Opportunities for Greener Alternatives from a Formulator's Perspective

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The ACS Green Chemistry Institute® Formulator's Roundtable (Roundtable) is a partnership between the ACS Green Chemistry Institute® (ACS GCI) and the formulated products industry designed to be the driving force to use green chemistry in creating innovative products that are environmentally sustainable throughout the entire product life cycle and safer to make and use. The ACS GCI Formulator's Roundtable welcomes the active participation of any corporation, or subsidiary, division or unit thereof, significantly engaged in the formulation of soap, detergents and cleaning preparations and/or perfumes, cosmetics, and other toilet preparations under his or its own brand names. This includes all corporations identifying with SIC Industry Group 284.

The Roundtable has identified five strategic priorities in order to achieve the mission of the organization to be a driving force in the formulated products industry to use Green Chemistry in creating innovative products that are environmentally sustainable throughout its product life cycle and safer to make and use.

- **Promote transparency and consistency through a set of green chemistry principles for formulated products.** The Roundtable recognizes the importance of establishing a unified voice on the principles of an environmentally preferable product for clarity and credibility across all stakeholder groups. The Roundtable will work collaboratively to establish these principles.
- **Drive good science in the development of environmentally preferred products standard/ certification.** The Roundtable recognizes the importance that "good science" is used in decision making and ensuring technical rigor in influencing environmentally preferred products certification and/or standard development. Leverage the independent position of ACS GCI to gain recognition that the ACS GCI Formulator's Roundtable be a resource to standard-setting bodies. Collaborate with global stakeholders, including governments and other organizations, to support harmonization in standard setting with an emphasis on continuous improvement that resonates with consumer expectations.
- **Inform and influence suppliers and academia to develop greener alternatives.** The Roundtable acknowledges its position to generate an aggregate demand for greener alternatives to currently used raw materials. The Roundtable will develop collaborations and/or funding opportunities to engage the suppliers, academia, and the larger scientific community in this endeavor to identify greener materials. Focus will be on identifying greener alternatives for commodity types of raw materials and will avoid any proprietary ingredients.
- **Be recognized leaders in Green Chemistry.** Proactively influence green chemistry related debate with regulators, non-government organizations, customers, and consumers. Influence suppliers, regulators, retailers and academic research. Establish recognized leadership for driving Green Chemistry. Use our collective learning to promote Green Chemistry.
- **Incorporate risk-based decision making into green chemistry.** The Roundtable seeks to expand the current use of hazard assessments in determination of "greenness" to incorporate risk-based decision-making and the precautionary principle when appropriate. The level of technical rigor used in sustainability assessments should be related to the quantity and quality of chemical information available. The Roundtable encourages the development and improved access to data to support decision making on products and ingredients. This may be accomplished by, but is not limited to, the development of tools, funding research, collaborating with suppliers, supporting curriculum development, etc.

To initiate progress towards informing and influencing suppliers and academia to develop greener alternatives, the Roundtable believed it was imperative to define the top areas for opportunities for greener alternatives as identified from a formulator's perspective. The components of existing formulated products are considered safe and effective; however, it is the intention of the Roundtable to foster the development of innovative greener components to enhance the overall sustainable profile of formulated products. The following list was developed with input and review from all member companies. These opportunities are common to the industry and do not represent one particular company's interests. This document reflects the consensus view of the Roundtable members in October 2010 and reflects data available at that time. Any information referenced in this document may have been superseded. It is the hope of the Roundtable that this list of top formulation opportunities initiates dialogue, research, and development of renewable and less hazardous alternatives.

The Roundtable recognizes this as an opportunity for collaboration where appropriate, for funding where feasible, and for global communication as needed to engage the broader audience in this effort to bring greener alternatives into the marketplace. The member company formulators recognize this is not something that can be achieved in a vacuum and seek the support and input from partners in industry, academia, government, and other organizations as appropriate.

The following are general recommendations for greener alternatives and are applicable, where appropriate, to all categories of materials.

