The Chemistry of Stain Removals

Jump To:

Oxidizable Stains and Bleaches

Common examples of oxidizable stains include coffee, lipstick, red wine, and tea stains [1]. Oxidizable stains go through chemical reactions, specifically oxidation-reduction reactions, or redox reactions. An oxidation reaction is the loss of an electron by a molecule or atom. Simultaneously, a reduction reaction is the gain of an electron by a molecule or atom.

What causes stains to be oxidizable?

The color in the pigment of the stain is caused when molecules absorb light in the visible wavelength range (400-780 nm) [10]. The wavelengths that are not absorbed will be reflected instead and are visible to the human eye. For example, red wine stains are red because the molecules absorb every wavelength that is not in the red range, and the red wavelengths (500-600 nm) are then reflected to see.

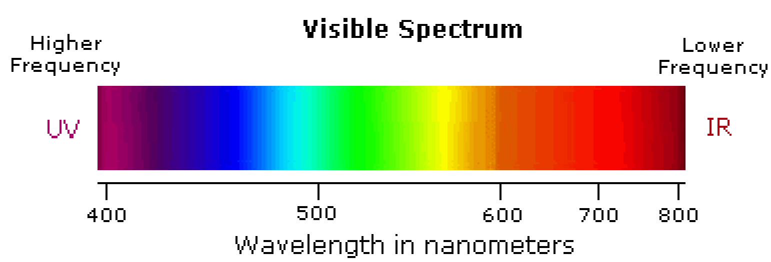

Figure 1: Visible Wavelength [10]

Light is absorbed by chemical molecules which contain an organic compound called chromophores that can cause coloration [1]. As seen in Figure 2 below, chromophores have alternating single and double carbon bonds.

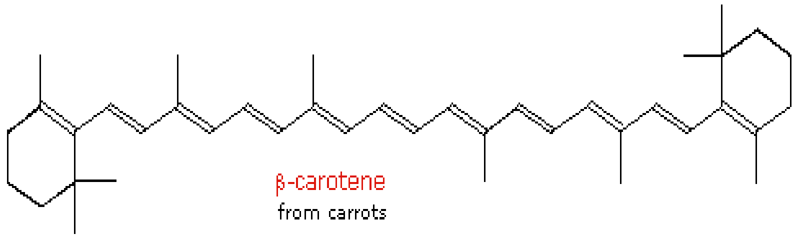

Figure 2: Chromophore Molecule of Carrot Pigments [10]

Bleaches

The best way to remove oxidizable stains is through oxidizing agents, which gain electrons to create the new product, becoming more negative. Oxidizing agents causes reactions to form new chemical compounds. A common oxidizing agent to remove oxidizable stains is bleach. Bleach oxidizes colored substances to become colorless. Bleach functions as a stain remover by breaking bonds within the chromophore to produces smaller fragments which do not absorb light in the visible region of light that people can see [1]. Bleach removes the double bonds from chromophores through a redox reaction by breaking the double bonds into single bonds that do not emit color [9]. In Figure 3, notice the differences between the top and bottom chromophore with the red circle on the bottom that emphasizes the broken chromophore.

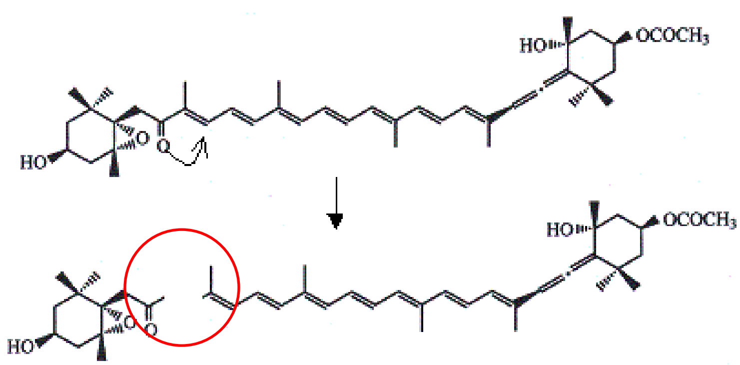

Figure 3: Broken Chromophore [11]

This reaction of broken chromophores is why bleach can leave white spots on colored clothing, so be careful when using bleach. There are two different types of laundry bleaches: chlorine bleach and oxygen bleach.

