Section 17.2

Laundry

Whether you wash your clothes at home or send them to a laundry, you expect them to come out clean and crisp, looking and feeling as they did when they were new. The dirt, oils, perspiration, and stains should all have vanished, leaving the fabrics and their colors completely intact. Moreover, the clothes should retain their shapes, sizes, structures, and surface textures. With so many expectations, it's no wonder that the word "miracle" appears so frequently in advertisements for laundry detergents.

Achieving these many goals is something of a balancing act. The chemicals that contaminate clothes aren't always so different from those that give them their structures and colors. Trying to remove one chemical while leaving the other isn't easy and washday in the nineteenth century was hardly a treat for the garments being cleaned. However, in recent years laundering has developed from a simple art to an advanced technology. The miracles promised by the detergent commercials are almost reality. In this section, we'll examine physical and chemical mechanisms that make those miracles possible.

Questions to Think About: *How do soaps and detergents help to clean clothes? What is the difference between a soap and a detergent? What is hard water and how do you "soften" it? Why does soap form soap scum in hard water? How do detergents keep soil from redepositing on the clothes? Is dry cleaning really "dry"? Why do some clothes wrinkle and shrink when you wash them in water but not when you dry clean them? How does bleach remove stains? Why do fabric softeners increase the volume and fluffiness of towels? Why do fabric softeners reduce static cling? How do "brighteners" make clothes appear whiter than white?*

Experiments to Do: *You don't have to do laundry to know that soaps and detergents help to remove oil and grease from just about anything. Spread a little oil on a rag or your hand and try to wash it off with water. You'll find that the oil is difficult to remove with water because it doesn't dissolve in water—oil and water don't mix. But if you add a little soap or detergent to the water and try washing again, you'll find that the oil is carried away in the water. The soap or detergent molecules surround tiny droplets of oil and allow the water to remove them.*

Soaps and detergents are remarkable materials. They are "at home" in both water and oil and they assist water in handling oil. That simple fact is the basis for laundering and the central issue in this section.

Soap

One of the most difficult problems in laundering clothes is how to remove all of the different soils in a single operation. Some soils consist of polar molecules, those that have electric charges or electrically charged regions, while others consist of nonpolar molecules, those that are effectively neutral throughout. These two types of soils are so different from one another that a liquid that dissolves one is unlikely to dissolve the other. To make things worse, there are also soils that don't dissolve well in anything, or at least not in anything that you could imagine putting on your clothes. Getting all of these soils out of the clothes without harming the clothes is what laundry is all about.

Polar soil molecules include salts from perspiration and ground dirt. These salts generally dissolve in water, where they become ions that are carried away in

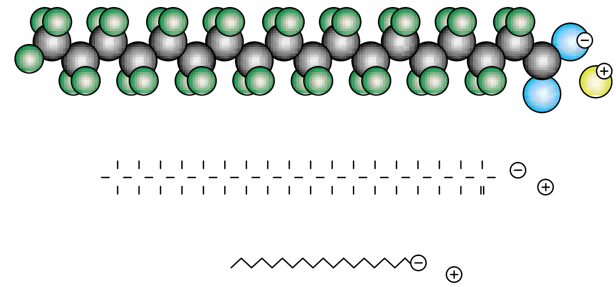


Fig. 17.2.1 - Soap is a peculiar salt. Its negative ion consists of a long hydrophobic (water avoiding) hydrocarbon chain attached to a hydrophilic (water loving) carboxylate group. A nearby positive ion, usually sodium (Na), balances the negative charge of the carboxylate group. A soap molecule can be represented as (*a*) balls, (*b*) letters, or (*c*) a zigzag hydrocarbon chain with charges attached to it.

shells of water molecules. Because they are basically at home in water, these polar soils are described as **hydrophilic** (water loving). Because carbohydrates such as sugar have electrically charged regions and form hydrogen bonds with water, they dissolve easily in water and are thus also hydrophilic.

Nonpolar soil molecules include oils, fats, and waxes from skin, foods, and plants. These oily molecules tend to dissolve in nonpolar solvents such as gasoline or kerosene. Because they can't form hydrogen bond with water molecules, they don't bind well with water and are essentially insoluble in it. These nonpolar soils are described as **hydrophobic** (water avoiding).

You could launder your clothes by first washing them in water to dissolve and remove hydrophilic soils and then laundering them in gasoline to dissolve and remove hydrophobic soils. But this would take a long time and would be very hard on the fabric. After the process was over, your clothes would have aged considerably, yet some of the soils would still remain. Cleaning clothes requires something more than water and gasoline. That's why we use soaps, detergents, bleaches, and brighteners in our laundry.

Soap is a peculiar type of salt. Like all salts, soap contains a mixture of positively and negatively charged ions (Fig. 17.2.1). There is nothing special about the positive ions, which are usually just sodium or potassium atoms that are missing an electron. What makes soap so unusual and so effective at cleaning is its negative ions. The negative ions in soap have the negative charge located at one end of a very long molecule. The other end of the molecule is an uncharged hydrocarbon chain such as those encountered in oil molecules.

The negative soap ion is so long that its two ends operate independently. Its charged end is polar and hydrophilic. Water molecules cling to this end's electric charge and try to carry it into solution. But the soap ion's hydrocarbon end is nonpolar and hydrophobic. This end of the soap molecule is expelled from water but binds nicely to oil molecules.

The one half of a soap ion is at home in water and the other half is at home in oil. The hydrophilic end is attracted to water while the hydrophobic oil end is attracted to oil. This split affinity causes soap ions to accumulate at interfaces between water and oil (Fig. 17.2.2). The negative ions spontaneously orient themselves at such an interface with their electrically charged ends in the water and their hydrocarbon ends in the oil. The positive ions hover around in the water near the interface to keep everything electrically neutral.

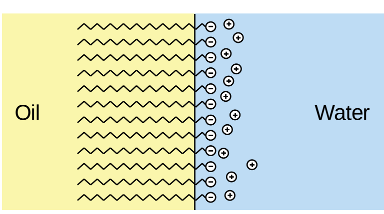


Fig. 17.2.2 - Soap negative ions move spontaneously to interfaces between water and oil. Their hydrophobic ends project into the oil and their hydrophilic ends project into the water.

This tendency for soap ions to order themselves at interfaces is an example of *self-organizing behavior*. While mixtures of table salt and water are random and homogeneous, mixtures of soap and water are not. Even when there's no oil present, soap ions migrate to water's surface because individual soap ions don't mix freely with the water. Since water molecules don't bond well to the nonpolar hydrocarbon chains, the water molecules push the soap ions to the water's surface.

