DETERGENTS AND ANTISEPTICS

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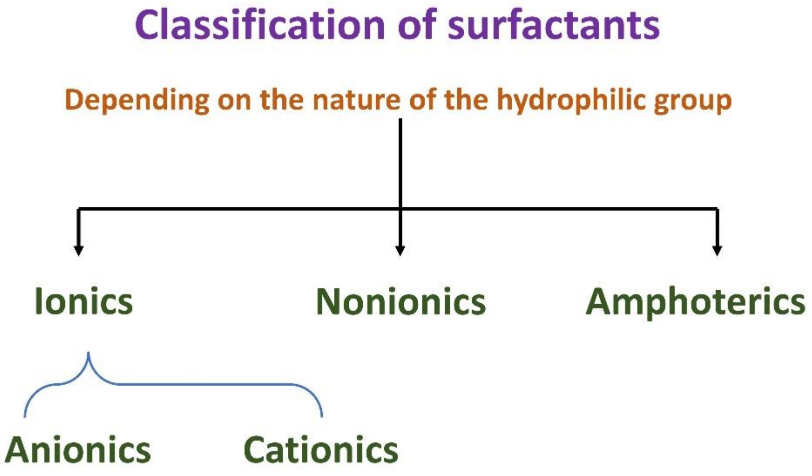
Course Outline

- **Surfactant Types and Structures**
  - Anionic
  - Cationic
  - Non-ionic
  - Amphoteric
- **Introduction to Detergents**
  - Common Detergents Ingredients
  - Representative Detergent Formulations
  - Laundry Detergent Formulations
  - Dishwash Detergent Formulations
  - Hard Surface Cleaning Formulations
- **Examples of Some Market Detergents Products**
  - Laundry Detergent Formulations
  - Dishwashing Detergents for Household Applications
- **Antiseptic and Disinfection**
  - Quaternary ammonium system
  - Phenols
  - Chlorin compounds
  - Hydrogen peroxides
  - Acids
  - Aldehydes

Surfactant Types and Structures

There are several types of surfactants, each with unique chemical structures and properties. The most common types of surfactants include:



Anionic surfactants:

Anionic surfactants are the most commonly used type of surfactant. These surfactants have a negatively charged head group and are typically used as detergents and cleaning agents. Examples of anionic surfactants include sodium lauryl sulfate and sodium dodecylbenzenesulfonate.

Cationic surfactants:

These surfactants have a positively charged head group and are often used as disinfectants and fabric softeners. Examples of cationic surfactants include cetyltrimethylammonium bromide and benzalkonium chloride.

Nonionic surfactants:

These surfactants have an uncharged head group and are often used as emulsifiers, solubilizers, and wetting agents in industrial applications. Examples of nonionic surfactants include polyethylene glycol (PEG) and alkyl polyglucosides.

Amphoteric surfactants:

These surfactants have both a positively and negatively charged head group and are often used as mild detergents and personal care products. Examples of amphoteric surfactants include cocamidopropyl betaine and disodium cocoamphodiacetate.

Surfactants are amphiphilic, meaning they have both hydrophilic and hydrophobic properties. The hydrophilic head group is usually polar or charged, while the hydrophobic tail is typically a long hydrocarbon chain. The structure of the surfactant is designed to allow it to interact with both polar and non-polar substances, which gives it its unique surface-active properties.

Surfactants work by adsorbing onto the surface of a liquid or solid to reduce its surface tension. This can help to facilitate the spreading, wetting, or emulsification of the substance. The effectiveness of a surfactant depends on its concentration, chemical structure, and the properties of the substances it is interacting with. Surfactants are used in a wide range of applications, including personal care products (such as shampoos, soaps, and lotions), household and industrial cleaning products, paints and coatings, food processing, and agricultural products.

Overall, surfactants play an important role in many everyday products and industrial processes, and their properties and structures can be carefully designed and tailored to suit specific applications and outcomes.

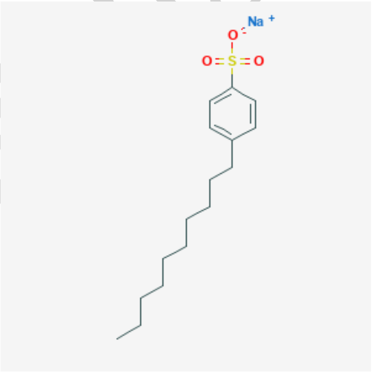
In our course, we will focus on every type of the surfactant in some details.

Anionic surfactants:

Anionic surfactants are a type of surfactant that contains a negatively charged ion in the hydrophilic (water-loving) part of the molecule. **This charge is usually provided by a sulfonate, sulfate, or carboxylate group,** which makes the molecule water-soluble and able to form stable micelles in water.

1- Sulfonates surfactants: $-SO_3^-$

A- Alkylbenzene sulfonates (LABS)



Linear alkylbenzene sulfonate (LABS): This is a common anionic surfactant that is used in a wide range of applications, including laundry detergents, dishwashing liquids, and household industrial cleaners. It is effective at removing dirt and oil and is compatible with hard water.

Synthesis of LABS:

Here are the general production steps of LABS:

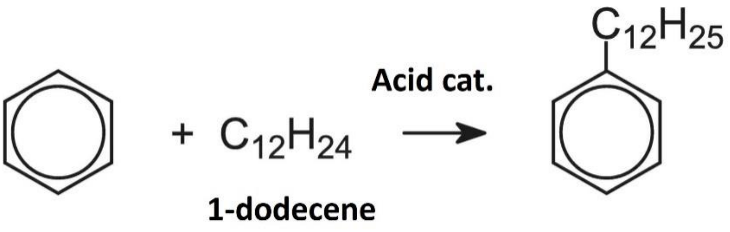
Alkylation: In this step, benzene is alkylated with a linear alkyl chain, usually derived from an olefin (e.g. propyl**ene**, butyl**ene**) *via* a catalytic process. The alkyl chain length typically ranges from 10 to 14 carbon atoms. The process of alkylation is typically carried out in a liquid-phase reactor containing benzene and the olefinic feed, along with a suitable catalyst (e.g. hydrofluoric acid, aluminum chloride). The catalyst promotes the reaction between benzene and the olefin, leading to the formation of LAB. The resulting LAB stream is then neutralized to remove any unreacted acid or catalyst.

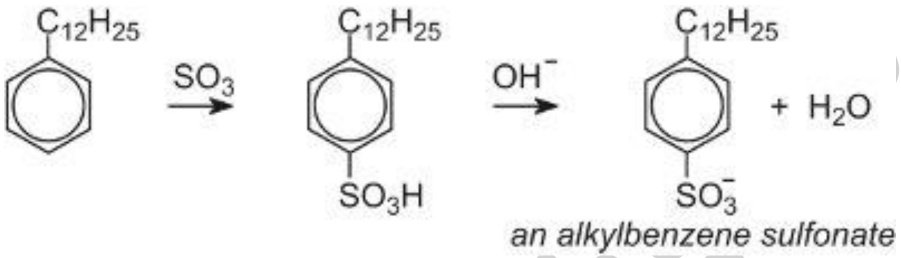
Sulfonation: The LAB is then sulfonated to produce sulfonic acid, which is then neutralized to form LABSA. The sulfonation reaction is typically carried out using concentrated sulfuric acid as a catalyst and sulfur trioxide (SO_3) as the sulfonating agent. The reaction is typically carried out in a reactor at temperatures ranging from 90 to 120°C, and the reaction time is carefully controlled to ensure that the desired level of sulfonation is achieved. After sulfonation, the reaction mixture is cooled and neutralized with an alkali, usually sodium hydroxide, to form the sodium salt of LABSA.

Separation and purification: The LABSA is then separated from the reaction mixture by a series of steps, including neutralization, filtration, and drying. In this step, the LABSA is separated from the reaction mixture by adding an alkali (usually sodium hydroxide), which neutralizes the sulfuric acid and precipitates the LABSA. The precipitate is then washed with water to remove any residual sulfuric acid and sodium sulfate, which is a by-product of the neutralization reaction. The LABSA is then dried and the resulting powder is milled to the desired particle size.

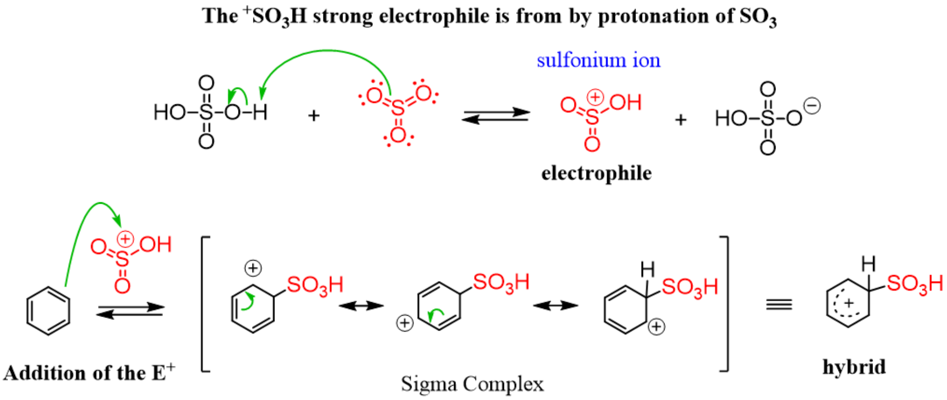
Optional steps: Depending on the specific application of the LABSA, additional steps may be carried out to modify its properties. For example, LABSA used in liquid laundry detergents may be subjected to an ethoxylation process to increase its solubility in water and improve its performance in cold water. In this process, the LABSA is reacted with ethylene oxide, which adds ethylene oxide molecules to the LABSA molecule, resulting in an ethoxylated LABSA (or "AELAS"). The degree of ethoxylation can be controlled to modify the physical properties of the resulting AELAS.

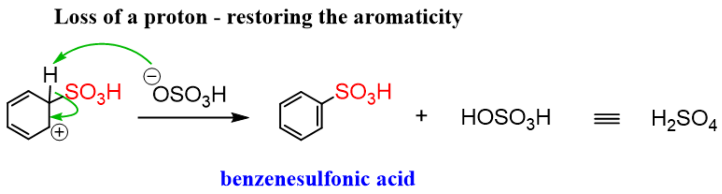
Overall, the production of LABSA is a complex process that requires careful control of the reaction conditions and the separation and purification steps to ensure a high-quality product.





The reaction mechanism of Benzene sulphonic acid formation:

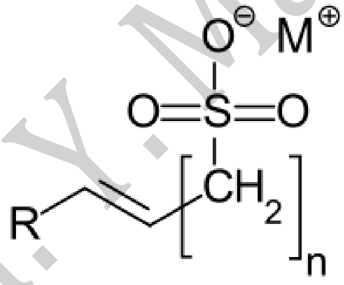




B- Alpha Olefin Sulfonates (AOS):

These are anionic surfactants that are commonly used in laundry detergents and household cleaning products. They are effective at removing tough stains and grease, and can work well in hard water conditions.

The compounds contain a - mostly linear, primary - alkyl R and a monovalent cation M, preferably sodium. The most frequently used example of this group of substances is sodium α-olefin sulfonate (INCI: Sodium C14-16 Olefin Sulfonate).



General chemical structure of α-olefin sulfonates

R= Alkyl, M= Na+, n = 1 or 2

<u>Description</u>

In addition to a longer hydrocarbon chain in which there must be at least one double bond (hence the name "olefin"), it has an anionic sulfonate headgroup with a sodium ion as a counterion. The sulfonate group is negative in aqueous solution, which is why the α-olefin sulfonates are among the anionic surfactants. In contrast to most other surfactants in which the C12-alkyl chains have the highest surface activity, olefin sulfonates shows maximal activity when using C14 and C16-olefins.

Production and composition

α-Olefin sulfonates are produced by sulfonation of alpha-olefins, typically using sulfur trioxide. Subsequent alkaline hydrolysis gives a mixture of alkene sulfonates (60-65%) and hydroxyalkane sulfonates (35-40%). The commercially available olefin sulfonates are mostly solutions with about 40% active ingredient content.

Usage

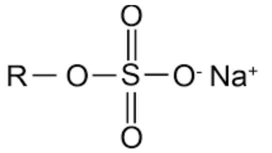
α-Olefin sulfonates with linear alkenyl radicals from C12 to C18 are used as anionic surfactants in various areas of application due to their pronounced foam formation and foam stability (even with high water hardness), excellent fat-dissolving power and oil dissolving power as well as a favorable ecological profile and low aquatic toxicity and human toxicity. They are typically used in detergents and cleaning agents, for degreasing, in the emulsion polymerization, the conditioning of concrete and mortar as well as in the **formulation of pesticides**.

Sodium C14-16 olefin sulfonate is being introduced in some shampoos as an alternative to sodium laureth sulfate. Some groups and sellers suggest that it is better for someone's health, but this claim lacks evidence.

2- Sulfate surfactants: $-OSO_3^-$

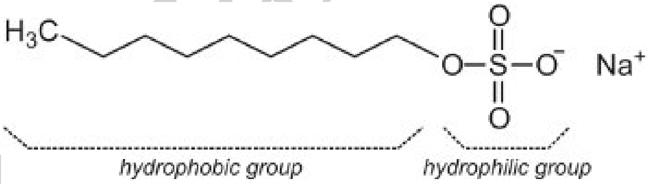
A- Alkyl sulphate:

These are anionic surfactants that are commonly used in personal care products, such as shampoo and body wash. They are effective at removing dirt and oil from the skin and hair but can also be harsh and irritating if used at high concentrations.

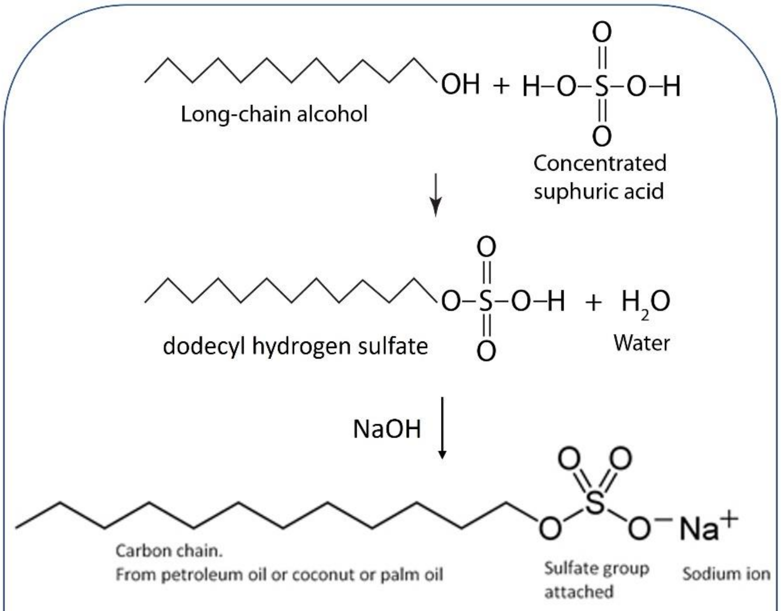


$R-O-S(=O)_2-O^-\ Na^+$

Sodium Alkyl Sulphate
(Detergent)



an alkyl sulfate



Sodium Lauryl Sulfate (SLS)

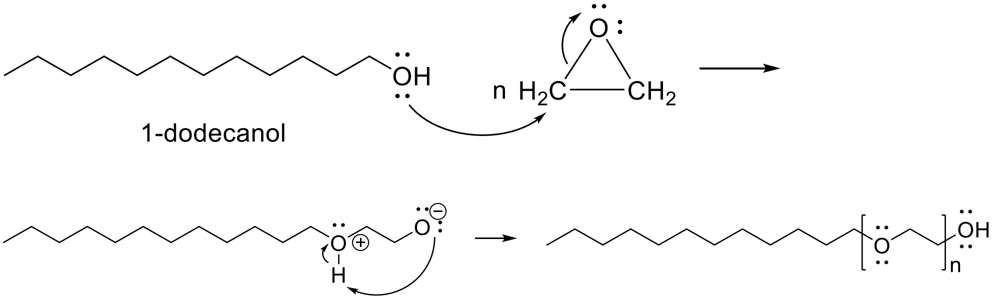
Sodium Dodecyl Sulfate (SDS)

B- Sodium lauryl ether sulfate (SLES):

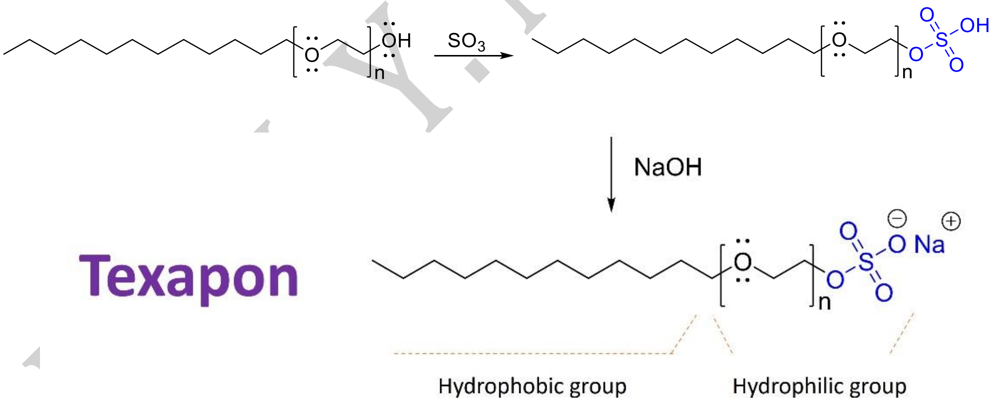
This is a milder form of anionic surfactant that is often used in personal care products such as shampoos and body washes. It has good foaming properties and is effective at removing dirt and oil but is less harsh on the skin than some other anionic surfactants.

<u>Sodium lauryl ether sulfate (SLES) production steps</u>

Ethoxylation: In this step, lauryl alcohol is ethoxylated by reacting with ethylene oxide in the presence of a catalyst. The reaction is typically carried out in a stirred-tank reactor at elevated temperatures and pressures. The degree of ethoxylation is carefully controlled to achieve the desired level of ethoxylation.



Sulfation: The ethoxylated lauryl alcohol is then sulfated by reacting with sulfur trioxide gas or sulfuric acid. The sulfation reaction is typically carried out in a falling-film reactor, where a thin film of the ethoxylated lauryl alcohol is exposed to the sulfating agent. The reaction conditions are carefully controlled to ensure that the desired level of sulfation is achieved.



Sodium **L**auryl **E**ther **S**ulfate (**SLES**)

Neutralization: The resulting sulfated product is then neutralized with an alkali, typically sodium hydroxide or ammonium hydroxide, to form the sodium or ammonium salt of SLES. The neutralization reaction is typically carried out in a mixing tank, where the sulfated product is mixed with the alkali.

Concentration and purification: The resulting SLES solution is then concentrated and purified to remove any impurities. This is typically achieved by a combination of heat, vacuum, and filtration. The purified SLES is then dried and milled to the desired particle size.

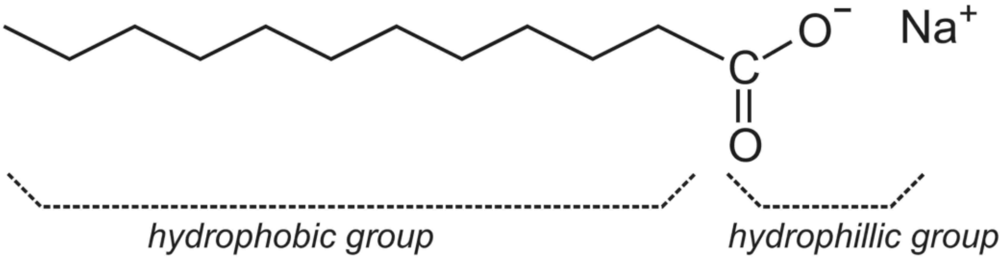
Optional steps: Depending on the desired properties of the SLES, additional steps may be carried out. For example, the SLES may be further ethoxylated or propoxylated to modify its physical properties. It may also be formulated with other surfactants, such as betaines or sulfosuccinates, to improve its performance in specific applications.

Overall, the production of SLES is a complex process that requires careful control of the reaction conditions and the separation and purification steps to ensure a high-quality product.

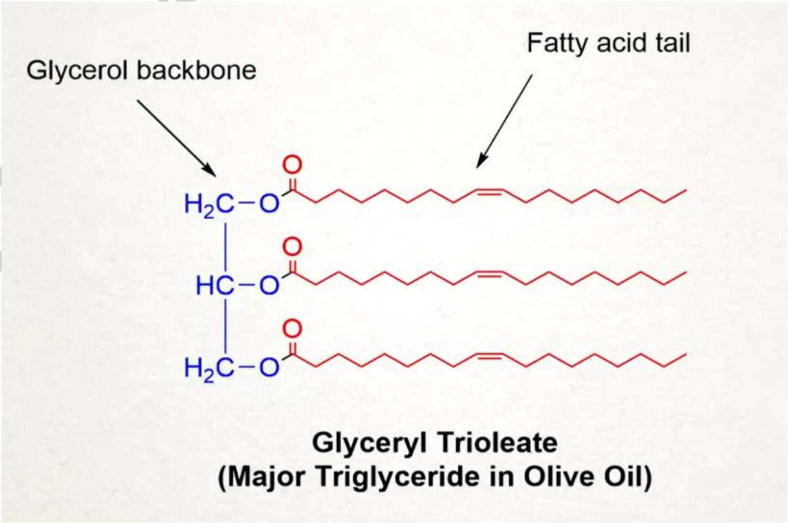
Note: It's worth mentioning that the production process for SLES may vary slightly depending on the specific manufacturer and production method. The steps mentioned above represent a general overview of the process.

3- Carboxylate surfactants: (R-COO$^-$)

Fatty acid soaps: These are anionic surfactants that are commonly used in bar soaps and liquid hand soaps. They are mild and gentle on the skin, but can also leave a residue if not rinsed off properly.

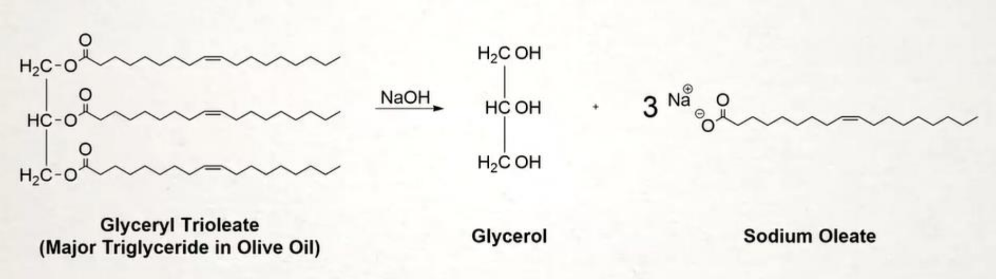


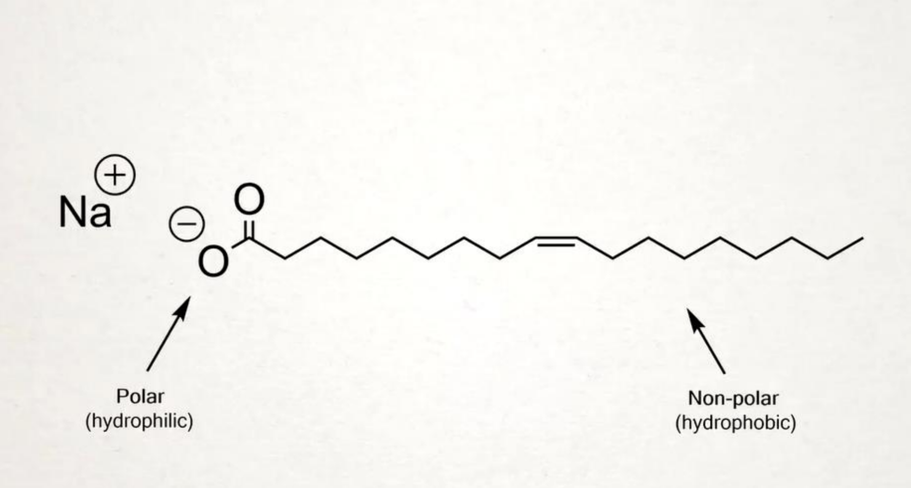
a soap



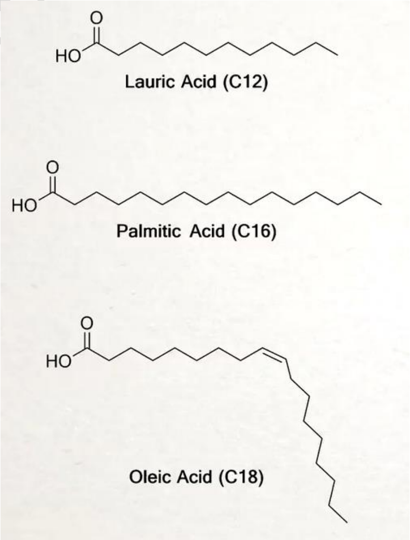
Glyceryl Trioleate
(Major Triglyceride in Olive Oil)

Saponification reaction:



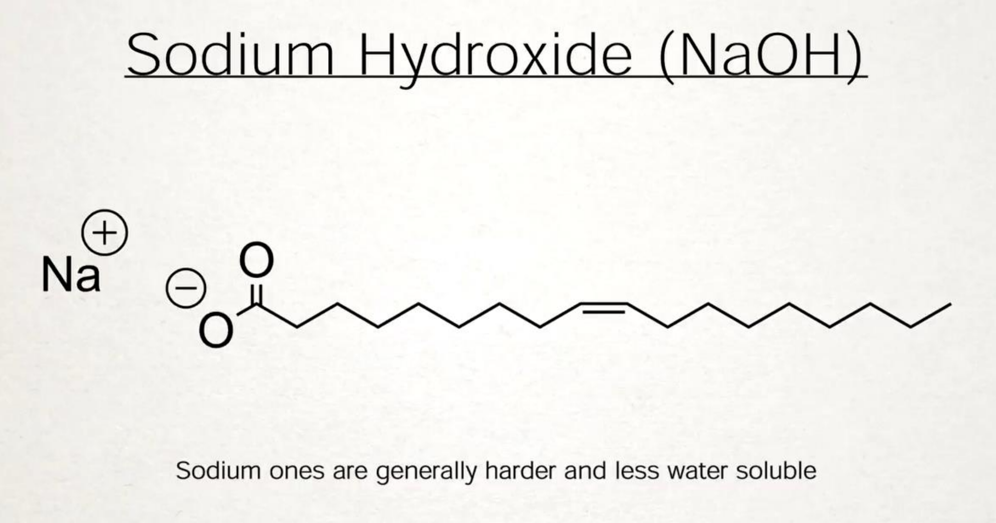


Examples of Fatty acids:



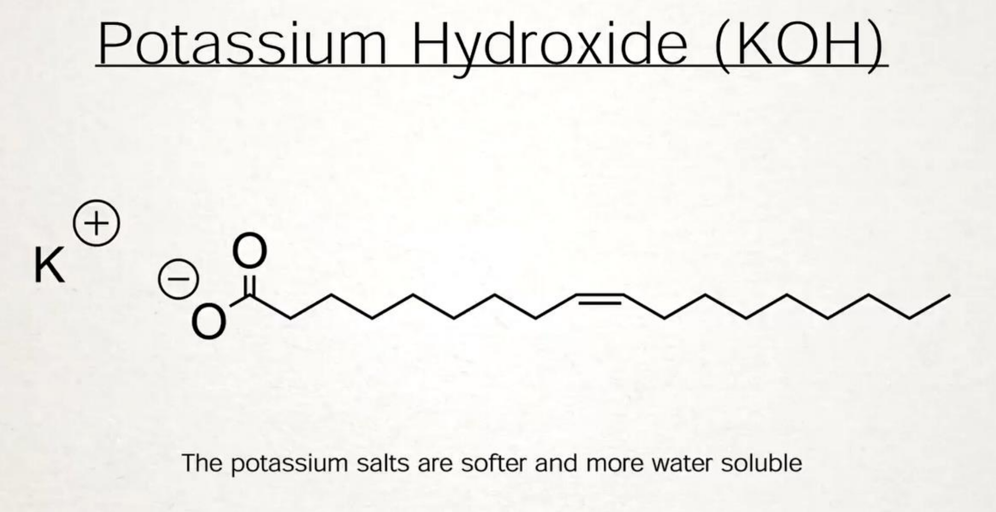
The final product of fatty acid salt is depending on the base used as follow:

Sodium salt is suitable for making solid bar soap.