Chlorine bleach is one of the most powerful stain removals. Clorox and Pure Bright are examples of chlorine bleach. It typically is available in liquid form. Chlorine bleach is based on sodium hypochlorite (NaClO) that is diluted with water to create an approximately 5.25% concentration [3]. With an electrochemical reaction, which is a process that is accompanied by the passage of an electric current to transfer electrons between two substances [4], salt water can produce chlorine gas [5]. By combining chlorine gas (Cl_2) and sodium hydroxide (NaOH), sodium hypochlorite is made, as seen in the reaction below.

$$2\ NaOH + Cl_2 \rightarrow NaCl + NaClO + H_2O$$

Chlorine bleach must be always added with water and mixed well before washing clothes. When the chlorine reacts with water and is diluted even further, hydrochloric acid and oxygen are produced. The oxygen that is then produced reacts with the chromophores to eliminate the portion of its structure that causes the color [4]. Pouring chlorine bleach directly onto fabrics can remove the color completely and dissolve the fabrics. When chlorine bleach is used to wash clothes, it acts as a disinfectant on both bacteria and viruses. Chlorine bleach even whitens most natural fibers like cotton [6]. Because of its powerfulness, chlorine bleach should typically be used on whites to remove stains and odors. Chlorine bleach lifts colors away using oxidation, and even in low concentration bleach can deteriorate garments and fade the color of the fabric over time. The main constituent of chlorine bleach is sodium hypochlorite. Sodium hypochlorite has a pH level of about 11, making it basic, and is very unstable and reactive, making it a strong oxidizer [2]. The intramolecular force, forces within the molecule, consists of an ionic bond with the hypochlorite ion (ClO-) and the sodium ion (Na+). The intermolecular forces, forces between the molecules, are polar dipoles, making NaClO water soluble. Polarity refers to an unequal distribution of electrons due to the partial positive and partial negative charges. Water is also polar due to its partial positive and partial negative charges between positive hydrogen and negative oxygens. Solubility refers to the ability to dissolve, and in this case, dissolve in water.

The other type of bleach is oxygen bleach, which include Oxiclean and Tide Oxi. Oxygen-based bleaches is safer to use on many fabrics. It is typically found in a solid powder state that becomes activated once combined with water. Oxygen bleach is based on sodium percarbonate ($Na_2CO_3 \cdot 1.5H_2O_2$). As shown below, when sodium percarbonate is combined with water, it is broken down into sodium carbonate (Na_2CO_3) and hydrogen peroxide (H_2O_2) [1].

$$2Na_2CO_3.3H_2O_2(aq) \rightarrow 2Na_2CO_3(aq) + 3H_2O_2(aq)$$

The released hydrogen peroxide then becomes the active oxidizing agent, which removes the stain by breaking down the colored section of the chromophores. The main constituent of oxygen bleach is hydrogen peroxide. It is a polar molecule and water soluble due to the hydrogen bonding between hydrogen and oxygen. Therefore, it also reacts well with water, similarly to chlorine bleach. Oxygen bleach is not as strong as chlorine bleach due to different chemical properties. Oxygen bleach is less corrosive, less damaging to fibers, and more environmentally friendly [7]. It is safer to use oxygen bleach on clothes. However, an issue with hydrogen peroxide as an oxygen bleach is that it does not function as a good stain remover below 40˚C. Tetraacetylethylenediamine ($C_{10}H_{16}N_2O_4$), or TAED, can be used as a bleach activator during the bleaching process [1]. TAED can react with hydrogen peroxide to produce peracetic acid, an even stronger bleaching agent than hydrogen peroxide. TAED is not a catalyst, an additive that speeds up a chemical reaction, during the oxidation reaction because TAED is consumed during the oxidation process; catalysts are never used up during reactions. Activators help boost bleach productivity by speeding up the bleaching reaction so that it can take place effectively at lower temperatures.

Surfactants

Another common type of stain on clothing includes stains from oils, grease, or dirt stains. These stains are best removed from the use of surfactants. This is due to the fact that oils and grease have a characteristic of non-polarity, so solely washing the clothing will not remove the stains, because water is polar and only mixes with other polar substances. On the other hand, the surfactants allow for the stains to be suspended using phospholipids, a class of lipids (fats) that have a glycerol, hydrophilic (attracted to water) head, and two fatty acid chains that are hydrophobic (repel water), and easily washed away.