A tiny amount of soap added to a bowl of water soon creates an ultra-thin layer of soap ions on the surface of the water—a layer that's only a single molecule thick. The soap ions arrange themselves with their polar ends in the water and their nonpolar ends in the air. The uppermost water molecules in the bowl

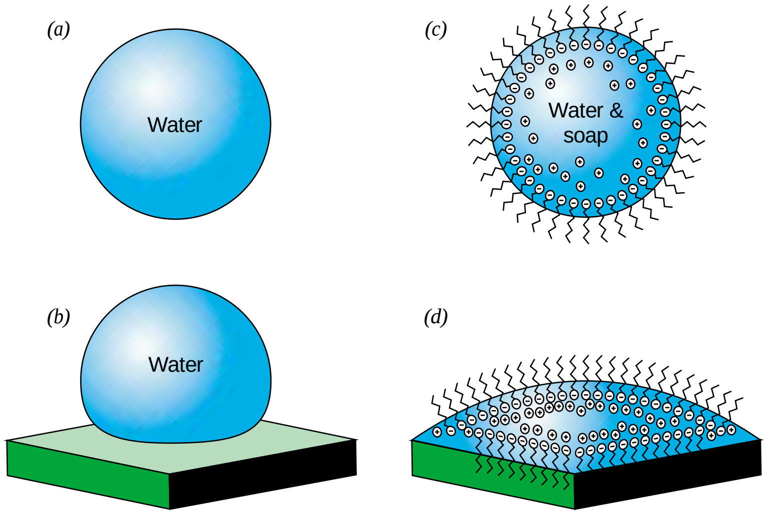


Fig. 17.2.3 - (*a*) Surface tension in pure water causes its droplets to be spherical. (*b*) These water droplets remain almost spherical on many surfaces. (*c*) Soap ions coat the outside of a water droplet and dramatically reduce the surface tension. (*d*) The soapy droplet is able to spread out more easily and wets many surfaces completely.

are then able to hydrogen bond to the soap ions above them and don't pull together as strongly as they would if they had only air above them. Thus the water molecules contribute little to the liquid's surface tension.

The hydrocarbon chains of the soap ions now form the uppermost layer in the liquid. With nothing above them to stick to, these chains pull together and create surface tension. However they attract one another with van der Waals forces, not hydrogen bonds, and create a surface tension only about 30% that of water molecules. The soap's presence in the water significantly reduces its surface tension.

This reduced surface tension is soap's first contribution to the laundering process. Pure water keeps to itself, beading up on any surface that doesn't bind strongly to water molecules (Fig. 17.2.3*a*,*b*). Surface tension makes falling water droplets spherical and they remain almost spherical on oily, hydrophobic surfaces. But adding just a tiny bit of soap to the water reduces each droplet's surface tension and allows it to wet the surface (Fig. 17.2.3*c*,*d*). A soapy droplet spreads outward because van der Waals forces attracting the droplet to the surface are strong enough to stretch it out into a flat puddle.

In effect, soapy water is "wetter" than pure water. Soapy water doesn't bead up on fabrics; it soaks right in. When you are cleaning clothes and want the water to wet every fiber in the fabric, you add soap to the water. Because soap helps water to wet surfaces, it's a **wetting agent**. It's also a **surfactant** or *surface-active agent* because of its tendency to modify the properties of surfaces or interfaces. There are other kinds of surfactants, but soaps and soap-like materials are the most important group.

However, not all soap molecules make it to the water's surface. If you put lots of soap in the water, or the surface is far away, the soap ions assemble themselves into spherical structures called **micelles** and remain inside the water (Fig. 17.2.4). In these micelles, all of the soap ions are oriented with their charged, polar ends pointing outward and their uncharged, nonpolar ends pointing inward. The water molecules stick to the micelles' polar outsides and carry the micelles about. As usual, the positive soap ions hover about nearby to keep everything electrically neutral.

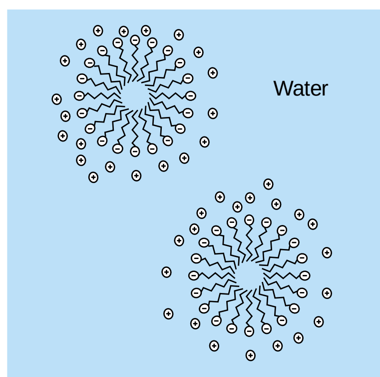


Fig. 17.2.4 - In water, negative soap ions form spherical micelles. The hydrophobic chains form the centers of these micelles and tend to accumulate oily soil molecules.

These micelles are soap's second contribution to the laundering process. They tend to trap and collect oily soil molecules. The inside of a micelle is a nonpolar environment and ideal for oil molecules. When an oil molecule bumps into a micelle, the water pushes it into the center of the micelle and there it remains.

The micelles in soapy water move randomly, collecting any oil molecules they encounter in their travels. With a little thermal or mechanical agitation, micelles can even pluck oil molecules from the surfaces of fabrics. Naturally, this is helpful when you are doing laundry. Little by little, the oily soils in the clothes become trapped in micelles in the water.

Soap also helps to remove insoluble debris from clothes. Micelles form around dust particles and help the water to carry these particles away. Since most dust particles don't dissolve in any liquids, soap micelles are essential to their removal from clothing.

Since soap micelles are composed of negatively charged soap ions, they are negatively charged objects and tend to repel one another in the water. They remain separate and mobile and are easily washed down the drain along with their contents. In fact, most fabrics also become negatively charged in water. Their fibers include weakly attached hydrogen atoms that are carried away as positive ions by the water. The fibers are left with negative charges and they tend to repel the negatively charged soap micelles. This repulsion prevents soils from redepositing on the clothes.

This arrangement, soap micelles in water, is a stable emulsion. Unlike a simple mixture of oil and water, it doesn't separate when you let it sit. A surfactant that helps to form and stabilize emulsions is called an **emulsifier**. Emulsifiers are particularly important in food preparation, where egg yolks, lecithin, and various gums are used to make mayonnaise, chocolate, and other foods smooth and creamy.

Soap is clearly useful in laundering clothes, but where does it come from and what is its structure? Soap is made from naturally occurring oils and fats. Each molecule of oil or fat consists of three **fatty acid** molecules bound to a glycerin molecule. A fatty acid molecule resembles a paraffin or olefin molecule, with its long chain of carbon atoms surrounded by hydrogen atoms. But the fatty acid molecule has a special arrangement of carbon, oxygen, and hydrogen atoms, a *carboxylate group*, at one end that makes it an organic acid (Fig. 17.2.5).

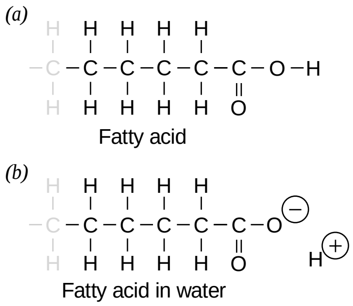


Fig. 17.2.5 - (*a*) A fatty acid is a long hydrocarbon chain ending in a carboxylate group. (*b*) In water, the carboxylate group's hydrogen atom is carried away by water molecules as a positive ion, leaving the rest of the molecule negatively charged.