Sodium Hydroxide (NaOH)

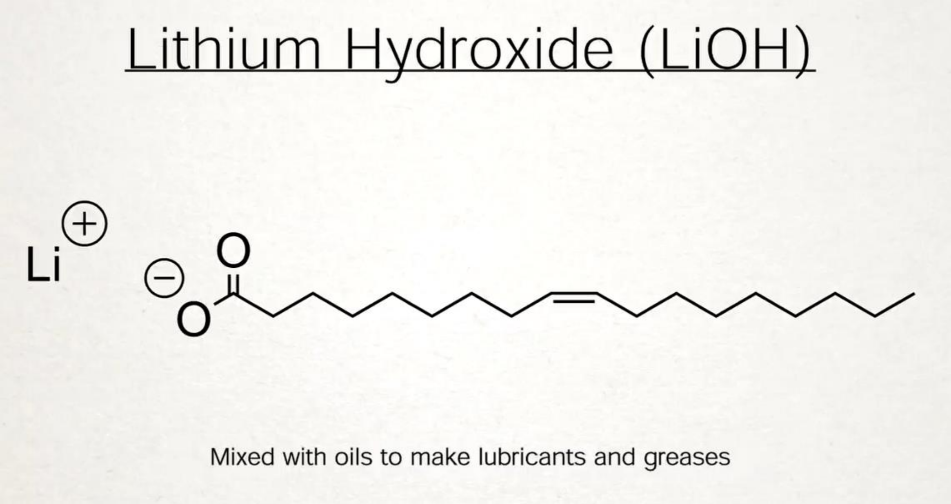
Sodium ones are generally harder and less water soluble

Potassium salt is suitable for making liquid soap.


Potassium Hydroxide (KOH)

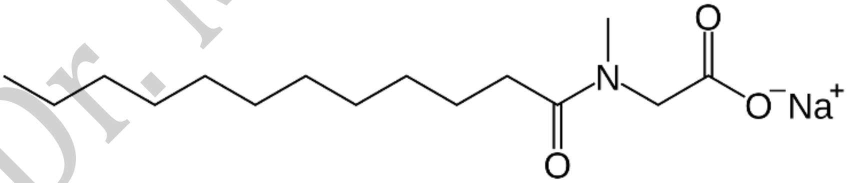
The potassium salts are softer and more water soluble

Lithium salt is suitable for making lubricants and greases.


Lithium Hydroxide (LiOH)

Mixed with oils to make lubricants and greases

Sodium lauroyl sarcosinate, also known as sarcosyl, is an anionic surfactant derived from sarcosine used as a foaming and cleansing agent in shampoo, shaving foam, toothpaste, and foam wash products. It is mild and gentle on the skin, and produces a mild foam.



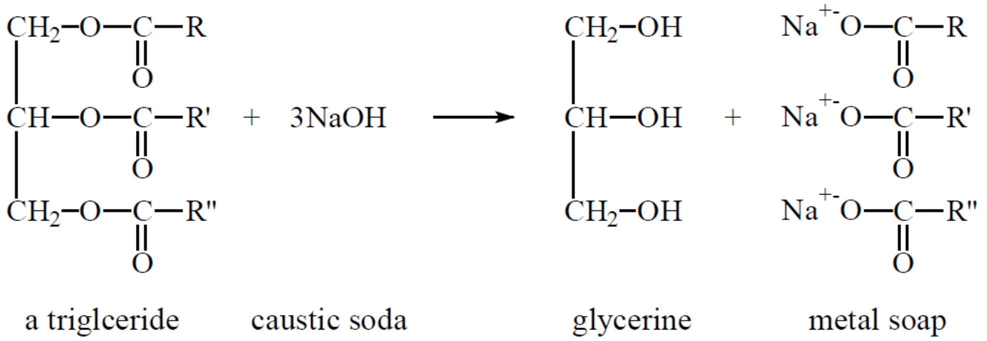
This surfactant is amphiphilic due to the hydrophobic 12-carbon chain (lauroyl) and the hydrophilic carboxylate. Since the nitrogen atom is in an amide linkage, the nitrogen is not pH active and is neutrally charged in all aqueous solutions regardless of pH. The carboxylate has a pKa of about 3.6 and is therefore negatively charged in solutions of pH greater than about 5.5.

Soap production

Soap production typically involves a reaction between a fatty acid and an alkali. Here are the basic steps involved in soap production:

Weighing and mixing the ingredients: The fatty acids (such as coconut oil, palm oil, or tallow) are first weighed and mixed in a large container. Then, the alkali (such as sodium hydroxide or potassium hydroxide) is added to water and dissolved to form a solution.

Saponification: The fatty acids are then heated and the alkali solution is slowly added to them while stirring continuously. This initiates the saponification reaction, which results in the formation of soap and glycerol.



Salting out: After saponification, salt (such as sodium chloride) is added to the mixture. This causes the soap to separate from the glycerol and other impurities, and rise to the top.

Settling and separation: The mixture is left to settle and the soap is separated from the glycerol and other impurities. The impurities are drained off, and the remaining soap is washed with water to remove any residual impurities.

Finishing: The soap is then shaped, cut, stamped, and dried to give it its final form. This may involve the use of molds or extruders, and the addition of fragrances or colors.

It is important to note that soap production is a complex process that can involve variations in the specific ingredients and methods used. Additionally, there are many different types of soap that can be produced, each with its own unique characteristics and production methods.

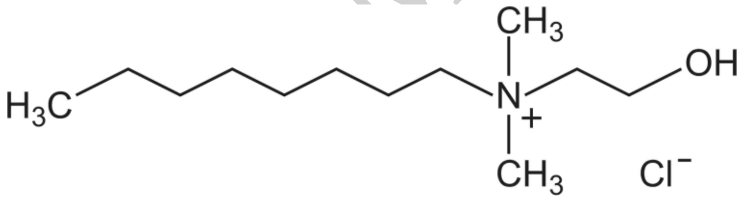
Sulfosuccinates: These are anionic surfactants that are often used in personal care products such as shampoos and body washes. They are mild and gentle, and produce a rich, creamy lather.

Cationic surfactants:

The hydrophilic head is positively charged, have quaternary ammonium (quats) as the polar end.

A) Alkyl quaternary systems

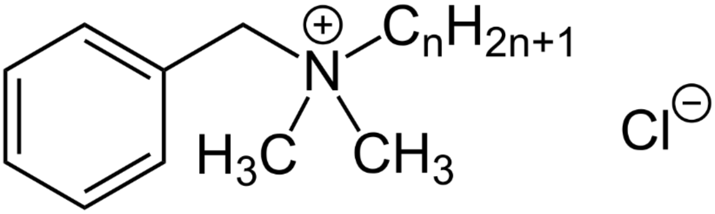
Quaternary ammonium compounds (quats): These are cationic surfactants that are commonly used as disinfectants in household cleaning products, as well as in personal care products such as hair conditioners and fabric softeners. They are effective against a wide range of bacteria and viruses, but can also be toxic to aquatic life if not disposed of properly.



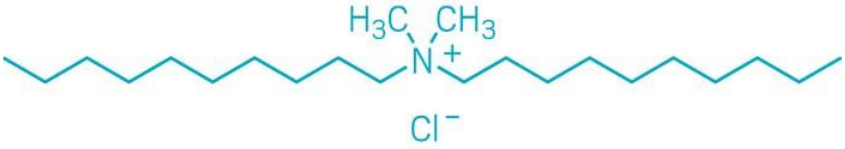
an alkyl quaternary system

Benzalkonium chloride: commonly used as a disinfectant and antiseptic in medical and personal care products.

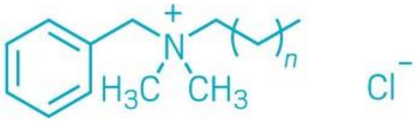
Cetyltrimethylammonium bromide: commonly used as a fabric softener and in hair conditioning products.



$n = 8, 10, 12, 14, 16, 18$



Didecyldimethylammonium chloride (DDAC)



Alkyldimethylbenzylammonium chloride (ADBAC)

$n = 6, 8, 10, 12, 14, 16$

1-Cetylpyridinium chloride (CPC)

Production of Quaternary ammonium compounds (quats)

The production of quats typically involves the following steps:

Alkylation: The first step in the production of quats is the alkylation of a tertiary amine with an alkyl halide or sulfate. This reaction is typically carried out in the presence of a strong base, such as sodium hydroxide or potassium hydroxide. The resulting product is a quaternary ammonium salt.

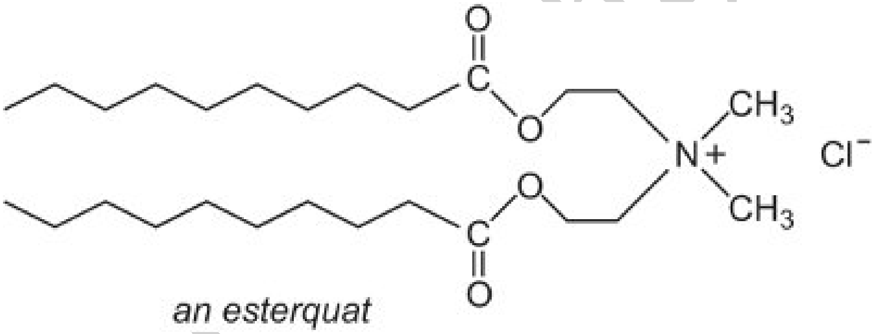
Neutralization: The quaternary ammonium salt is then neutralized with an acid, such as hydrochloric acid, to produce the corresponding quaternary ammonium compound. This step is necessary to convert the salt to the free base form.

Purification: The quaternary ammonium compound is then purified to remove any impurities or unreacted starting materials. Purification methods may include distillation, extraction, or chromatography.

Formulation: The purified quaternary ammonium compound can then be formulated into a variety of products, such as fabric softeners, hair conditioners, or antimicrobial agents. Formulation may involve blending the quaternary ammonium compound with other ingredients, such as emulsifiers, preservatives, or fragrances.

The specific process for producing quats may vary depending on the type of quat and the intended application. For example, some quats may be synthesized using different alkylating agents or purification methods. However, the general steps outlined above are commonly used in the production of many different quats.

Cationic surfactant esters (Esterquats): There is an ester linkage between the alkyl chains and the quaternary head-group. These are cationic surfactants that are commonly used in hair conditioners and other personal care products. They can help to smooth and detangle hair, but can also be heavy and greasy if used at high concentrations.



an esterquat

<u>Here are some examples of formulations that contain quats:</u>

Fabric softeners: Quats are commonly used in fabric softeners to provide a soft, smooth feel to fabrics. In these formulations, the quat is typically blended with a carrier, such as water or a solvent, and may be combined with other ingredients, such as emulsifiers, fragrances, or colorants.

Disinfectants: Quats are effective antimicrobial agents and are used in a variety of disinfectant formulations, including sprays, wipes, and foams. In these formulations, the quat is typically blended with a carrier, such as water or a solvent, and may be combined with other ingredients, such as fragrances, surfactants, or chelating agents.

Hair conditioners: Quats are commonly used in hair conditioners to provide conditioning and detangling benefits. In these formulations, the quat is typically blended with a carrier, such as water or a solvent, and may be combined with other ingredients, such as emollients, humectants, or proteins.

Shampoos: Quats can also be used in shampoo formulations to provide conditioning benefits and improve wet combability. In these formulations, the quat is typically blended with other surfactants, such as sulfates or betaines, and may be combined with other ingredients, such as thickeners, fragrances, or preservatives.

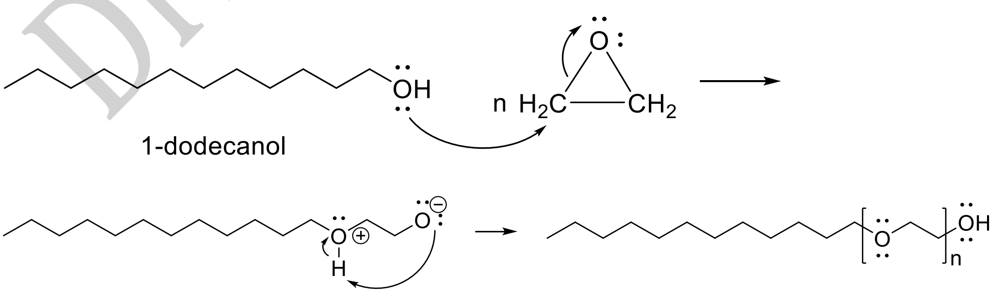
Industrial formulations: Quats are used in a wide range of industrial formulations, including oilfield chemicals, water treatment chemicals, and agricultural chemicals. In these formulations, the quat is typically blended with a carrier, such as water or a solvent, and may be combined with other ingredients, such as surfactants, dispersants, or corrosion inhibitors.

Nonionic surfactants:

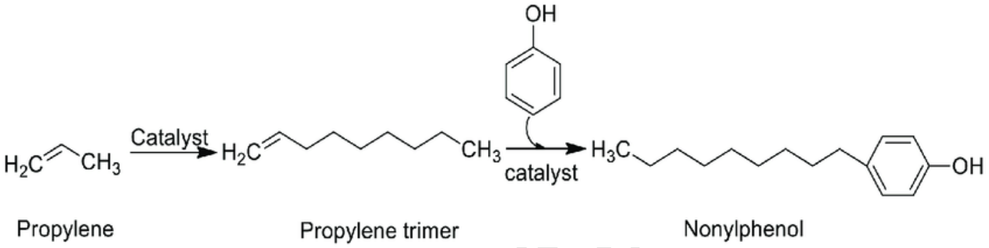
These surfactants do not bear an electrical charge and are often used together with anionic surfactants. The major group of nonionics are the ethoxylates.

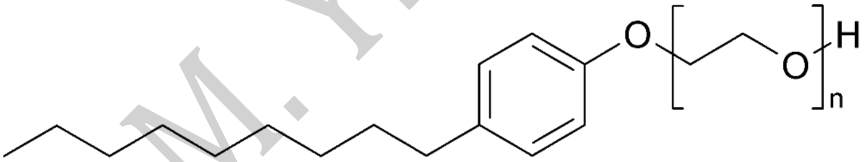
Ethoxylated alcohols: These are nonionic surfactants that are commonly used in laundry detergents and industrial cleaners. They are effective at removing oily and greasy stains, and can work well in hard water conditions.

Silicone surfactants: These are nonionic surfactants that are commonly used in personal care products, such as hair conditioners and skin lotions. They can help to smooth and soften the hair and skin, but can also be expensive and difficult to formulate.



Alkyl phenol ethoxylates: Alkyl phenol ethoxylates are another class of nonionic surfactants that are derived from alkyl phenols. They are similar to alkyl ethoxylates, but have a hydrophobic alkyl phenol group instead of a fatty alcohol. Alkyl phenol ethoxylates are often used in industrial formulations, such as emulsion polymerization, as well as in agricultural and oilfield chemicals.





Polysorbate 20: commonly used as an emulsifier and solubilizer in personal care products, such as facial cleansers and lotions.

Alkyl polyglucosides (APGs): commonly used in household cleaning products and as a foaming agent in personal care products.

As the temperature of the surfactant solution is increased the hydrogen bonds gradually break causing the surfactant to come out of solution. This is commonly referred to as the cloud point and is characteristic for each nonionic surfactant. Nonionics are more surface active and better emulsifiers than anionics at similar concentrations. They are less soluble than anionics in hot water and produce less foam. They are also more efficient in removing oily and organic dirt than anionics.

Alkyl ethoxylates production steps

Here are the general production steps for alkyl ethoxylates:

Raw material preparation: The first step in the production of alkyl ethoxylates is to obtain the starting materials, which are typically linear or branched alcohols and ethylene oxide. The alcohols are typically obtained from natural fats and oils, such as coconut oil or palm kernel oil, and are then purified and distilled to obtain the desired chain length.

Ethoxylation: The alcohols are then reacted with ethylene oxide in the presence of a catalyst, such as potassium hydroxide, to produce the alkyl ethoxylate. The reaction takes place in a stirred reactor under controlled temperature and pressure conditions.

The amount of ethylene oxide used in the reaction can be varied to produce alkyl ethoxylates with different levels of ethoxylation.

Neutralization: The alkyl ethoxylate is then neutralized with an acid, such as phosphoric acid, to remove any residual catalyst and adjust the pH of the product.

Purification: The alkyl ethoxylate is then purified to remove any impurities and byproducts, such as unreacted alcohol or ethylene oxide. This can be done through a variety of methods, such as distillation or crystallization.

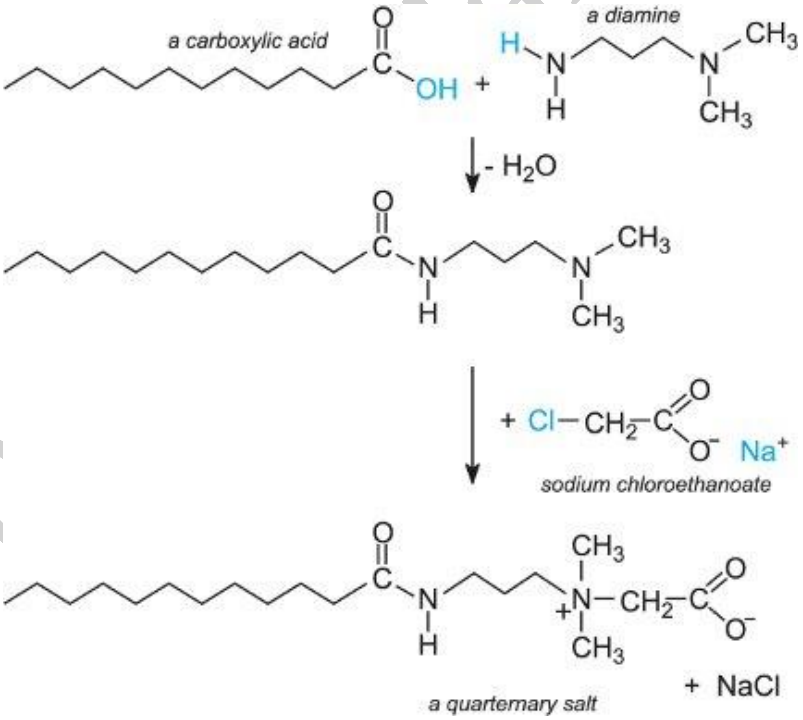
Formulation: The purified alkyl ethoxylate can then be formulated into a final product, such as a detergent or personal care product, by blending it with other ingredients, such as other surfactants, builders, and fragrances.

The specific production steps and conditions for alkyl ethoxylates can vary depending on the specific product and application, but the general process involves the preparation of raw materials, ethoxylation, neutralization, purification, and formulation.

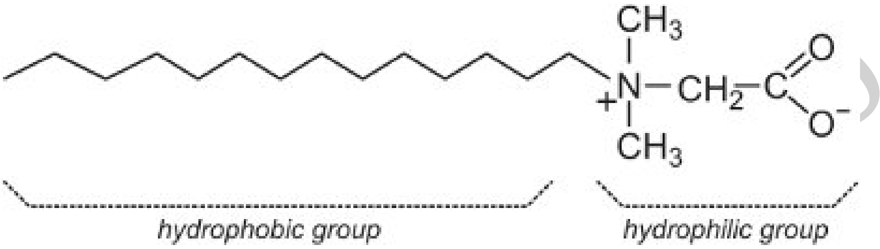
Amphoteric (Zwitterionic) Surfactants:

The head-group carries both a negative and positive charge. The positive charge is almost quaternary ammonium ion and negatively charged group can be carboxylate, $-CO_2^-$, sulfate, $-OSO_3^-$ or sulfonate, $-SO_3^-$.

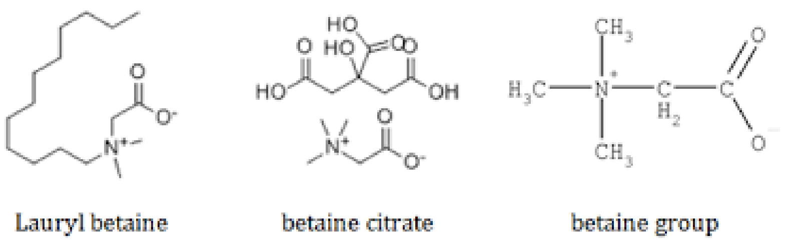
Amphoteric: These are amphoteric surfactants that are commonly used in industrial cleaners and hard surface cleaners. They are effective at removing dirt and grime from a wide range of surfaces, and can work well in hard water conditions.



Cocamidopropyl betaine: commonly used as a mild detergent and conditioner in personal care products, such as shampoo and body wash. Betaines are neutral compounds with a cationic and an anionic group which are not adjacent to one another.



an alkyl betaine



<u>Here are the general steps involved in the production of betaines:</u>

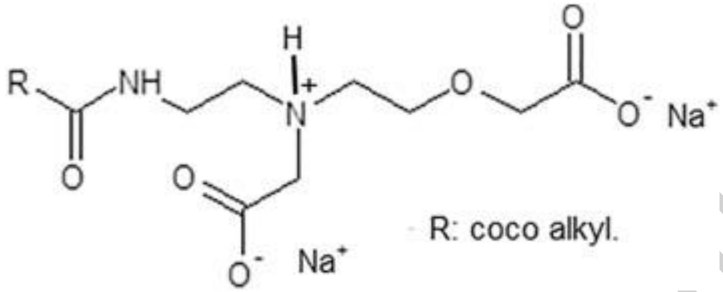
Synthesis of amine: The first step is to synthesize the amine that will be used as a starting material. This can be done by reacting an alkyl halide or an alkyl sulfonate with ammonia or a primary amine, using conditions such as high temperature and pressure or the presence of a catalyst.

Reaction with carboxylic acid: The amine is then reacted with a carboxylic acid such as glycine or sarcosine, which has a carboxylate group and a hydrogen atom that can be substituted by the amine. The reaction is typically carried out in the presence of a strong base such as sodium hydroxide, and may require a coupling agent or an activating reagent such as dicyclohexylcarbodiimide (DCC) or 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC) to facilitate the reaction.

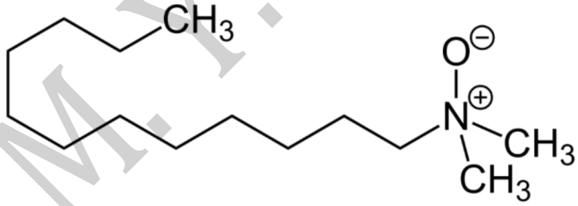
Purification and isolation: The resulting product is a quaternary ammonium compound with both positive and negative charges in its molecular structure, which is typically purified and isolated by methods such as extraction, precipitation, or chromatography.

The specific conditions and reagents used in the production of betaines can vary depending on the desired product, as well as the equipment and resources available in the manufacturing facility.

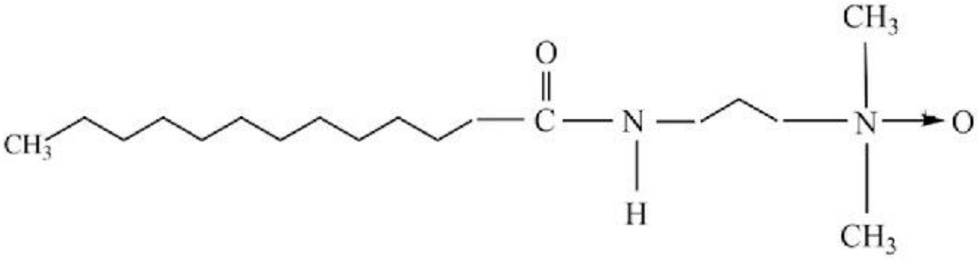
Disodium cocoamphodiacetate: commonly used in personal care products, such as facial cleansers and makeup removers.



Amine oxides: Amine oxides are cationic surfactants that contain an amine group and an oxide group. They are used as foam boosters, viscosity builders, and detergents in a variety of applications. Examples of amine oxides include lauryldimethylamine oxide and cocamidopropylamine oxide.



Lauryldimethylamine oxide



Cocamidopropylamine oxide

1

Introduction to Detergents

Michael S. Showell

CONTENTS

I. INTRODUCTION

Generally, the term “detergents” is applied to materials and/or products that provide the following functions:

1. Promote removal of material from a surface, e.g., soil from a fabric, food from a dish, or soap scum from a hard surface;
2. Disperse and stabilize materials in a bulk matrix, e.g., suspension of oil droplets in a mobile phase like water.

The ability of a detergent to perform either of these functions depends on the composition of the formulation, the conditions of use, the nature of the surfaces being treated, the nature of the substance to be removed and/or dispersed, and the nature of the bulk phase. Accordingly, detergent formulation is a complex process driven by the specific needs of the end user, economics, environmental considerations, and the availability of specific “actives” that can provide the required functionality.

By far the most common and familiar detergents are those used in household cleaning and personal care. These products can be grouped into four general categories:

1. Laundry detergents and laundry aids. These comprise mainframe laundry detergents in powder, liquid, tablet, gel, and bar form, fabric conditioner products typically in liquid or sheet form, and an array of specialty products like pretreaters (as sticks, gels, sprays, bars), presoaks (liquids, powders), and bleaches (liquids, powders). Typical laundry detergents are formulated to provide general cleaning, which includes removal of soils and stains as well as the ability to maintain whiteness and brightness. In addition, many premium laundry detergents offer additional benefits like fabric softening, dye lock, fiber protection, and disinfectancy.
2. Dishwashing products. These include detergents for hand and machine dishwashing and are typically provided in liquid, gel, powder, or tablet form. Hand dish wash products are formulated to remove and suspend food soils from a variety of surfaces. They also must deliver long-lasting suds, even at high soil loads, and they must be mild to skin. Products designed for automatic dishwashing must provide soil removal and suspension, control of water hardness and sheeting of water off dish surfaces in order to achieve a spot- and film-free finish, and produce little or no suds that would otherwise interfere with the operation of the machine. Rinse aids are specialty detergent formulations for automatic dishwashing designed to promote drainage of water from surfaces via lowering of surface tension. This helps minimize spotting and filming during drying.
3. Household cleaning products. Because no single product can provide the range of cleaning required on the various surfaces found in the home a broad range of household cleaning products are currently marketed. These are typically formulated either in liquid or powder form although gel, solid, sheet, and pad products are also available. So-called “all-purpose” cleaners are designed to penetrate and loosen soil, control water hardness, and prevent soil from redepositing onto clean surfaces. Many of these products also contain low levels of antibacterial actives like Triclosan to sustain disinfectancy claims. Powdered abrasive cleaners remove heavy accumulations of soil via the use of mineral or metallic abrasive particles. Some of these products may also bleach and disinfect through the incorporation of a bleach precursor like sodium perborate, sodium percabonate, or sodium dichloroisocyanurate.