- The performance of ingredients should be equal to or better than existing materials.
- Ingredients should be stable and function in a pH of >2 and < 11.5.
- Ingredients shall strive to be non-VOCs, not HAP's, and not be TRI listed chemicals.
- Ingredients shall not be Ozone Depleting Agents as defined by Montreal Protocol.
- Ingredients shall not contain toxic elements such as heavy metals.
- Ingredients shall not be classified as carcinogens, mutagens or reproductive toxins by established authorities such as IARC, NTP. If ingredient contains a contaminant which is classified as a carcinogen, mutagen or reproductive toxin it must be below an established "no effects level".
- Ingredients shall not be classified as persistent, bioaccumulative, toxic (PBTs) by the US EPA, or Persistent Organic Pollutants (POP) as defined by UNEP.
- Ingredients should be cost effective.

The opportunities for greener alternatives as identified by the ACS GCI Formulator's Roundtable include:

- Greener "Antimicrobials"
- Greener Solvents
- Greener Small Amines, MEA, DEA, TEA
- Greener Chelants
- Greener Boron Alternatives- enzyme stabilization, perborate replacement
- Greener Fragrance Raw Materials
- Greener Corrosion Inhibitors
- Greener Alkanolamide Replacement
- Greener Surfactants
- Greener UV Filters

This list of opportunities for greener alternatives from a formulator's perspective is not intended to be exclusionary, but rather provide an initiation point. Refer to the Appendix for a more detailed description of each category and preferred characteristics of each. For general toxicity and environmental criteria refer to the US EPA's General Screen for Safer Ingredients, February 3, 2009.

For more information about the Roundtable or to suggest ways to collaboratively address these opportunities to bring greener alternatives to the marketplace, please go to www.acs.org/gciformulators or e-mail gcifr@acs.org.

Description of Use:
The primary purpose of the document is to communicate opportunities for greener alternatives from a formulator’s perspective to the scientific community at large including industry, academia, government, and non government organization. The Roundtable seeks to encourage further research and development to identify and otherwise make available greener alternatives. The final document is open to the public.

Member companies are free to use the document at their discretion and are encouraged to increase visibility of the document as they see appropriate. The Roundtable will work to increase publicity of the final document in scientific journals, trade journals, and appropriate industrial and scientific conferences.

Appendix

Companies Endorsing this Document

Greener "Antimicrobials"

Greener Solvents

Greener Small Amines, MEA, DEA, TEA

Greener Chelants and Sequestering Agents

Greener Boron Alternatives- enzyme stabilization, perborate replacement

Greener Fragrance Raw Materials

Greener Corrosion Inhibitors

Greener Alternatives for Alkanolamides

Greener Surfactants (not specific to nonionic surfactants)

Greener UV screens (Sunscreens)

Companies Endorsing this Document

The following members of the ACS GCI Formulator's Roundtable endorse this document.

Amway

Bissell Homecare, Inc.

Church & Dwight Co. Inc.

The Clorox Company

Ecolab

Florida Chemical Company, Inc.

Johnson & Johnson Consumer Companies

Rug Doctor, Inc.

S.C. Johnson & Son, Inc.

Seventh Generation, Inc.

State Industrial Products Corp.

Zep Inc.

Greener "Antimicrobials"

Preservatives, by their very nature, are designed to kill things. By definition, most are stable compounds and potent toxicants to microorganisms. These ingredients are often similarly toxic to indicator aquatic organisms such as Daphnia species (water fleas) Specifically they work by killing cells and preventing them from multiplying and are intended to prevent the growth of bacteria and fungi in commercial products – mainly Candida albicans, Pseudomonas aeruginosa, Escherechia coli, Aspergillus niger and Stephylococcus aureus – which could potentially cause serious infections on the skin and in the body. How do products become contaminated? A significant amount of contamination actually occurs during manufacture – a problem that should be, but is rarely, addressed at the factory floor level rather than by simply adding more chemicals to the finished product.

All of the most commonly used preservatives have some health or toxicity concerns. Some are sensitizers, cause dermatitis and other skin reactions; some carry larger risks. Some preservatives form formaldehyde when challenged with bacteria. These are known as formaldehyde donors. However, formaldehyde is a known carcinogen.

Currently there are few "greener" alternatives for preservatives. The ACS GCI Formulator's Roundtable is seeking new preservatives with the following characteristics and that are designed considering the 12 Principles of Green Chemistry.