An acid is a molecule that can easily lose a positively charged hydrogen ion when it is mixed with water. One of the hydrogen atoms at the special end of the fatty acid falls off easily because the adjacent oxygen atom has largely removed its electron. Oxygen and hydrogen form a covalent bond, with a pair of electrons between them, but the oxygen atom attracts the pair of electrons more strongly than the hydrogen atom does. As a result, the hydrogen atom's nucleus is relatively exposed and is easily carried away by passing water molecules. This loss leaves a negatively charged fatty acid ion.

In an oil or fat, these three fatty acid molecules are not ionized. Instead, they have reacted with a glycerin molecule like three large ships docking at a small port. The glycerin molecule has a chain of three carbon atoms and each of these carbon atoms plays host to one of the fatty acids (Fig. 17.2.6). The resulting structure is called a **triglyceride**. Assembled in this manner, the triglyceride is nonpolar and virtually insoluble in water. It looks and feels like petroleum oil

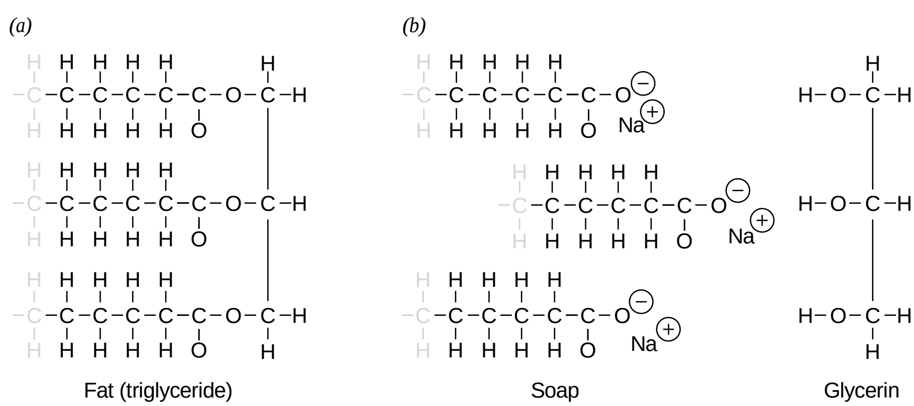


Fig. 17.2.6 - (*a*) A fat molecule or triglyceride consists of three fatty acids bonded to a glycerin molecule. When the triglyceride reacts with sodium hydroxide (lye), the fatty acids break free of the glycerin and produce a mixture of soap and glycerin (*b*).

because both have the same long hydrocarbon chains. However triglycerides are digestible while petroleum oils are not.

Triglycerides composed entirely of paraffin-like fatty acids are called **saturated fats** because they have only single covalent bonds and as many hydrogen atoms as possible. Such molecules experiences strong van der Waals forces, forming fats that remain solid at relatively high temperatures. These fats are found in animals and tropical plants such as palms and coconuts.

Triglycerides containing olefin-like fatty acids are called **unsaturated fats** because they have double bonds that reduce their hydrogen atoms count. Double bonds stiffen the hydrocarbon chains and prevent them from bonding as strongly to one another. Oils contain these molecules melt at relatively low temperatures and are found in fish and temperate plants such as soybeans and corn. Unfortunately, people find the less healthy saturated fats more tasty and satisfying than the unsaturated fats. Converting unsaturated fats to saturated fats, a process called **hydrogenation**, is commonly used to stiffen oils for use in foods such as margarine and candy.

Soap enters into this picture when triglycerides react with sodium hydroxide (lye). Sodium hydroxide is a salt consisting of positive sodium ions and negative hydroxyl ions (a hydrogen and an oxygen atom together) and it rapidly dissolves into independent ions when you put it in water. When you mix fat, water, and lye together, the hydroxyl ions from the lye attack the fat molecules and remove the fatty acids from the glycerin as negative ions (Fig. 17.2.6*c*). Soon the water is filled with glycerin molecules, negative fatty acid ions, and positive sodium ions. When the reaction is complete and most of the water is removed, the result is soap. The glycerin may or may not be removed.

The hardness of the soap depends on the fats from which it was made. Saturated fats produce hard bar soaps while unsaturated fats produce soft liquid soaps. Soft hand soaps often include the glycerin. While most modern soaps are made with lye and are thus sodium salts, earlier soaps where made with potassium hydroxide obtained from wood ash and lime and were potassium salts.

CHECK YOUR UNDERSTANDING #1: Walking On Water
A water strider is a bug that walks along the surface of water, supported by surface tension. When add a little soap to the water, the bug can no longer stand on the water. Why not?

Water Softening

Unfortunately, laundering clothes isn't quite this easy. While soap is wonderful at removing oils and fats from fabric, it has problems in hard water. **Hard water** is any water with more than about 120 milligrams of positively charged calcium and magnesium ions per liter. These two metal ions, and a few others, bind with the negative soap ions and form insoluble soap scums that deposit themselves on sinks, showers, bathtubs, washing machines, and clothing. If you try to launder clothes with soap in hard water, you are in for a messy surprise.

The problem occurs because calcium and magnesium ions behave differently from the ions of sodium and potassium normally found in soap. Sodium and potassium atoms each have one more electron than they need to complete an electronic shell—a quantum physical structure that is particularly stable. That extra electron is relatively easily removed, creating a positively charged ion that is easily drawn into solution in water. Water is so strongly attracted to sodium ions that almost every sodium salt in existence dissolves in water. Sodium's fantastic solubility explains why there is so much sodium in seawater. Potassium

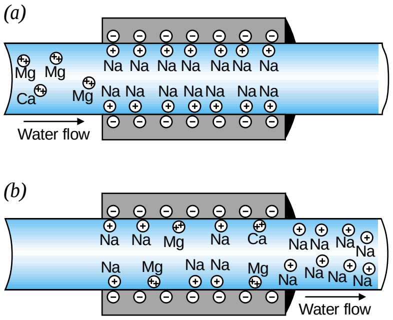


Fig. 17.2.7 - (*a*) A fresh ion exchange water softener contains sodium ions, located near negatively charged sites in a resin or zeolite ceramic. (*b*) As water containing magnesium (Mg) and calcium (Ca) ions passes through the softener, the sodium ions are released and the magnesium and calcium ions remain behind.

ions are almost as soluble as sodium ions. Salts consisting of sodium or potassium positive ions and soap negative ions are extremely soluble in water.

But calcium and magnesium atoms have two more electrons than they need to complete an electronic shell. They give up those two electrons somewhat reluctantly to form positively charged ions and aren't particularly soluble in water. While some calcium and magnesium salts are modestly soluble in water, calcium and magnesium soap salts are not.