4. Personal cleansing products. These include products for hand and body washing as well as shampoos, conditioners, and toothpastes. They are marketed primarily in bar, gel, and liquid forms. A major consideration in formulation of such products is the desired consumer aesthetic such as lather, skin feel, rinsability, smell, and taste. Formulations designed for cleaning may also provide moisturizing benefits, disinfectancy, conditioning, and styling effects.

Within each of these categories products are formulated with specific ingredients selected on the basis of their ability to perform the desired function and deliver "consumer preferred" aesthetics while meeting specific cost constraints, environmental regulations, and human safety guidelines.

In addition to these familiar consumer products, detergent formulations are used in a number of other applications and industries. These include:

1. Environmental remediation. Surfactant systems have been developed to aid in the clean up of contaminated groundwater supplies [1].
2. Enhanced oil recovery. Micellar and surfactant "floods" are among the most successful methods of enhancing recovery of oil from depleted reservoirs [2].
3. Nanoegineering. Researchers have used the phase behavior of surfactants to generate self-assembling nanosystems [3].
4. Formulation of paints and printing inks. Paints and inks comprise formulations wherein a pigment is dispersed into a liquid phase. The dispersion is typically achieved with surfactants and/or dispersing polymers [4].
5. Preparation and application of synthetic polymers. Emulsion polymerization and the preparation of latexes represent one of the largest uses for surfactants outside the cleaning arena [5].
6. Industrial/metal parts cleaning. Detergent compositions based on a CO_2 bulk phase have application in the cleaning of microelectronic components [1].
7. Medical applications. Mimics of human lung surfactants have been developed to treat respiratory distress syndrome in premature infants [1].
8. Lubricants. While highly diverse, lubricant formulations utilize the same basic additives: surfactants, dispersants, antiwear actives, antioxidants, corrosion inhibitors, and viscosity modifiers.
9. Textile processing. Detergent formulations are used to clean fibers prior to manufacture into finished textiles as well as lubricate the fibers during spinning and weaving.
10. Agricultural preparations. Pesticide and herbicide preparations are often formulated as aqueous dispersions with specific functional actives to promote even distribution of the active during application and fast penetration of the active upon contact with plants [6].

This diversity of application of detergents presents a rather formidable challenge when compiling a volume such as this on detergent formulations. Accordingly, rather than try to cover authoritatively all aspects of detergent formulations—a monumental task in its own right— I have elected instead in this chapter to provide some general background on detergency, the common ingredients used in detergent formulations, and general approaches to detergent processing or manufacture. This should provide a solid framework for the more in-depth discussions found in later chapters of this book. In addition, there are several good reference books available on the topic of detergent formulations [7– 9].

II. COMMON DETERGENT INGREDIENTS

Modern detergents can comprise 20 or more ingredients depending on what benefits the detergent is meant to deliver. It is not within the scope of this chapter to provide an extensive review of the myriad ingredients used in detergent formulations. Rather, the intent of this section is to provide a general overview of the more common elements— surfactants, dispersing polymers, builders and chelants, bleaching systems, solvents, and performance enhancing minors — in order to familiarize the reader with the general chemistry of detergent formulation. Subsequent chapters will provide significantly more detail on many of these ingredients and there are several reference books available on the topic [6–12].

A. Surfactants

Surfactants are arguably the most common ingredient of the detergent formulations described in this book. Their primary function is to modify the interface between two or more phases in order to promote the dispersion of one phase into another. In cleaning formulations, for example, surfactants serve to wet surfaces and reduce the interfacial tension between soil and water such that the soil is removed from the surface to be cleaned and dispersed in the aqueous phase. The ability of surfactants to concentrate at interfaces derives from their amphiphilic character—the combination of hydrophilic and hydrophobic moieties within the same molecule.

Generally, surfactants are classified according to their hydrophilic component as nonionic, anionic, cationic, or amphoteric. The nonionic surfactants have a hydrophilic component that is not ionized. Typical nonionic groups consist of polyoxyethylene, polyoxypropylene, alkanolamides, or sugar esters. As the name implies, the hydrophilic component of anionic surfactants comprises an anionic group, typically a sulfate, sulfonate, or carboxylate moiety. Likewise, the cationic surfactants comprise molecules containing a positively charged group such as a quaternary amine. The amphoteric surfactants are perhaps the most unique in that they comprise a hydrophilic group containing both anionic and cationic character such as the amino acids.

Typical hydrophobes for surfactants are the alkyl chains between C10 and C20. However, in some specialty surfactants the hydrophobe may consist of polysiloxane or perfluorocarbon backbones. Examples of common surfactants are shown in Table 1.

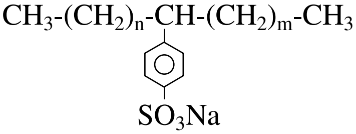
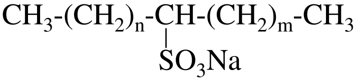
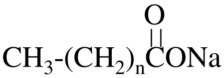
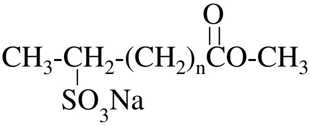
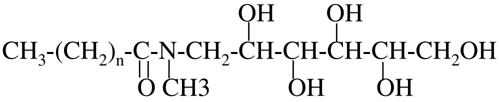
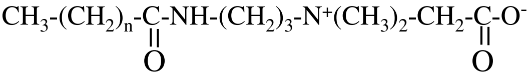
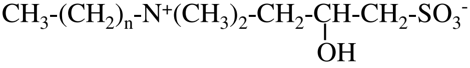
Until the 1940s detergents were formulated principally with the sodium or potassium salts of C12–C18 chain length fatty acids. The synthesis of surfactants from petroleum feed stocks in the late 1940s spurred the development of soap-free synthetic detergents that proved much more effective for cleaning in cooler wash temperatures and in hard water. Today, the linear alkyl benzene sulfonates, alkyl sulfates, alkyl ethoxy sulfates, and alkyl ether ethoxylates are the workhorse surfactants for most detergent formulations. Alkyl polyglucosides, alkyl glucosamides, and methyl ester sulfonates are also widely used [13]. Recent attention has been given to the use of internal methyl branched alkyl chains as the hydrophobe for certain anionic surfactants [14]. Such branching promotes improved solubility, particularly in cold, hard water.

For systems where water is not the continuous phase a variety of specialty surfactants are used. Examples include the polydimethylsiloxane-based surfactants for use in highly hydrophobic media and the acrylate-polystyrene co-polymers designed by DiSimone and colleagues for applications in cleaning systems utilizing condensed phase CO_2 [15].

B. Dispersing Polymers

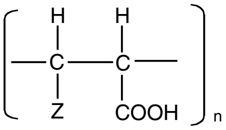
The suspension of solids or liquids in a continuous phase is a critical aspect in the formulation of paints, inks, coatings, and agricultural products such as herbicides. Suspension of soil after removal from a surface is important in cleaning applications to

Table 1 Common Surfactants Used in Detergent Formulations

Type	Structure
Anionic	
Linear Alkyl Benzene Sulfonate	
Paraffinsulfonate	 $CH_3\text{-}(CH_2)_n\text{-}\underset{SO_3Na}{CH}\text{-}(CH_2)_m\text{-}CH_3$
Alkyl Ether Sulfate	$CH_3\text{-}(CH_2)_n\text{-}O\text{-}(CH_2\text{-}CH_2\text{-}O)_xSO_3Na$
Fatty Acid Soap	 $CH_3\text{-}(CH_2)_n\overset{O}{\overset{\Vert}{C}}ONa$
Methyl ester sulfonate	 $CH_3\text{-}\underset{SO_3Na}{CH_2}\text{-}(CH_2)_n\overset{O}{\overset{\Vert}{C}}O\text{-}CH_3$
Cationic	
Quaternary monoalkylammonium chloride	$CH_3\text{-}(CH_2)_n\text{-}N^+(CH_3)_3Cl^-$
Nonionic	
Fatty alcohol ethoxylate	$CH_3\text{-}(CH_2)_n\text{-}O\text{-}(CH_2\text{-}CH_2O)_nH$
Amine oxide	$CH_3\text{-}(CH_2)_n\text{-}N(CH_3)_2 \rightarrow O$
Alkyl monoethanolamide	 $CH_3\text{-}(CH_2)_n\text{-}\underset{O}{\underset{\Vert}{C}}\text{-}NH\text{-}CH_2\text{-}CH_2OH$
N-methylglucosamide	 $CH_3\text{-}(CH_2)_n\text{-}\underset{O}{\underset{\Vert}{C}}\text{-}\underset{CH3}{N}\text{-}CH_2\text{-}\overset{OH}{CH}\text{-}\underset{OH}{CH}\text{-}\overset{OH}{CH}\text{-}\underset{OH}{CH}\text{-}CH_2OH$
Amphoteric	
Amidopropyl betaine	 $CH_3\text{-}(CH_2)_n\text{-}\underset{O}{\underset{\Vert}{C}}\text{-}NH\text{-}(CH_2)_3\text{-}N^+(CH_3)_2\text{-}CH_2\text{-}\underset{O}{\underset{\Vert}{C}}\text{-}O^-$
Alkyl sulfobetaine	 $CH_3\text{-}(CH_2)_n\text{-}N^+(CH_3)_2\text{-}CH_2\text{-}\underset{OH}{CH}\text{-}CH_2\text{-}SO_3^-$

avoid redeposition of the soil back onto the cleaned surface. Generally speaking, the particles to be suspended are sufficiently large that definite surfaces of separation exist between the dispersed phase and the dispersion medium [16]. In order to keep the dispersed phase stable it is important to adsorb functional actives at these surfaces to prevent aggregation. This is one of the critical functions of surfactants. However, another class of detergent actives has been developed to assist in particle suspension—the polymeric dispersants.

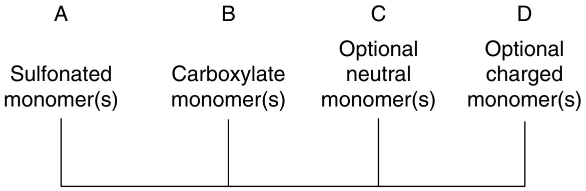
In general two types of polymeric dispersants are used in detergent formulations—polymers comprising ionically charged groups and nonionic polymers. Typical of the ionic dispersing polymers are the homopolymers of acrylic acid and copolymers of acrylic and maleic acids which are widely used in laundry detergent formulations:



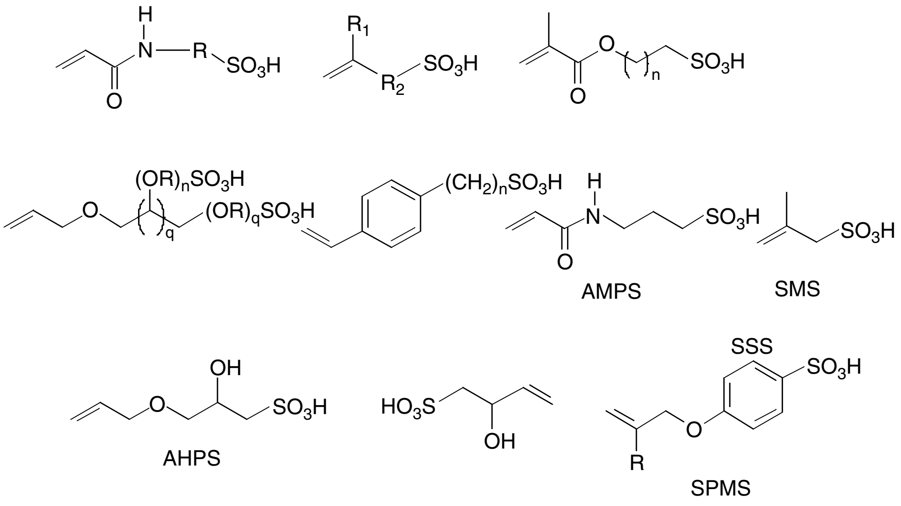
$$\left[-\underset{Z}{\overset{H}{\underset{|}{\overset{|}{C}}}}-\underset{COOH}{\overset{H}{\underset{|}{\overset{|}{C}}}}- \right]_n$$

where Z is either hydrogen, in the case of homopolymers of acrylic acid, or a carboxyl group in the case where the monomer unit is maleic acid. Polymers of this type are commonly found in powdered laundry detergent formulations where they assist in cleaning by acting as a dispersant for soil and inorganic salts, provide alkalinity control, and serve as crystal growth inhibitors [17].

Anionic dispersing polymers comprising carboxyl and sulfonate groups in the same backbone have been developed for use in water treatment where they act to prevent formation of inorganic scale. The polymers are generally of the following hybrid type:

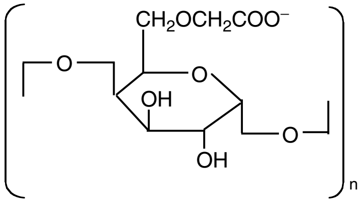


The key features are A and B. A, the sulfonated monomers, include the following groups:



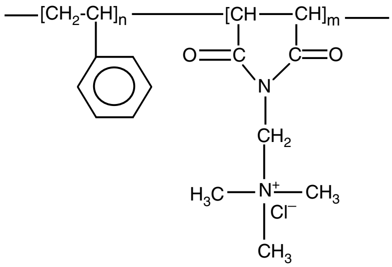
B usually comprises maleic, acrylic, or methacrylic acid. C and D are optional but can include acrylamide, vinyl acetate (alcohol), acrylate esters, cationics, or phosphonates [18].

Carboxymethylcellulose is another example of an anionic dispersing polymer widely used in laundry detergent applications

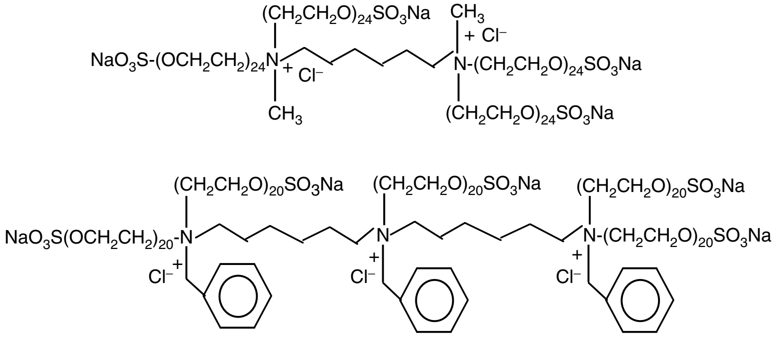


Considerable attention has been paid over the years to the preparation of biodegradable dispersants [19–21]. Examples include polyamino acid polymers such as polyaspartate prepared from the catalytic condensation of polyaspartic acid [22] and functionalized polysaccharides such as oxidized starches [23]. Recently, a novel process was reported for the preparation of functionalized polyaspartic acid polymers that expands the utility of these materials as dispersants for a variety of applications [24].

Cationic dispersants are less commonly used although some amphiphilic structures have been described as effective dispersants in high salt content media [25]:



Amphoteric dispersing polymers of the types shown below have also been reported to be good clay and particulate dispersants in certain laundry detergent formulations [26]:

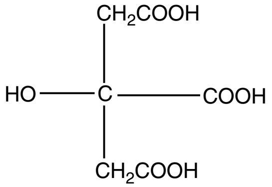


Nonionic polymers include polyethylene glycol, polyvinyl alcohol, and random and block ethoxy propoxy copolymers. Graft copolymers of polyalkylene oxide and vinyl acetate are reported to be effective antiredeposition agents for hydrophobic surfaces like polyester fabric [27].

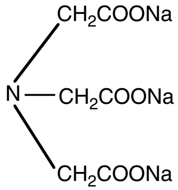
C. Builders and Chelants

Metal ion control is a common need in many detergent formulations. For example, in aqueous cleaning applications the presence of Ca^{2+} in the water can lead to the precipitation of anionic surfactant reducing the effective concentration available for cleaning. Fatty acids can precipitate as calcium soaps resulting in the formation of soap scum on hard surfaces, and many soils, especially inorganic clays, will precipitate with calcium leading to redeposition of the soil onto the surface being cleaned. Builders—a generic term used to refer to any number of materials whose primary function is the removal of Ca^{2+} and Mg^{2+} ions from aqueous solutions—and chelants are widely used in the formulation of various detergents.

Sodium tripolyphosphate (STPP) is among the best known and widely used detergent builder. In laundry detergent formulations it serves not only as an extremely effective calcium control agent but also provides dispersion, suspension, and anti-encrustation benefits. However, environmental concerns associated with large-scale release of phosphates into the environment lead to the development of a number of substitutes. Citric acid and sodium nitrilotriacetate are representative of soluble detergent builders



Citric Acid

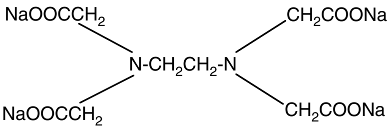


Sodium nitrilotriacetate

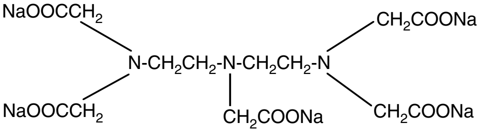
Sodium carbonates and noncrystalline sodium silicate form sparingly soluble precipitates with calcium and are frequently used in powdered detergent formulations where they also provide a source of alkalinity. However, to avoid encrustation of the calcium carbonate/silicate onto surfaces these building agents generally are co-formulated with a dispersing polymer like the polyacrylate/maleic acid copolymers described above and crystal growth inhibitors like HEDP (1-hydroxyethane diphosphonic acid).

Insoluble builders include the zeolites and layered silicates, which bind calcium via an ion exchange mechanism [28]. Zeolite A, $Na_{12}(AlO_2)_{12}(SiO_2)_{12}\bullet 27H_2O$, is the principal alternative to phosphate as a detergent builder. The Na^+ ions are exchangeable for Ca^{2+} while the larger hydration shell around Mg^{2+} tends to impede exchange.

Citric acid is also an excellent chelant for metal ions other than calcium and can be employed where the removal of transition metals such as copper, zinc, and iron is important. Other commonly used detergent chelants include ethylenediaminetetraacetate (EDTA)



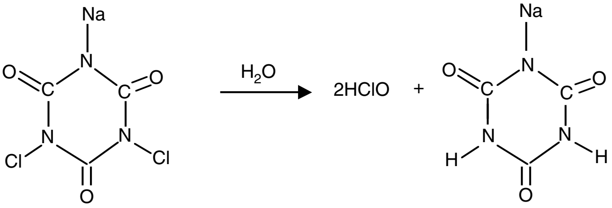
and diethylenetriaminepentaacetate (DTPA)



D. Bleaching Systems

Bleaches are common components of laundry, automatic dish wash, and hard surface cleaning detergent formulations where they act to destroy chromophoric groups responsible for color in soils via oxidative attack. Four basic technology approaches have been taken to deliver bleaching in these products—chlorine-based bleaches, peroxide-based bleaches, activated peroxide systems, and metal catalysts.

Chlorine-based systems are common in some powdered abrasive hard surface cleaners and automatic dishwashing products. Typically, hypochlorite bleach is delivered via precursor like sodium dichloroisocyanurate according to the reaction:



Peroxide-based bleaches either use hydrogen peroxide directly or appropriate precursors like perborate monohydrate, which generate peroxide according to the reaction:

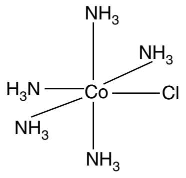
$$(NaBO_2H_2O_2)_2 \rightarrow H_2O2NaBO_2 + 2H_2O_2 + H_2O$$

Activated peroxide systems rely on perhydrolysis of a precursor molecule (generally referred to as an "activator" to generate a peracid bleach *in situ*:

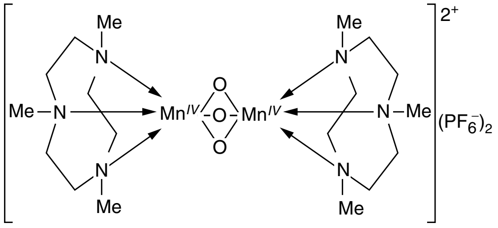
$$RCO_2H + H_2O_2 \rightarrow RCO_3H + H_2O$$

The two most common activators used in laundry detergents are N′N″-tetraacetyl ethylene diamine (TAED) and nonanoyloxybenzene sulfonate (NOBS). In an aqueous environment TAED undergoes perhydrolysis with the perhydroxyl anion from peroxide to generate peracetic acid. NOBS reacts in much the same way but generates the more hydrophobic pernonanoic acid.

A frequently studied approach to bleaching involves the use of transition metal catalysts [29]. Complexes of metals like Mn, Fe, Cu, and Co with certain organic ligands can react with peroxygen compounds to form reactive intermediates, which can potentially result in powerful bleaching action. Typical of these systems are the structures shown below:



From US Patent 5, 798, 326



From US Patent 5, 246, 612

E. Solvents

The selection of solvents for use in detergent formulation depends on the nature of the actives being formulated, the intended application of the detergent, and economics. Water is the dominant solvent in most household and industrial cleaning formulations. Generally speaking, water-based detergents are less toxic, more environmentally friendly, cheaper, more surface compatible, and easier to handle than petroleum-based solvents. However, many common detergent actives have limited solubility in water requiring formulation of a co-solvent and/or hydrotrope. Typical co-solvents used in household cleaning formulations include ethanol, glycerol, and 1,2-propanediol.

A hydrotrope, also called a “coupling agent,” is an organic compound that increases the ability of water to dissolve other molecules. Hydrotropes are commonly used in aqueous-based detergent formulations containing high concentrations of surfactant in order to achieve a shelf-stable, clear, isotropic fluid. Common hydrotropes are sodium xylene sulfonate, sodium toluene sulfonate, and sodium cumene sulfonate. A typical liquid dishwashing formulation, shown below in Table 2, is a good example of a surfactant-rich aqueous-based detergent system comprising both a co-solvent (in this case ethanol) and a hydrotrope (sodium cumene sulfonate):

Of course there are applications where water must be avoided. Perhaps the most recognizable of these is in the dry cleaning of fine textiles like silk and wool. Historically, this process has used volatile organic solvents like perchloroethylene as the bulk cleaning fluid. Concerns that such solvents may represent human and environmental safety hazards has recently lead to the development of alternative processes utilizing condensed phase CO_2 [30] and certain silicone oils like cyclic decamethylpentasiloxane, D5 [31]. Detergent formulations for use in such systems will typically comprise a solvent compatible with the bulk phase (e.g., polydimethylsiloxane in the case of the D5 system) and capable of solublizing the cleaning actives to be introduced into the bulk phase.

Table 2 Typical Hand Dishwash Formulation

Ingredient	Weight %
C_{12}-C_{13} Alkyl ethoxy (E1.4) sulfate	33
C_{12}-C_{14} Polyhydroxy fatty acid amide	4
C_{14} Amine oxide	5
C_{11} Alcohol ethoxylate E9	1
$MgCl_2$	0.7
Calcium citrate	0.4
Polymeric suds booster	0.5
Ethanol	1
Sodium cumene sulfonate	0.5
Minors and water	Balance

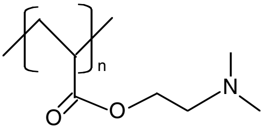
Other areas where water is not a suitable solvent include the cleaning of certain metal parts and electronic circuit boards. Here chlorinated hydrocarbons like perchloroethylene or methylene chloride, or volatile organics like methyl ethyl ketone have historically been used but regulatory pressure has resulted in a shift to more environmentally friendly solvents like terpenes and dibasic esters.

F. Performance Enhancing Minor Ingredients

Depending upon the end use of the detergent formulation and the benefits to be delivered a number of performance enhancing minor ingredients may be used. These include:

1. Enzymes. Used primarily in cleaning formulations enzymes promote soil removal by the catalytic breakdown of specific soil components. Proteases (enzymes that degrade protein) are the most common of all the detergent enzymes but amylases (starch degrading), lipases (lipid degrading), and cellulases (cellulase degrading) are also used [32].
2. Brighteners/fabric whitening actives. These materials enhance the visual appearance of white surfaces, typically cotton fabrics, by absorbing ultraviolet (UV) radiation and emitting via fluorescence in the visible portion of the spectrum. Typical whitening actives are built from direct linkage or ethylenic bridging of aromatic or heteroaromatic moieties. Among the most commonly used whiteners in laundry detergents are the derivatives of 4,4-diaminostilbene-2,2-disulfonic acid.
3. Foam boosters. In some applications, most notably hand dishwashing and shampoos; it is desirable for the detergent formulation to generate a large-volume, stable foam. While most surfactants are capable of generating and sustaining foam in the absence of soil, these foams rapidly collapse in the presence of soil, especially particulate and fatty soils. In applications where foam must be maintained throughout the course of detergent use, specific boosters may be added. Proteins have been shown to promote foaming in certain systems [33] especially in food and beverage applications [34]. Alkanolamides, particularly mono- and diethanolamides, are effective foam stabilizers used in dishwashing liquids and

shampoos [7]. Polymeric foam boosters of the type shown below have also proved effective in hand dish wash applications [35]:



4. Antifoam agents. In many applications it is desirable to minimize foam generation. For example, in automatic dishwashing foam generation can interfere with rotation of the spray arm leading to degradation in the performance of the dishwasher. Antifoam agents act to reduce or eliminate foams. They either prevent formation of the foam or accelerate its collapse. Alkyl ethoxylate nonionic surfactants are commonly used as foam control agents in detergents where application temperatures exceed the cloud point of the surfactant—the temperature at which the surfactant becomes insoluble. The insoluble nonionic-rich surfactant phase acts to break foam lamella promoting foam collapse.

   Hydrophobic particulate antifoam agents physically break foams by lodging in the foam film promoting rapid localized draining in the region of the film in contact with the particles. The calcium soaps of long-chain fatty acids are effective at foam control as are hydrophobic silica particles. Particularly effective antifoams are comprised of colloidal hydrophobic silica particles suspended in a silicone oil like polydimethyl siloxane. The hydrophobic oil promotes spreading of the particles at the air-water interface thereby ensuring entrapment in the foam film and subsequent foam disruption [7].
5. Thickeners. It is often desirable to modify the rheology of a detergent formulation to fit a particular application. For example, gel-type automatic dishwashing detergents are thickened to help suspend phosphate and other solids that would otherwise separate out from the liquid phase. Thickening can be achieved through the use of inorganic electrolytes, e.g., NaCl; clays, such as laponite or hectorite; or a high-molecular-weight polymer like carboxymethylcellulose, guar, or xanthan gum. The Carbopol® series of polymers from Noveon, homo- and copolymers of acrylic acid cross linked with polyalkenyl polyether, are particularly effective thickeners for household cleaning detergent formulations.
6. Soil release polymers. Soil release refers to the enhanced removal of soil from a surface as a result of modification of that surface with a specific agent, typically a polymer that alters surface polarity thereby decreasing adherence of soil. Used primarily in laundry detergent formulations soil release polymers provide significant changes in surface energy, which in turn can lead to dramatic improvements in the removal of soils. Carboxymethyl cellulose (CMC) is the archetypical soil release polymer. CMC absorbs onto cotton fabric owing to the similarity in structure between the cellulose backbone of CMC and the cellulose polymer of cotton fibers. Once absorbed, the carboxyl moiety creates a high net negative charge on the fabric surface effectively repelling negatively charged soils, especially clays [7].

Other soil release polymers used in detergents are derivatives of polyester-polyether block copolymers that are capped with nonionic (ethoxylates), anionic (typically sulfonates), or cationic (typically quaternary amines) groups to achieve deposition and release from specific formulations [36].

