Detergent Basics

Detergents are designed with one primary purpose: to remove soil from some type of surface. From that simple premise all formulas are designed, although the variety of soils and surfaces encountered will give an almost infinite range of formulating possibilities.

An effective, general-purpose detergent must be capable of four basic cleaning functions. First, since most soil is acidic in nature, it must be able to neutralize acidic soil components. Secondly, to clean oil and grease from a surface, it must be able to emulsify, or homogenize, oil and grease into tiny water dispersible particles. Third, it must deflocculate, or break down, particulate soils such as carbon, dust and clay, into very fine particles. Fourth, once the above three functions are accomplished; the detergent should keep the soil in suspension so that redeposition onto the surface just cleaned does not occur during rinsing.

Detergents universally use two components to accomplish these functions: surfactants and builders. Surfactants can be either a liquid or a powdered ingredient comprised of organic molecules. Builders are inorganic ingredients, usually in powdered form, such as phosphates, silicates, carbonates, and orthophosphates. The combination of surfactants and builders is the basis of detergent compounding.

As a detergent is formulated, different weight may be given to each of the four basic cleaning functions, depending on the intended use of the detergent. Consideration will also be given to the type of surface to be cleaned to prevent possible damage to the substrate. In addition, there are three other factors that influence the effectiveness of a detergent: agitation, time, and heat. For example, if a soak tank is set up and a greasy panel is immersed into a detergent solution, the detergent will show a certain level of cleaning effectiveness after a set period. Increase the time, and the effectiveness goes up. Add agitation and heat, and maximum effectiveness is achieved. The combined action of detergent, agitation, time, and heat gives the best results. Leave one factor out, and you must compensate with more of the others.

These variables account for the different products produced today. There are hand dish-washing detergents and machine dish-washing detergents, baby shampoos and pet shampoos, engine degreasers and car wash detergents; all purpose cleaners, metal cleaners, solvent-based cleaners, hand cleaners, concentrated products and RTU (ready to use) cleaners, each different, but all accomplishing the basic function of removing soil from a surface.

It is important to note the difference between the terms detergent and soap. In this book, the emphasis is on formulating synthetic detergents, not soap. Soap is commonly produced when a sodium or potassium base neutralizes a fatty acid. Up until the 1940s, soap was the primary cleansing agent used for most types of cleaning. The introduction
of synthetic surfactants, with their superior cleaning and rinsing capability, has sharply reduced the use of soap products. However, the terms soap and detergent are oftentimes used interchangeably, and many times detergent formulations will actually contain a varying amount of soap.

**Surfactants**

Water, by itself, does not have sufficient detergency to produce the results we normally would desire. That is not to say that water alone is not capable of cleaning. Anybody who has taken the garden hose to the family car will admit it looks better after a quick rinse. Moreover, a good rainstorm removes a great amount of dirt and grime. Nevertheless, the cleaning ability of plain water can be improved tremendously by the small addition of a surfactant.

The word surfactant is a contraction of "surface active agent." There are many different types of surfactants, but they can be grouped into four main classes: anionic, nonionic, cationic, and amphoteric. The anionics have a negative charge. Nonionics have no charge. Cationics are positively charged. Amphoterics can be either negatively or positively charged. Surfactants lower the surface tension of a liquid. Added to water, for example, water will seem "wetter" and penetrate through to surfaces and surround soil particles for better cleaning. Surfactants also reduce the interfacial tension between two liquids. Whereas oil will normally float on water, a small addition of surfactant will allow the oil and water to "mix," forming an emulsion.

Let us look at one type of surfactants called ethoxylated nonylphenols. They are the workhorses of industrial detergents. They are nonionic, and are comprised with molecules having an oil-soluble (lipophile), hydrocarbon end, and a water-soluble (hydrophile) polyalkoxylate chain. The lipophile used is nonylphenol; the hydrophile used is ethylene oxide. The more ethylene oxide, the greater the water solubility of the surfactant. A nonylphenol modified (ethoxylated) with four moles of ethylene oxide per mole of nonylphenol is soluble in kerosene, but not in water. A nonylphenol modified with 13 moles of ethylene oxide is soluble in water, but not in kerosene. Incidentally, the term “mole” is not short for molecule. It is a unit of measurement (see the section on Chemical Descriptions, Terms, & Definitions). The mix between the hydrophile (ethylene oxide) and the lipophile (nonyl phenol) is expressed as the hydrophile/lipophile balance, or HLB. HLB’s range from 1 – 20; the higher numbers represent higher water solubility.