When you put soap in hard water, the positive calcium and magnesium ions in the water combine with the negative soap ions and quickly form insoluble salts. These salts are pasty solids that cling to everything. If you want to do laundry in a place where the water contains substantial amounts of dissolved minerals, you must either remove the calcium and magnesium ions from the water or replace the soap with something else. Actually, you often do both.

Removing the calcium and magnesium ions is the first option. This step is called *water softening* and is done routinely in most industrial laundries long before the water enters the washing equipment. There are several different ways to soften water, but the most interesting scheme and the one used most often in houses is called **ion exchange**. The water passes through an ion exchange material that replaces the calcium and magnesium ions with sodium ions (Fig. 17.2.7).

The ion exchange material is a special ceramic (zeolite) or plastic resin with many negatively charged regions in its porous structure. To keep the material electrically neutral, a positive ion is located near each negative region. The negative regions are part of the material, so they can't go anywhere, but the positive ions are mobile.

When the ion exchange material is fresh, nearly all of the positive ions inside it are sodium ions. As hard water flows through the material, the sodium ions are gradually replaced by calcium and magnesium ions. Since the sodium ions are more soluble in water than the calcium and magnesium ions, the sodium ions tend to enter the water and the calcium and magnesium ions tend to leave it. Each calcium or magnesium ion that sticks to the ion exchange material releases two sodium ions, which leave the water softener in the water itself.

While the water leaving an ion exchange water softener still contains dissolved ions, they are sodium ions rather than calcium or magnesium ions. The sodium ions cause no trouble when laundering clothes or washing your skin, but people who are on low sodium diets should avoid softened water. Moreover, you shouldn't use softened water in a steam iron.

When all of the sodium ions in the ion exchange material have been replaced by calcium or magnesium ions, the water softener stops softening the water. To regenerate the ion exchange material, you must flush it with very concentrated salt water. The many sodium ions in the salt water dislodge most of the calcium and magnesium ions and return the ion exchange material to its original condition—it is once more full of sodium ions and ready to soften water.

Because many homes don't have water softeners, most laundry soaps soften the water themselves. They contain chemicals called **builders** that bind to the calcium and magnesium ions and keeping them away from the soap ions. The most effective of these builders is sodium tripolyphosphate and, at one time, most household detergents contained large amounts of it. However, phosphates encourage the growth of algae, threatening the ecologies of rivers, lakes, and bays, and have been banned from detergents in many regions. Builders such as sodium carbonate, citric acid, and sodium citrate are now often used instead.

Another building technique used in some products is to incorporate small zeolite ceramic particles directly in the detergent. These builder particles exchange sodium ions for calcium and magnesium ions and soften the water directly in the washer. They fall to the bottom of the washer and are rinsed away

CHECK YOUR UNDERSTANDING #2: Hard to Lather
When you wash your hands in well water, you often find that the bar of soap makes very little lather and leaves a waxy white scum on the sink. What is going on?

Detergents

But water softening is only half the solution. Because it's hard to eliminate all of the calcium and magnesium from water, the manufacturers also eliminate the soap from the laundry powder. That's right—most laundry detergents aren't soap at all. Instead, they are synthetic **detergents** that are structurally related to natural soap but aren't quite the same.

Actually, soap is a type of detergent. Detergents are a broad class of molecules that stabilize mixtures of oil and water. There are many other kinds of molecules that can perform this task and thus many types of detergents.

The most common laundry detergents are the linear alkylbenzenesulfonates (Fig. 17.2.8*a*). These petroleum products are sodium salts, just like most soaps, but the structures of the negative ions are different. Recall that a negative soap ion is a long hydrocarbon chain attached to a negatively charged carboxylate group. The detergent ion is also a long hydrocarbon chain, attached to an aromatic or benzene ring, attached to a negatively charged sulfonate group. The sulfonate group involves one sulfur atom and three oxygen atoms.

The two important parts of the detergent molecule are the charged head and the long nonpolar tail. The charged end is a *sulfonate group* in which a sulfur atom attaches to four other atoms: a carbon atom and three oxygen atoms. This arrangement is roughly tetrahedral in shape. But sulfur normally attaches to only two atoms, so how is this arrangement possible?

First, the sulfur atom forms normal covalent bonds with the carbon atom and with one of the oxygen atoms. That oxygen atom has an extra electron, making it a negatively charged ion that can only form a single covalent bond.

Second, the sulfur atom allows each of the two other oxygen atoms to share a pair of its electrons. Because these shared electrons can travel between both atoms, their wavelengths increase and their kinetic energies decrease. In this manner, the oxygen atoms become attached to the sulfur atom. The overall result is a negatively charged structure that's easily carried about by water molecules.

The detergent molecule's long nonpolar tail is essentially an unbranched paraffin chain, also referred to as a *linear alkyl group*. This chain provides the oily

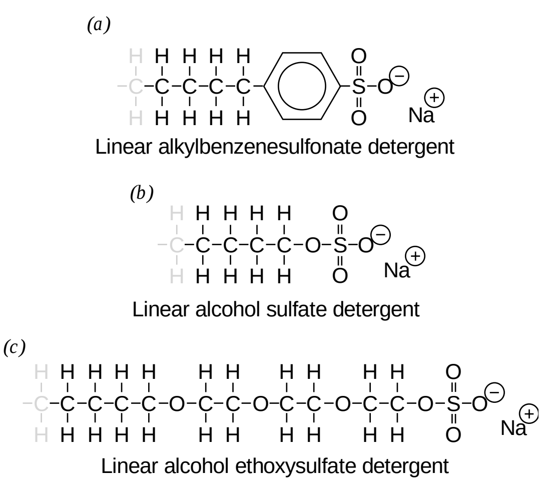


Fig. 17.2.8 - (*a*) The most common laundry detergent has an aromatic or benzene ring connecting a long hydrophobic hydrocarbon chain to a hydrophilic sulfonate group. Common shampoo detergents connect the chain to the sulfonate with either (*b*) an oxygen atom or (*c*) a string of oxygen and carbon atoms.

tail of the detergent molecule. While early alkylbenzenesulfonate detergents included branched paraffin chains, these proved to be less biodegradable than the linear versions. Bacteria can metabolize long linear chains because those chains are common in animals and plants, but branched chains are rare in nature and bacteria are unprepared for them. To keep detergent foam out of streams and lakes, manufacturers have learned to produce purely linear detergent molecules.

The last piece of the detergent molecule is the aromatic or benzene ring. This ring is a vestige of the manufacturing process. It's much easier to attached the linear alkyl tail and the sulfonate head separately to an aromatic ring than it is to attach them directly to one another. Unfortunately, the ring actually reduces the biodegradability of the molecule somewhat. There are other detergents, such as linear alcohol sulfates and linear alcohol ethoxysulfates, in which the aromatic ring is replaced by an oxygen atom (Fig. 17.2.8*b*) or a string of oxygen and carbon atoms (Fig. 17.2.8*c*). The most common linear alcohol sulfate is sodium lauryl sulfate, with 14 carbon atoms in its hydrophobic chain. Sodium laureth sulfate is a common linear alcohol ethoxysulfate, also with 14 carbon atoms in its chain. These detergents are derived from tropical oils and often used in shampoos and dishwashing liquids.