III. REPRESENTATIVE DETERGENT FORMULATIONS

This section provides examples of detergent formulations comprising the ingredients discussed in Section II. This is by no means an exhaustive compilation. Rather, the intent is to illustrate the variety of detergent formulations and how the composition of the formulation varies depending on the intended use. Subsequent chapters of this book will provide more detail on detergent formulations for specific applications.

A. Laundry Detergent Formulations

Examples of granular laundry detergent formulations are shown in Table 3.

Table 4 illustrates typical liquid laundry detergent formulations.

B. Dishwash Detergent Formulations

Examples of typical liquid hand dishwash formulations are provided in Table 5.

Examples of granular detergent formulations for use in automatic dishwashing applications are illustrated in Table 6.

C. Hard Surface Cleaning Formulations

Examples of liquid hard surface cleaning formulations are illustrated in Table 7.

D. Personal Care Detergent Formulations

Table 8 provides examples of typical shampoo formulations.

Examples of body washes are provided in Table 9.

E. Oral Care Detergent Formulations

An oral mouthwash formulation is illustrated in Table 10.

Examples of Toothpaste formulations are provided in Table 11.

In the toothpaste formulations illustrated in Table 11 note the use of silica as an abrasive cleaning agent.

F. Agricultural Detergent Formulations

Herbicidal compositions typically comprise an aqueous emulsion of the active with appropriate surfactants to insure effective spreading and penetration of the herbicide into plants. Typical compositions comprising the well-known herbicidal active glyphosphate are illustrated in Table 12.

G. Automobile Detergent Formulations

A variety of detergent compositions are used in the care and maintenance of automobiles. Chapter 8 provides an extensive review of the components used in such formulations. The composition in Table 13 illustrates a formulation designed to clean and provide a waxed finish to the exterior of automobiles.

A formulation designed to remove grease from automobile engines and engine compartments is illustrated in Table 14.

Table 3 Representative Granular Laundry Detergent Formulations

Ingredients Examples	Weight %		
	A	B	C
C_{11}-C_{13} Linear alkyl benzene sulfonate	8	10	—
C_{12}-C_{16} Alkyl ethoxy (E2) sulfate	—	—	5.3
C_{14}-C_{16} Secondary alkyl sulfate	2	—	—
C_{14}-C_{15} Alkyl sulfate	—	7	—
C_{16}-C_{18} Alkyl sulfate	2	—	—
C_{14}-C_{15} Alkyl ethoxy (E2) sulfate	—	1	—
C_{12}-C_{15} Alcohol ethoxylate E7	3.4	—	—
C_{14}-C_{15} Alcohol ethoxylate E7	—	1	3.3
STPP	—	—	10.7
Zeolite A	18	22	10.7
Carbonate	13	19	6
Silicate	1.4	1	7
Sodium sulfate	26	10	40
Na perborate tetrahydrate	9	—	5
Na perborate monohydrate	—	1	—
TAED	1.5	—	0.5
NOBS	—	4	—
HEDP	0.3	—	—
DTPA	—	0.4	—
Protease[a]	0.8	0.3	0.3
Amylase[a]	0.8	0.1	0.1
Lipase[a]	0.2	—	0.2
Cellulase[a]	0.15	—	0.3
Acrylic/maleic copolymer	0.3	1	0.8
CMC	0.2	—	0.2
Polyester-based soil release polymer	0.2	0.4	—
Minors	Balance	Balance	Balance

[a] Enzymes are added in granulated form where typical enzyme level in the granulate ranges from 1 to about 8% by weight of the granulate formulation.

Source: From U.S. Patents 6,326,348 B1 and 6,376,445 B1.

H. Detergent Formulations for Cleaning Food Processing Equipment

Processing of food contaminates surfaces with lipids, carbohydrates, and proteins. A variety of detergent formulations have been developed specifically for cleaning food processing and preparation equipment. Table 15 provides an example of one such detergent utilizing high alkalinity as the major detersive component:

More user friendly and environmentally compatible formulations can be built around enzyme technology to facilitate the removal of protein bound to surfaces. Examples are illustrated in Table 16.

Table 4 Representative Liquid Laundry Detergent Formulations

Ingredients Examples	Weight %		
	A	B	C
C_{11}-C_{13} Linear alkyl benzene sulfonate	12	—	28
C_{12}-C_{15} Alkyl sulfate	—	18	—
C_{14}-C_{15} Alkyl sulfate	—	—	14
C_{14}-C_{15} Alkyl ethoxy (E2.5) sulfate	12	2	—
C_{12}-C_{13} Alcohol ethoxylate (E7)	3	4	—
C_{11}-C_{13} Alcohol ethoxylate (E8)	—	—	3
C16-C18 Alkyl N-methyl glucamide	—	8	2
C_{12}-C_{14} Fatty acids	2	11	—
Oleic acid		—	3.4
Citric acid	3	5	5.4
Sodium cumene sulfonate	4	—	—
NaOH	6	—	0.4
Ethanol	—	3	7
1,2 propanediol	3	10	6
Monoethanolamine	3	9	17
Protease[a]	0.8	0.8	1
Amylase[a]	—	0.3	—
Lipase[a]	—	0.1	—
Cellulase[a]	—	0.1	—
Polyester-based soil release polymer	0.2	0.2	—
Water + minors	Balance	Balance	Balance

[a] Enzymes are added from liquid stocks where typical enzyme levels in the stock ranges from 1 to about 8% by weight of the liquid stock formulation.

Source: From U.S. Patent 6,376,445 B1.

I. Detergent Formulations for Metal Component Cleaning

Industries involved in repair and replacement of mechanical parts often require that those parts be cleaned prior to inspections, repair, or replacement. Generally, mechanical parts have been exposed to a wide variety of contaminants including dirt, oil, ink, and grease that must be removed for effective repair or service. A variety of metal cleaners have been developed to clean such surfaces. For example, solvent-based cleaners containing either halogenated or nonhalogenated hydrocarbons are common. However, the use of these cleaners carries certain environmental and worker safety issues. Where appropriate, aqueous-based cleaners are preferred for cost, safety, and environmental concerns. Table 17 provides example formulations of aqueous-based metal cleaning formulations:

IV. DETERGENCY THEORY AND MECHANISMS

As noted in the introduction the two major functions of detergents are to remove materials from surfaces and keep materials suspended in a bulk phase. Each function requires work

Table 5 Representative Liquid Hand Dishwash Detergent Formulations

Ingredients Examples	**Weight %** A	**B**	**C**
C_{12}-C_{13} Alkyl ethoxy (E3.5) carboxylate	22	—	—
C_{11}-C_{17} Alkyl ethoxy (E2.5) sulfate	—	29	34
C_{12}-C_{13} Alcohol ethoxylate (E3.5)	1.3	—	—
Polyhydroxy fatty acid amide	—	—	7
C_{12}-C_{13} Alkyl sulfate	6	—	—
C_{12}-C_{14} Amidopropyl diemethyl betaine	3	0.9	2
C_{14} Amine oxide	3	3	3
$MgCl_2$	0.6	3.3	—
$Mg(OH)_2$	—	—	2
Methyldiethanol amine	10	—	—
Ethanol	9	4	9
Xylene sulfonate	—	2	2
Water + minors	Balance	Balance	Balance

Source: From U.S. Patents 5,376,310 and 6,376,445 B1.

Table 6 Representative Granular Automatic Dishwashing Detergent Compositions

Ingredients Examples	**Weight %** **A**	**B**
STPP	54	30
Carbonate	14	31
Silicate	15	7.4
Sodium perborate monohydrate	8	4.4
Alcohol ethoxylate	2	1.2
Metal bleach catalyst	0.01	—
TAED	—	1
Protease[a]	2	2.5
Amylase[a]	0.3	0.5
Sulfate	5	23.4
Minors	Balance	Balance

[a] Enzymes are added in granulated form where typical enzyme level in the granulate ranges from 1 to about 8% by weight of the granulate formulation.

Source: From U.S. Patent 6,376,445 B1.

Table 7 Representative Liquid Hard Surface Cleaning Compositions

Ingredients Examples	Weight % A	Weight % B	Weight % C
Hydrogen peroxide	7	—	—
C_{10} Alkyl sulfate	2	—	—
Na octyl sulfate	—	2	—
Na dodecyl sulfate	—	4	—
C_{12}-C_{13} Alcohol ethoxylate (E3)	2	—	—
C_9-C_{11} Alcohol ethoxylate (E10)	2	—	—
Betaine	—	—	0.8
Butyl octanol	0.5	—	—
Butyl carbitol	—	4	—
Isopropanol	—	—	30
Butoxypropanol	—	—	15
Sodium hydroxide	—	0.8	—
Silicate	—	0.04	—
Monoethanolamine	—	—	2.5
Quaternary ammonium disinfectant	—	—	0.5
Tartaric acid	—	—	0.1
Water + minors	Balance	Balance	Balance

Source: From U.S. Patents 6,277,805 and 6,376,445.

Table 8 Representative Shampoo Formulations

Ingredients Examples	Weight % A	Weight % B	Weight % C	Weight % D
Ammonium lauryl sulfate	14	12.5	48	50
Isostearamidopropyl morpholine lactate	—	—	3	6
Cocoamidopropylbetaine	2.7	4.2	—	—
Sodium cocosulfate	—	—	4	3
Polyquaternium-10	0.3	0.3	—	—
Trimethylolpropane caprylate caprate	0.3	0.3	—	—
Cocamide MEA	0.8	—	—	—
Cetyl alcohol	—	0.4	—	—
Stearyl alcohol	—	0.2	—	—
Glycerol stearate	—	—	1.5	1.5
Ethylene glycol distearate	1.5	1.5	—	—
Dimethicone	1	1	—	—
EDTA	—	—	—	0.4
Water + minors	Balance	Balance	Balance	Balance

Source: From U.S. Patent 6,007,802 and HAPPI, February 2001.

Table 9 Representative Body Wash Formulations

Ingredients Examples	**Weight %**	
	A	**B**
Sodium cocoamphoacetate	5	14
Cocaminopropyl betaine	10	10
Disodium lauryl sulfosuccinate	—	30
Disodium oleamido MEA sulfosuccinate	5	—
Disodium laureth sulfosuccinate	5	—
Sodium laureth sulfate	17	—
Isostearamidopropyl morpholine lactate	2	6
Hydrolyzed wheat protein derivative	1	—
Polyquaternium–7	2	3
Glycol distearate	—	3.5
Sodium chloride	—	3
Water + minors	Balance	Balance

Source: Courtesy of T. Schoenberg, The McIntyre Group Ltd.

Table 10 Oral Mouthwash Formulation

Ingredients tb	**Weight %**
	10
Glycerine	10
Betaine	1.4
Ethanol	10
Propylene glycol	7
Flavoring	0.2
Triclosan	0.06
Water	Balance

Source: From U.S. Patent 5,681,548.

(W) to be done on the system. In the case of removal that work, defined here as W_R, is a measure of the energy required to move a substance from a surface into the bulk phase. In general, surface-active agents like surfactants promote removal from surfaces by lowering the interfacial energy between the substrate and the bulk phase. In the case of suspension, the work, W_S, to suspend in the bulk phase is a measure of the energy required to keep materials from aggregating, flocculating, or adhering to a surface. Generally, suspension is achieved either by electrostatic repulsive effects or steric stabilization. Subsequent chapters of this book provide extensive detail on how to remove and suspend materials via chemical means. The purpose of this section is to provide a general thermodynamic underpinning to the phenomena of soil removal and particulate suspension so that the reader can better understand the mechanisms by which detergent chemicals function.

Table 11 Representative Toothpaste Formulations

Ingredients Examples	Weight %		
	A	B	C
Glycerin	27	29	29
Polyethylene glycol	2	1	3
Xanthan gum	0.3	0.4	0.3
CMC	0.2	0.2	0.2
Water	5	7	5
Sodium saccharin	0.5	0.4	0.5
Sodium fluoride	0.2	0.2	0.2
Xylitol	10	10	10
Poloxamer	2	3	—
Sodium alkyl sulfate	6	4	4
Cocamidopropyl betaine	—	—	2
Flavoring	1.1	1	1
Sodium carbonate	2.6	3	3
Titanium dioxide	1	1	1
Silica	20	20	20
Sodium bicarbonate	1.5	1	1
Propylene glycol	15	11	12
Tetrasodium pyrophosphate	5	7	7
Calcium peroxide	0.5	1	1

Source: From U.S. Patent 5,849,269.

Table 12 Representative Herbicidal Formulations

Ingredients Examples	Weight %		
	A	B	C
Butyl stearate	18	1	7.5
Span 80	3	—	3
Tween 20	5	—	5
C12-15 Alcohol ethoxylate (E20)	—	10	—
Glyphosphate (as g a.e./liter)	100	163	160
Water	Balance	Balance	Balance

Note: a.e. = active ether

Source: From U.S. Patent 6,479,434.

A. Removal Mechanisms

For simplicity, in the following discussion, materials to be removed from a surface will be generically referred to as soils. The basic concept illustrated here will be for surfactant-

Table 13 Detergent Formulation for Cleaning and Care of Automobile Exteriors

Ingredients	Weight %
Micronized polymer wax	6
Amino functional silicone	3
Polydimethylsiloxane	1
Paraffinic hydrocarbon solvent	15
Alkyl alcohol ethoxylate	0.5
Fluoroamide polymer	0.2
Water	Balance

Source: From U.S. Patent 5,782,962.

Table 14 Automobile Engine Cleaner

Ingredients	Weight %
Dodecyl oxydibenzene disulfonate	6
Nonylphenol-9 ethoxylate	1.2
Sodium orthosilicate	1.2
Tetra potassium pyrophosphate	8
C18 tall oil	9.5
Heavy aromatic naphtha	14
Water	Balance

Source: From U..S Patent 3,717,590.

Table 15 Detergents for Cleaning Food Processing Equipment

Examples	A	B	C
Sodium hydroxide	15	15	15
Sodium polyacrylate	2.7	2.7	2.7
1,2,4 Tricarboxylic acid	0.8	—	—
1-Hydroxyethylidene-1,1-disphosphonic acid	—	0.3	0.8
Sodium hypochlorite	2	3	3
Water	Balance	Balance	Balance

Source: From U.S. Patent 4,935,065 to Ecolab Inc.

Table 16 Enzymatic Based Detergents for Cleaning Food Processing Equipment

Ingredients	Weight %			
Examples	A	B	C	D
Triethanolamine	2	2	2	2
Sodium metabisulfite	1	1	1	1
Propylene glycol	12	12	15	15
Sodium xylene sulfonate	20	20	20	20
Ethoxylated propoxylated nonionic	25	25	25	25
Protease	6.3	6.3	3.1	3.1
Water	Balance	Balance	Balance	Balance

Source: From U.S. Patent 6,197,739 B1 to Ecolab Inc.

Table 17 Representative Aqueous-Based Metal Cleaning Detergents

Ingredients	Weight %			
Examples	A	B	C	D
Sodium carbonate	3	3	3	3
Borax	0.3	0.3	0.3	0.3
N-octylpyrrolidone	—	—	—	2
1,2,3-Benzotriazole	0.3	0.3	0.3	0.3
C_9-C_{11} Alcohol ethoxylate (E2.5)	2	—	—	2
C_9-C_{11} Alcohol ethoxylate (E6)	2	—	—	2
C_{12}-C_{15} Alcohol ethoxylate (E9)	—	4	—	—
C_{14}-C_{15} Alcohol ethoxylate (E7)	—	—	4	—
Acrylic acid polymer	0.5	0.5	0.5	0.5
NaOH	0.5	0.5	0.5	0.5
Sodium silicate	2	2	2	2
Sodium nonanoate	6.5	6.5	6.5	6.5
Water	Balance	Balance	Balance	Balance

Source: From U.S. Patent 6,124,253 to Church & Dwight Co.

mediated removal of soil from a surface. Soil removal mechanisms can be considered to comprise several steps:

1. Surfactant transport to an interface. This can occur with the surfactant in the monomeric form, in which case kinetics of transport are fairly rapid (10^{-5} cm^2/sec), or with the surfactant in aggregated or micellar form in which case the kinetics of transport are relatively slow (10^{-7} cm^2/sec). The kinetics of surfactant transport and adsorption at the interface can be measured via dynamic interfacial tensiometry [37–41].
2. Adsorption of surfactant at the solution/soil interface, solution/atmosphere interface, and surface/solution interface. This step results in lowering of the interfa-

cial energies at each of these interfaces. Adsorption is driven by the surfactant packing parameter ($P = V/a_oI$) where V is the volume described by the hydrophobic portion (alkyl chain) of the surfactant, a_o is the mean cross-sectional area of the surfactant head group, and l is the all trans alkyl chain length of the hydrophobe (alkyl chain) [42]. Surfactants with $0 < P < 1/3$ form micelles in aqueous solution. Surfactants with $1/3 < P < 1/2$ form wormlike micelles and surfactants with $\frac{1}{2} < P < 1$ display vesicle formation. Controlling the surfactant packing parameter close to 1 (flat surfactant film) promotes strong adsorption and delivers very low-soil/bulk phase equilibrium interfacial tensions.

3. Formation of a surfactant:soil complex. This typically is represented as surfactant coating the soil to be removed either in a monolayer, or, at high enough surfactant concentrations with bilayer structures. During this step surfactant can promote solid soil softening and liquifaction. This is a critical step to promote roll-up or emulsification that takes place only with liquid soils.
4. Desorption of the surfactant:soil complex. For oily soils this occurs either via the classical roll-up mechanism or by solubilization of the oil into micellar surfactant aggregates. In the case of liquid soil, the energy required to remove the soil can be expressed as $\gamma_{ow}(1+\cos\theta)$ where γ_{ow} is the soil/solution interfacial tension and θ is the soil/substrate contact angle. For large contact angle (180°) roll-up of the soil occurs. For small contact angles emulsification via low γ_{ow} is the major mechanism of soil removal.
5. Transport of the surfactant:soil complex away from the surface. In the case of greasy soils that have lower density than the bulk solution, the soil simply floats to the surface. In other cases, mechanical energy or agitation is critical to move the surfactant:soil complex away from the interface.
6. Stabilization of the dispersed soil to prevent redeposition (see Section IV B).

The work, W_R, to move soil (o) from the surface (s) to the bulk phase (w) can be directly related to the interfacial tensions of the various interfaces through the following [7]:

$$W_R = \gamma_{sw} + \gamma_{ow} - \gamma_{os} \tag{1}$$

where γ_{sw} is the interfacial tension between the surface and bulk phase, γ_{ow} is the interfacial tension between the soil and the bulk phase, and γ_{os} is the interfacial tension between the soil and the surface. From this equation it can be seen that the work required to remove soil from a surface is reduced when the interfacial tensions between the surface and bulk phase and soil and bulk phase are minimized and the interfacial tension of the soil-surface is increased. This is exactly the effect that surfactants have. By adsorbing at the surface, bulk-phase, and soil interfaces surfactant lowers interfacial energies, decreasing the free energy associated with moving the soil from the surface into the bulk phase. Surfactant adsorption causes the surface/bulk phase (γ_{sw}) and soil/bulk phase (γ_{ow}) interfacial tensions to drop while the interfacial tension between soil and surface (γ_{os}) increases thereby facilitating movement of the soil into the bulk phase.

One aspect of the above that is often ignored is step one, transport of surfactant to the various interfaces. The presence of monomeric surfactant is critical to rapid transport of surfactant to the interface and rapid lowering of the interfacial tensions (IFT). However, solubilization is dependent on the presence of micelles. As surfactant concentration in solution is raised aggregates (micelles) form and at a certain concentration (critical micelle concentration, CMC) the monomer concentration of surfactant remains constant and additional surfactant resides in micelles. The formation of micelles reduces the capacity of the surfactant to adsorb at the interface and reduce IFT that is critical in step 2. Therefore, there is an optimum CMC that must be achieved in order to optimize steps 1 and 2 above while still allowing efficient solubilization. This optimum is dependent on the nature of the soil being removed, the substrate (hydrophobicity), and the surfactant system used.

The mechanism outlined above is generally applicable for oily soils. For particulate soils consideration of the electrostatic and van der Waals forces of attraction between the particle and the surface need to be considered because most particulate dirt and most surfaces tend to be charged due to the presence of surface exposed silicic acid, hydroxyl, or carboxyl groups [43]. .

Again, the process can be described in a series of steps [44]. In the first step a soil particle, P, adhering to a surface, S, is removed a distance δ with no penetration of liquid between the soil and the surface. The process requires work input, ω_1, to overcome the van der Waals attraction between P and S. Then detergent solution penetrates the space between P and S, allowing surfactant to adsorb at the solution-particle interface and the surface-solution interface, and a net sum of work, ω_2 , is obtained. The total work done in this first step is:

$$W_1 = \omega_1 - \omega_2 \tag{2}$$

In the second step the particle is removed from the surface to a distance large enough that there are effectively no forces of interaction between P and S. The work for this second step, W_2, is composed of contributions from van der Waals attractions and the electrostatic repulsions between P and S, and is equal to the total potential energy of the system at the distance δ such that $W_2 = -\varphi_\delta$ and the work done for the total process of removing an adhering particle, P, from surface S is equal to the sum of W_1 and W_2 or:

$$\Sigma_W = W_1 + W_2 = \omega_1 - \omega_2 - \varphi_\delta \tag{3}$$

The work, ω_2, created when surfactant adsorbs onto the particle and the surface can, in the first approximation, be described as the sum of various interfacial energies, similar to Eq. (1):

$$\omega_2 = \gamma_{sp} - \gamma_{sw} - \gamma_{pw} \tag{4}$$

where γ_{pw} is the interfacial tension between the particle and the solution phase. According to Eq. (3) the removal of particulate soil becomes easier as the total work to remove the particle, Σ_W, becomes smaller. The addition of surfactant reduces both γ_{sw} and γ_{pw} such that ω_2 increases, which helps to lower the total work of removal. In addition, the total potential energy of the system φ_δ is the sum of the attractive van der Waals interactions, $\varphi_{\delta,A}$, and the repulsive interactions, $\varphi_{\delta,R}$, due to surface charges. The adsorption of surfactant, especially anionic surfactant, at the surface-solution and particle-solution interfaces serves to decrease the attractive force and increase the repulsive force thereby promoting removal to a distance where there are no longer any attractive forces between particle and surface.

B. Suspension Mechanisms

Once material is removed from a surface it must be suspended in the bulk phase to avoid redeposition. For hydrophobic liquid soils in aqueous media, suspension is typically accomplished by entrapment of the soil within the surfactant micelle or vesicle. For particulate soils suspension is often best achieved by adsorption of a charged polymer onto the surface of the particle thereby increasing electrostatic repulsion between particle-

particle and particle-surface interactions. There are two general mechanisms for suspending soil in solution— electrostatic repulsion and steric stabilization.

In polar media, most substances will acquire a surface electric charge as a result of ionization of surface chemical groups, ion adsorption, and ion dissolution [16]. In aqueous solutions most surfaces and most soil particles are negatively charged. As a result both soil and surface possess an electrical double layer. The electrical double layer is comprised of a compact layer of ions of opposite charge to the surface and a more diffuse double layer comprised of counter- and co-ions distributed in a diffuse manner in the polar medium. As described in Section IV A, the total potential energy for a system comprised of a particle at some distance, δ, from a surface is the sum of the attractive force, $\varphi_{\delta,A}$, and the repulsive force $\varphi_{\delta,R}$. When two particles of the same net surface charge approach one another, or when a particle approaches a charged surface, they repel each other as their double layers start to overlap. The particles have to overcome this electrical barrier in order to get close enough for van der Waals attraction to take over. When the potential energy barrier $\varphi_{\delta,R}$ is high particles tend to stay dispersed in the bulk phase. However, if the electrical double layer is compressed by high ionic strength or shielded by adsorption of an organic layer coalescence and aggregation can occur resulting in redeposition of soil particles back onto the surface. Electrostatic repulsion is best achieved in low ionic strength media where the electrical double layer on particles and surfaces is diffuse. An alternative strategy is to adsorb a charged polymer, such as the acrylic acid polymers described in Section II B, or a charged surfactant onto the surface.

When particles having adsorbed layers (polymer or surfactant) collide, their adsorbed layers may be compressed without penetrating. This results in reduced configurations available to the adsorbed layer. In thermodynamic terms the reduction in potential configurations is expressed as a decrease in entropy for the system or an increase in free energy. This increased free energy of stabilization results from the "elastic" effect of colliding adsorbed layers and is referred to as steric stabilization. The positive free energy change is related to both the enthalpy and entropy change by $\Delta G = \Delta H - T\Delta S$. Stabilization can therefore come either as a result of a positive change in enthalpy or a decrease in entropy. A positive ΔH reflects the release of bound solvent from the polymer chains as they interact and a negative ΔS results from the loss of configurational freedom of the polymer [16]. Steric stabilizers are usually block copolymers that make up a hydrophobic part (e.g., polyethyleneterepthalate) which attaches to the particle surface and a hydrophilic part (e.g., polyethylene glycol) which trails out into the bulk solution.

Effective detergency results when the detergent formulation is designed to maximize four basic properties; penetration, wetting, dispersion, and emulsification. These four factors combined determine the ultimate effectiveness of the detergent formulation. Subsequent chapters of this book provide significantly more detail on how to design effective detergents for a variety of specific applications.

ACKNOWLEDGMENTS

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3

Laundry Detergent Formulations

Randall A. Watson

CONTENTS

I. INTRODUCTION

A. Scope of Chapter

A chapter on laundry detergent formulations would have been significantly shorter and less complex a few decades ago. It wasn't so long ago that the same basic detergent was used for clothes, dishes, floors, and even the body! In the search for ever better cleaning and value, and larger market shares, there has been an incredible multiplication of laundry detergents. Not all of the forms and formulations are available or relevant in every market. Nonetheless, today in most markets the choices presented to consumers in the laundry detergent section of their local store is nothing short of bewildering. Likewise, the number of choices and demands faced by the detergent formulator continues to grow.

This chapter is designed to first present the logic behind the plethora of laundry detergent forms and formulations. Despite the growing diversity of forms and formulas, the underlying chemistry and general concepts remain essentially unchanged. A brief discussion of the key unifying formulation concepts is therefore presented, along with a brief description of the key ingredients used in these formulations. The bulk of this chapter is devoted to discussion and examples of each of the key laundry detergent forms available today. Some general conclusions and discussion of future trends closes the chapter.

The reader will appreciate that each of the topics covered in this chapter could be, and in many cases are, the subject of entire chapters or books in and of themselves. As such, it is not the aim of this chapter to provide an exhaustive discussion of each topic. Rather, it is intended to provide an overview of the many different products and product forms that fall generally under the heading of "home laundry detergent." For those looking for still more details, the references will direct them to more in-depth reviews.

B. Why Different Forms?

The number of different laundry products and types available today is nothing short of remarkable. So is the level of effort from the large number of different formulators in different companies around the world. On one level the reason for this is clear. Consumers have become more demanding and more discriminating in their purchases of all types of consumer goods. They are also looking for more and more customization. "One size fits all" no longer works in much of the world. These trends are also reflected in laundry products. As companies have responded to these new consumer demands they have also realized that the company who best meets their needs can reap rich rewards. Why there should be so many different formulas and forms is perhaps less obvious, though for most there are equally clear answers. These answers are usually related to differences in consumer habits and wash conditions, differences in the targeted benefits, and differences in consumer preferences.