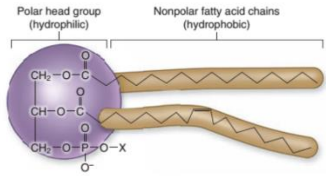

Figure 4: A picture of the phospholipid, with a hydrophobic tail and hydrophilic tail. [17]

So what are surfactants?

Surfactants, called surface active agents, are derived from fats having both polar and nonpolar characteristics. This property allows surfactants to lower the surface tension- the attraction between molecules that causes a cohesive force between a liquid's molecules- within the interaction of oil and water. Another property is its ability to form an elastic-like membrane [16] between liquids to allow the grease or dirt to be captured in the micelle [12]. The micelle forms a structure such that, the phospholipid molecules arrange themselves in spherical form with the hydrophobic (repel water) heads facing out and the hydrophilic (affinity for water) tails facing inside the sphere. However, there are multiple types of surfactants depending on the characteristic of their hydrophilic head group and their interactions with ions [13]. The different types of surfactants include anionic, nonionic, cationic, and amphoteric.

How do surfactants work?

Due to their hydrophobic and hydrophilic tail and head groups and their ability to form micelles, surfactants are quite useful when incorporated into laundry detergents.

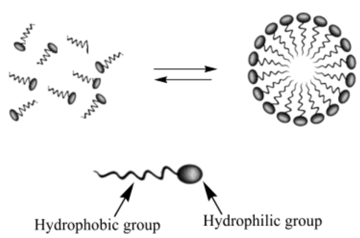

Figure 5: The spherical micelle that forms around the oil stain which is in the center of the micelle suspended [18].

A micelle, is the spherical structure (as seen in figure 2) that forms around the oil stains as the hydrophobic tails are able to interact with the nonpolar oil stains. As a part of laundry detergent, the surfactants can perform multiple roles to remove the stains out of clothing. Their three-step process includes being able to penetrate and wet the fabric, loosen the soil/dirt in the fabric, and bring the soil particulates together to suspend them in the solution [15]. So, when the surfactants in detergent are mixed with water, the hydrophilic head groups attract to the polar water and the hydrophobic tails face away from the water. These surfactant molecules gather near the surface of the water and the accumulation of surfactants causes a weakening of the hydrogen bonding between the water molecules causing there to be lower surface tension [15]. The lowering of the surface tension allows the surfactants to get through and 'wet' the fabric. Next, when the surfactants come into contact with the oil or grease stain, the hydrophobic tails of surfactants attract to the nonpolar oil molecules [15]. Thus, the surfactants create almost a sphere around the oil molecules with the nonpolar hydrophobic tails facing in and the polar hydrophilic heads facing out as they are attracted to the water molecules. So, although the polar and nonpolar substances do not mix, the oil molecules become suspended in the water since they are surrounded by the surfactant molecules [15]. This suspension effectively allows the fabric to be cleaned as the surfactant molecules have surrounded the oil stain which can easily be washed away.

Anionic surfactants

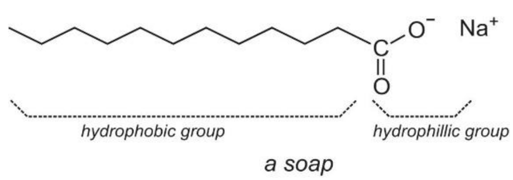

Figure 6: Anionic Surfactant [18]

An anionic surfactant is one whose hydrophilic head is negatively charged. As can be seen in figure 3, the surfactant has a negatively charged head group that is balanced out by the positive cation Na^+. These anionic heads have functional groups ranging from sulfates, and phosphates, to carboxylates. Anionic surfactants are the most abundant in laundry detergents because of their ability to emulsify (suspend) the stains and be good wetting agents [14]. Important anionic surfactants for detergents include alkyl carboxylates (soaps), and linear alkylbenzene sulfonates.

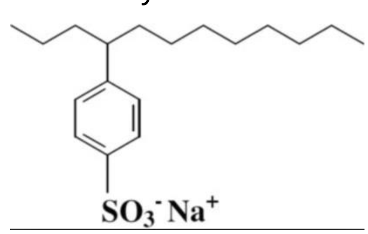

Figure 7: Linear Alkylbenzene Sulfonate Structure [14]

The linear alkylbenzene sulfonates (LAS) are quite abundant in detergents today as they are the component of detergents that help to best wet the fabric and lower the surface tension. The ideal range of carbons for the LAS to be good wetting agents is 9-12 carbons and 15-18 carbons for ones that are good emulsifiers or good at lowering the surface tension [14]. Although anionic surfactants have a negatively charged head group, they interact with the stains in a similar way as described. When the anionic surfactants interact with water, they ionize, meaning they convert into a charged molecule, and become negatively charged. Thus, the hydrophobic tail binds to the soil stains because they are positively charged, and the hydrophilic tails bind to the water molecules. They perform the same process as described in the section how do surfactants work to remove the stain.