Since calcium and magnesium ions don't cause these sulfonate or sulfate detergents to form insoluble detergent scums, why do laundry detergents still worry about softening the water? Unfortunately, calcium and magnesium ions interfere with the micelles, making it difficult for them to extract soil from fabric and keep it suspended in water. Because each calcium or magnesium ion has twice the positive charge of a sodium or potassium ion, these highly charged ions approach the micelles closely and partially neutralize their surfaces. Since these neutralized micelles don't repel one another or the fabric well, they do a poor job of cleaning clothes. That's why laundries and laundry detergent still work to remove the calcium and magnesium ions.

Before leaving detergents, it's worth noting that not all detergents are negative ions (**anions**). It's also possible to construct detergent molecules that are positive ions (**cations**) and even ones that aren't ions at all. However, cationic detergents and surfactants aren't used in laundry detergents because they tend to stick to fabric—we'll discuss their use as fabric softeners later on. But nonionic detergents are often used to launder clothes.

The only requirement for a detergent is that its molecules stabilize a mixture of oil and water. Nonionic surfactant molecules don't have an electric charge, but they do have a hydrophilic end and a hydrophobic end (Fig. 17.2.9). Like most detergents, the hydrophobic end is just a long hydrocarbon chain. But the hydrophilic end is also a long chain, consisting of oxygen and carbon molecules attached one after the next and decorated with hydrogen atoms. The oxygen atoms in this special chain form hydrogen bonds with water molecules, giving that end of the molecule its hydrophilic character. These nonionic molecules form micelles and are very effective at removing grease.

Nonionic surfactants are unaffected by hard water and are actually better than anionic detergents at removing some soils—they are particularly good at removing skin oils from synthetic fabrics. However, they aren't salts and exist either as liquids or waxy solids. As a result, nonionic surfactants are difficult to formulate into powdered detergents but are common in liquid detergents.

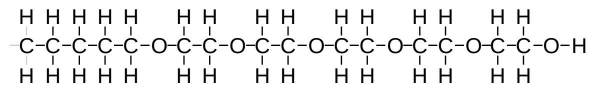


Fig. 17.2.9 - Nonionic surfactants have a hydrophobic hydrocarbon chain (on the left) attached to a hydrophilic chain containing oxygen atoms (on the right).

CHECK YOUR UNDERSTANDING #3: Getting the Grease Out

Oils are not soluble in water yet they are easily removed from fabric by water that contains even a small amount of detergent. Why does this small amount of detergent make such a difference?

Bleaches and Enzymes

Not all soils can be removed from fabrics with detergent and water. Molecules that form covalent bonds with the fabric create stains that can only be eliminated with bleaches or enzymes. **Bleaches** act to destroy the coloration of stain molecules or to cut them free from the fabric. **Enzymes** act to dice up large stain molecules into smaller fragments that can be washed away. With a little luck, these steps can be taken without destroying the fabric or its color.

Unlike soaps and detergents, bleaches react chemically with the soil molecules. They are particularly aggressive at converting double bonds to single bonds by attaching oxygen and chlorine molecules to the two atoms involved. Double bonds often give organic molecules their colors so this sort of rearrangement tends to make them colorless.

Just as atoms absorb and emit photons of light that are characteristic of their electronic states, so molecules absorb and emit photons that are characteristic of their electronic states. Each electron in a molecule is sensitive to passing electromagnetic radiation and responds to photons that can transfer it to some unoccupied state with more energy. If the electron finds such a photon, it may undergo a radiative transition to the excited electronic state and absorb the photon. The electron will eventually return to its original state, converting the extra energy into thermal energy, but the photon will be gone forever. If a particular molecule contains electrons that can absorb photons of visible light in this manner, it will appear colored.

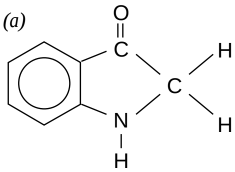
In most single covalent bonds, the two electrons are bound so tightly between the two nuclei that any transition to a new electronic state requires more energy than a photon of visible light can provide. Only ultraviolet light can cause radiative transitions in these electrons. Molecules based entirely on single covalent bonds are normally unaffected by visible light and are thus colorless.

However, the outer electrons in a double covalent bond aren't so tightly bound and can be transferred to other electronic states relatively easily—a photon of visible light may well be able to cause the transfer. A double bond that absorbs blue photons from passing light appears yellow. One that absorbs red photons appears cyan. The usual rules of subtractive color apply.

Just how much energy it takes to cause this transfer depends on the chemical nature and environment of the double bond. Most important are the two atoms joined by the double bond. In addition to double bonds involving a pair of carbon atoms, there are also carbon-oxygen, carbon-nitrogen, nitrogen-oxygen, and nitrogen-nitrogen double bonds. These double bonds are often colored, particularly the latter two. Groups of atoms that give rise to color in molecules are called **chromophores**.

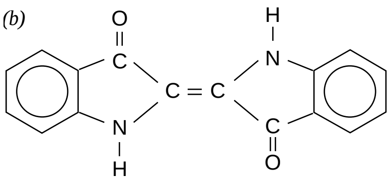
However the exact color of a double bond is determined by the detailed structure of the molecule around it. Since all of the electrons in that molecule affect one another through electrostatic forces and the Pauli exclusion principle, the whole molecular structure contributes to the color of the electrons in the double bond itself. A subtle change in a molecule's structure may change its color from

(a)



Indoxyl

(b)



Indigo

Fig. 17.2.10 - (*a*) Indoxyl is a colorless, water-soluble chemical obtained from a fermented plant extract. When indoxyl is exposed to oxygen in the air, it reacts pairwise to form water-insoluble indigo (*b*), the blue dye used in blue jeans. The double bonded carbon atoms at the center of this molecule are the chromophore and the rest of the molecule determines the precise color of the dye. Bleaches and ultraviolet light can destroy the double bond, giving blue jeans a faded look.

red to orange. That's how organic dye manufacturers construct rich pallets of colors from a small number of different chromophores (Fig. 17.2.10).

Colored molecules are wonderful if you are an artist, but you don't want extraneous ones attached to your clothes. That's where bleach comes in. Bleach attacks double bonds, destroying the chromophores in the stain molecules. The molecules may remain on the fabric but they no longer absorb visible light.