Preferred characteristics for greener preservatives

- Rapid acting at the first sign of contamination
- In container sanitization of gram positive bacteria, gram negative bacteria, yeast, mold preferably in less than 2 days, at least less than 7 days after challenge
- Broad spectrum, effective on multiple bacteria or fungi or both
- Non-sensitizing
- Non-toxic and non-irritating to humans
- Compatible with the other ingredients in the mix
- Stable – not break down during storage, stays active in a wide pH range
  - For fabric softener, pH 2.5-4.0
  - For dish detergent, pH 6.0-8.0
  - Laundry detergent, pH 7.0-9.5
- Inactive, except as an antimicrobial – i.e. not interact with other ingredients
- Soluble – mix well with whatever base (water or oil) it is in
- Acceptable in odor and color. No impact on finished product aesthetics (color, odor, viscosity)
- Cost effective

Greener Solvents

The term "*solvent*" encompasses many classes of chemicals: alcohols, amides, amines, esters, glycols, glycol ethers, hydrocarbons, oxygenated hydrocarbons, terpenes, etc. The broad functionality of traditional solvents, such as petroleum distillates, makes them useful necessary ingredients in many product applications. Many formulators find these materials crucial to formulating high performance products that deliver concentrated cleaning. It is their varied attributes that make them indispensable in cleaning and personal care formulations. Solvents are used for dissolving raw materials (e.g., resins and waxes) and various soils (e.g., adhesives, grease and inks) for removal, and as a carrier for essential oils among other uses.

Solvents can be fossil-based or bio-based **–** water-soluble or oil-soluble. Most are 100% active although some contain azeotropic water:

Unfortunately fossil-based solvents are not without issues. The traditional hydrocarbon solvents and oxygenated hydrocarbons, such as petroleum distillates, glycol ethers, isopropyl alcohol, etc., are fossil-based and as such have a high global warming potential (GWP). All of the most commonly used solvents have health, safety and environmental concerns. Most petroleum distillates are found to be non-carcinogenic hydrocarbon blends, but because they are distillates, can contain small amounts of carcinogens such as benzene or HAPs such as xylene. Petroleum distillates are a safety concern for many reasons: some have inhalant/respiratory issues, and most cause defatting of the skin, dermatitis and other skin reactions. Most fossil-based solvents are VOCs or LVP VOCs and some carry larger risks such as flammability. Made from non-renewable sources they have environmentally unfavorable life-cycles.

Many companies are looking to bio-based solvents from renewable feedstocks. Formulators need an assortment of solvents to meet the variety of applications required for green cleaning and personal care products.

Ethanol and ethyl lactate can be derived from fermentation of a food substance (cellulosic ethanol has not yet been commercialized). Others, such as soy methyl esters and propanediols are biobased, but require a chemical reaction and process for their production. Together they have lower GWPs than their fossil-based counterparts, but all impact food crops. Others, such as citrus oils and conifer (pine) derivatives, are expressed from waste biomass without a chemical reaction and have even lower GWPs. All are bio-based and derived from renewable agricultural materials (including plant, animal and marine materials) or forestry materials.

Bio-based solvents can have negative impacts on the environment even though they come from a renewable source. Often the environmental impact is reducing biodiversity of the area due to monoculture or cutting of natural areas and replanting with the crop of choice. Another negative impact can be on a food supply if the crop is more valuable for its chemical value than its food value. When renewable feedstocks are used a life cycle assessment should be considered as well as an environmental impact assessment.

The ACS GCI Formulator's Roundtable is seeking greener alternatives for commonly used solvents. In addition to meeting as many of the 12 Principles of Green Chemistry as possible, the following summarizes some of the key characteristics of suitable alternatives.

<u>Preferred characteristics for greener solvents</u>

- Sourced from renewable raw materials avoiding petroleum feed stocks where possible
- Non-sensitizing
- Non-toxic and non-irritating to humans
- Minimal odor and color, thus minimal impact on the finished product aesthetic
- Life cycle assessments (LCA) of cradle-to-gate, cradle-to-grave, and cradle-to-cradle would be helpful.
- Cleaning benefits such as grease-cutting and solubilizing. Soy methyl esters and terpenes were cited as especially effective among the biobased solvents
- Modifying physical properties (i.e. reduced viscosity, freeze-thaw recovery, freeze point depression) of finished formulations
- Stabilizing formulations by keeping solids in solution and preventing precipitates
- Meets the US Environmental Protection Agency Design for the Environment criteria for acceptable
- Cost effective

Greener Small Amines, MEA, DEA, TEA

The broad functionality of small amines (such as MEA, DEA, TEA, AMP, etc) - low pH alkalinity, corrosion protection, grease removal, film/streak inhibition, storage stability and dissolution in water without phase issues - make them necessary ingredients in many product applications. Many formulators find these materials to be crucial to formulating high solids products to deliver concentrated cleaning.