Cationic surfactants

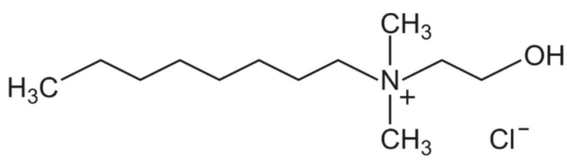

Figure 8: Cationic Surfactant [13]

A cationic surfactant is one that has a hydrophilic head that is positively charged. These surfactants only account for 5-6% of surfactant production for laundry detergents because they are not very good at being detergents. The reason for this is that the cationic surfactants soak into the fabric and the stain but are not able to desorb from it [13]. Thus, these cationic surfactants are better used as fabric softeners because of their ability to strongly absorb into the fabric. However, one way that the cationic surfactants are utilized in detergents are through short carbon chain cationic surfactants mixed with anionic surfactants. This helps to better the packing of the anionic surfactants that are interacting with the stain [13].

Nonionic surfactants

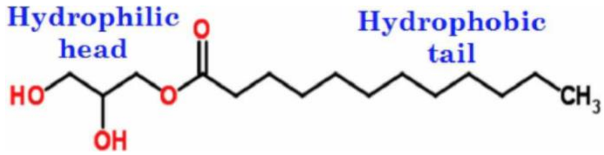

Figure 9: Nonionic Surfactant [19]

A nonionic surfactant means it does not disassociate into ions in an aqueous solution. This is due to their head group not being charged and thus, they are able to be mixed with other molecules including cationic or anionic surfactants. Since they are nonionic and have no charge, they also work well in hard water because they do not interact with the calcium or magnesium ions in hard water [13]. Also, the largest group of nonionic surfactants are ethoxylates. Thus, the hydrophilic part contains derivatives of polyoxyethylene. These are derivatives of the formula $HO\text{-}(CH_2CH_2O)_n\text{-}H$. The hydrophobic part contains fatty acids or alcohols [13]. A fatty acid is a long hydrocarbon chain of CH_2 with a carboxylic acid group (-COOH) group at the end. Fatty alcohols are long chain of carbons (usually an even number) with a –OH group at the end. Its structure and formula allow nonionic surfactants to have characteristics like low foaming and great ability to suspend the soil stains. They interact with the stains in the same way described in the section how do surfactants work.

Amphoteric surfactants

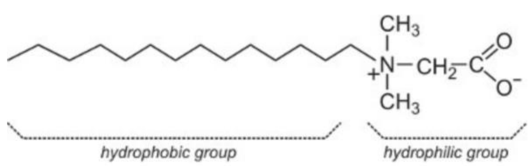

Figure 10: Amphoteric Surfactant [13]

Amphoteric means the hydrophilic head group is both negative and positive. So, one functional group is favored over the other, but it all depends on the pH. Thus, if it is an alkaline (basic) pH then it is anionic. However, if it is near an acidic pH then it favors the cationic group. However, at the isoelectric point, the amphoteric surfactant is neutral because the cationic and anionic charge cancel each other out [14]. These surfactants are mostly derived from amino acids and thus have properties quite different from the other surfactants. Amphoteric surfactants are rather mild but are good foaming agents and detergent at very high pH. When put into detergents they follow the same procedure as in the section how do surfactants work. However, since they amphoteric surfactants are very mild they are not commonly used in detergents.

Enzymatic Stains

The most common commercial use for enzymes today is the laundry industry [20]. But what exactly is an enzyme, and how do they work?