The two major classes of bleaches are chlorine bleaches and oxygen bleaches. The chlorine bleaches tend to put chlorine and oxygen atoms on the two atoms involved in a double bond. The double bond vanishes as one of its atom binds to a chlorine atom and its other atom binds to the oxygen atom of a hydroxyl group (OH).

Unfortunately, chlorine bleaches are so effective at attacking chemicals that they damage the clothes, too. Sometimes they destroy the chromophores in dye molecules, turning colored fabric white. Other times they modify the dye molecules and change the fabric's color. But chlorine bleaches also damage natural fibers themselves, breaking up their molecules and weakening the fabric. While chlorine bleach may succeed in cutting stain molecules free from your clothing, it may also cut holes in the clothing itself.

Oxygen bleaches used hydrogen peroxide to attack double bonds. A hydrogen peroxide molecule is a water molecule with an extra oxygen atom inserted between the oxygen atom and one of the hydrogen atoms. This molecule decomposes in water and its fragments, either ions or free radicals, attack double bonds. Once again, they destroy chromophores and decolorize stains.

Hydrogen peroxide is less reactive than chlorine bleach and causes less fabric damage. It's also less damaging to commercial dye molecules than chlorine bleach. However, since hydrogen peroxide is often used to bleach hair, oxygen bleaches can obviously destroy the colors in some natural fibers.

Hydrogen peroxide itself is rather unstable and is often generated right in the washer by the decomposition of another molecule, sodium perborate. This decomposition occurs only above about 50 °C, so bleaching must be done in hot water. Some laundry detergents contain activators that help sodium perborate decompose in cooler water but it still works best in hot water.

Enzymes are biological catalysts. Your body uses a great many different enzymes to catalyze various chemical reactions that would otherwise rarely occur at body temperature or that might proceed along the wrong paths without help. Enzymes help to construct molecules, to take them apart, or to rearrange their components.

The enzymes used most often in detergents are those that degrade proteins. Protein molecules cling tightly to fabrics, are insoluble in water, and prevent detergents from penetrating to the fibers. They act as binders for other molecules, creating stains that are hard to remove. Familiar proteinaceous stains include blood, milk, eggs, and gravy.

The most effective way to remove these stains is by taking the protein molecules apart. This decomposition is done by *proteolytic enzymes*—enzymes that catalyze reactions between water and protein. In these reactions, protein molecules are broken up and water molecule fragments cap the severed ends. In time, proteolytic enzymes can dice up long protein molecules into their constituent parts: *amino acids* and short sequences of amino acids called *peptides*. The stain falls apart and is carried away by the water and detergents. Meat tenderizers operate in a similar fashion, using papain—a proteolytic enzyme extracted from unripe papaya—to degrade protein in meat before cooking.

However, proteolytic enzymes may have an effect on the people who use them. You certainly don't want the protein in your body decomposed while you do laundry or while you wear freshly laundered clothes. Although studies seem to indicate that the enzymes in household detergents pose no serious health threat, they're used sparingly in detergents to avoid any possible adverse effects.

CHECK YOUR UNDERSTANDING #4: Fading to White
Long exposure to light often bleaches the colors out of clothes. Why does this happen?

Brighteners and Fabric Softeners

Not all laundry chemicals disappear down the drain when the wash is done. Brighteners and fabric softeners do their jobs by remaining on the clothes long after they leave the drier. Brighteners affect the appearances of the clothes while fabric softeners affect their feels.

With age, white fabrics such as cotton tend to absorb more and more blue light and begin to look yellow (Fig. 17.2.11*b*). Cleaning and bleaching do little to reduce this effect. In fact, bleached fabric molecules tend to appear slightly yellow themselves. The old fashioned solution to the yellowing problems was to adding *bluing* to the wash. This blue dye absorbed red and green light, balancing the blue absorption of the fabric itself so that the fabric appeared colorless. To mask the yellowing of age, bluing darkened the whole fabric to a light gray—the amount of light reflected by the fabric was noticeably less than that striking it.

Instead of using bluing, virtually all modern laundry detergents add chemicals that optically brighten the fabric. These **brighteners** are actually fluorescent dyes, designed to absorb ultraviolet light and emit bluish-white visible light. Instead of absorbing red and green light to balance the white appearance of a fabric, the brighteners reintroduce the missing blue light (Fig. 17.2.11*c*). They work best in sunlight, which is rich in ultraviolet light. A brightener molecule absorbs a photon of ultraviolet light and reemits it as a photon of blue light. The energy not reemerging from the molecule in the second photon is converted through vibrations into internal energy in the clothes.

When clothes are washed in these fluorescent dyes, the dye molecules stick to the fabric to create brightened fabric. We can't see the ultraviolet light that the brightened fabric absorbs but we can see the bluish light that it emits. With the missing blue light restored by this fluorescence processes, the brightened fabric appears dazzlingly white. In fact, it may emit more blue light than it is exposed to, making it effectively "whiter than white." In a room illuminated only by ultraviolet light, the brighteners give clothes an eerie violet glow.

Fabric softeners are also chemicals that remain on fabrics after laundering. They are primarily cationic surfactants called *quaternary ammonium compounds*. These compounds are based on the positive ammonium ion, which is itself based on a positive nitrogen ion. A normal nitrogen atom has five valence electrons and must share three of these to reach the four pairs needed to complete an electronic shell. If it shares those electrons with three hydrogen atoms, it forms an ammonia molecule (Fig. 17.2.12*a*). But if it's missing an electron, the nitrogen atom must share four electrons to complete its shell and can actually bind to four hydrogen atoms. In that case, it forms a positive ammonium ion (Fig. 17.2.12*b*).

In quaternary ammonium compounds, a positive nitrogen ion forms covalent bonds with four other atoms. However, these atoms aren't necessarily hydrogen atoms. In fabric softeners, the central nitrogen ion binds to four hydrocarbon chains (Fig. 17.2.12*c*). Two of these chains are short, only one carbon atom

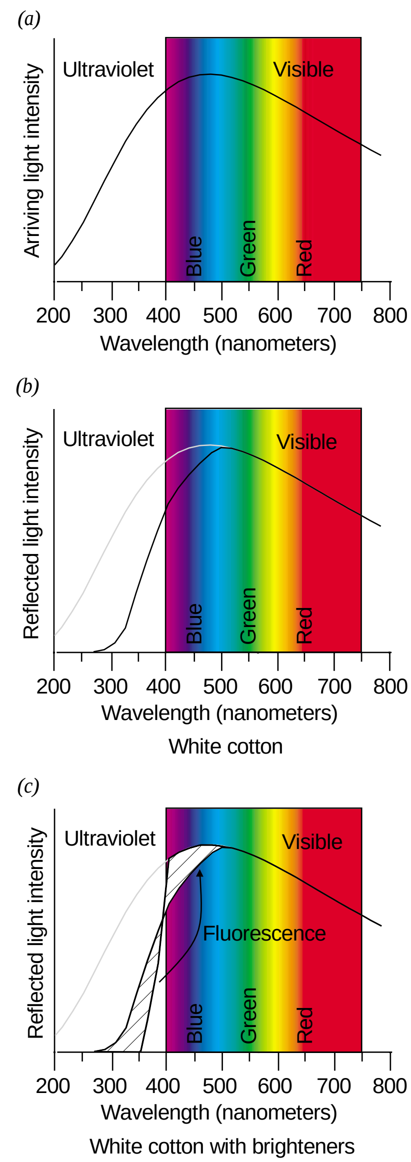


Fig. 17.2.11 - When white cotton cloth is exposed to sunlight (*a*), it reflects a little less blue light than it should (*b*) and appears slightly yellow. This yellowness increases with age. But when fluorescent brighteners are added to the cotton (*c*), they convert ultraviolet light into blue light and make the cloth appear dazzlingly white.

