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# **Detergents**

**by Clair Wood**

The next time you are in the supermarket, take a quick tour through the soap and detergent section. The *detergents* may take up an entire aisle, and the *soaps* occupy at most a single shelf. Detergents have replaced soap for all but a few domestic and industrial uses.

Soap is an ancient cleaning agent that was traditionally made at home or by village tradespeople. It is made from animal fat or vegetable oil (See SOAP, *Chem Matters*, February 1985). Detergents, in contrast, are manufactured from petroleum and industrial chemicals. The detergent industry started about 60 years ago, when the first synthetic replacement for soap was developed for the textile industry where it was used to wash raw wool. Detergents challenged soap for the household market during World War II when shortages of animal fat led to the rationing of soap. Detergents have now captured over 90% of the home cleaning market.

When you visit the supermarket today, you are confronted by a bewildering array of boxes and bottles, each with its own claim to cleaning superiority. Look at the list of ingredients on the label. Names like polyphosphate, TEA, CMC, nonionic surfactant, or sodium lauryl sulfate serve to confuse the shopper even further. Although the chemical nature of soap is rather simple, the composition of detergents seems clouded in mystery.

To begin unraveling the mystery, we must understand that a detergent is not a compound but a *formulation*, that is a mixture of compounds, each with a specific role to play in the cleaning process. The key ingredient around which a detergent is formulated is the surface active agent or *surfactant*. The surfactant plays the same role in the cleaning process as does soap. It removes the dirt-trapping oil or grease. The other ingredients, called *builders*, play supporting roles that

make the surfactant's task easier. Some detergents also use *fillers*—chemicals that do not perform any cleaning function. Detergents differ in the amounts and kinds of surfactant, builders, and fillers they contain. Let's examine some of these ingredients more carefully.

## Surfactants

There are literally hundreds of different surfactants available to detergent manufacturers. They are classified as *anionics*, *cationics*, and *nonionics*. The anionics are so named because their active component is an *anion*, or negative ion. Cationic surfactants contain a *cation*, or positive ion. *Nonionics* contain no ion. The anionics account for nearly 70% of the surfactant market. They produce thick, copious suds that stand up well in heavy concentrations of fat and grease. Anionics are used in industrial detergents, heavy-duty laundry formulations, and a few household applications. Figure 1a shows a molecule of a common anionic surfactant called sodium dodecylbenzene sulfonate (DDBS). A comparison of DDBS with a typical soap, sodium stearate, shows many points of similarity. Both have long, nonpolar hydrocarbon chains that are soluble in fats and oils. Also, they both have a charged, water-soluble portion.

As you might suspect from this comparison, soaps and detergents attack grease and oil in much the same way. Normally, oil and water do not mix. If oil and water are stirred vigorously, tiny droplets of oil will spread throughout the water, giving a milky appearance. This combination, called an *emulsion*, is only temporary, and the oil will soon gather in a layer on the top of the water. When soap or detergent is added, the droplets of oil are stabilized and remain mixed with the water. The molecules of soap or surfactant perform this trick by dissolving their polar (charged) end in water and their nonpolar (uncharged) end in the oil, as shown in Figure 1b.

The other major surfactant type, *nonionics*, contains no ions. They rely on the presence of many polar oxygen atoms in their structure to make them soluble in water. Figure 2 shows a nonionic surfactant. Nonionics do not produce the heavy suds that anionics ionics do, nor do they remain as effective after heavy doses of fat and grease. They are used for lighter cleaning chores such as car washes, liquid laundry detergents, and detergents used for washing dishes by hand. The nonionics make up about 25% of the detergent market.

Several other types of surfactants account for about five percent of the total market. Chief among these are the *cationics* that go into the production of fabric softeners.

Despite the similarities between detergents and soap, detergents have one advantage over their soap counterparts that immediately made them popular. Household water often contains dissolved minerals. If the water has a high concentration of magnesium ions,  $\text{Mg}^{2+}$ , or calcium ions,  $\text{Ca}^{2+}$ , it is called *hard* water because it makes it hard to wash clothes properly. Instead of dissolving in the water, the soap combines with these ions to form an insoluble scum that settles onto the clothes, leaving them looking gray and dirty. The synthetic surfactants used in detergents are less likely to form scum in the presence of calcium and magnesium ions, and thus often avoid a washday headache.

## Builders

Table 1 lists some of the common builders and fillers that are mixed with the surfactant in a detergent formulation. The most important of these are the phosphates that play a dual role in the cleaning process. Some phosphates raise the pH of the wash solution. Cleaning agents work better at high pH because the alkalinity helps cut through fats and grease by saponification (partly changing them into soap) and loosens their grip on the surface to be cleaned. Other phosphates are *sequestering* agents. This means that they can attach to  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  so that these ions cannot combine with the surfactants. The hard water is chemically made “soft.”