Unfortunately they are not without issues. Small amine molecules are a safety concern primarily because of the potential to form nitrosamines. Nitrosamines have been shown to be carcinogenic; however, the amines themselves are not carcinogenic. In addition, it has been shown that secondary amines form nitrosamines somewhat easily with nitrite, while tertiary amines react more slowly by magnitudes and primary amines do not form nitrosamines. Formulating guidelines (Scientific Committee for Cosmetics and Non-Food Products of the European Commission) have been established to minimize potential issues; however, a safer/greener replacement is preferred.

The ACS GCI Formulator's Roundtable is seeking greener alternatives for small amines. In addition to meeting as many of the 12 Principles of Green Chemistry as possible, the following summarizes some of the key characteristics of suitable alternatives.

Preferred characteristics for greener small amines

- Sourced from renewable raw materials relative to petroleum feed stocks
- Non-sensitizing
- Non-toxic and non-irritating to humans
- Minimal odor and color, thus minimal impact on the finished product aesthetics
- Alkalinity at relatively low pH, neutralizing (providing a counter-ion for) anionic detergents, neutralizing fatty acids, etc.
- "Organic" alkalinity, yet water miscible thus tying up less water than inorganic counter-ions (i.e. sodium).
- Corrosion protection
- Cleaning benefits such as grease-cutting and solubilizing. AMP was cited as especially effective.
- Modifying physical properties (i.e. reduced viscosity, freeze-thaw recovery, freeze point depression) relative to inorganic sourced alkalinity
- Preventing scale or film formation. TEA has been shown to be effective in hard surface applications.
- Small amines are particularly important in formulations with high solids content. In concentrated formulations, small amines serve to lower viscosity, increase the solubility of the surfactant, and maintain uniform solids distribution. Laundry detergents typically have high solids content in comparison to other cleaning products. It is particularly difficult to formulate above a solids content of 30% and maintain physical properties without use of small amines.
- Meet the US Environmental Protection Agency Design for the Environment criteria for acceptable
- Cost effective

Greener Chelants and Sequestering Agents

Chelants or sequestering agents are used in products to tie up metal or hard water ion. They can be used industrially as scale inhibitors or they can be used in cleaning products to tie up calcium, magnesium, iron and other metals to improve cleaning performance. There are several concerns about chelants that are on the market for cleaning products. For example, chemical that can tie up the molecules of an element, such as iron, and keep it in solution past the point where it should naturally precipitate.

Chelants, according to ASTM-A-380, are "chemicals that form soluble, complex molecules with certain metal ions, inactivating the ions so that they cannot normally react with other elements or ions to produce precipitates or scale."

EDTA, ethylenediaminetetraacetic acid, tetrasocium salt dehydrate, is a polyamino acidic and a colorless, water-soluble solid. It is widely used to dissolve scale. Its usefulness arises because of its role as a chelating agent, i.e. its ability to "sequester" metal ions such as Ca^{2+} and Fe^{3+}. After being bound by EDTA, metal ions remain in solution but exhibit diminished reactivity. EDTA is produced as several salts, notably disodium EDTA and calcium disodium EDTA.

EDTA and other chelants have been linked to toxicity to internal organs such as kidneys and the liver. This should be an expected effect if the chemical is a good chelant and the dosage is high. Environmental concerns are around lack of biodegradability and tying up heavy metals in river and lake sediment and possibly re-suspending the heavy metals.

The US EPA's Design for the Environment, (DfE) program has unofficially rated chelants, although they do not have specific DfE criteria. The ratings are not provided here to avoid any unintended preferential identification of specific chelants. The DfE has a technical team working on the development of chelant criteria.

Many of the new more biodegradable chelants that have been developed over the past several years have one of two problems. The backbone of the molecule looks very much like NTA, Trisodium nitrilotriacetate monohydrate, a suspect carcinogen. The DfE is concerned about this exposure even though the molecule is very biodegradable in 14-28 days. The second issue with several of the new chelants is they are not as effective on the key ions, CA+, Mg+ or Fe+++. This means a higher concentration of chelation chemical needs to be used or the performance will be compromised. The final issue is price. New chelation agents usually can not compete against EDTA, a commodity and workhorse of chelants.