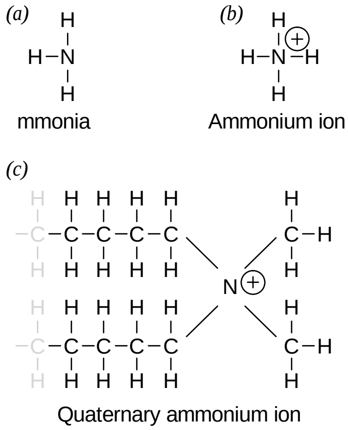


Fig. 17.2.12 - (*a*) An ammonia molecule is three hydrogen atoms bound to a nitrogen atom. (*b*) An ammonium ion is four hydrogen atoms bound to a positively charged nitrogen ion. (*c*) The quaternary ammonium ion used in fabric softeners is formed by replacing the four hydrogen atoms with hydrocarbon chains.

long, while the other two chains may contain as many as 18 carbon atoms. These long chains are hydrophobic and have the same oily character as most lubricants. This oily character is what gives these compounds their fabric softening ability.

When you apply the softener to wet fabric, its positively charged surfactant ions are drawn toward the negatively charged fibers and stick to them strongly. While anionic surfactants are repelled by wet fabric and help to clean it, cationic surfactants are attracted to wet fabric and help to soften it.

The surfactant molecules stick to the fabric with their long hydrophobic chains pointing outward. These molecules decorate every fiber in every thread of the clothing, giving them all an oily coating. The hydrocarbon chains lubricate the fabric so that each fiber slides easily within a thread and each thread slides easily within the fabric. This lubrication enhances the flexibility of the fabric and makes it feel softer and more flexible.

Fabric softeners also make fabric surfaces slightly hydrophobic, so that they dry more easily in the spin dry cycle of a washing machine. In this cycle, the clothes travel rapidly around in a circle, always accelerating toward the center of the circle and experiencing huge inward forces from the washer's metal drum. Water's inertia causes it to lag behind the accelerating clothes and it leaves the drum through perforations. By making the fabric slightly hydrophobic, the fabric softener helps the clothes to shed water as they spin, so that they don't have to spend as much time in a hot drier later on.

Fabric softeners also raise the nap on cotton terry towels. Cotton fibers are normally hydrophilic and cling tightly to water droplets. As water droplets dry up, they shrink and pull the cotton fibers toward one another. By the time an untreated towel is dry, its fibers have been crushed together by these forces and it has little nap. But a towel that has been coated by quaternary ammonium compounds is hydrophobic enough that the water droplets can't pull its fibers together as they dry. The nap remains loose and thick, giving the towel a fluffy appearance and feel. Unfortunately, this same hydrophobic coating slightly reduces the towel's absorbency—a real problem for cotton diapers. To keep it under control, don't use too much fabric softener.

Despite their hydrophobic chains, quaternary ammonium compounds actually attract a few water molecules to the surface of the fabric. They are **hygroscopic**, meaning that they attract water molecules directly out of the air. Since water conducts electricity very weakly, fabric that has been treated with fabric softeners is very slightly conducting. This conductivity reduces the accumulation of static electricity on the fabric and eliminates static cling.

In a drier, untreated clothes rub against one another and sliding friction transfers electric charge from one region of fabric to another. Large charge imbalances are created and the clothes leave the dry clinging to one another with electrostatic forces. However, treated clothes are lubricated in the drier and experience weaker frictional forces. They transfer less electric charge as they tumble and the small charge imbalances that are created quickly dissipate through the moisture attracted by the fabric softener.

Quaternary ammonium compounds are also used in conditioners and shampoos to soften hair and reduce static electricity problems—they will coat and lubricate just about anything. They are actually bactericidal because they coat bacteria and smother them. These compounds also deactivate some of the enzymes in bacteria and upset their metabolisms. Some antiseptic throat lozenges and mouth washes use quaternary ammonium compounds to kill germs.

❒ Softened fabrics were not always the most desirable. At one time, silk, cotton, and rayon were chemically treated to harden their fibers so that they would produce a rustling or swishing sound known as "scroop." This hardening increased the intrafabric friction so that the garments would crackle as they rubbed across one another.

Unfortunately, the positive charges of cationic quaternary ammonium compounds make them relatively incompatible with the negative charges of anionic detergents. When they're present together in the water, these two types of ions attract one another and may clump together. This clumping is avoided by keeping the two types of surfactants separate, which is why softeners are usually added during the rinse cycle, in the drier, or in a separate conditioner when washing your hair. However, some detergent and shampoo formulators have successfully combined cationic softeners and anionic detergents.

CHECK YOUR UNDERSTANDING #5: Looking Cool
When you enter a darkened room illuminated only by ultraviolet light (black light), all of the white fabrics glow blue-white. Why don't any glow red or green?

Detergent Additives

Formulated detergents contain a number of important components that work together to clean clothes. We've already examined the anionic and nonionic detergents (surfactants), the builders (water softeners), the bleaches, and the brighteners. But there are also foam stabilizers, corrosion inhibitors, soil redeposition inhibitors, and processing agents.

Foam stabilizers are there to control bubble formation. These chemicals can either enhance or suppress foaming. Believe it or not, foam is unrelated to a detergent's ability to clean clothes. The same goes for shampoos and dishwashing detergents. However, the amount of foam a detergent produces may influence its use. If the detergent foams excessively, you may think the detergent is more powerful than it is and cut back on the amount you use. As a result, you may not use enough to clean your clothes properly. If the detergent doesn't foam much, you may think that it isn't working and buy another brand. So the detergent and shampoo manufactures carefully control the foaminess of their products.

Air bubbles don't last long in pure water because water's surface tension causes them to tear. The final layers of water molecules on the bubble's outer and inner surfaces pull together so strongly that any tiny defect immediately initiates a rip that lets the air out of the bubble. By reducing water's surface tension, soaps and detergents remove its tendency to rip and stabilize air bubbles.