Union Carbide, a division of Dow Chemical Company, produces a line of nonylphenol surfactants under the **TERGITOL NP™** name. The number following the NP is the average number of moles of ethylene oxide added. Here is a list of those surfactants with a brief description of each:
TERGITOL NP-4™
Oil soluble, liquid surfactant, forms water in oil emulsions, HLB 8.9

TERGITOL NP-6™
Oil soluble, liquid surfactant, forms water in oil emulsions, HLB 10.9

TERGITOL NP-7™
Oil soluble, liquid surfactant with limited water solubility, HLB 11.7

TERGITOL NP-9™
Water soluble, liquid surfactant, limited oil solubility, HLB 12.9

TERGITOL NP-13™
Water soluble, liquid surfactant, forms oil in water emulsions, HLB 14.4

As a general guide, HLB numbers can be useful in determining the application of a surfactant. A surfactant with a HLB between 4-6 would be useful in dissolving water into a solvent (w/o emulsions). A range of 7-9 would make a good wetting agent. From 8-18 is good for dissolving oil into water (o/w emulsions). From 13-15 is good as an all-purpose detergent. 10-18 is good for solubilizing other ingredients.

It is also possible to combine surfactants with different HLB values. For example, a simple detergent formula that calls for ten parts NP-9 dissolved into 90 parts water would be improved by the addition of 2 parts NP-6. Normally, NP-6 would not be water soluble, but the NP-9 will act as a solubilizer. The NP-6 will increase the cleaning ability of the detergent on oils and grease.

Anionics, on the other hand, are high-foaming surfactants commonly used in hair shampoos, car wash detergents, and hand dish wash detergents. One of the most common anionic surfactant is sodium lauryl sulfate. Because anionics are negatively charged, they are deactivated by positively charged hard water ions. When using anionics, care must be taken to include chelating agents to deactivate hard water ions. Other common anionics are alcohol sulfates, alcohol ether sulfates, ordinary soap, and alkylaryl sulfonates (see section on LAS).

Cationic surfactants are generally used in anti-static products such as fabric softeners, hair conditioners, and in sanitizing compounds. Because they are positively charged, they are not compatible with anionics. Common cationics are quaternary ammonium compounds.

Amphoterics are a special class of surfactants. They are anionic at an alkaline pH, have no charge at neutral pH, and cationic at acidic pH. Due to their mildness and high foaming properties, amphoterics are used in personal care products and as substitutes for
anionics when cationics are present. Examples of amphoterics are lauroamphopropylsulfonate and cocoamphopropylsulfonate.

When evaluating surfactants, the following characteristics come into play:

**Foam:** Amphoterics and anionics will generate the highest amounts of foam. Some cationics foam well, although most are considered medium foamers. Nonionics generally are low to medium foamers.

**Wetting:** Anionics rate high as wetting agents, with nonionics just behind. Amphoterics are fair wetting agents, while cationics are usually rated poorly.

**Emulsification:** Nonionics lead here, followed by anionics and amphoterics. Cationics are not good emulsifiers.

**Detergency:** Nonionics, amphoterics, and anionics all exhibit good to excellent detergency. Cationics are not good detergents.

**Skin and Eye Irritation:** Amphoterics are considered very mild irritants. Nonionics, cationics, and anionics will rate from mild to severe.

**Compatibility With Other Surfactants:** Nonionics and amphoterics are generally compatible with all other surfactants. Anionics and cationics are incompatible with each other.

In general, nonionics are used heavily in industrial detergents, with anionics, amphoterics, and cationics used in personal care products. However, there can be significant crossover depending on the individual product.

**Builders**

Builders are ingredients that are added to cleaning products to enhance the performance of a surfactant/water blend. Builders accomplish this through several means.