<u>Preferred characteristics for greener chelants</u>

- Preferred Metal Chelation Capacity (see Table 1).

Table 1. Preferred Metal Chelation Capacity

Metal	**Part chelant per parts metal (w/w)**
Ca	16-20
Mg	25-35
Fe	10-20
Cu	10-15
Mn	10-15

- The chelant should be active from a neutral pH to a pH of 12 or from a neutral pH to a pH of 2. A chelant effective over the full pH range would be the best but technically very difficult.

Greener Boron Alternatives- enzyme stabilization, perborate replacement

Boron compounds useful in cleaning products are in the form of boric acid, borates and perborates. Boric acid acts as a non-alkali buffer and an enzyme stabilizer in liquid cleaning products. Borates (typically as borax) are useful as a cleaning/laundry aid to provide buffering and deodorizing. Perborates are employed as stable sources of oxygen bleach.

Boron is naturally present in silicates and is therefore also found in surface waters as boric acid and the borate anion. Boron is an essential element necessary for plant growth, but excess levels can be phytotoxic. In regards to perborate itself, human safety studies indicate it is irritating and may be sensitizing. Boron is toxic to mammals in relatively low doses, with a NOAEL of 9.6mg/kg bw/d set by the critical effect of reduced fetal weight in a developmental toxicity study.

Cleaning products can contribute boron via sewage effluent and therefore greener/safer alternatives are needed. No truly suitable alternative for boric acid for enzyme stabilization has been found. The standard perborate replacement, sodium percarbonate, has many issues most important of which are poor stability as well as very high alkalinity. The ACS GCI Formulators Roundtable is seeking greener alternatives for these boron compounds. In addition to meeting as many of the 12 Principles of Green Chemistry as possible, the following summarizes some of the key characteristics of suitable alternatives.

<u>Preferred characteristics for greener perborates</u>

- Non-sensitizing
- Non-toxic and non-irritating to humans
- Minimal odor and white in color, thus minimal impact on the finished product aesthetics
- Stable available oxygen (at least 10% AvO in neat form) as raw material and in powder finished product – shelf life 3 years. Both chemical and physical stability (flow, color, odor)
- Very water soluble – AvO release complete within 2 minutes in cold water (10'C)
- Safe handling and shipping as raw material
- Sourced from renewable raw materials
- Meet the US Environmental Protection Agency Design for the Environment criteria for acceptable
- Cost effective

<u>Preferred characteristics for greener boric acids</u>

- Non-sensitizing
- Non-toxic and non-irritating to humans
- Minimal odor and color, thus minimal impact on the finished product aesthetics
- Provide enzyme stability in aqueous based cleaning products for 3 years (ideal)
- Sourced from renewable raw materials
- Meet the US Environmental Protection Agency Design for the Environment criteria for acceptable
- Cost effective

Greener Fragrance Raw Materials

Section 3.16 of the US EPA Design for Environment (DfE) Screen for Fragrances defines a Fragrance raw material as "any substance, obtained by chemical synthesis or derived from a natural source, intentionally added or present in a fragrance at greater than 0.01 percent by weight whose primary purpose is to impart scent. In the context of this screen, fragrance raw materials include aroma chemicals, fragrant extracts (essential oils), and components of essential oils." See:
http://www.epa.gov/dfe/pubs/projects/gfcp/dfe_screen_for_fragrances_human_health_criteria_version_1.pdf

Preferred characteristics for greener fragrance raw materials

- Fragrances must meet the International Fragrance Association (IFRA) Standards.
- All fragrance raw materials present at 100 ppm (or 0.01 percent by weight) or greater in the fragrance should be screened for toxicity following the guidelines in the US EPA Design for Environment Human Health criteria.
- Fragrance ingredients present at or above 0.01% in the cleaning product should be screened to meet the DfE Environmental Toxicity and Fate (ETF) Criteria.
- Fragrance ingredients should be non-sensitizing and not listed on the EU 26 Allergens List.
- Fragrance ingredients should not be derived from non-sustainable sources (i.e. Ambergris from Sperm whales.) or sources which will endanger another species.
- Solvents used in fragrances should not be a volatile organic compound.
- Non-odor ingredients should be ready biodegradable.