But how long each air bubble lasts depends on many features of the mixture and not on its ability to clean things. Some surfactant molecules make particularly stable and long lasting bubbles while other molecules deliberately introduce defects that pop the bubbles. Methyl silicone polymers ("methicones") are particularly effective at weakening bubbles so that they tear and collapse. These polymers are common in antifoam additives and are even included in some antiacid tablets.

Foam boosters are common in detergents and shampoos that are used by hand, where foam is regarded as a sign of effectiveness. Antifoaming agents are often used in washing and dishwashing machine detergents where you don't see the foam anyway and foam interferes with the machine's operation.

Corrosion inhibitors are important in detergent because the ions in detergent would otherwise quickly rust the steel in a washing machine. Rusting is an electrochemical reaction of the type explored in the supplement on batteries. In normal rusting, the iron in steel is attacked by negatively charged hydroxyl ions. However other negatively charged ions, including detergent ions, can also attack iron and rust it. So detergents include corrosion inhibitors. These compounds are usually sodium silicates—water soluble glasses that are discussed in Section 17.2. They form thin glassy coatings on the washer parts and inhibit rusting.

Soil redeposition inhibitors enhance the negative charge of wet fabric fibers. Some fabrics, particularly synthetic ones, don't acquire a strong negative charge in water. They need this electrostatic charge to keep the negatively charged detergent micelles from redepositing their soils on the fabric. So detergents include carboxymethyl cellulose, which attaches itself to the fibers and adds to their negative charge.

Finally, processing agents simply give the detergents the right structures in their boxes or bottles. Sodium sulfate helps to bulk up powdered detergent and make it pour easily. Sodium xylene sulfonate helps to keep all of the components of very concentrated liquid detergents in solution.

CHECK YOUR UNDERSTANDING #6: Suds or Duds?

Some dishwashing liquids create lots of long lasting suds while others create relatively little foam. Which of these liquids cleans best?

Dry Cleaning

Washing clothes in water isn't always a good idea. Fibers such as cotton, wool, silk, and rayon, are very hydrophilic and soak up water molecules like sponges. These fibers form hydrogen bonds with water molecules at various sites on their molecules and accumulate large quantities of water. This water takes up space and causes the fibers to swell. Cotton, wool, and silk fibers increase by about 1% in length and about 15% in thickness. Rayon expands even more, by 3% in length and about 25% in thickness. This swelling distorts the fabric and changes its structure. When the fabric eventually dries, it may have shrunk or wrinkled.

To avoid damage caused by this cycle of expansion and contraction, you can send your clothes to be dry-cleaned. Dry cleaning takes place in a nonpolar solvent. Since this solvent doesn't form hydrogen bonds, it's only weakly attracted to the fibers by van der Waals forces and doesn't cause them to swell. The clothes don't lose their shapes.

The solvents used in dry cleaning have evolved over the years since petroleum oils were first found to remove stains. Early dry cleaning was done with gasoline, resulting in many dramatic fires. In 1928, a less flammable solvent became available. The Stoddard solvent, named for the president of the National Institute of Dry cleaning, W. J. Stoddard, is less volatile than gasoline because it contains larger hydrocarbon molecules. It's obtained by distilling crude oil and its vapor will not ignite in air at temperatures below 38 °C.

Nonetheless, Stoddard solvent is still dangerous during hot air drying so nonflammable nonpolar solvents have largely replaced it. The most common solvent in dry cleaning is now perchloroethylene. Its molecule consists of a pair of carbon molecules connected by a double bond and each attached to two chlorine atoms. The chlorine atoms bind so strongly to the carbon atoms that the molecule doesn't react with oxygen and forms a nonflammable liquid.

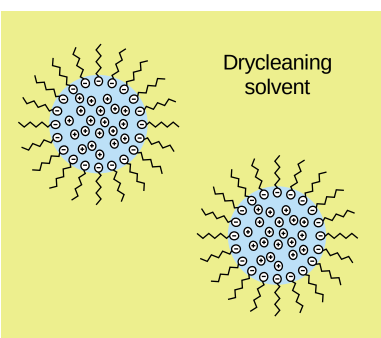


Fig. 17.2.13 - Detergents form inside-out micelles in dry cleaning solvent. The polar hydrophilic ends of the molecules project inward, toward a tiny drop of water. The nonpolar hydrophobic ends project outward into the solvent.

When you put clothes in either Stoddard solvent or perchloroethylene, the oily soils dissolve. These nonpolar solvents attract the oily molecules with van der Waals forces and carry them away. Chlorinated solvents clean better than hydrocarbons because they bind more strongly to oily soils. Chlorine atoms are more polarizable than hydrogen atoms and produce stronger van der Waals forces, which is why perchloroethylene doesn't boil until it is heated to 121 °C.

However, these nonpolar solvents are unable to dissolve salts and other polar soils. They are also poor at removing insoluble soils such as dust. To help in removing these other soils, dry cleaning solvents include detergents and a little water. The detergents form inside-out micelles in the nonpolar solvents, arranged with their nonpolar ends on the outside and their polar ends on the inside (Fig. 17.2.13). Each micelle surrounds a tiny droplet of water. Just as in water cleaning, detergents help to carry away substances that aren't soluble in the principal cleaning liquid.

The water in the dry cleaning mixture is carefully adjusted so that the clothes neither gain nor lose moisture during the cleaning process. In air, water molecules are continually leaving and returning to the clothing and an equilibrium is reached. At this equilibrium, the water molecules still move back and forth but the moisture in the clothing doesn't change significantly. The actual moisture level in the fabric then depends only on the relative humidity of the air, which is typically about 70% in a dry cleaning shop.

The same leaving and returning process takes place in the dry cleaning solvent. Water molecules move back and forth between the fabric and the solvent and establish an equilibrium. Like air, the dry cleaning solvent has a relative humidity and a dry cleaner tries to maintain this relative humidity at the same value as the air in the shop. That way, the fabrics don't accumulate too many water molecules and swell, nor do they lose too many water molecules and dry out. But the polar soils leave the fabrics, become trapped in the detergent micelles, and never return.

With the help of detergents, nonpolar dry cleaning solvents carry away nonpolar, polar, and insoluble soils from clothes without affecting the structure of the cloth. The dry cleaner then removes the solvent from the clothes by spinning them and drying them in hot air. Because solvents are expensive and environmentally damaging, dry cleaners collect the solvents for reused. They do this by filtering and distilling the liquid solvents and by condensing the gaseous solvent molecules onto chilled surfaces. When this type of solvent recycling is done effectively, a dry cleaner can operate for a long time on the same supply of solvent.

CHECK YOUR UNDERSTANDING #7: Salty Stuff

Without adding detergent to the dry cleaning solvent, it will have trouble removing perspiration from clothes. Perspiration is easily removed by water so why does the dry cleaning solvent have trouble with it?