Different laundry habits and conditions are the most obvious reasons for different laundry formulations. Wash conditions range in concentration from several thousand ppm of detergent in the typical European front-loading washing machine, to only a few hundred ppm in Japanese machines. These same two countries also illustrate the extremes in wash temperatures. Though the average washing temperature is falling everywhere in the world due to energy and environmental concerns, the typical front loading machine still includes a boil-wash cycle. On the other hand, in Japan and several others countries consumers often use ambient wash-water temperatures, meaning that in the winter the wash can be as low as 2°C. Add onto these variations the differences in wash/rinse times—where in a U.S. top-loading machine it can be as short as 12 minutes and in a European front loader as long as almost 2 hours—and one can easily see the challenge.

Of course many consumers in the world don't even use washing machines. When considering the various ways that handwash laundry is executed around the world the variables multiply even more. One of the more interesting variables the formulator encounters in handwash laundry is the reuse of the laundry liquor for more than one load. This is done both to conserve often-precious water supplies, and to stretch the value of their detergent purchase. In this situation consumers often start with a load of whites and then reuse the wash solution for one or more loads of their colored or more delicate items. Providing good performance throughout this habit is extremely challenging. Also, hand washers can spend several hours each week with their hands immersed in laundry liquors. Hand skin mildness is therefore another concern largely absent from machine wash geographies.

Even within a given laundry habit, a single detergent formulation that can work for all clothes under all conditions remains unobtainable. The same formulation that delivers superior dingy cleaning and whiteness can result in unacceptable fading of colored garments. In a similar vein, formulas containing protease enzymes provide superior stain removal, but can prove disastrous when used to wash fine wool or silk garments. For formulas that deliver through-the-wash softening via clay, the challenge is to provide acceptable base cleaning while still depositing enough softening clay for a benefit. These are just a few of the many dichotomous challenges faced by the formulator. The result is a number of detergents formulated specifically against targets such as softness, delicate care items, brightly colored items, etc.

Table 1 Average Global Machine Wash Conditions

	Europe	**North America**	**Japan**
Wash water volume (L)	13	64	49
Washing Time (min)			
–Total wash cycle	115[a]	35	na
–Main wash duration	75[a]	12	10
	[a]Long cycle		
Ave. wash temp. (˚C)	40–90	10–45	4–20
Water Hardness	2.5 mmol	1.0 mmol	0.5 mmol
Detergent Concentration (ppm)	5000–7500	1200–2000	600–1000

Table 2 Representative Global Handwash Conditions

	Russia	Brazil	China	India
Wash water volume (L)	24	20	5	4.5
Washing time (min)				
- Soak	—	22	10	30
- Wash Duration	24	n/a	10	n/a
Avg. wash temp. (°C)	40	22	25	25
Water hardness	2.5 mmol	0.3 mmol	1.4 mmol	0.5–3.4mmol
Detergent concentration (ppm)	8300	4000	4800	5555

Note: n/a, not applicable.

A final driver for multiple laundry formulations is consumers' preferences themselves. Some prefer granular detergents and others liquids. Still others, at least in the handwash world, prefer bars or pastes. Some want to be able to adjust their dosage freely and others prefer the simplicity of predetermined doses as found in laundry tablets or liquitabs. But perhaps the best example is odor. There are those consumers who want as much perfume odor on their clothes as possible, as well as those who will go to great lengths to avoid perfume altogether. Likewise, not every scent pleases every consumer, so often you can find the exact same cleaning formula sold under the same brand name, but in multiple scent variations. There are also consumers who have real or perceived skin sensitivity to perfumes, dyes or enzymes, and for these consumers "free" products are available that contain none of these items.

II. UNIFYING FORMULATION CONCEPTS

The key, unifying concept of all the different forms and formulations is that consumers expect their laundry detergent to clean their clothes. As such, the underlying chemistry of detergents is, not unexpectedly, quite similar. With a few exceptions that have been touched on above and will be discussed later, their primary job is the same—clean clothes. Briefly, following the laundry mechanism laid out by Venegas [1], all detergents in one way or another need to: (1) hydrate the soil, (2) remove the soil from the fabric, (3) fragment the soil to aid suspension, (4) prevent the redeposition of said soils, (5) bleach any residual soils to lessen their visual impact, and (6) provide any final modification to the fabric as desired (e.g., deposit perfume, brighteners, etc.). The general approach to meeting these needs looks quite similar in all detergents.

In all cases one or more surfactants provide the primary wetting and soil removal power (excluding the very large impact of water via machine or hand agitation alone). Surfactants provide the basis and bulwark of the cleaning power as illustrated in Figure 1 [2]. Builders of one sort or another are included to protect anionic surfactant from precipitation as calcium salts, aid in removal of calcium sensitive soils like clay and particulate soils, and depending on the builder, aid in peptization and suspension of soils. Very few if any detergents exist that lack one or the other of these two actives.

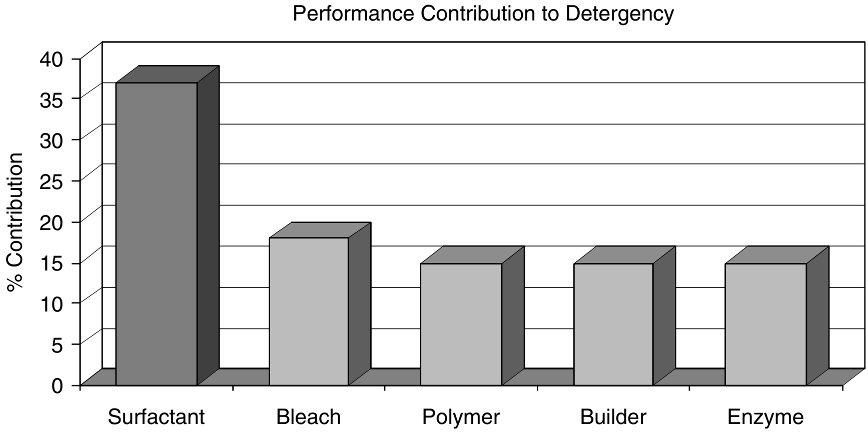


Figure 1 Relative Contribution of Actives to the Cleaning Process.

The actual selection of surfactant(s) and builder and their relative ratios can vary widely however.

The level of cleaning and overall price desired largely determines the presence and level of additional actives besides surfactant and builder. In less expensive, more basic detergents there may be nothing additional besides a buffer system to maintain pH and some level of perfume. In top-tier, flagship detergents, typically one or more enzymes, soil suspension polymers, and/or bleaching agents are also added. There are a number of variants of each available to the formulator (see below). The exact choice and number is often dictated by questions of availability of proprietary materials, mutual compatibility with other actives present in the detergent, and the particular role the detergent is designed for.

Technologies that work very well in one habit or in one form may not work at all in another. An obvious example is heavy duty granules (HDG) vs. heavy duty liquids (HDL), where there is a big difference in the actual wash pH. While both commonly use a protease enzyme, they must use different strains of the enzyme to obtain maximum activity at wash pH. The kinetics can also be vastly different between habits. In the short, cool wash cycles of Japan or North America, only technologies that work very quickly are useful. In the longer, warmer, European wash cycle the kinetics are still important, though not to the same degree. This difference can often be observed in the chain length of surfactants used, and also accounts for the relative efficiency of some builders in each habit.

Regardless of the form, for a detergent whose focus is primarily cleaning you can expect to see surfactant and builder at the core, with one or more cleaning adjuncts added to boost the performance further and some level of perfume. The exception to this is those detergents that are designed to deliver a different primary benefit, plus a base level of cleaning. Examples of this include 2-in-1 detergents, which seek to soften clothes as they clean, and color-care or fabric-care detergents that strive to maintain the look and feel of clothing as close to the original, store-bought, appearance as possible. In these cases the formulator is often forced to make tradeoffs in absolute cleaning (either for cost or chemical reasons) to facilitate delivering these benefits. More will be said about this in the section on specialty detergents (Section VIII).

III. TYPICAL LAUNDRY DETERGENT INGREDIENTS

A. Surfactants

A number of excellent reference works are available covering every aspect of surfactant chemistry and use [3]. Today's formulator has an extensive pallet of surfactants to choose from. What surfactant is chosen, and what level is used in product, is determined by a number of different factors. These include cost and supply availability of course. Additional requirements are often dictated by machine type and wash conditions, compatibility with the rest of the formulation, concerns with mildness where handwash is involved, and existing local regulations regarding biodegradability, to name a few.

1. Anionic Surfactants

Anionic surfactants, especially the sulfates and sulfonates, dominate laundry detergent formulations. Their ready supply, generally low cost, and excellent performance make them a clear choice [4]. Linear alkylbenzene sulfonate (LAS) remains the most important of the anionic surfactants. When used as the sole surfactant it suffers due to its hardness sensitivity and generally poor surface activity. As a result LAS is usually formulated along with a lower level of cosurfactant to ameliorate these weaknesses. A recent interesting development involves introducing a mono-methyl substitution in the alkyl chain and increasing the percentage of terminal-phenyl isomers to nearly 100%. [5] This has the effect of improving the overall surface activity and eliminating the internal phenyl isomers that are most responsible for the hardness sensitivity of LAS.

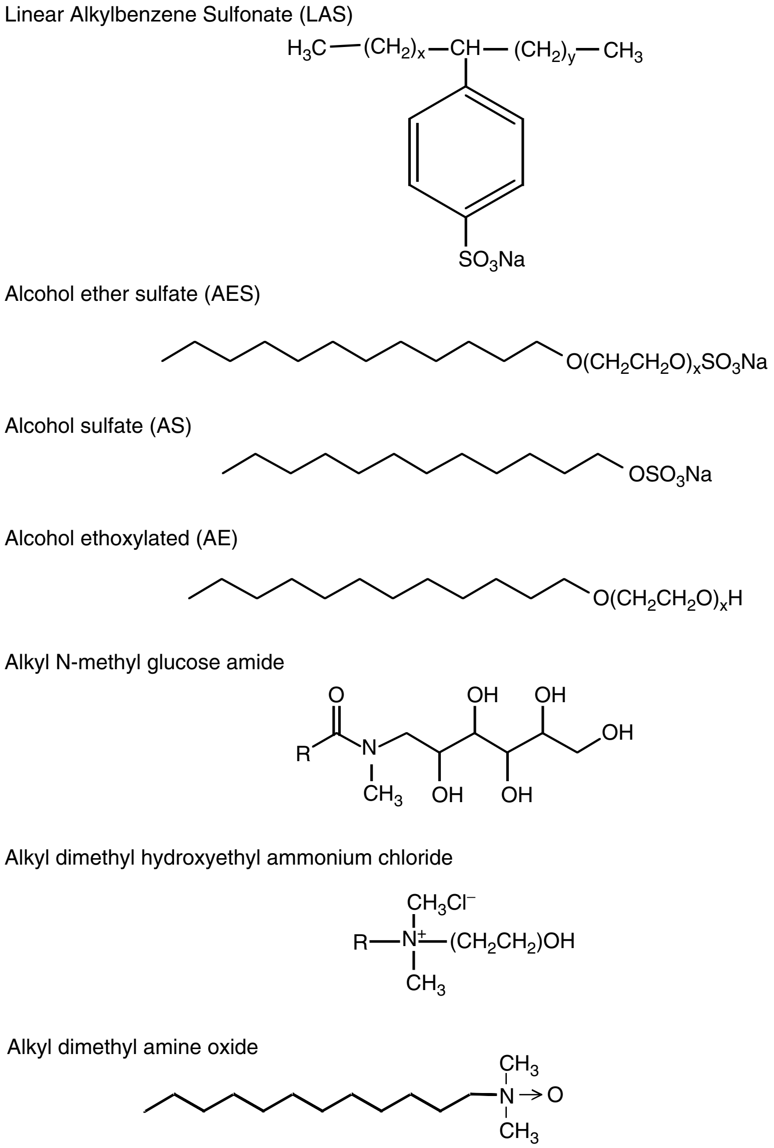
The alcohol sulfates and alcohol ether sulfates account for most of the remaining anionic surfactants in common detergent usage. The ether sulfates in particular are useful for boosting the hardness tolerance of LAS containing systems. They also have the benefit (or issue, depending on your point of view) of being high foaming. Other sulfates and sulfonates such as secondary alkane sulfonates, and sulfo fatty acid esters (e.g., MES) [6], are also known, but are currently less widely used. Methyl substituted versions of AS and AES, similar to the methyl-substituted LAS discussed above, have also been developed [7].

There are several other anionic surfactants known (e.g., phosphate esters, sulfosuccinates, taurates, isethionates, carboxylates), but aside from the simplest of the carboxylates—soap—they are seldom widely used. Soap is sensitive to low pH, and to polyvalent cations such as calcium, and hence is not used much as the primary surfactant in laundry detergents. Having said that, in situations where these factors can be controlled, soap provides excellent cleaning properties. In Japan, for instance, soap bars represent the gold standard for collar and cuff soil removal. Figure 2 presents exemplary structures of common surfactants in detergents.

2. Nonionic Surfactants

Almost by definition nonionic surfactants [8] are insensitive to hardness ions. As such they can make excellent cosurfactants with anionics as discussed above. They also have the advantage of being relatively mild toward dyes and delicate fabrics, making them good candidates for color-care or delicate garment formulations. Nonionics are generally kinetically slower than anionics though, sometimes limiting their cleaning contribution in short-wash cycle, cold water conditions.

Alcohol ethoxylates are by far the most important of the nonionic surfactants. By proper balance of the alkyl chain length with the number of ethoxy groups a wide range of surfactants with varying properties is possible. As a result, interaction and compatibility


Linear Alkylbenzene Sulfonate (LAS)

Alcohol ether sulfate (AES)

Alcohol sulfate (AS)

Alcohol ethoxylated (AE)

Alkyl N-methyl glucose amide

Alkyl dimethyl hydroxyethyl ammonium chloride

Alkyl dimethyl amine oxide

Figure 2 Exemplary Structures of Common Surfactants in Detergents

with other surfactants and detergent actives, overall performance for a given wash condition, and stain removal performance on various soils, can be accurately optimized. Versions using an alkyl phenol instead of a simple alcohol are known to provide even better performance, but environmental concerns have limited their use in household products.

There are other important nonionics as well, though their significantly higher cost and lower supply availability limit the actual volumes used. Included here are amine oxides, alkanolamides, EO/PO block copolymers, and various surfactants made from polysaccharides. Amine oxides are often used as suds boosters, and can sometimes play a similar role in surfactancy as cationic surfactants.

3. *Cationic Surfactants*

Cationic surfactants [9] present a series of different opportunities and challenges to the formulator. Since most fabric surfaces and many soils are negatively charged at wash pH, cationic surfactants have a natural affinity and can build up in significant amounts. This can be a positive or a negative depending on the desired outcome. Likewise, the interaction of cationics with anionic surfactants is important (formulating a laundry detergent with all cationic surfactants is not done). When used at the right ratio cationics can significantly boost the cleaning power of an anionic surfactant like LAS. Use at too high a level results in precipitation and loss of both.

The most common cationic surfactants are quaternized ammonium compounds. These can be as simple as a single alkyl chain of typical detergent length, along with three methyl groups on the nitrogen. Others incorporate various levels of ethoxylation on the nitrogen along with methyl groups. These quaternary compounds are often referred to as "true quats." Regardless of the pH of the wash solution they remain cationic. A "pseudoquat" then, is a surfactant like an alkyl amine, which becomes protonated below it's pKa and behaves as a quat. Above its pKa it is a neutral surfactant. Materials like this can be important, for example, in heavy duty liquids where formulating a true quat along with anionic surfactant can pose significant formula stability issues.

4. *Others*

The simple classification of anionic, cationic, and nonionic above easily captures the lion's share of surfactants actually used in laundry detergent formulations today. There are also amphoteric surfactants [10] like the betaines and sultaines that are also used occasionally. There are some specialty surfactants like the chelating surfactant N-acyl ED3A marketed by Hampshire Chemical (Nashua, NH) [11], and short-chain surfactants that are more often used as hydrotropes, though they can provide good cleaning benefits if present in high enough concentration as in a specialty pretreater. Research continues as well on Gemini, twin-tail surfactants, on polymeric surfactants, and others. To date none of these new developments offers a suitable cost/performance value to be used extensively in laundry detergents.

B. Builders

The primary role of builders in a laundry detergent is sequestering calcium and magnesium ions. All other considerations are secondary. There are numerous reasons why this is important, not the least of which is that calcium and magnesium lead to precipitation of anionic surfactants, or help form multilamellar vesicles, both situations leading to significant loss of performance. Both the rate of sequestration and the absolute capacity for sequestration are important considerations in the choice of builder. Beyond removal of hardness ions, builders can also play a variety of additional roles. Depending on the builder they can also provide dispersancy and peptization of soils, can serve as a source of alkalinity, and in granular and tablet detergents can be important carriers of other organic actives in the formula. The number of practically important builders for laundry detergents remains relatively small [12].

Sodium tripolyphosphate (STPP) is the standard by which all other builders are measured. It delivers rapid sequestration of hardness ions while also serving as an excellent peptization and soil suspension agent. It is also inexpensive, readily available and easy to formulate in a granular product (isotropic liquid products are a different matter as discussed later in this chapter). Today it is largely limited in use to handwash countries due to concerns over its role in eutrophication of waterways. As a result of these concerns, the development and use of a variety of substitutes has ensued.

Zeolites, primarily Zeolite A and Zeolite MAP, are the primary replacement for STPP in granular detergents today. Like STPP, Zeolite A is readily available and relatively cheap, and it has high capacity for calcium ions. The primary drawback of zeolite builders is that they are kinetically slower in the uptake of calcium (something that becomes more and more important as wash temperatures and wash times decrease), and are relatively ineffective in removal of magnesium. Also, because they are insoluble, concerns with deposition and buildup on fabrics is also always present. Recent work [13] has looked at reducing the primary particle size of the zeolite in an attempt to increase the rate of calcium ion exchange, but as of this writing it is not yet commercially common.

Builders based on carboxylic acids become more important for liquid detergents than granular ones, but they are used in both. The simplest form of this type of builder is soap. In liquid detergents, fatty acids sometimes represent the only builder present in the formula. Citric acid is also an effective carboxylate builder, used most often in liquid detergents. Polycarboxylate polymers are effective dispersants that also deliver some building power. Use is largely limited to granules due to formulatability concerns in liquids. Amino carboxylic acids, like nitrilo triacetic acid (NTA), are excellent builders, though their use is limited by toxicological concerns.

Other builders include amorphous silicates, materials common in granular detergents as a source of alkalinity and as anticorrosion aids. Layered silicates are a more recent development used in some markets. Calcium carbonate is ubiquitous in granular detergents and tablets, and its role as a builder is sometimes overlooked. By forming insoluble calcium carbonate it efficiently removes calcium from solution, but brings with it the concern of inorganic encrustation of fabrics. As often as not, this trait of carbonate is viewed more as a liability in detergents than as a positive.

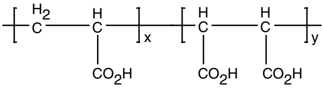
C. Polymers

The use of polymers has increased as detergent formulations have evolved. Initially, as phosphate use was curtailed, the focus was on polyacrylate-type polymers with the goal of replacing some of the lost building and dispersancy power of STPP. Carboxymethyl cellulose is another of the oldest polymers and represents one of earlier attempts at soil release. From these successful beginnings, a large number of polymers for a variety of purposes have emerged [14]. Several new dispersants have been commercialized, as have polymers for dye transfer inhibition, soil release and soil repulsion, for structuring liquid detergents and for aiding dissolution of tablets. For every new polymer actually commercialized there are myriad additional ones patented, attesting to the level of interest in the area.

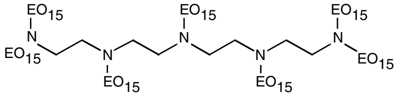
Dispersancy and soil removal remains the primary role of polymers today [15]. The choice of dispersant is governed by a number of factors. The formulator must first be clear on what it is they want to disperse and where. Is it clay-type soils in the wash, solids in the crutcher of their spray-tower, dyes in the rinse, hydrophobic soils in the wash, etc.? Poly(acrylic acid) or poly(acrylic/maleic) copolymers are the most popular dispersants for granules, but their use in liquids is limited due to solubility concerns and limited efficacy at the lower pH. For HDLs, smaller polymers, such as ethoxylated polyamines are more common. Recently, more specialized (and more expensive) polymers have been developed to broaden the spectrum of soils against which they work. These include a variety of ethoxylated polyamines, and zwitterionic polymers [16]. Figure 3 presents exemplary structures of common polymers in detergents.

Soil release polymers are another important class [17]. In simple terms, these are polymers deposited on fabrics through the wash cycle (this discussion excludes polymers applied in the mill for similar benefits) such that they form a “protective layer” between the fabric and subsequently encountered soil. In it’s most common application the polymer

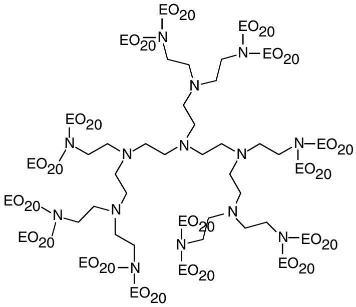
Poly(acrylic)/Poly(maleic) acid (PAA/PMA)



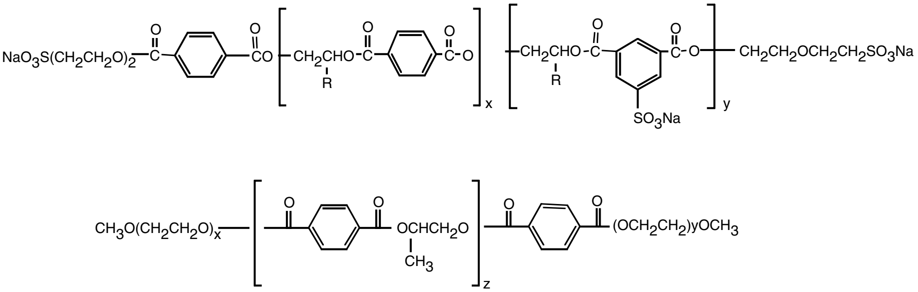
Ethoxylated tetraethylene pentaimine



Ethoxylated Polyethyleneimine



Soil Release Polymers



PVNO

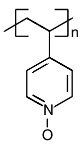


Figure 3 Exemplary Structures of Common Polymers in Detergents

is based on a terephthalate polyester backbone and builds up primarily on synthetic fabrics over multiple cycles. This buildup makes the otherwise hydrophobic (and therefore hard to wet and clean) fabric more hydrophilic thereby aiding in soil removal. CMC has also been claimed to provide some soil release benefits on cotton, though the size of benefits are rather limited.

The last main class of polymers currently in use are dye transfer inhibition polymers. These polymers are included to trap fugitive dyes released from fabrics and prevent them from depositing on other fabrics. The fugitive dyes can be released due to the nature of dye used on a new garment initially, or due to the action of the detergent itself. Whatever the primary cause of dye release, these polymers work by complexing with the dyes, usually via dipole-dipole interactions, and keeping them well solubilized. The most common DTI polymers are based on poly(vinylpyridine) and related derivatives.

New developments in nondispersant polymers are focused on delivering totally new "fabric-care" benefits. The ultimate goal is to repair damaged fibers and/or prevent damage in the first place to keep clothes looking like new. Work in this area is still in the early stages, but some materials have already been introduced into the market. Recent developments in this area are covered in Section IXA—Care Detergents.

D. Enzymes

Enzymes offer a great deal to the detergent formulator. By definition they work catalytically and hence take up little formulation space. They are also biodegradable, making them a good choice for today's increasingly environmentally conscious consumer. Enzymes have also proven beneficial in keeping performance high as wash temperatures have fallen. Some have predicted that enzymes will become the single most important detergent component as environmental pressures continue to mount on other actives. While this may still be some time away, detergents containing as many as four or five different enzymes are already on the market.

Several different enzymes are commercially available today for detergents and research continues apace to discover and develop new ones [18]. In choosing an enzyme the formulator needs to consider what the target soil or benefit is. The answer to this question determines what enzymatic activity is required. The formulator also needs to consider the wash pH and wash temperature. All enzymes have a pH and temperature window in which activity is maximized. Moving too far out of this window can make the enzyme so inefficient that it becomes cost prohibitive, or perhaps even impossible, to formulate an efficacious amount. Finally, the formulator needs to consider the mutual compatibility of the enzyme and other detergent actives.

By far the most common enzyme in use today is protease. Not coincidentally it was also the first enzyme to be successfully commercialized in detergents. Protease works by cleaving peptide chains found in proteins, producing smaller, more soluble or easy to disperse fragments. Since proteins are found in some of the most common and important consumer stains (e.g., grass, blood, skin cells, sweat, many foods) it is a natural fit in most detergents. Protease presents a unique challenge for formulators (especially of liquid detergents) since it can also undergo autolysis and degrades other enzymes that are present in the formula. This is a well-understood phenomenon and solutions generally take the form of a reversible inhibitor that releases the protease on dilution into the wash.

Amylases, more specifically alpha-amylases, are the second most commonly used enzyme in detergents. By hydrolyzing glycosidic bonds in starch, amylase can deliver significant stain removal benefits on food stains such as chocolate, gravy, and spaghetti, as well as body soil removal benefits. Also, amylase can sometimes deliver multicycle whiteness benefits by removing starch that could otherwise serve as a "glue" to attract other soils to the garment. Because amylases require calcium ions to maintain their three-dimensional structure, care must be given to how they are formulated, with liquid detergents again providing the largest challenge.

Lipases offer great potential in principle, though their actual impact in detergents thus far has been limited. Lipases work by hydrolyzing triglycerides and fatty esters to the corresponding fatty acids. The fats and oils that are susceptible to hydrolysis by lipase are often difficult to remove by surfactants alone, especially in colder water. Hydrolyzing them to fatty acid and glycerol makes removal by surfactants much easier. The issue has been that today's lipases require multiple cycles to provide benefits. Also, lipases generally require the presence of calcium ions for maximum activity, and these same calcium ions can form a hard soap layer over the oily stain, blocking further action.

Cellulase rounds out the roll call of today's commonly used enzymes. It is different from those listed above in that it does not work directly on any stains, but rather directly on the fabric itself. By hydrolyzing the glycosidic β-1,4 bonds of cellulose, cellulase can remove the topmost layer of microfibers from cotton garments. The result can include stain removal by loosening the cloth "fingers" that help trap soils, but the focus has generally been on depilling, color restoration and softness. The obvious challenge with cellulases is balancing the benefits obtained with damage to the strength of the cotton garment itself over several cycles.

As mentioned above, there is a great deal of ongoing work by enzyme suppliers, academics, and detergent makers themselves to discover and develop new enzymes. This work involves screening of natural isolates and "evolution" of existing enzymes, with the goal of both improving on existing activities (where improving can mean higher activity, greater stability, wider temperature and pH applicability, etc.) and developing new ones. One recent example of a newly commercialized enzyme activity for detergents is mannanase [19]. Mannanase hydrolyzes the mannan backbone of galactomannans and glucomannans. Because these materials are common rheology modifiers in a variety of foods and consumer care products, they can form a gluey film on fabrics. By removing this film, mannanase helps prevent fabric dinginess.

E. Bleach

Bleach contributes to stain removal by either oxidatively modifying the stain such that it becomes more water soluble and easier to remove, or by decolorizing the stain such that it is no longer visible. In some cases the oxidative bleach can also provide antibacterial benefits. There are also reductive bleaches available, but generally speaking they are not popular in laundry detergents for a variety of reasons. There are several oxidative bleaches available to the formulator today, though like most actives discussed in this chapter, a relative few dominate commercially [20].