Greener Corrosion Inhibitors

Corrosion is the destruction, degradation or deterioration of substrate material at its interface with the environment, due to chemical reaction between the material and its environment.

Corrosion can be prevented or inhibited by (A) Coating the substrate with a non-reactive medium (B) passivating the substrate and (C) the use of Chemical Corrosion Inhibitors.

Corrosion inhibitors can delay or prevent metal corrosion rate. They are broadly divided by their electrochemical theoretical mechanisms as anodic inhibitors, cathodic inhibitors and mixed inhibitors.

Considering the annual cost of corrosion in the US alone is in excess of $275 Billion, corrosion inhibitors support sustainability by the very nature of their function. However, many corrosion inhibitors are manufactured using energy intensive methods, have environmentally unfavorable life-cycles and though they prevent corrosion are themselves made from nonrenewable resources. Many are corrosive, toxic, not biodegradable and can bio-accumulate.

Some industrial applications have no choice but to use corrosive inhibitors. To increase sustainability, these applications need to evaluate alternative techniques. One method is to determine how to reduce the negative affects of these corrosion inhibitors; another is to try to improve activity of corrosion inhibitors, and use less consequently.

The field of corrosion inhibitors encompasses too many classes of chemicals and individual chemicals to list. Even though sustainability development in this class of chemicals is at the nascent stage, several new classes of compounds useful in corrosion inhibition were introduced recently. Amino acid salts from renewable resources, natural soy-based polymers; casein-based polymers, marine polysaccharides have demonstrably outperformed traditional corrosion inhibitors in various corrosion tests.

The availability of recently introduced "green" corrosion inhibitors has weakened the old argument that corrosion inhibitors help sustainability so their harmful and non-desirable effects should be acceptable. Development of acceptability criteria is perhaps the best way to confer a "sustainable" or green tag to an inhibitor chemical. For example, the North Sea Standard (primarily minimizing marine toxicity) acceptability criteria are as follows:

- Biodegradability: > 60% in 28 days
- Marine toxicity: Effective Concentration, 50% (EC50)/Lethal Concentration, 50% (LC50)>10 mg/L to North Sea species
- Bioaccumulation: Log Octanol/Water Partition Coefficient (Pow)<3

<u>Preferred characteristics for a greener corrosion inhibitors</u>

Since the Roundtable is primarily concerned with formulations of HI&I products, limits need to be established for:

- Corrosivity
- Skin/Eye Irritation
- Toxicity (All kinds)
- Biodegradability
- LCA analysis (energy used to manufacture, store, use concentration, length of useful life, post use disposal)
- Renewability (for example 50% or more of the raw materials need to be from renewable or natural sources)

Greener Alternatives for Alkanolamides

Alkanolamides have traditionally been used by cleaning product formulators to increase viscosity and/or stabilize foam. They also provide solubilization of oily components. In the product itself, this can aid the incorporation of fragrance and other non-polar ingredients. In the end use application they can improve the removal of an oily soil from a substrate. In addition, they are virtually 100% "active" (no water). These attributes have made them valuable components in shampoos, dishwashing liquid, laundry hand wash detergents and other products that are enhanced by stable foam, increased viscosity or high concentrations.

In recent years, alkanolamides have been identified as needing safer alternatives. These materials will contain some small amine molecules which are a safety concern primarily because of the potential to form nitrosamines. Nitrosamines have been shown to be carcinogenic; however, the amines themselves are not carcinogenic.

The ACS GCI Formulators Roundtable is seeking greener alternatives for alkanolamides. In addition to meeting as many of the 12 Principles of Green Chemistry as possible, the following summarizes some of the key characteristics of suitable alternatives.

<u>Preferred characteristics for greener alkanolamides</u>

- Sourced from renewable raw materials rather than petroleum feed stocks
- Non-sensitizing
- Non-toxic and non-irritating to humans
- Minimal odor and color, thus reducing impact on the finished product aesthetics
- High activity (alkanolamides are essentially 100% active)
- Compatible with anionic and nonionic surfactants
- Cleaning benefits such as oil solubilizing (low HLB)
- Modify physical properties (i.e. viscosity, freeze-thaw recovery, freeze point depression) of finished formulations
- Meet the US Environmental Protection Agency Design for the Environment criteria for acceptability
- Cost effective

Greener Surfactants (not specific to nonionic surfactants)

Surfactants are widely used in personal care and cleaning products, for a wide range of functions (e.g., antistatic, cleansing, emulsifying, foaming, hair conditioning). Most are readily biodegradable, but are potent toxicants to aquatic organisms. Today formulators have numerous choices for surfactants that have less impact on the environment and are safer for the users, however the majority are synthetic surfactants have been derived from petroleum. As "green" or "natural" has become popular there are more surfactants that are being derived from renewable resources such as the alkyl polyglucocide and surfactants from palm and other plant oils. Surfactants that are produced from renewable resources may be plant based, animal fats or even derived from microorganisms.