Enzymes are proteins, meaning that they are made out of various combinations of the 20 amino acids that then fold into a specific three-dimensional structure. Their function is to increase the rate or efficiency of chemical reactions. Each enzyme has an area on it known as the active site, which is where it interacts with a specific molecule of interest called a substrate. Each type of enzyme can only act on a particular type of substrate; that is, proteases will work on proteins but not lipids, and so on. Because of this, detergents often utilize multiple categories of enzymes to carry out stain removal. These usually include, but are not limited to, proteases, lipases, amylases, and cellulases. As described in the following sections, their importance in the detergent industry arises from the fact that they take larger molecules from stains and break them apart into smaller sections that the detergent can handle [21].

In addition to being useful cleaners, enzymes alleviate the environmental impact of laundry detergent. First, renewable energy drives the production of the organisms that produce commercial enzymes. Also, the ability of enzymes to be highly effective in small quantities means they consume a small fraction of the space that other cleaning chemicals in detergent would need [22]. Furthermore, as washing machines and other appliances have begun to operate at lower temperatures to save energy, enzymes have aided in allowing detergents to be equally as effective while using less heat [20].

Proteases eliminate stains caused by proteins, including grass, blood, egg, sweat, and chocolate [23]. Proteases break up proteins through hydrolysis, which is the process of using H_2O to break bonds between amino acids. This reaction is energetically favorable, but will not happen on its own at a fast enough rate, which necessitates the use of protease enzymes [24]. A visualization of the hydrolysis of a peptide bond, which is representative of hydrolysis reactions in general, is pictured below:

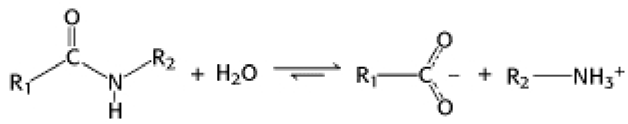

Figure 11: Mechanism by which a protease enzyme works. The water molecule splits the amino acid into two components, which each incorporate either the hydrogen or the oxygen atoms of the water into their new structure [24].

For protease to maintain its structure and thus its function, it needs a calcium ion. Since detergents contain ingredients that can break apart the calcium ion from the protease, negatively-charged substances have to be added to detergent proteases to maintain the enzyme's attraction to the calcium ion. Another challenge to protease in detergent is the enzyme's ability to attack other ingredients in the detergent. To solve this, proteases can be sheltered using a capsule, or protease inhibitors can be added to the detergent. Since the water from the washing machine dilutes protease inhibitors, they do not compromise the overall effect of protease on stain removal [25].

Lipases are responsible for targeting oil, fat, or grease stains. The need for lipases in the detergent industry emerged when it became environmentally unfavorable to get rid of grease stains the old fashioned way, which involved using extremely hot water for a long period of time. Subsequent genetic engineering produced lipases that use the process of hydrolysis to break up fats. Problematic fat molecules called triglycerides do not dissolve in water because of their hydrophobic (water-fearing) nature, and they can adhere to clothing for multiple wash cycles. Lipases turn triglycerides into mono- or diglycerides, or simple fatty acids. Unlike triglycerides, these can be pulled away from fabric at lower temperatures. However, low water temperatures inhibit the activity of lipase, reducing its effectiveness. Additionally, surfactants in detergent also alter lipase activity. When surfactants prevent lipase from initiating lipid hydrolysis, the lipase remains on the clothing in the dryer, where it can then act on the lipid stain. A second wash is then required to complete the stain removal. This is why lipid stains often need to be pre-treated in order to completely disappear in one wash [26].

Amylases destroy stains caused by starches, including potatoes, oatmeal, pasta, and gravy [21][27]. A string of glucose molecules linked by bonds called alpha-1,4-glycosidic bonds form starch molecules. Amylase uses hydrolysis to break these glycosidic bonds into shorter molecules called dextrins or oligosaccharides, which dissolve in water and allow for stain removal [21]. Much like proteases, amylases need calcium ions to maintain their functional integrity. These ions allow amylase to work at a range of temperatures and to fend itself from other enzymes that may target it. Also like proteases, amylases have had to be engineered so that they have negatively-charged amino acids that can better hold onto calcium ions [27].

Cellulases do not target a specific stain; instead they prevent whites and brights from fading by targeting cellulose microfibrils. When clothing made out of cotton experiences normal wear and tear, this physically manifests as structures called microfibrils, which occur when glucose chains called cellulose become stuck to each other via hydrogen bonds. These hydrogen bonds make cellulose more tough than an ordinary starch molecule, which is also just a chain of glucose [28]. Microfibrils can directly cause stains by capturing other material and holding it to the clothing. They can also form a barrier of cellulose microfibrils that blocks chemicals from removing other stains. Cellulase gets rid of these microfibrils through the process of hydrolysis of cellulose, which then allows the stains to be removed [23][29].