First, most builders act as water softeners. That is to say, the builders either precipitate, or sequester, calcium and magnesium ions in hard water, and prevent them from interfering with the surfactants, especially anionics. When precipitation occurs, the hardness ions form insoluble salts that drop out of solution. Sequestration, on the other hand, occurs when the positively charged hardness ions are surrounded by the negatively charged builder, and are thereby made inactive. Sequestration is preferable over precipitation because precipitated salts tend to redeposit onto surfaces being cleaned, forming that hard, white-looking scale buildup. Sequestered hardness ions stay in solution, and are rinsed away.
Second, builders impart a reserve alkalinity to the cleaning solution. Acidic soils lower the pH of a cleaning solution to below the optimum level needed for the surfactant to perform well. Builders act as a buffer against acidic soils by neutralizing them and maintaining the pH at a designed level of alkalinity.

Third, builders tend to break down larger clumps of soil into tiny particles. This is called deflocculation, which is a fancy word for disperse.

Fourth, builders can contribute towards soil anti-redeposition by increasing the negative charge that already exists on particulate soils. When this happens, particulate soils tend to repel each other and are less likely to bind together or redeposit onto a freshly cleaned surface.

And fifth, builders peptize, or keep in suspension, soil particles. Good suspension of soil particles means better rinsing ability.

The term "built detergent" refers to a detergent containing a surfactant that has been "built" by the addition of one or more builders. The most common builders are listed below:

**Sodium Trisodium Pyrophosphate**

One of the most frequently used builders, especially in powdered formulations, sodium trisodium pyrophosphate (STPP) acts as an excellent water softener by sequestering hardness ions. In addition, STPP breaks up soils into small particles and keeps them in suspension. It is often combined with sodium metasilicate. The two together produce a synergistic effect, where the combination of the two works better than corresponding amounts of either component used alone. STPP cannot solubilize fatty soils by itself, but a combination of SDDBS (sodium dodecyl benzene sulfonate) and STPP dramatically increases the ability of SDDBS to solubilize fatty soils. STPP can be dissolved into water at the rate of 14 grams STPP per 100 grams of water (14% maximum solubility). A 1% solution of STPP produces a pH of 9.7.

**Potassium Trisodium Pyrophosphate**

Another frequently used builder, although more expensive than STPP, potassium trisodium pyrophosphate (KTPP) is an excellent sequestrant of hardness ions. It is also a good deflocculant and peptizing agent. KTPP is more water-soluble than STPP, with a solubility of over 60%. A 1% solution of KTPP produces a pH of 9.6.

**Tetrasodium Pyrophosphate**

Where as polyphosphates contain three phosphorus atoms, pyrophosphates contain only two. The pH of tetrasodium pyrophosphate (TSPP) is slightly higher than
STPP at 10.2, and water solubility is 8g per 100g of water. TSPP is a better sequestering agent than STPP.

**Tetrapotassium Pyrophosphate**

Due to its high water solubility (over 60%), tetrapotassium pyrophosphate (TKPP) is used in liquid formulations as a sequestrant and deflocculant. The pH is 10.2.

**Trisodium Phosphate**

A common household cleaner, trisodium phosphate is a sodium orthophosphate, which in turn, is the single, double or the triple salt of phosphoric acid. The "tri" indicates it is the triple salt. TSP softens hard water by precipitation. It has a pH of 11.4, and a water solubility of 14g per 100g of water.

**Disodium Phosphate**

DSP is the double salt of phosphoric acid. It has a lower pH than TSP, at about 9.2. It also softens water by precipitating hardness ions. The water solubility is 14g per 100g of water.

**Monosodium Phosphate**

MSP is the single salt of phosphoric acid, with the lowest pH of 4.6. Again, it precipitates hardness ions, and has a water solubility of 87g per 100g of water. NOTE: tri, di, and mono sodium phosphate are also available in potassium versions with similar pH values but greater water solubility.

**Sodium Carbonate**

The biggest single used builder in heavy-duty laundry products, sodium carbonate, or soda ash, is a low cost, high alkaline builder that softens water by precipitation. However, soda ash is often combined with sodium trypolyphosphate to eliminate any formation of scale. Sodium carbonate has a pH of 11.4, and a water solubility of about 7%.

**Sodium Bicarbonate**

Sodium Bicarbonate is a low alkaline version of sodium carbonate. It has a pH of 8.4; it has a water solubility of 10%. It also precipitates hardness ions. Sodium bicarbonate is a useful builder in aluminum, brass, and other soft metal cleaners, where low pH is desired.