The simplest and most common bleach is hydrogen peroxide. The ability of peroxide to decolorize and help remove hydrophilic stains like tea, coffee, and wine has been known for a very long time. It has been used in granular detergents for over 100 years. Of course hydrogen peroxide itself cannot be formulated in a granular detergent, so it is usually formulated as the stable perborate salt. Also available is percarbonate, which is actually carbonate with the hydrogen peroxide trapped in the crystal lattice. Just which material is used is based on a number of factors. Stability, dissolution rates, environmental legislation all comes into play. Whichever form one chooses, the performance of the resulting peroxide is most powerful at high temperature and long wash times. In all other situations, an additional bleaching agent is needed for strong performance.

This "additional bleaching agent" takes the form of a bleach activator. A bleach activator is a peracid precursor that reacts with peroxide in the wash solution to form a peracid. They have the advantage being more reactive and therefore more effective than peroxide. Also, because they are hydrophobic, they offer better performance on body soils and hydrophobic stains. The combined bleaching profile of hydrogen peroxide and peracid gives a much broader performance profile, both in terms of stains affected and conditions in which good performance is observed. By far the two most common bleach activators are tetraacetylethylenediamine (TAED) that generates two equivalents of peracid, and nonanoyloxybenzenesulfonate (NOBS) that generates one [21].

Preformed peracids are also known. They offer a weight efficiency advantage since no hydrogen peroxide is required and there is no "wasted" leaving group. The main issue with preformed peracids is stability—both of the raw material itself and in finished product. Phthalimidoperoxycaproic acid (PAP) is probably the best known. Metal bleach catalysts also offer great promise of weight efficiency. Bleach catalysts are transition metal compounds, typically Mn, Fe, Cu, or Co, with various chelating organic ligands. They react with appropriate oxygen sources to form high valent metal oxides that are potent oxidizing agents. Most are designed for use with hydrogen peroxide, but the obvious goal is to develop a catalyst that works with molecular oxygen. To date there is no successful commercial example, but the search continues within many academic and corporate labs. In some regards photobleaches (normally metal phthalocyanines) could be considered as bleach catalysts. They generate singlet oxygen, a powerful bleaching species, on exposure to light and air. Because of the need for sunlight, and because the bleach is only really effective while the clothing is still wet, the utility of photobleach is greatest in areas where consumers air dry their laundry outside. Figure 4 presents the exemplary structure of common bleaches and chelants.

F. Chelating Agents

Chelants are often formulated in detergents because metal ions in the wash are almost always a detriment to end performance. Many highly colored stains incorporate metals. Removal of the metal can often decolorize the stain and/or make it easier to remove by destabilizing its structure. Examples include porphyrins found in blood and tannins in tea. Metal ions can also catalytically decompose bleach in a formulation, leading to significantly reduced performance. Finally, metals often find their way onto fabric surfaces, either as insoluble salts as with calcium or magnesium fatty acids, or as metal oxides. Both lead to a multicycle dinginess and fabric feel issues.

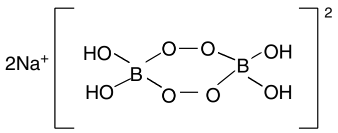
What chelant is used depends largely on local environmental regulations. Diethylene triamine pentaacetic acid (DTPA) is commonly used in North America. It's an analog of the more well-known ethylenediaminetetraacetate (EDTA), but has a better environmental profile. In Europe, however, DTPA is banned due to concerns with aquatic toxicity. As a result, European formulations rely more on phosphonate-based chelants such as diethylene triamine penta(methylene phosphonic) acid (DTPMP) or ethylene diamine tetra(methylene phosphonic) acid (DDTMP). In an interesting twist, these materials cannot be used in North America due to bans on phosphorous in laundry detergents.

In environmental terms, ethylene diamine disuccinic acid (EDDS) represents the best achievement thus far. The molecule has two chiral centers and only the S,S-isomer is fully biodegradable. This makes it a more expensive chelant than the phosphonate chelants mentioned previously. It is used in some European granules today. HEDP, 1-hydroxyethyidene-1,1-diphosphonic acid, is not truly a chelant in the sense of the materials mentioned above, but because it also helps control deposition of metals on fabrics it deserves mention in the same section. HEDP works more by inhibiting crystal growth.

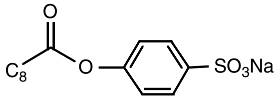
G. Perfumes

In a technical sense perfumes add no cleaning power to a detergent. However, from a consumer point of view perfumes have a major impact on the overall impression of how well a detergent works. Even a perfectly clean garment can be judged substandard due to lack of a "fresh and clean" odor. Odor has been proven to be an important driver for consumer acceptance, and thus should be carefully considered when formulating a product. As a result, as much effort is put into formulating different perfumes [22] as goes into formulating the rest of the laundry product, it's just done by a different set of people—perfumers. Perfumers

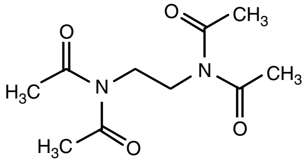
PB1



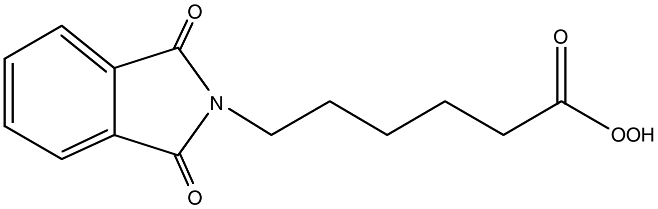
NOBS



TAED



PAP



Photobleach

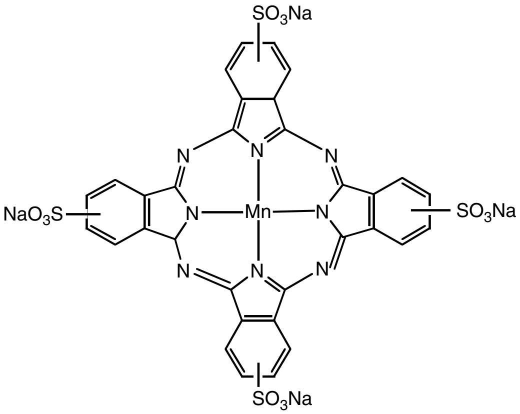
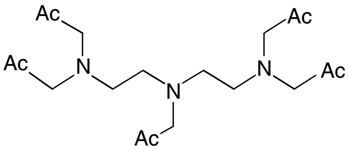


Figure 4A Exemplary Structure of Common Bleaches and Chelants.

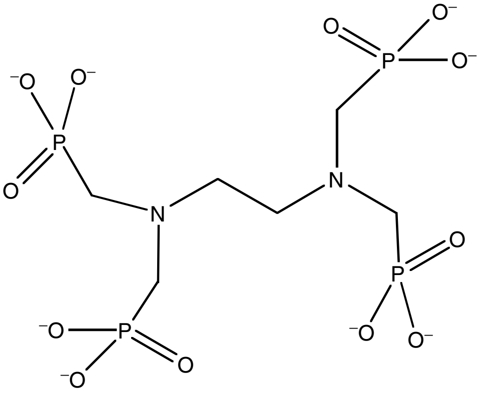
are highly trained technologists skilled in the science and art of creating unique winning perfumes with odor performance profiles meeting consumer needs.

Perfumes are complex mixtures of organic compounds. For example, a detergent perfume may be composed of 30, 50, or even over 100 different organic materials. Given this nature, perfumes can have complex interactions with detergent actives that affect both the perfume character and possibly the actives' performance. In addition, detergent actives often have odor properties themselves, and these "base odors" should also be considered

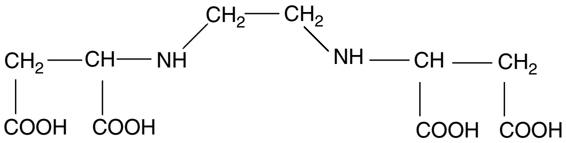
DTPA



DDTMP



EDDS



$CH_2(COOH)-CH(COOH)-NH-CH_2-CH_2-NH-CH(COOH)-CH_2(COOH)$

Figure 4B

when formulating detergents since they can impact the final product odor profile. The detergent formulator should work in partnership with the perfumer to ensure the final product odor profile best meets consumer's needs.

Most of the perfume formulated in laundry detergent ends up being washed down the drain. Deposition onto fabric is inefficient. To further complicate things, what perfume does deposit on a fabric is relatively short lived. As a result, there has been a great deal of research in recent years to aid in delivery and sustained release of perfumes. The result is a number of additional technologies available to the formulator, including those that aid in deposition of traditional perfumes, those that extend the longevity (usually via delayed release) of perfume on fabrics, and even those that only generate perfume after some triggering event such as heat, sun, or moisture exposure. All of these new developments are beyond the scope of this chapter to describe.

H. "Minors"

Whether a detergent ingredient is a "minor" or not is all in the eye of the beholder. In this section, "minor" simply refers to actives that are included at a relatively low level in detergent, or have no direct cleaning benefit (these items are sometimes referred to as "fillers"). "Minor" should not be taken as statement of the importance of these actives, as their absence will generally result in overall poorer performance. Discussion here is limited and the list should not be considered as exhaustive.

Fluorescent whitening agents (FWA) are included at some level in most detergents today [23]. The primary benefit of FWAs is observed over multiple cycles as white garments begin to become dingy. By absorbing ultraviolet (UV) light and emitting it in the violet-blue visible region, FWAs increase the apparent whiteness of a garment. FWAs are also added at the mill as garments are made, but these FWAs are removed with multiple washes and need to be replenished. FWAs additionally have a benefit in solid detergents by making the granule appear whiter, and hence more attractive to consumers. The watch out, especially in liquid detergents that are often used for pretreating fabrics, is that when applied in excess to light-colored clothing, the fluorescence in the violet-blue region can appear as a light-colored stain. By careful selection of the right FWA this issue is easily avoided in most situations.

In liquid detergents there is often a need for solvents or hydrotropes to ensure formula stability across the wide range of temperatures it will experience from plant to the consumer's home. Typical solvents and hydrotropes include ethanol, propanediol, toluene sulfonate, or xylene sulfonate. The effect of solvents and hydrotropes on liquid stability and physical properties (e.g., viscosity) is not always straightforward. Effects can reverse depending on the formulation, and stability issues may not materialize for many months. Optimization of the solvent system for a product is therefore an involved process involving many samples and various rapid aging techniques. Liquid detergents, especially the more dilute ones where water makes up a greater fraction of the total product, also often contain an antibacterial agent of some sort to protect against microbial growth over the lifetime of the product [24]. Liquids are also the biggest users of dyes, pigments, or colorants [25].

In all detergents, maintaining the optimum pH for performance is crucial. As such, most contain a buffering system of some sort. This is much easier in a granular detergent than a liquid where solubility of common buffering salts is problematic. In granules this is accomplished with carbonate, silicate, and STPP. In liquids there is essentially no buffering capacity in the real sense of the word. What pH control exists comes from the degree of neutralization of acid surfactants and fatty acid, as well as the nature of the neutralizing agent itself.

Suds control [26] is important as consumers make many judgments relating to the performance of their detergent based on the suds profile. Unfortunately not all consumers want the same suds profile, so knowing the consumer preference is key. It's not just important from a consumer preference point of view, but in machine wash it is often necessary for correct machine performance. For example, a typical handwash or North American detergent will result in suds flowing out of a European machine, at best making a mess and at worst locking-up the machine such that it shuts down. Some degree of suds control is possible via careful selection of surfactant type and level, but often a separate suds control material is required. The most important type of suds suppressor is based on organic silicone compounds, though metallic soaps of carboxylic acids, insoluble nitrogenous compounds, and branched alcohols are also used.

IV. HEAVY DUTY GRANULES

Heavy duty granules (HDG) were the first mass marketed consumer laundry detergents. They remain the dominant laundry form in most markets today, with a few notable exceptions such as in North America where heavy duty liquids have overtaken them in volume sold. Even in markets such as North America, however, HDGs remain a very important and dominant form. The range of different formulations on the market around the world today is quite wide. Extremely basic formulas that contain little more than carbonate, some LAS, and a bit of sulfate that are simply made by stirring them all together are sold very cheaply in some developing markets. Somewhat more complex (but developmentally still very simple) formulas made by spray-drying LAS, STPP, carbonate and fillers are found widely around the world in handwash geographies. In developed machine wash countries one can find very complex products with mixed surfactant systems, mixed builder systems, multiple enzymes, and polymers, and made via agglomeration techniques. As the formulas gain in complexity they also gain in cleaning power, benefits delivered, and cost.

In general the HDG form leverages high pH and high builder levels, both made possible by the relative ease of formulating solid buffer like carbonate and solid builders such as STPP or zeolite. Surfactant levels and types are determined in part by cost considerations of course, but manufacturing and flowability concerns have a significant impact as well. As will be seen, these considerations generally limit total surfactant levels to under 25%, and nonionic surfactant to less than 5%. Additional performance is provided by bleach, and a wide variety of enzymes and polymers. Most recent patent art is focused on new developments in these areas versus the fundamental formulation. Processes for making granules also dominate the patent art.

In an attempt to bring some clarity, discussion of HDG formulations in this chapter is focused on the basic formulation and is grouped according to three key questions. First, does the desired formulation contain phosphate (usually as STPP) or not? In many markets today the use of phosphate builder is banned or severely limited. Whether or not phosphate is present can have major implications on the remainder of the formulation. Second, is this a low-density (aka “fluffy”) product or a high-density (aka “compact”) product? All markets used to be made up of fluffy products, with a density of around 350— 500 g/L. In the late 1980s there was a significant shift to compacts with a density of around 600 to 900 g/L [27]. Finally, is this a product intended for use in washing machines or for use in handwashing of clothes? The delineation provided by these questions is somewhat arbitrary as the answers can be combined in many different ways. There are both high-density and low-density phosphate containing formulas for machine wash for example. Likewise, there are both phosphate and nil-phosphate low-density formulas for handwash, and so on. Examples of all these formulations abound in the patent literature. The discussion below is illustrative of the more common approaches.

A. Phosphate vs. Nil-Phosphate

Phosphate, typically STPP, has been the preferred builder of formulators for many years. STPP readily sequesters hardness, acts as a soil peptizer and dispersant, provides some buffering capacity and helps carry the organic load in granules. It is still the preferred builder in many parts of the world today. In others, such as North America, the use of phosphate in laundry detergents has been banned and so alternative such as zeolite A are used. Zeolite A replaces the builder function and organic carrying function of STPP, but other actives are required for buffering, soil peptization, and soil suspension. Also, since the calcium binding kinetics and capacity of zeolite is not as high as STPP, more hardness tolerant surfactant systems are often used in nil-P products. Hence, to get equal performance from a nil-P product can mean additional formulation cost to pay for the chemistry needed to offset the loss of STPP.

Table 3 illustrates a high-end, phosphate built detergent [28]. Compared to the nil-P detergent in Table 4 [29], the biggest apparent difference in the core formula (aside from replacing STPP with zeolite A) is the presence in the nil-P formula of a polyacrylic/maleic acid copolymer and of the soda ash/silicate co-granulate sold commercially by Rhodia under the name Nabion 15. These extra actives help compensate for the dispersancy power lost when STPP is removed. Even with such additions, it is very difficult to achieve the same level of clay stain removal from a nil-P product at equal cost to a P product without

Table 3 Example of Phosphate Built HDG

Ingredient	Percent
Sodium C11-13 alkylbenzene sulfonate	13.7
Sodium C14-15 alcohol sulfate	4.0
Sodium C14-15 alcohol ethoxylate (0.5) sulfate	2.0
Sodium C14-15 alcohol ethoxylate (6.5)	0.5
STPP	41.0
Sodium carbonate	12.4
Sodium silicate (1:6 ratio NaO/SiO_2) (46%)	6.4
Sodium sulfate	10.9
PEG 4000 (50%)	0.4
Dispersant polymer	0.76
Soil release polymer	0.10
Suds suppressor	0.60
Water and minors	Balance

Table 4 Example of Nil-Phosphate HDG

Ingredient	Percent
C9-13 Alkylbenzene sulfonate	13.6
C12-18 Alcohol sulfate	3.9
C12-18 Alcohol ethoxylate (5)	3.6
C12-18 Fatty acid	0.7
PEG 400	1.5
Zeolite A	17.6
Nabion 15 (Rhodia)	12.0
Acrylic/maleic copolymer	3.5
Silicate	1.5
PB1	17.4
Chelant	0.5
Dusting agent	1.5
EDTA	7.0
Protease	1.6
Suds suppressor	3.6
Water, misc.	10.3

Note: EDTA, ethylenediaminetetraacetate.

compromising in other areas (e.g., surfactancy). Mixed STPP and zeolite products are also known as illustrated in Table 5 [30]. This complex formula also illustrates the trend to using a mix of agglomerated and/or spray dried particles of varying composition to form the total formulation. This approach provides increased flexibility over a single spray-dried or agglomerated particle.

Table 5 Example of Mixed Builder HDG

Ingredient	Percent
Base Powder	*51.2*
STPP	28.3
Sodium LAS	27.8
Sodium silicate	11.0
Sodium sulfate	21.0
Moisture, minors	11.8
LAS Granule	*11.1*
Sodium LAS	70.0
Zeolite 4A	20.0
Zeolite MAP	5.0
Moisture, etc.	5.0
Nonionic granule	*12.0*
Sodium carbonate	62.8
Citric acid	8.1
AE3	20.9
Water	8.2
Admixes	
Dense sodium carbonate	10.7
Sodium sulfate	13.86
Savinase	0.754
Lipase	0.166
Perfume	0.22

Relying on the building capacity of carbonate is another, less common, approach to nil-P formulas. Whereas STPP is a soluble builder that remains soluble when complexed with calcium, and zeolite is an insoluble builder from the start, carbonate is a precipitating builder. That is to say, it remains soluble until it interacts with calcium. As such it has the additional challenge of controlling the growth of calcium carbonate crystals and the fabric incrustation that can result when too large crystals are formed. Table 6 illustrates one approach that relies on polyacrylic acid and a maleic acid/olefin copolymer to limit encrustation [31]. Another approach to carbonate builders involves the use of very small calcite particles that act as seeds for calcium carbonate growth, resulting in more controlled and smaller crystal sizes [32]. Many other nil-P builders are known: soluble, precipitating, and zeolitic. However, they all come with significant additional cost and are used far less commonly.

B. Low Density vs. High Density

The choice between high- and low-density products is primarily market driven. In most of the developed world today consumers prefer high-density products. The products take up less shelf space in their homes, have less packaging waste, lower dosages, and are seen as better for the environment and as a better value. Not long ago in these same markets

Table 6 Example of Carbonate Built HDG

Ingredient	Percent
Nonionic EO5	4.0
Sodium carbonate	25.6
Sodium bicarbonate	4.0
Acusol 445ND (polyacrylic acid)	3.4
Acusol 460ND (maleic acid/olefin copolymer)	0.9
PB1	4.0
Sodium silicate	9.6
Sodium sulfate	48.5

consumers looked for large boxes at low prices, and in much of the handwash world this is still the case. The formulation strategy for high- and low-density products is essentially the same. However, because of limitations in the end density that can be provided with different processes, some changes are required.

Most low-density products are made via spray-drying. The products contain large amounts of carbonate and sulfate, and the surfactant system is limited somewhat by what can safely and stably go through the spray-drying tower. Additional surfactant and other organics can be sprayed onto the surface of the tower made granule, but only at low levels. Otherwise the granule can become "wet" and sticky, resulting in poor flowability and poor aesthetics. "Dusting" the finished particle with zeolite or other flow-aids is commonly done to prevent stickiness.

High-density products are typically made via agglomeration processes, though post-spray-tower densification processes are also used. Low-efficiency actives such as sulfate and carbonate are significantly reduced in high-density products relative to their low-density counterparts. Within the practical limits of marketed detergents there is not a large difference in the overall formulation beyond this. There is a great deal of patent art related to the challenges of making agglomerated powders that flow and dissolve as readily as low-density, tower-made granules [33].

C. Machine Wash vs. Handwash

Much of the world today still does laundry by hand. In most cases handwash consumers use the presence of suds as a signal that sufficient detergent is present in the wash. To meet the cleaning and sudsing needs of handwash consumers, formulators have added high levels of anionic surfactants such as LAS. However, many anionic surfactants can be harsh to skin at high concentrations, especially when the skin is repeatedly exposed for relatively long periods of time as in handwashing. As a result, the formulator needs to be aware and adjust accordingly. In addition, the handwash consumer often has a much higher soil load, either due to environmental reasons or due to a lower overall frequency of garment washing. This results in increased demand on the detergent actives, including enzymes and bleach.

A handwash detergent could use the same formulation as a machine wash detergent minus the suds suppressor in the simplest situation. More often though, handwash formulations include higher levels of builder and dispersants, and special care is taken to limit the level of protease and other actives that can be harsh to skin under certain conditions.

Table 7 Example of a Simple Handwash HDG

Ingredient	Percent
Sodium LAS	15.0
STPP	17.0
CMC	0.1
Polyacrylic acid	0.1
Protease	0.1
Carbonate	12.0
Silicate	8.0
Sulfate	38.0
FWA	0.1
Perfume	0.2
Water	Balance

Because the handwash habit is predominately found in lower income markets, many handwash formulas are relatively simple, as shown in Table 7. With lower priced formulations consumers frequently "titrate" the dosage and the amount of time scrubbing to get the end benefit they desire. Top performing handwash detergents, however, contain a mixed enzyme system, bleach, chelant and other performance boosting actives. The increased performance allows consumers to dose less and spend less time scrubbing while still obtaining the desired end result. Combined with a surfactant system designed to maximize cleaning while still being mild to hands results in a very mild formulation. Table 8 illustrates this approach [34].

V. HEAVY DUTY LIQUIDS

The first heavy duty liquids (HDL) were introduced as early as the 1950s, though it wasn't until the early eighties that the form really took hold in the United States and Europe. Formulators of HDLs generally fall into two different schools of thought. The first focuses on the intrinsic benefits of the liquid form, allowing for the incorporation of surfactants at high levels and for pretreatment (i.e., direct application of the HDL to the stain prior to addition to the washing machine). This route leads to low viscosity, isotropic liquids and has been the preferred route for Procter & Gamble and Henkel for example. The second school of thought is to make the HDG into a liquid form. This route leads to structured liquid detergents containing high levels of suspended builders such as STPP or zeolites, a route championed by Unilever. These two schools remain dominant today, roughly 50 years after the introduction of the first HDLs [35]. Recently, however, new concepts have emerged including "liquigels" or "liquitabs," essentially an HDL in a soluble pouch (a form covered in the section on Unit Dose Detergents), and HDLs packaged in dual compartment bottles.

A. Isotropic Liquids

Isotropic liquids are by far the largest in terms of market share and number of formulations on the market. In many markets in North America in particular, isotropic HDLs have

Table 8 Example of Handwash HDG Designed for Mildness

Ingredient	Percent
C16-18 N-methyl glucose amide	2.3
C12-14 Dimethyl amine oxide	1.9
C12-15 Alkyl ethoxylated (EO = 5)	7.3
C14-15 Alkyl ethoxy (EO = 1) sulfate	14.0
STPP	15.0
Sodium polyacrylate (MW = 4500)	15.0
DTPA	1.6
CMC	0.4
Protease	1.0
Cellulase	0.15
Amylase	0.15
Sodium silicate	7.0
Soil release polymer	0.3
PB1	2.0
NOBS bleach	3.2
FWA 15	0.15
FWA 49	0.05
Misc. (sulfate, water, perfume, etc.)	15.1

become the leading seller, surpassing HDGs. HDLs offer a number of intrinsic advantages over HDGs. The form itself makes the pretreatment of stains easy and effective, allowing levels of stain removal not otherwise possible. The advent of dosing cups with built-in rollerballs or pour spouts makes this even easier. Rapid and complete dissolution is another inherent advantage of isotropic liquids. As wash cycles become shorter and temperatures cooler this takes on increasing importance. Liquids also offer the opportunity to formulate much higher levels of surfactant than is possible in a granule, resulting in much better greasy stain removal. Ease of dosing and less mess are also advantages noticed by consumers. The key disadvantage liquids have faced versus powders is poorer cleaning due to lack of bleach. This is the origin for much research in liquids as will be discussed below.

The biggest challenge for the formulator of an isotropic liquid is stability—both physical and chemical. These considerations are the primary driving force behind what today's isotropic liquid formulations look like. Stability must be maintained across a wide range of conditions and for a considerable period of time. From the time product is made and stored in bulk at the manufacturing plant, through bottling and warehouse storage, on to retail outlets and finally into consumer's homes, the HDL can experience wide swings in storage conditions. Temperatures ranging from below freezing to over 40°C are not unheard of. In well-developed markets where product is made on demand, the time gap between manufacturing and use can be relatively short. In less developed markets, where perhaps product is imported from a manufacturing site in another country, the time gap can stretch to several months.

Water is the primary solvent in HDLs, though various cosolvents such as propanediol, and hydrotropes like toluene- or xylen-sulfonate, are also used at low levels.

Maintaining solubility of all actives, especially as formulas become more compact (i.e., more concentrated so lower volume doses are needed for each wash), is the main challenge. Surfactants with high Krafft temperatures are particularly troublesome, and longer-chain length hydrophobes are strictly limited. Surfactants that tie up large amounts of water, such as highly ethoxylated nonionics are also troublesome, as can be some of the more commonly used polymers in HDGs.

The problem becomes further aggravated as other actives are included and as the ionic strength increases. Several "tricks" can be used such as using monoethanolamine (MEA) or triethanolamine (TEA) neutralized surfactants. Because they have lower hydration demand, these counterions have been key in the development of concentrated HDL formulas. Using potassium instead of sodium as the counterion is also done, but this has limited effect for the increased cost. These solubility issues are a main reason why most HDLs in the market today have a pH of around 7 to 9. It is impractical to try to formulate the amount of buffer that would be required to raise the pH to 10 or higher that is common for HDGs. The lower pH and lack of in-wash buffering is not a major issue though, provided the formulator keeps it in mind when selecting actives such as enzymes. In fact, this lower pH can often have a beneficial effect in reducing dye bleeding and damage to fabrics.

Delivering the HDL with the right viscosity is also important. If the viscosity is too low consumers view the product as being dilute and therefore poor cleaning. If the viscosity is too high the rate of dissolution under stressed conditions (e.g., low temperature, short wash cycle, low agitation) can be negatively impacted. Most isotropic HDLs in the market today have a viscosity of between 100 and 400 centipoise (cps), though examples are available outside of this at either extreme. In simple HDLs with high water levels the issue is increasing viscosity without adding expensive thickening chemicals. In top-end HDLs with numerous cleaning actives the issue is often keeping the viscosity from becoming too high. Careful balance of solvent and hydrotrope types and levels, often determined by laborious trial and error, is usually sufficient.

Maintaining chemical stability, that is preventing or limiting interactions among the various actives included in an HDL, is also a challenge. The challenge is much higher in isotropic HDLs than in other detergent forms since all actives are dissolved in solution and free to interact with everything else in solution. The most commonly encountered chemical stability issues are reactivity and stability of enzymes, formulation of oppositely charged actives, hydrolysis of actives, and microbial growth. The formulation of bleach also falls into this category, but because there are no isotropic HDLs containing bleach this will be covered in the section on bleach containing liquids (Section V.C.).

The issue of autoproteolysis in protease containing HDLs was mentioned briefly in the section on laundry detergent ingredients (Section III). If formulated without a stabilizing system, protease will rapidly consume itself and other enzymes the formulator may have added. A number of different strategies have been examined to overcome this issue. A reversible inhibitor of protease is the most common solution employed. In the relatively concentrated neat formula the inhibitor binds to the active site of the protease, preventing any unwanted reactivity. Once dosed into the wash solution the detergent is diluted and the inhibitor releases, freeing the protease active site. Boric acid and boronic acids are the most commonly used reversible inhibitors. These are added in the form of borate or boric acid and propylene glycol, which form the active stabilizer species *in situ*. Novozymes has recently begun offering "prestabilized" proteases for sale, which include 4-formyl phenyl boronic acid as the enzyme stabilizer already mixed into the enzyme solution [36].