Particulate stains and builders

What are builders and what do they do?

Another type of stain is particulate stains. These stains are best removed through the use of builders. Builders are often added to cleaning compounds to enhance or maintain the cleaning efficiency of other chemicals in detergent, like surfactants. Builders do this by preventing other charged molecules (like surfactants) to be interfered by cations.

Builders have a number of functions including softening, buffering, and emulsifying [37].

Softening

The primary function of builders is to reduce water hardness [31]. Water hardness is the amount of dissolved calcium and magnesium in the water [33]. Harder water contains a higher amount of dissolved minerals because calcium, magnesium, and other metal compounds contribute to water hardness.

Builders soften water by deactivating hardness minerals, which are metal ions like calcium and magnesium [37]. They do this through a couple of ways:

1) Sequestration – holding metal ions in solution.
2) Precipitation – removing metal ions from solution as insoluble materials [37].
3) ion exchange -- trading electrically charged particles [31].

Buffering

In addition to softening water, builders also help in cleaning stains (stain removal) by providing a desirable level of alkalinity (increasing the pH of the solution) and acting as a buffer to maintain the proper alkalinity in wash water [37]. Alkalinity assists in several things including (1) cleaning, especially of acid soils, and (2) helping to keep removed soil from redepositing during washing.

Emulsifying

Along with acting as a buffer, builders also help emulsify oily and greasy soil by breaking it up into tiny globules [37]. Many builders will suspend loosened dirt and keep it from settling back on the cleaned surface [37].

Other functions of builders

Builders can also help remove soil stains from clothes. Soil stains are often bound to fabrics by calcium ion bridging, so by removing the calcium ions, builders therefore help to remove the dirt.

Where can builders be found?

Builders are often found in washing detergents. Washing detergents used to commonly use sodium triphosphate as a builder [30]. But then researchers found out that if an excessive amount of sodium triphosphate is released into the environment, it can lead to eutrophication.

Due to the many concerns of sodium triphosphate being released to the environment, many companies now use other agents as builders in washing detergents instead. Some of these agents can include sodium carbonate, polycarboxylates, and also zeolites. [30]

Examples of builders

Types

On the basis of characteristics and properties, detergent builders can be categorized into two types [40]:

- Organic detergent builders
- Inorganic detergent builders

Inorganic builders:

Inorganic builders can be classified to 4 groups: Phosphates, Silicates, Carbonates, and Oxygen Releasing Materials [32].

Phosphates

There are two classes of phosphates, which are the orthophosphates and the complex phosphates [32].

Orthophosphates phosphates-- trisodium phosphate and disodium phosphate

1) Trisodium phosphate-
    - Little used these days because phosphates can cause eutrophication of water
    - Has the property of softening water by precipitating metallic ions (as a gelatinous precipitate) [32]
    - Helps in dispersing soil
    - Aids in the saponification of fatty acids
2) Disodium phosphates-
    - Are rarely used
    - Produce lower alkalinity

Complex phosphates--

- Have a lower alkalinity than trisodium phosphate
- Enhance the detergency of soap type detergents
- Can regenerate useable soup [32]. If a piece of cloth has some calcium (in the form of an insoluble calcium soap) imbedded in it, the phosphate molecule re-dissolves the calcium and releases sodium which re-combines with the fatty acid anion of the soap molecule.

Phosphate have become out of favor biologically because of eutrophication, but suitable alternatives are hard to find that will completely replace them [32].

Silicates

The addition of silicates to synthetic detergents has proved to be very beneficial.

- Aid in softening water through forming precipitates that can be easily rinsed away.
- Have great suspending and anti-re-deposition qualities, so they tend not to deposit on the fibers of the cloth being washed.
- Are used in dish-washing powders for their wetting and emulsifying properties [32].

- Most soils in laundering processes are acidic, and Silicates have excellent buffering action against acidic compounds.

Carbonate

1) Soda ash (sodium carbonate)- provides high alkalinity [32].
- If the pH of the solution is greater than pH 9 (and that it is maintained), Soda ash then can soften water by precipitating calcium and magnesium carbonates.
- Synthetic soda ash, which is chemically produced, is of superior quality to mined natural soda ash.
- Two grades are commonly used- light soda ash and dense soda ash [32].
- Light soda ash can absorb large amounts of liquid material onto its surface and remain dry to the touch, and keep its free-flowing properties [32].
- It is also used as a neutralizing agent for the absorption of DDBSA (anionic surfactant) [32].