Plant based surfactants can have a negative impact on the environment even though they coming from a renewable resource. Often the environmental impact is reducing biodiversity of the area due to monoculture or cutting of natural areas and replanting with the crop of choice. Another negative impact is on the food supply if the crop is more valuable for it chemical value than its food value. Any time renewable feedstocks are being used a Life Cycle Assessment should be considered as well as an environmental impact assessment.

Many surfactants from renewable feedstocks are anionic surfactants including sulfates, sulfonate, esters, phosphate esters, and carboxylates. Many formulators are looking for nonionic and cationic surfactants from renewable feedstocks. The variety of surfactants from renewable feedstocks is limited in their physical properties when compared to synthetic surfactants. Formulators need a variety of surfactants to meet the variety of applications needed for cleaning and personal care products.

Biosurfactants are often amphiphilic compounds produced on living surfaces, mostly microbial cell surface or excreted extracellularly and contain hydrophobic and hydrophilic moieties that reduce surface tension and interfacial tension between individual molecules at the surface and interface respectively. Several biosurfactants have high surface activity and low critical micelle concentration (CMC) and are therefore, promising substitutes for synthetic surfactants.

The physical properties of the ideal surfactant are varied because different uses will dictate a wide range in physical properties. However the important physical properties of a surfactant include the following:

- **%** Active
- Cloud Point
- HLB
- Pour Point
- Moles of EO
- CMC, ppm at 25º C
- Viscosity at 25 Cº cP
- Density at 20 º C (g/ml)
- Flash Pt, Closed Cup, ASTM D93
- Surface Tension: dynes/cm at 1% at 25º C
- Ross-Miles foam heights in mm at 0.1% actives at 25ºC, initial and at 5 minutes

<u>Preferred characteristics for greener surfactants</u>

- Biodegradability (readily biodegradable)
- Aquatic toxicity (LC50 >10mg/l)
- From feedstock that has no food value
- Feedstock will not have a negative impact on eco-diversity.
- Manufacturing processes should be designed considering the 12 Principles of Green Chemistry.

Greener UV screens (Sunscreens)

Sunscreens contain one or more ultraviolet (UV) filters. UV filters absorb potentially harmful ultraviolet rays from penetrating the skin. UV screens include both organic compounds (e.g., octinoxate, octocrylene, ethylhexyl triazone) and inorganics (e.g., zinc oxide, titanium dioxide). The inorganic UV screens are often used in the form of nano-scale particles. Few data exist to characterize the persistence, bioaccumulation potential, and aquatic toxicity of organic UV screens. According to widely used predictive models, nearly every UV screen is a potent aquatic toxicant. Model predictions indicate that many UV screens are also expected to be persistent and/or bioaccumulative. Recent research indicates that certain UV screens have the potential to cause chronic reproductive effects to aquatic life at low exposure levels. A desirable alternative would be well-characterized as readily biodegradable, of low toxicity to aquatic organisms, and not endocrine active.

<u>Preferred characteristics for greener UV screens</u>

- Readily biodegradable
- Low octanol-water partition coefficient (Kow) (*e.g.,* log Kow less than 3.5)
- Low acute toxicity to aquatic organisms (*e.g.*, lethal and adverse effects concentrations to 50% of a test population – LC_{50} and EC_{50} values – greater than 100 mg/L)
- Does not elicit a positive response in endocrine disruption screening tests (*e.g.,* estrogen receptor binding assay)
- Non-sensitizing
- Non-toxic and non-irritating to humans
- Minimal odor and white in color, thus minimal impact on the finished product aesthetics
- Safe handling and shipping as raw material
- Sourced from renewable raw materials
- Meet the US Environmental Protection Agency Design for the Environment criteria for acceptable
- Cost effective