Other enzymes have additional stability concerns. Amylase for example, requires low levels of free calcium to stabilize their tertiary structure. Without the calcium they

Table 9 Example of Dilute Isotropic HDL

Ingredient	Percent
AES	5.0
AS	5.0
AE	1.0
Citric acid (50%)	0.75
Protease	0.24
Propylene glycol	0.28
Monoethanol amine	0.32
Borax (38%)	0.6
NaOH (50%)	1.4
Na formate (36%)	1.25
Suds suppressor	0.02
Dye	0.016
Perfume w/benzyl salicylate	0.30
FWA	0.10
Water	Balance

essentially denature and become inactive. Low levels of calcium are often formulated for this reason. The challenge comes when chelating agents, fatty acids, citric acid, etc. are also formulated. These materials can all effectively bind calcium. Careful consideration and balance are required to include all these actives.

The formulation of oppositely charged actives can also present difficulties. Interactions between anionic and cationic surfactants, resulting in the precipitation of their large uncharged complex are an obvious example. Most HDLs today do not include cationic surfactants, but there are examples that have been marketed in the past, where low levels of cationic surfactant were successfully formulated. Pseudoquats, namely tertiary amines that are not fully protonated at the pH of the formulation, are also used. Less obvious are problems that can arise from FWAs, which are also anionic species.

The formula shown in Table 9 is illustrative of one way to formulate a “low-cost” dilute HDL while maintaining suitable aesthetics [37]. The challenge in a formula with over 80% water and around 10% surfactant is getting an acceptable viscosity. In this particular case the formulators found that certain perfume raw materials had an added benefit of thickening to greater than 160 cps. Finding actives that can play a dual role such as this is always a challenge. Adding a thickening polymer is also a possible solution. However, since most thickening polymers add nothing in terms of cleaning or odor, this represents an extra cost that is usually avoided.

At the other extreme are formulas containing 20 to 30% surfactant, soil release polymer and/or dispersant, chelant, and multiple enzymes. Table 10 illustrates such a detergent that contains a pseudoquat amine surfactant [38]. Compared to the simple formula of Table 9, the increased use of solvent is apparent. There are numerous variations existing between these two formulas with variations on surfactant system, enzyme stabilization system (e.g., see Table 11 where sucrose is added [39]), solvents, and perfume. In all cases the underlying formulation strategy and challenges remain basically the same.

Table 10 Example of "Fully Loaded" Isotropic HDL

Ingredient	Percent
LAS	18.0
C8-10 Propyldimethyl amine	2.0
C12-14 Alkyl ethoxylated	12.0
C12-18 Fatty acid	11.0
Citric acid	5.0
DTPA	1.0
Monoethanol amine	11.0
NaOH	1.0
Propane diol	12.7
Ethanol	1.8
Amylase enzyme	0.1
Lipase enzyme	0.15
Protease enzyme	0.5
Endo-A glucanase enzyme	0.05
Carezyme	0.09
Terepthalate polymer	0.5
Boric acid	2.4
Suds suppressor	1.0
Water/various	balance

Table 11 Example of Isotropic HDL with Sucrose

Ingredient	Percent
NaLAS	7.0
NaAES	11.6
AE7	7.0
Na borate	2.0
Sucrose	3.2
Na citrate	5
Propylene glycol	3.42
Monoethanol amine	0.24
Coconut fatty acid	0.85
Protease enzyme	0.3
Lipase enzyme	0.4
NaOH	to pH 8.0
Water	Balance

Both batch and continuous processes are used in the manufacturing of isotropic liquids. The manufacturing process is relatively straightforward and does not normally add additional constraints to the formulator. The primary concern is that the order of addition is defined to avoid formation of highly viscous phases or generate insoluble precipitates. Since neutralization of acid surfactants can generate considerable heat, care must also be taken to add heat sensitive materials only after the batch has been sufficiently cooled. This usually means items like enzymes and perfumes are added very late in the making process.

B. Structured Liquids

Those formulators who prefer to formulate the liquid more along the lines of an HDG favor structured liquids. The key difference in structured liquids is the opportunity to suspend solids and possibly to formulate a higher concentration of cleaning actives without stability issues. This makes it possible to include actives that would otherwise not be soluble in an isotropic liquid, and to add actives that might otherwise be too reactive in their dissolved form. The resulting liquids are typically opaque and highly viscous, hence offering an entirely different aesthetic appearance to the consumer as well as a different performance profile. The higher viscosity of typically 500 to 9000 cps can also result in lower pretreat performance since the liquid does not penetrate the fabric as well as an isotropic liquid.

The most common structured liquids are based on liquid crystalline surfactant phases. The structure comes from the dispersion of surfactant vesicles in the aqueous phase. The advantage of this method of structuring is that the structurant is also a cleaning agent and does not add extra cost. The surfactant (including fatty acid for purposes of this discussion) concentration is increased, and/or the electrolyte concentration is increased to push the system to form enough of these vesicles to become space filling. In practice this occurs when the vesicles have a solution volume fraction of above around 0.6 [40]. As the volume fraction of vesicles increases, the viscosity increases, as does the stability. Because the viscosity must be low enough to make the product easily pourable from the product bottle, there is a compromise that must be made between stability and pourability. The other common issue is flocculation of the vesicles that can result in significantly increased product viscosity due to the formation of networks, or can result in the destabilization of the structure due to a decrease in the total number of vesicles. Overcoming the viscosity/stability compromise and the flocculation issue is where most recent patent art is focused.

Deflocculating or decoupling polymers are the most commonly used solution. These polymers are typically comb-type polymers with a hydrophilic backbone and hydrophobic teeth and there are numerous examples in the patent art. They are thought to perform two functions. First, they stabilize against flocculation by providing a barrier between individual vesicles in solution. Second, by inserting the hydrophobic teeth into the lamellar sheets that make up the vesicle walls, they can increase the size of individual vesicles, thereby increasing stability. The hydrophilic backbone is often a polyacrylate derivative and the hydrophobic teeth a long alkyl chain. Table 12 shows an example of a phosphate containing HDL [41] made in this way. Adding even a fraction of this level of STPP in an isotropic HDL would not be possible. A similar, nil-phosphate version is illustrated in Table 13 [42].

There are alternatives to structuring via surfactant phase. These alternatives typically involve creating a network throughout the solution that reduces the tendency of other materials in solution to coalesce or phase-split. This network can be established via some soluble polymers [43], though this approach is typically very expensive and is not always sheer-thinning, thus making pouring difficult. A more common means of creating this network involves the use of insoluble or sparingly soluble solids. The use of organically modified clay particles to create a "house-of-cards" structure in a liquid is well known and will be discussed briefly in the section on 2-in-1 detergents. A more recent example

Table 12 Example of a Phosphate Containing Structured HDL

Ingredient	Percent
NaLAS	6.3
K Laurate	3.8
K Oleate	5.5
AE7	10.0
Glycerol	5.0
Boric acid	2.28
KOH	1.0
STPP	19.0
Gasil 200	2.0
Silicon oil	0.25
FWA	0.1
NaCMC	0.3
Dequest 2060S	0.4
Protease enzyme	0.5
Perfume	0.3
Deflocculating polymer	0.75
Water	Balance

Table 13 Example of Nil-Phosphate Structured HDL

Ingredient	Percent
LAS	20.0
AES	5.5
AE	10.0
Na citrate	10.0
Borax	2.0
Glycerine	4.0
Protease enzyme	1.5
Deflocculating polymer	1.0
FWA	0.4
Colorant	0.75
Preservative	0.05
Fragrance	0.4
Water	Balance

involves the controlled crystallization of hydroxyl-modified oils to create a fibrous or entangled thread-like network *in situ* [44]. One such example is trihydroxystearin, sold under the trade name Thixcin by Rheox, Inc.

It is possible to generate a stable structured gel without the use of decoupling polymers or other external structurants. An example is shown in Table 14 [45]. In this

Table 14 Example of Structured Gel HDL without Deflocculating Polymer

Ingredient	Percent
C25E1.8S	23.5
C12 LAS	3.0
C23 E9	2.0
C10 Amidopropylamine	1.5
Citric acid	2.5
DTPA	0.5
C12-16 FA	5.0
Rapeseed FA	6.5
Protease enzyme	0.88
Amylase enzyme	0.1
Cellulase enzyme	0.05
FWA	0.15
Soil suspending polymer	1.2
Ethanol	0.5
Propane diol	4.0
Monoethanol amine	0.48
NaOH	7.0
Na sulfate	1.75
Borax	2.5
Suds suppressor	0.06
Perfume	0.5
Dye	0.02
Water	balance

example the careful balancing of electrolyte levels via citric acid and sodium sulfate is used to move the surfactant into a planar lamellar phase. The result is a shear thinning gel that remains transparent. Gels of this type can be sensitive to fluctuations in raw material quality and process variations that affect electrolyte levels. Otherwise they offer an interesting alternative to the more traditional opaque structured liquids.

Transparent gels packaged in transparent bottles open the possibility of delivering unique aesthetics via the suspension of visible particles of various sizes and compositions. Robust, clear gels based on lamellar phase droplets dispersed in an isotropic aqueous phase have been reported [46]. The key is to reduce the size of the lamellar phase droplets via either very high sheer rate during processing, and/or by use of deflocculating polymers. Careful matching of refractive index between the droplets and the continuous phase via addition of sugars can also help. An interesting new issue of such a clear product in a clear product is the effect of UV light on the actives. Degradation of actives such as enzymes or dyes when exposed to normal daylight is well know and must be avoided. Addition of fluorescent dyes, UV absorbers, and antioxidants are all shown to aid stability [47]. Encapsulation of actives in polymers or other protective shells can also work [48].

The production of structured liquids is more problematic than that of isotropic liquids. Depending on the structuring method used the process required can vary dramatically. Also, some systems need to “age” before their full structuring capability is realized. In systems where solids will be suspended this is an important consideration. In a typical batch mixer with blade agitation, large amounts of air can be incorporated into the product. This needs to be removed before the structuring step or it can become entrapped in the liquid. As it slowly deaerates an undesirable foam layer can form on top of the liquid, and the process of deaerating can destabilize suspended solids.

C. Bleach-Containing Liquids

As mentioned above, one of the largest challenges in liquid detergents is the inclusion of bleach. There are two primary reasons for this, and two primary avenues used to overcome them. First, most of the nonchlorine oxidizing bleaches are unstable as the aqueous solution. Second, even if the bleach is stable, the other actives in the formula are typically not stable toward the bleach. In both cases, by the time the detergent reaches the consumer's home there is little bleaching power remaining, and often little of anything else. Conceptually the solutions are straightforward—keep the bleach separate from the rest of the detergent and/or make the detergent nonaqueous. Executionally things are less straightforward.

One way to keep the bleach separated from the rest of the detergent is to use a bleach that is either insoluble or only very slightly soluble in the detergent matrix. Provided the insoluble bleach is present in small enough (i.e., submicron) particle size it can be suspended directly in a non-structured liquid. More commonly, a structured liquid is utilized. If totally insoluble, such a bleach could theoretically be added into any structured HDL with appropriate suspending power. The bleach is typically an organic peroxy acid, examples of which include: *N*,*N′*-terephthaloyl-di-(6-aminopercarboxycaproic acid) (TPCAP); 1,12-diperoxydodecenoic acid (DPDA); and *N*,*N*-pthaloylaminoperoxycaproic acid (PAP).

The reality is that these bleaches do have limited water solubility—enough to be of concern. Hence thought has to be given to their chemical stability as well. The stability of these peracids is much higher at low pH (i.e., pH 3–6), but for good performance of the detergent the wash pH needs to be higher (i.e., pH 7–9). So formulators have developed "pH-jump" systems. In a pH-jump system the neat product pH remains low, but on dilution in the wash jumps to a suitably high pH of 7 to 8. This is commonly accomplished by formulating borax and a polyol. The polyol complexes the borate in the concentrated neat liquid, keeping the pH low. On dilution they dissociate, releasing borate into solution and thereby raising the pH. Table 15 illustrates a bleach containing HDL formulated around this concept [49].

Another potential problem area for bleach stability is the presence of trace transition metals in the formulation. Even with careful attention to water sources and raw material quality, the presence of trace transition metals in the formulation is all but unavoidable. Transition metals decompose the peracid bleaches via a radical mechanism. To shut down the decomposition pathway the formulator can either add a chelant to sequester the transition metals, or add a radical scavenger such as an amine-oxide or an antioxidant like BHT. An example of a formulation with the later is shown in Table 16 [50].

Suspending the bleach in an anhydrous liquid detergent is another possibility. This also opens the possibility to formulate a bleach activator such as TAED or NOBS for better performance. The challenge in this case is insuring there is no free water to begin decomposition of the bleach, and ensuring the liquid remains stable at a pourable viscosity. These two items are often related since decomposition of activators such as NOBS leads to formation of colloidal fatty acid derivatives that leads to irreversible thickening upon aging. Stable products are obtained by the careful choice of organic solvent and liquid raw materials (such as some nonionic surfactants). The rest of the raw materials are added as fine powders. Table 17 illustrates a formula where butoxy-propoxy-propanol is the primary solvent, and NOBS/percarbonate makes up the bleach system [51]. Processing of

Table 15 Example of pH-Jump with Bleach HDL

Ingredient	Percent
DPDA	2.0
LAS	16.1
C25 E9	6.9
Na borate $10H_2O$	5.0
sorbital	20.0
Na sulfate	0–5
Na polyacrylate	0 – 0.20
Decoupling polymer	0.5 – 1.0
Chelant	0.30
Minors	0.5
Water	Balance

Table 16 Example of Stabilized HDL with Bleach

Ingredient	Percent
HLAS	29.5
Sorbitol (70%)	16.1
DI H_2O	15.2
AE9	12.9
Na citrate	9.7
NaOH (50%)	7.4
Decoupling polymer	1.8
Sodium borate	3.7
BHT	0.84
TPCAP	3000 ppm AvO

anhydrous formulas such as this is much more complex than for isotropic liquids or even for most structured liquids described above.

Bleach catalysts offer perhaps the most promising approach to an HDL with bleach, though to date none have appeared on the market. The reasons for this are tied to the design and performance of the bleach catalyst more than to the HDL itself [52]. As already discussed in the section on raw materials, catalysts react with appropriate oxygen sources to form high valent metal oxides that are potent oxidizing agents. These metal oxides provide enhanced performance at lower temperatures and in shorter time. More importantly for HDLs they take up far less formulation space since they are catalytic. The ultimate goal for an HDL is to have a catalyst that forms the metal oxide bleaching species using molecular oxygen or the low levels of peroxides that preexist in stains. Such a catalyst would remove the challenge of formulating either peroxide sources or preformed peracids in the HDL.

Table 17 Example of Anhydrous with Bleach HDL

Ingredient	Percent
NaLAS	16.0
C11E5	21.0
BPP	19.0
Na citrate	4.0
NOBS	6.0
Soil suspension polymer	1.2
EDDS	1.0
Na carbonate	7.0
Acrylate polymer	3.0
Protease enzyme prills	0.4
Amylase enzyme prills	0.8
Cellulase enzyme prills	0.5
Na percarbonate	16.0
Suds suppressor	1.5
Perfume	0.5
TiO2	0.5
FWA	0.14
Thixatrol ST	0.1
Speckles	0.4
Misc.	to 100%

D. Dual-Bottle Liquids

One of the goals mentioned above for structured and anhydrous liquids is to keep reactive or incompatible ingredients separate. The same goal can be accomplished in a chemically simpler way by keeping the different actives physically separated via the packaging. That is to say, the bottle is made up of two (or more) separate compartments such that their contents mix only on dosing. This opens up several degrees of freedom to the formulator, but adds packaging complexity and cost. With such a packaging system in hand a number of possibilities emerge. The utility of the dual-bottle approach is currently limited by packaging and production constraints much more so than formulation constraints.

Formulating for a dual-bottle approach is not as straightforward as putting a normal HDL in one bottle and a solution of the incompatible active in the other. Unless the dosage volume is doubled, the result would be to dilute the HDL with the second bottle. Where possible then, the main cleaning actives are often formulated into both bottles, with the main incompatible actives formulated more concentrated in separate bottles. In this way, deliver of sufficient actives can be balanced against dosage volume. The degree to which this is an issue depends on the volume ratio delivered by the two bottles on dosing and on how concentrated the particular formula can be. Matching the viscosity between the two liquids is also an important challenge to maintain optimum pouring and mixing properties.

An example of a dual-bottle approach delivering softening benefits is shown in Table 18 [53]. In this case the second compartment contains a quaternary softening active that

Table 18 Example of Dual-bottle HDL with Softener Active

Ingredient	Percent A	Percent B
AE	15.0	5.0
Alkyl amine oxide	5.0	—
Citric acid	—	10.0
Ethoxylated alkyl amine	1.0	—
Chelant	0.4	—
N,N-dimethyl N,N-di(tallowacyloxyethyl) ammonium chloride	—	15.0
Protease enzyme	0.10	—
Amylase enzyme	0.22	—
Boric acid	2.0	—
Ethanol	—	5.0
Propanediol	10.0	—
Sodium cumene sulfonate	2.0	2.0
NaOH	—	to pH 3.0
Monoethanolamine	to pH 7.5	—
Perfume/minors	1.5	1.5
Water	Balance	Balance

would otherwise precipitate with the anionic surfactant in a single bottle HDL. Note that the dual-bottle approach also allows for formulating at the optimum pH for chemical stability of the softener active on the one hand, and the detergent enzymes on the other. Incorporation of a bleach such as PAP in the second bottle is also of key interest [54]. Another interesting possibility disclosed in the same patent application is delivery of "signals" that reinforce to consumers that the detergent is working as intended. Examples could include release of a specific consumer appreciated fragrance, or production of a color that indicates mixing is complete. Table 19 illustrates a formula where the signal is effervescent foaming created by the reaction of catalase enzyme with hydrogen peroxide. The foam is created as the gas generated from the decomposition of peroxide bubbles through the concentrated surfactant solution of the HDL.

VI. UNIT DOSE DETERGENTS

A. Tablets

Laundry tablets are small "briquettes" of solid laundry detergent. Shapes vary, but the typical tablet contains roughly 40 G of detergent making the normal dose two per wash load. The primary advantage of tablets comes in ease of dosing—aside from deciding how many tablets to add to the wash there is no measuring. Given their highly compact nature, tablets also offer some economy in shipping and storage, but this is secondary. The basic idea of laundry tablets has been around since the 1960s. Initial launches failed due to poor solubility and poor consumer acceptance. Tablets were relaunched in Europe in the late 1990s, where they have taken a firm place in the market. Improvements in

Table 19 Example of Dual-bottle Effervescent HDL

Ingredient	Percent
Bottle A	
MEA	1.1
C10 APA	0.5
Na C25 AE1.8S	19.35
Propylene glycol	7.5
Neodol 23-9	0.63
FWA	0.15
Na toluene sulfonate	2.25
NaOH	2.79
N-cocoyl N-methyl glucamine	2.5
Citric acid	3.0
C12–16 real soap	2.0
Borax	2.5
Ethanol	3.25
Ca formate	0.09
Ethoxylated polyethyleneimine	1.3
Ethoxylated tetraethylene pentaimine	0.6
Na formate	0.115
Fumed silica	0.0015
Soil release polymer	0.08
Water	46.08
Dye	0.016
Protease enzyme	1.24
Cellulase enzyme	0.043
Amylase enzyme	0.15
Silicone	0.119
Perfume	0.35
DTPA	0.3
Catalase enzyme	0.15
Bottle B	
NaOH	3.46
Hydrogen peroxide	4.0
Water	72.69
Titanium dioxide	2.5
Xanthan gum	0.45

tablet design and changes in consumer habits and preferences have contributed to the new success.

Tablets are the same as HDGs in terms of actual cleaning chemistry delivered to the wash process. The basic cleaning chemistry is reapplied from HDG developments, described previously in this chapter. Most developments in the field of tablets are targeted at overcoming the manufacturing and dosing/dissolution constraints inherent in the form. The first step of manufacturing tablets often involves making a traditional laundry granule via either spray-drying or agglomeration. These granules are then combined with other actives, a binder of some kind (e.g., polyethylene glycol, water soluble polyacrylates, etc.), and the combination is then "pressed" with high pressures into the tablet form. Due to the force used to compact the tablets, they dissolve slower in the wash compared to the same actives in granule form. If less force is used a more porous, faster dissolving tablet results. Unfortunately such tablets are usually not physically robust enough to withstand the packaging and shipping operations. Developing a tablet with good handling characteristics and good dissolution profile at the same time is the primary challenge.

A number of approaches have been developed against this challenge, many of them learned from the pharmaceutical industry that faces related challenges in medicinal tablets. Some solutions do not affect the tablet per se, but rather how the tablet is physically added to the wash. These range from hard plastic devices to simple mesh bags [55]. In all cases the idea is to insert the tablet into the device to help break-up the tablet and to prevent large chunks from becoming lodged in nonproductive places in the washing machine. Once broken into small enough pieces the same dynamics affect dissolution as in HDGs. Approaches that affect the tablet itself usually rely on an added swelling agent, hydrotropes, or disintegrant to help the tablet break apart rapidly and completely in the presence of water. This is the preferred approach for tablets of uniform density and hardness. There are also approaches that involve more complex processing of the tablet to include layers of different hardness, or coatings to protect softer interiors. Combinations of all these approaches are also known.

In phosphate-containing tablets it is possible to use materials high in Phase I STPP to aid in rapid disintegration [56]. Phase I STPP, available commercially for example as Rhodiaphos HPA 3.5, is the high temperature stable version of crystalline anhydrous STPP. It hydrates and dissolves more rapidly than phase II material and has been shown to aid dissolution of granules. Additional dissolution aides can also be used at the same time as shown in the example in Table 20, which includes an effervescent system. This example also highlights another common feature of tablet design, the use of multiple layers to separate actives (e.g., the phase I STPP is best separated from other hydrated species), or to provide additional mechanical stability. Table 21 illustrates the use of phase I STPP in a zeolite-containing tablet [57].

In nil-P products a different approach is required. In this case, the use of other higher water-soluble salts is found to be beneficial [58]. Sodium acetate trihydrate is claimed for use in this role [59]. Another approach is to use swellable polymers, which on wetting serve as an "explosive agent" to aid disintegration of the tablet. Henkel, for example, use a form of compacted cellulose sold as "Arbocell" by Rettenmaier, for this purpose [60]. A wide variety of other disintegrants are known from the pharmaceutical industry, including starches, and gums [61].

Generating a tablet with a softer, more readily dispersed and dissolved interior, coated with a harder protective "shell" is another approach to the problem. The shell coating is designed to provide mechanical stability during manufacturing, shipping, and handling, and also to provide some level of moisture protection. The coating should be easily broken in the washing machine, via mechanical action and via interaction with water, to release the softer contents rapidly. The coating can be applied over the already formed tablet interior either in the molten form, or as an aqueous solution. Dicarboxylic acids, such as adipic acid, are the preferred coatings in many applications [62]. The coating can also include a disintegrant as discussed above to aid the breakup of the coating. Likewise, reinforcing fibers (e.g., 100 to 400 µm synthetic or natural fibers) can also be included to help avoid premature cracking of the coating during handling. It should be noted that tablets using a coating such as this generally require a flow wrap of some sort for moisture protection to prevent premature swelling and cracking.

Table 20 Example of Tablet with Phase I STPP and Effervescent System

Ingredient	Percent
Base powder	
Na-LAS	23.55
Nonionic surfactant	10.42
Soap	0.72
AA/MA copolymer (70:30)	3.22
STPP (builder)	40.63
Na silicate	8.63
Na carboxymethyl cellulose	0.67
Moisture	12.15
Total	100.0

Tablet

	Thick Layer	Thin Layer	Overall
Base powder	39.00	22.00	35.60
Na percarbonate	—	49.00	9.80
TAED granules (83%)	4.40	—	3.52
Rhodiaphos HPA 3.5	49.00	—	39.20
Citric acid	—	9.62	1.92
Na bicarbonate	—	19.30	3.96
Minors + moisture	7.60	0.08	6.10
Total	100.00	100.00	100.00

An interesting possibility being explored recently is development of tablets with controlled release of actives. Increased performance and/or delivery of additional benefits can be obtained by controlling the order and timing in which various actives enter the wash process. Tablets offer some additional avenues by which to do this. For example, by changing the pressure used to compress different layers of a tablet, different dissolution rates can be obtained. Generally speaking the higher the compression force used the slower the dissolution. The addition of different binding agents at different levels can complement this effect. Likewise, by using different coating or even the same coating with varying thickness the dissolution rate of different layers of the tablet can be retarded by varying amounts of time. Finally, disintegrants can be added to selected layers to help them dissolve more rapidly.

An example of this approach is illustrated in Table 22 [63]. This particular example is a four-phase tablet wherein the surfactants and nonprotease enzymes are released almost immediately in the wash, followed 5 to 10 min later by protease enzyme, builder, and alkali. Bleach follows closely in the third phase, and finally a fabric softener active is added in the final rinse. The advantage to this approach is the separation of actives that normally interfere with each other. The nonprotease enzymes have time to function before protease is added and begins degrading them. All of the enzymes have time to function before bleach is added, and the cationic fabric softener is well separated from the anionic surfactants, thereby preserving the function of both.

Table 21 Example of Tablet with Mixed Zeolite/STPP System

Ingredient	Percent
Base Powder	
Na-LAS	22
Nonionic surfactant	5
Soap	3
Zeolite 4A	35
Na carbonate	20
STPP (fully hydrated)	10
Moisture/minors	5
Total	100%
Tablet	
Base powder	66
Rhodiaphos HPA 3.5	31
Blue speckles	1.5
Sequestrant, enzymes, perfume	3.5
Total	100%

Table 22 Example of Tablet Utilizing Controlled Release of Actives

Ingredient	Amount (G/Wash Load)	Phase I	Phase II	Phase III	Phase IV
C12-18 Alkylbenzene sulfonate	9.75	x			
C12-18 Alkyl sulfate	1.95	x			
C12-18 Alkyl ethoxylate EO7	2.93	x			
Zeolite A	14.63		x		
Sodium carbonate	7.31		x		
Water glass	2.91		x		
Polycarboxylate polymer	2.44	x			
Sodium percarbonate	11.25			x	
TAED	4.5			x	
Protease	0.75		x		
Amylase	0.23	x			
Lipase	0.75	x			
Cellulase	0.23	x			
Auxiliary materials (antifoam, perfume)	3.75	x			
Water	6.5	x			
Sodium sulfate	to 100	x			
Esterquat softener	7				x

4

Dishwashing Detergents for Household Applications

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CONTENTS

I. SUMMARY

Dishwashing detergents play an essential role in consumers' everyday lives. Both hand and automatic dishwashing detergents help consumers clean and care for a wide range of kitchenware, including dishes, pots, pans, and utensils. Over the years, dishwashing detergent manufacturers and suppliers have conducted extensive research and development activities to improve product performance in order to satisfy consumers' needs better. New technologies and new product forms have emerged in recent years, fueling the dynamic growth of hand and automatic dishwashing detergents in the global marketplace.