2) Sodium bicarbonate- rarely used
3) Potassium carbonate- used in polish manufacture as a source of alkalinity because it is more soluble

Oxygen Releasing Material

1) Sodium perborate-
- Has been used in laundering as a bleach for many years
- Acts as a hydrogen peroxide bleach because it releases nascent oxygen at elevated temperatures
- Its main disadvantage is that its bleaching action only takes place at elevated temperatures [32].
- If an activator is added, its bleaching action then can be released at lower temperatures.

2) Sodium Percarbonate-
    - It works in solutions as if sodium carbonate and hydrogen peroxide had been added separately

- Percarbonate releases oxygen at a lower temperature, and is effective as a laundry bleach [32].

Three of the most common builders used in today's heavy-duty detergents:

1) **Phosphates**, usually sodium tripolyphosphate (STPP), have been used as builders extensively in heavy-duty industrial detergents [37].
    - Combine with hardness minerals to form a soluble complex which is removed with the wash water.
    - Sequester dissolved iron and manganese which can interfere with detergency [37].

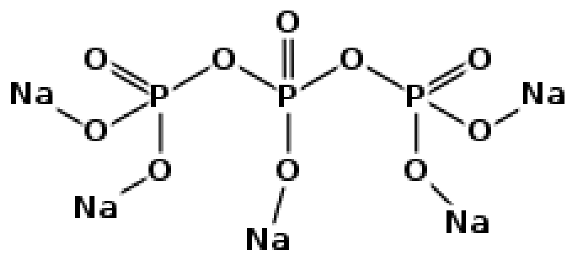

Figure 12: structure of a sodium tripolyphosphate compound [38]

2) **Sodium carbonate (soda ash)**
    - Can only soften water through precipitation
    - Not used in laundry detergents because precipitated calcium and magnesium particles can build up on surfaces, especially clothing.

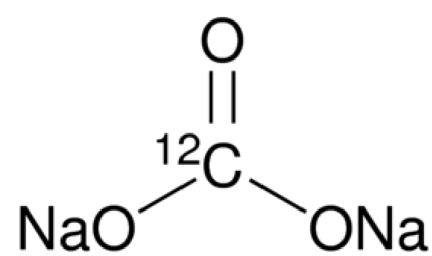

Figure 13: structure of a sodium carbonate compound [39]

3) Sodium silicate

- Serves as a builder in detergents when used in high concentrations.
- When used in lower concentrations, it inhibits corrosion and adds crispness to detergent granules [37].

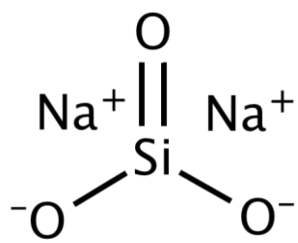

Figure 14: structure of a sodium silicate compound [41]

Appendix

Carbon bonds: Each vertex in a chromophore molecule represents one carbon atom. A single bond of carbon is represented by a single line. A double bond of carbon is represented by a double line. In a chromophore molecule, the straight

carbon chain alternates in single and double bonded carbons.

Redox reactions: A type of chemical reaction that involves the transfer of electrons between two components involves both an oxidation and a reduction reaction. A molecule, atom, or ion will either gain or lose electron(s).

Electron: Atoms have subatomic particle(s) with a negative charge.

Nonpolar: an equal sharing of electrons between the atoms so they are not charged.

Polar: an unequal sharing of electrons causing a difference in positive and negative charge on the atoms.

Emulsion: A suspension of tiny droplets of one liquid in a second liquid.

Desorb: the release or removal of an adsorbed substance by the reverse of absorption pH scale: it means potential hydrogen and is a relative measure of how acidic or basic a substance is.

Eutrophication: Eutrophication is the enrichment of an ecosystem with chemical nutrients, typically compounds containing nitrogen, phosphorus, or both. Eutrophication is a type of pollution that stimulates an explosive growth of algae (algal blooms) that depletes the water of oxygen when the algae die and are eaten by bacteria. Eutrophication is a leading cause of impairment of many freshwater and coastal marine ecosystems in the world.

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