Another common builder is sodium carbonate,  $\text{Na}_2\text{CO}_3$ , an inexpensive compound that is used to give high pH values in heavy-duty detergent formulations. Silicates are also present in some detergents because they increase alkalinity and protect the metal parts of washing machines against corrosion. An important ingredient in many household formulations is carboxymethyl cellulose (CMC). This derivative of plant cellulose is used to thicken liquid laundry and dishwashing formulations. It also acts as an *antiredeposition* agent, that is, it prevents dirt from settling back on fabric or dishes once it has been removed. CMC is the compound that prevents “spotting” on glasses and dishes washed in automatic dishwashers. The most common *filler* (no cleaning function) is sodium sulfate,  $\text{Na}_2\text{SO}_4$ . It adds bulk to the detergent and helps prevent powdered detergent from caking, but it serves no cleaning function. Other additives that do not add to the cleaning action are whiteners, dyes, fragrances, and germicides.

## The phosphate dilemma

Some states have now banned phosphates from detergents sold within their borders because they lead to an environmental problem called *eutrophication*. Phosphates are excellent plant fertilizers. When waste

water containing used detergents enters a stream or lake, algae start to grow rapidly. This quickly uses up the oxygen dissolved in the water, and fish and plant life die. In liquid formulations, phosphates are often replaced by a chemical with the initials EDTA (discussed in "Lead Poisoning," *Chem Matters*, December 1983) that also sequesters magnesium and calcium. For powdered detergents, there are no substitutes as effective as phosphates, and this is an area of active research.

### **Mystery foam**

In the early 1960s, a problem arose that could have spelled doom for laundry detergents if chemists had not found a solution. Streams, rivers, and lakes around the country developed mysterious blankets of foam. The chemical culprit was soon identified as a surfactant used in laundry detergents. The chemical was turning up in waterways making suds long after the wash water was discarded. Manufacturers had assumed that bacteria in soil and water would decompose the surfactant molecule just as they had decomposed soap molecules for centuries. However, a basic difference in the structures of the soaps and surfactants made the latter immune to bacterial attack. Bacteria simply did not have the necessary enzymes to break down this type of surfactant, called *alkylbenzene sulfonates* (ABS). Like other surfactants, molecules of ABS have a long hydrocarbon chain but, unlike soap, they also have "branches" projecting from the chain, as shown in Figure 3. Although this difference may appear slight, it is enough to prevent biodegradation. Thus the ABS molecule had to be replaced with an unbranched hydrocarbon chain such as the DDBS pictured in Figure 1a.

### **Million\$ for suds**

When a chemist sets out to blend a successful detergent formulation, many factors must be considered. Unusual regional conditions such as extremely hard water or the presence of iron, manganese, and other minerals can alter the formulation. State laws against phosphates must be considered. It is not unusual for many years and millions of dollars to be spent in research and test marketing before a new product is offered to the public.

Detergent formulations are significantly better cleaners than any pure soap product. Today, manufacturers offer effective, well-proven formulations with a "little something extra" added to give their product a competitive edge.

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## CAPTIONS

Tide laundry detergent ingredients: Cleaning agents (anionic surfactants) Water softeners (complex sodium phosphates, sodium carbonate) Processing aids (sodium sulfate) Washer protection agents, fabric whitener, perfume, and an agent to prevent redeposition The surfactants in Tide are biodegradable Contains 8.2% phosphorus, equivalent to 6.3 g per 3/4-cup use

Figure 1a. Soap is attracted to polar water molecules by ionic charges (white) on the carboxylic acid group. The detergent surfactant relies on ionic charges of the sulfonate group,  $-\text{SO}_3^-$

Figure 1b. The nonpolar end of the surfactant is represented by a zigzag line, the polar end by a circle. The stabilized oil droplet, called a *micelle*, can be washed away

Figure 2. A nonionic surfactant molecule. The region near each oxygen atom has a partial electrical charge. The molecule contains no ions, but the polar region (white) makes this end of the molecule attractive to water. The hydrogen atoms have been omitted for clarity.

Table 1. Some common ingredients found in detergent formulations

Figure 3. ABS, a very effective surfactant, was used in many laundry detergents. Because natural bacteria could not break it down, it accumulated in streams and produced suds

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## BIOGRAPHY

**Clair G. Wood** worked several years for a detergent manufacturing firm and wrote the article "SOAP" for the February 1985 issue of Chem Matters. He currently teaches chemistry at Eastern Maine Vocational Technical Institute in Bangor, Me.

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