This chapter reviews the key new technologies and new product forms for both hand and automatic dishwashing detergents over the last 10 to 15 years. Significant progress has been made since the earlier reviews on hand dishwashing detergents by Lai et al. (1997), on liquid automatic dishwashing detergents by Gorlin et al. (1997), and on general automatic dishwashing detergents by Heitland and Marsen (1987). For hand dishwashing detergents, this review covers key new cleaning technologies such as new surfactants, low interfacial tension (IFT) technologies based on divalent cations, suds boosting polymers, dissolution aids, enzymes, and bleaches. For automatic dishwashing detergents, we review new product forms such as gels and tablets and new cleaning technologies such as bleach catalysts, low-foaming non-ionic surfactants and glass surface care technologies. Summaries will also be provided on the key patent activities in both hand and automatic dishwashing detergents.

II. INTRODUCTION

Dishwashing detergents play an essential role in the consumer's everyday life. The primary purpose of dishwashing is to remove soils, mainly food material residues, from kitchenware surfaces, including dishes, pots, pans, utensils, and a wide range of other items. Although dishwashing detergents can be traced to ancient times, the first modern-day liquid hand dishwashing detergent was developed in the 1940s (Lai et al., 1997; Mizuno, 1975). The mechanical dishwasher was invented in the early 1900s, and this mechanization of the dishwashing process significantly simplifies the consumers' lives. However, even in the twenty-first century after many innovations in the electronics and control systems of the dishwasher, it still does not fully replace hand dishwashing. Instead, machine and hand dishwashing coexist in many consumer's homes, addressing the wide variety of consumers' everyday dish care needs.

The efficiency and efficacy of the dishwashing process is determined by several key factors. First, the efficacy of the detergents is crucial to dishwashing. These detergents are generally designed to facilitate soil removal and make the dishwashing job easier and more enjoyable for the consumer. Second, the amount of mechanical action is highly variable in the dishwashing process. For difficult to remove soils, consumers generally apply a large amount of mechanical action by scrubbing, often with the help of an implement. With the automatic dishwasher, the amount of mechanical action is in general much higher than dishwashing by hand. Third, soil removal efficacy is highly influenced by wash temperature. For greasy soils, higher wash temperatures help to melt the grease particles, making them easier to remove with detergent solutions.

High-performance dishwashing detergents are generally carefully formulated to work with all the key factors or variables in the dishwashing process. For example, given the large amount of mechanical action and high wash temperatures involved in the automatic dishwasher, the composition of an automatic dishwashing detergent is very different from that of a hand dish detergent. To ensure that high performance detergents truly meet the needs of the consumer, detergent formulators have devoted considerable resources to the study and monitoring of consumer habits and practices for both hand and automatic dishwashing.

Over the last 20 years or so, society has been undergoing fundamental changes on a global basis, and these changes are profoundly impacting consumers' dish care habits and practices. Leading dish detergent formulators monitor these relevant consumer trends closely to aid their product development efforts. Several key consumer trends are summarized briefly below.

A. Market Penetration of Residential Automatic Dishwashers

Since the early to mid-1900s, ownership of residential dishwashers has been steadily increasing, similar to other major household appliances. Today dishwasher ownership is one of the major measures of consumer living standard around the globe (Bauman, 2003). In recent years, the household penetration rates of dishwashers continue to increase in many countries, as shown in Fig. 1. However, an equally important take-away from this figure is that the market penetration rate of residential dishwashers is still quite low when compared to other major appliances. This is the case even in major industrialized countries such as the United Kingdom, Spain, and Italy, where dishwasher market penetration remains below 40% (AEA Technology, 2001).

Despite the increasing trends in dishwasher penetration rates, hand and automatic dishwashing detergents are expected to remain equally important to consumers in the foreseeable future. A majority of dishwasher owners often wash some of their kitchenware items by hand. This is especially the case for large, difficult-to-clean items such as those with cooked-on and baked-on greasy soils and for items such as fine crystal stemware and silver flatware. Furthermore, as the size of consumer household decreases (see discussions later in this section), consumer's dishwashing loads are expected to become smaller and

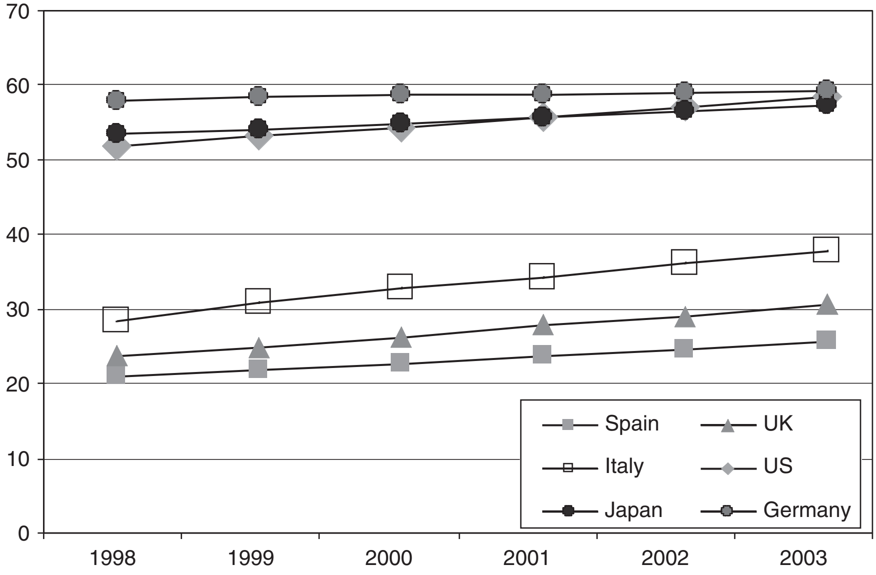


Figure 1 Dishwasher market penetration rates in key global markets

smaller. Many consumers find it more convenient to wash smaller dish loads by hand, instead of using dishwashers.

B. Smaller Households

The size of an average consumer household has decreased steadily in many industrialized countries over the last half a century. For example, the average household size in the United States has fallen from 3.32 in 1965, to 2.69 in 1985, and to 2.58 in 2002 (U.S. Census Bureau, 2002). Similar trends can be found in many industrialized countries. In the European Union, the average household size has decreased from 2.82 in 1980, to 2.68 in 1985 and 2.49 in 1995 (OECD, 1998).

The size of consumer household significantly impacts the habits and practices of dishwashing detergent users. As the size of the household decreases, the number of dirty dishes also decreases on average. This could lead to smaller, but more frequent, dishwashing jobs. As the dishwasher is generally more suited for larger dishwashing jobs, a smaller consumer household may do more hand dishwashing, or at least experience less frequent use of automatic dishwashing machines.

C. Busier Consumer Lifestyles

Several important factors contribute to consumers' increasingly busier lifestyles. First, more and more women have joined the labor force. For example, in the United States, women's share of the labor force was 28.8% in 1967. This share increased to 40.7% in 1997 (U.S. Census Bureau, 1998). Similar trends exist in other industrialized countries. Second, many consumers have busier activity schedules, such as children's after-school activities. Consumers' busier lifestyles often lead to less frequent formal meals at home and more income spent on eating outside the house.

The consumer and market trends as discussed above have significant implications for the formulation of hand and automatic dishwashing detergents. The busier consumer lifestyles lead the demand for faster and simpler dishwashing jobs, with reduced efforts.

At the same time, many consumers still want the reassurance and emotional satisfaction that their dishwashing jobs are accomplished to personal satisfaction and their families are well taken care of.

III. HAND DISHWASHING DETERGENTS

Hand dishwashing detergents are primarily used by consumers to wash dishes, pots, pans, flatware, and other kitchenware items. They are also often used to wash delicate fabrics and to a lesser extent for general household cleaning and washing automobiles.

The first hand dish detergent was developed in the 1940s. Like other liquid detergents, hand dishwashing detergents offer the advantage of convenience and are well accepted by consumers in both the developed and developing countries. As discussed above, many consumers use hand and automatic dishwashing detergents together to meet their various dish care needs in the kitchen.

Two major articles have been devoted specifically to manual dishwashing detergents, one by Heitland and Marsen (1987) and the other by Lai et al. (1997). Since then, there have been significant advances in both cleaning technologies and product forms, as documented in the patent literature. This section provides a detailed review on these cleaning technology advancements and novel product forms in the market place.

A. Chemistry of Hand Dishwashing

1. Hand Dishwashing Process

In simple terms, dishwashing by hand is a process in which soils are removed from dish surfaces through various washing methods that combine the mechanical action of stirring and/or scrubbing with chemical action afforded by the cleaning ingredients of a detergent. As illustrated by Lai et al. (1997), the effectiveness of the hand dishwashing process is ultimately impacted by four key parameters: the soil type, the mechanical action, the type of dish surfaces and detergent composition, in additional to other parameters such as quality of the wash water (e.g., hardness).

In a typical consumer's home, the principal types of soils involved in dishwashing are oily soil, including various types of animal fats (e.g. chicken, pork, and beef fats) and vegetable oils, proteins, carbohydrates, and particulate soils. Baked-on or cooked fatty soils require vigorous treatment actions, either mechanical or chemical. This also includes soaking to allow soil rehydration and removal by the detergent formulation. The oily soils are almost exclusively triglycerides, which contain predominantly C_{10}-C_{18} saturated and unsaturated alkyl carbon chains. These triglycerides are considerably more polar and have higher molecular weights than hydrocarbon soils encountered in other cleaning processes such as fabric laundry. As a result, the chemistry of manual dishwashing presents unique and interesting challenges for product formulators and raw material suppliers.

Mechanical action is another very important factor in hand dishwashing. When consumers wash dishes, they actively stir the wash water or rub the dish surface. A wash implement (e.g., sponge, wash cloth, etc) is often used to aid the process. Mechanical action serves two distinct purposes. First, it helps to soften the soils. As discussed by Lai et al.. (1997) and Heitland and Marsen (1987), mechanical action alone can remove a significant amount of soils, especially for particulate soils encountered around the kitchen. The second purpose of mechanical action is to mix the cleaning ingredients with soils, especially difficult-to-remove soils, enhancing the cleaning efficacy.

The amount of mechanical action employed in hand dishwashing is extremely variable, from consumer to consumer and from one cleaning job to another. For example, difficult-to-clean dish items may be soaked in a wash solution in which very little mechanical action is applied. Under such conditions, the surface chemistry actions of cleaning ingredients are critical. After soaking, consumers may apply a large amount of mechanical action by scrubbing the still difficult-to-clean soils off dish surfaces. Every consumer has his or her favorite dishwashing techniques and preferred mechanical activities for dishwashing. Nevertheless, detergents are generally designed to increase the efficiency of the consumer's mechanical actions, and as a result to reduce the amount of mechanical actions needed for difficult-to-clean soils. In essence, dish detergents make the consumer's dishwashing jobs easier and more enjoyable.

The type of dish surface is also a key consideration for hand dishwashing. Typical consumer kitchenware materials include metals (aluminum, stainless steel, carbon steel, cast iron, silver, and tin), glass and ceramics, and various plastics (polypropylene, polyethylene terephthalate [PET], etc.). These materials have a wide range of hydrophobicity or hydrophilicity. For example, surfaces of new metal, glass and ceramic items are typically hydrophilic, while those of plastic items are highly hydrophobic. Oily soils are especially difficult to clean off plastic items, primarily due to the tight bonding of greasy soils to the hydrophobic surfaces.

2. *Methods of Hand Dishwashing*

As discussed above, consumers typically have their own favorite method for hand dishwashing. These methods can be broadly classified into three categories: the full sink (FS) method, the direct application (DA) method, and the concentrated minisolution (CMS) method.

a. Full Sink (FS) Method. In this method, the consumer first fills the sink with hot or warm water and then applies an appropriate amount of detergent to make a dilute wash solution. Soiled dishes and other kitchenware are placed in the sink for soaking and washing. An implement (e.g., sponge) is often used to aid the cleaning action. The washed items may be rinsed one by one to remove detergent suds. Detergent concentration used by the consumer varies widely, typically ranging from 0.05 to 0.5% in the full sink method (Lai, et al., 1997).

b. Direct Application (DA) Method. The consumer typically applies an appropriate amount of detergent on the implement (e.g., sponge), which is then squeezed to generate suds and applied to dish surfaces for the cleaning action. Rinse water is often applied to remove soils and detergent suds after cleaning action is complete. Detergent concentration in the direct application method is typically much higher than the dilute wash solution used in the full sink method, ranging from 0.5 to 5% (Lai et al., 1997).

c. Concentrated Minisolution (CMS) Method. The consumer typically prepares a small amount of concentrated wash solution in a container by the side of the wash sink. An implement/sponge is then used to pick up the concentrated mini-solution and apply to soiled dish surfaces for washing. The dishes are often rinsed one by one at the end of the wash process. Detergent concentration in the CMS method is typically lower than the DA method, but much higher than in the dilute wash solutions used in the full sink method.

The consumer's hand dishwashing methods are typically a combination of the three methods as discussed above. Typical hand dishwashing methods are summarized in Table 1 for several representative countries, based on unpublished data from Westfield and Ruiz-Pardo (2004). As is evident from Table 1, the consumer's hand dishwashing methods are highly variable from country to country.

Table 1 Typical Consumer Hand Dishwashing Methods in Selected Countries

Countries	Full Sink (FS)[a]	Direct Application (DA)[a]	Concentrated Minisolution (CMS)*
United States	72	27	1
United Kingdom	82	14	4
Germany	93	7	—
France	51	38	11
Spain	35	50	15
Japan	3	90	7
Mexico	1	15	83

[a] Data are percentages (%) of dish wash loads by consumers.

3. *Mechanisms of Cleaning by Hand Dishwashing Detergents*

Detailed discussions have been presented by Lai et al. (1997) on the various cleaning mechanisms of hand dishwashing detergents. A brief summary is presented below.

a. Emulsification. Like many other detergents, emulsification is the primary cleaning mechanism for greasy soils in hand dishwashing. In this mechanism, surfactants partition onto the soil-water interface, and reduce the interfacial tension (IFT). This enables the soils to form an emulsion of small particles in the wash water (Neiditch, 1975). These emulsion particles are <0.5 μm in size and thermodynamically unstable. However, given the relatively short wash time, this thermodynamic instability does not significantly impact the soil cleaning efficiency. The key driver for the emulsification mechanism is the low IFT between greasy soils and wash water. Over the last 10 to 15 years, low-IFT technologies (e.g., Mg^{2+} and organic diamines) have played a critical role in improving the cleaning performance of hand dishwashing detergents.

b. Grease "Roll-Up". For greasy soils on highly hydrophobic surfaces (e.g., plastics), the emulsification mechanism is generally not effective. To improve cleaning, wetting agents and/or surfactants with strong surface wetting capabilities are typically needed to increase the contact angle and binding strength between the greasy soil and the hydrophobic surface. When the contact angle increases to between 90° and 180°, the greasy soil can effectively "roll-off" from the surface with small mechanical agitation. The "roll-off" mechanism is illustrated in Fig. 2.

The theory of surface wetting has been discussed extensively by Clint (1992) and by Holmberg et al. (2003). Most surfactants have some ability to induce wetting on hydrophobic surfaces. However, the wetting ability of surfactants varies widely depending on their amphophilic structures.

c. Solubilization. In detergency, the solubilization mechanism refers surfactant-aided dissolution of insoluble soils in wash water. This dissolution is achieved when soils partition inside the core of or around the surfactant micelles (Lai et al. 1997; Neiditch, 1972). The solubilization mechanism differs from emulsification in that the solubilized soil particles are thermodynamically stable in water. The size of these particles are generally similar to surfactant micelles, i.e., 5 to 100 nm in diameter. The efficiency of the

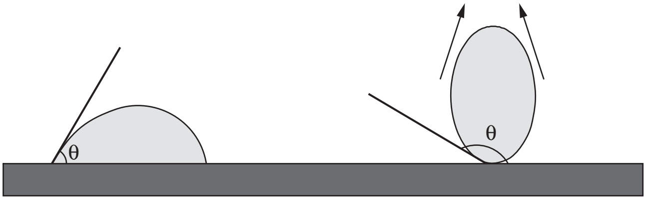


Figure 2 Schematic of the "roll-up" mechanism. With poor surface wetting, the contact angle θ is <90° and removal is difficult. When θ increases to >90°, soil "roll-up" becomes possible, with easier removal by low mechanical agitation.

solubilization mechanism depends on a complex set of surfactant parameters such as the micelle structure and the critical micelle concentration (CMC). More detailed discussions about this mechanism can be found in the work by Dunaway et al. (1995).

d. Formation of Surfactant-Rich Intermediate Phases. A review by Miller and Raney (1993) discussed a novel cleaning mechanism in which a surfactant-rich intermediate phase is formed between the soil and wash water. Such intermediate phases may be a microemulsion or liquid crystal and can improve dish soil cleaning as they grow to large sizes such that small mechanical agitation can break them off the surface. The intermediate phase mechanism is efficient for many hydrocarbon soils with nonionic surfactant systems, but relatively high temperatures (>65°C) are typically required. This mechanism is much less efficient with triglyceride soils and anionic surfactant systems that are typical of hand dishwashing detergents.

B. Basic Building Blocks of Hand Dishwashing Detergents

A typical hand dishwashing detergent in today's market place contains ingredients for cleaning, foaming, product dissolution, and other minor functions (preservation, color, fragrance, anti-irritation, etc.). Some products also contain antibacterial agent(s). The typical physical properties and composition of hand dishwashing detergents are summarized in the Table 2 (see Modler et al., 2002).

1. Surfactants

Surfactants are the primary cleaning ingredients in hand dishwashing detergents to provide cleaning performance. They are also the primary drivers for suds or foams, which are important sensory signals for consumers on the cleaning power of hand dishwashing detergents. Beyond cleaning and suds performance, mildness to human skin is another key requirement for surfactants in hand dishwashing detergents. Mildness is an increasingly important consideration for hand dish detergent consumers across all market segments around the globe.

Three main classes of surfactants have found widespread applications in hand dishwashing detergents: anionic, nonionic and amphoteric surfactants. The most commonly used surfactants are summarized in Table 3, based on recent surveys by Lai et al. (1997) and Modler et al. (2002). Cationic surfactants as a class have not been widely used in hand dishwashing detergents, primarily due to their generally detrimental impact on detergent suds.

Anionic surfactants are the workhorses for grease cleaning performance of hand dishwashing detergents. They help to reduce the interfacial tension (IFT) between greasy soils and wash water to achieve effective cleaning. In most hand dishwashing detergents, anionic surfactants are often used in combination with nonionic or amphoteric surfactants such as amine oxides and alkyl polyglucosides (APGs). As discussed by Holmberg, et al.

Table 2 Typical Properties and Ingredients of Hand Dishwashing Detergents

Ingredients or Properties	Typical Values
Viscosity (cps)	100–1,200
Product pH (10% solution)	6–10
Cloud point (˚C)	<5
Surfactants	10–50%
Foam/suds stabilizers	0–5%
Hydrotropes and dissolution aids	0–10%
Salts	<3%
Preservatives	<0.1%
Fragrance	0.1–1%
Dyes	<0.1%
Other additives	0–5%
Water	Balance

(2003) and Holland and Rubingh (1992), these mixed surfactant systems help to achieve very low IFT between greasy soils and wash water and thus significantly improve the detergent's cleaning efficiency.

Amphoteric surfactants typically exhibit both good cleaning for greasy soils and foaming/sudsing properties. More importantly, they offer excellent mildness for human skin (Holmberg et al., 2003). In recent years, these surfactants have found more widespread applications in hand dishwashing detergents due to increasing consumer need for product mildness. As shown in Table 3, the most widely used amphoterics are betaines, which are generally more expensive than other surfactants. This has prevented them from being used more widely.

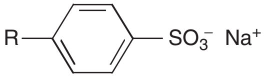
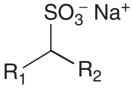
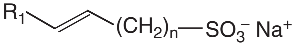
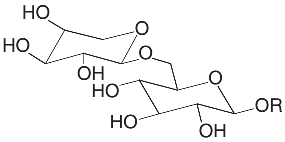
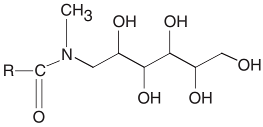
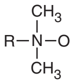
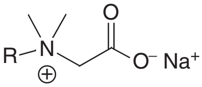
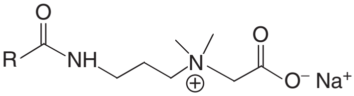
2. *Foam or Suds Stabilizers*

Detergent foam (or suds) is an important sensory signal that consumers often use to judge the performance of hand dishwashing detergents. They typically use the amount of initial foam to determine the amount of detergent to use for a specific dishwashing job. Suds longevity or mileage is also used as an indicator of the cleaning power of the product. Because of the great importance that consumers attach to suds, formulators and suppliers of hand dishwashing detergents have conducted extensive research to improve the detergent's initial foam generation and the foam's longevity or mileage in the wash process.

Most hand dishwashing detergents marketed today utilize several unique high-foaming surfactants to "boost" suds formation. The surfactants below are often referred to as "suds boosting" surfactants.

- <u>Amine oxides</u>: With unique combinations with anionic surfactants, amine oxides have been proven to be very effective in boosting suds performance of hand dishwashing detergents. The mostly widely used are C_{10}-C_{16} dimethyl amine oxides, which are commercially available from several manufacturers (see Modler, et al. [2002] for more details).
- <u>Fatty alkanol amides</u>: Similar to amine oxides, fatty alkanol amides are good foam boosters with unique values to hand dishwashing detergents. As pointed

Table 3 Major Surfactants Used in Hand Dishwashing Detergents

Surfactant Description	Chemical Structures
Anionic Surfactants	
Linear alkylbenzene sulfonate (LAS)	
Alkylethoxy sulfate (AES)	$R — [OCH_2CH_2]_nOSO_3^- Na^+$
Alkyl sulfate (AS)	$R-OSO_3^- Na^+$
Sodium paraffin sulfonate	
α-Olefin sulfonate	
Nonionic surfactants	
Alcohol ethoxylate (AE)	$R — [OCH_2CH_2]_nOH$
Alkyl polyglucoside (APG)	
Fatty acid glucamide	
Amine oxide	 $R-\overset{CH_3}{\underset{CH_3}{N}}-O$
Amphoteric surfactants	
Alkyl dimethyl betaine	
Alkyl dimethyl amidopropyl betaine	

> out by Modler et al. (2002), theses amide surfactants are typically used in conjunction with LAS-based formulations (likely due to the unique foaming properties of this surfactant combination). Most commonly used are lauric/myristic and coco mono- or di-ethanol amides.

In recent years, detergent formulators have developed polymeric technologies to increase or "boost" the suds mileage or longevity of hand dishwashing detergents. More discussion will be provided on this subject later in this chapter.

3. Hydrotropes and Dissolution Aids

Hydrotropes play a crucial role in the performance of hand dishwashing detergents, which are typically designed to be used in diluted form, but are often sold to the consumer as thickened compositions to facilitate product dispensing and to achieve product aesthetic benefits. It is therefore necessary that the detergent composition dissolves quickly and efficiently in water.

The dissolution functions of hydrotropes in liquid detergents have been discussed extensively in the past by Friberg and Brancewicz (1997). The most commonly used and cost effective hydrotropes include sodium cumene sulfonate (SCS), sodium xylene sulfonate (SXS), and sodium toluene sulfonate (STS). Several solvent hydrotropes have also found application in hand dishwashing detergents, including ethanol, isopropanol, propylene glycol, and polyethylene glycol ethers.

C. Recent Developments in Key Hand Dishwashing Technologies

1. Surfactants

As discussed by Lai et al. (1997), most hand dishwashing detergents utilize unique surfactant mixtures to achieve their performance objectives. These surfactant systems often contain a broad mixture of alkyl chain lengths in the surfactant hydrophobes, because micelles with mixed hydrophobe chain lengths are energetically favored in general when compared to those with the same hydrophobe chain lengths (see Schambil and Schwuger, 1987).

Over the last 5 to 10 years, there has been a large amount of patent activity on novel combinations of existing main frame surfactants as discussed in the previous section (see Section III.E for a detailed summary of the patent activities for hand dishwashing detergents since 1995). Key new developments have focused on improving surfactant water solubility and co-surfactant development. Drivers for these co-surfactants included (1) additional surfactant functionality (e.g., chelating surfactants) to improve grease cleaning and (2) improvement in the mildness of surfactants to human skin.

a. High-Solubility Anionic Surfactants. Mid-branched anionic surfactants in cleaning applications have been the recent focus of a large amount of patent activity and scientific literature. The key innovative feature of these anionic surfactants is the introduction of a limited amount of alkyl branching (e.g., methyl) in the middle of the hydrophobic alkyl chain. An example of such surfactant structures is shown in Fig. 3. The limited alkyl branching on the hydrophobe increases the water solubility of the anionic surfactants dramatically, while maintaining the ready biodegradability of these surfactants (Connor et al, 2001; Schmidt et al., 2000; Shi et al., 2000).

Applications of these high-solubility anionic surfactants in dishwashing detergents have been described in detail in the patent literature (see, e.g., Connor et al., 2001). Due

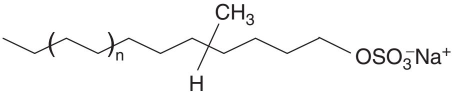


Figure 3 An example structure of high-solubility mid-branched anionic surfactants.

to high water solubility, these mid-branched anionic surfactants are highly available in the wash solution for grease removal.

b. Chelating Surfactants. Anionic surfactants with additional functionality have attracted attention for application in hand dishwashing detergents in recent years. Examples for such surfactants are acyl ethylene diamine triacetate (e.g., LED3A) and alkyl ethoxy caboxylates (AECs). Both of these surfactants have head groups (ethylene diamine triacetate (ED3A) and carboxylate, respectively) that exhibit significant chelating capacities. Applications of AECs in hand dishwashing detergents have been described in detail by Wise and Cripe (1993). Similarly, D'Ambrogio and Connors (2001) have described applications of LED3A in hand dishwashing detergent compositions for excellent grease cleaning and skin mildness. Despite the unique functionalities of these chelating surfactants, their commercial applications in current dishwashing detergents are rather limited, primarily due to relatively high costs when compared to other workhorse anionic surfactants.

The strong grease cutting ability of chelating surfactants is believed to be related to their ability to pack tightly at the grease/water interface. This leads to low interfacial tension (IFT) and thus good removal of grease by the emulsion mechanism described in Section III.A.3. For typical greasy soils encountered in dishware, fatty acids are present at significant levels (see Institute of Shortening and Edible Oils, 1999). These fatty acids are known to partition at the grease/water interface due to their amphiphilic properties. In the presence of hardness ions (Ca^{2+} and Mg^{2+}), the fatty acids turn into a thin layer of soap, preventing the tight packing of anionic surfactants at the grease/water interface. The chelating surfactants can disrupt this thin soap layer at the grease/water interface, thus yielding low IFT for the mixture surfactant system and excellent grease cleaning.

c. New Amphoteric Surfactants. Amphoteric surfactants are believed to be superior suds boosters and exceptionally mild to human skin (Lai et al., 1997). Efforts continue over the last several years to explore the applications of such surfactants in hand dishwashing detergents. Beyond the traditional amphoteric betaines, cocoamidopropyl dimethyl hydroxyl sultaine has also been explored by Arvanitidou et al. (2001) in hand dishwashing detergents. Good suds profiles and grease cutting were observed in detergents formulated with sultaine in conjunction with other relevant surfactants.

2. *Low-IFT Grease Cleaning Technologies*

Historically, anionic surfactants have been the predominant surfactants for hand dishwashing detergents. This is largely a result of their availability and economics. The anionic surfactants commonly used are alkyl ethoxy sulfate (AES), linear alky benzene sulfonate (LAS) and sodium paraffin sulfonate (SPS). However, these surfactants by themselves have critical micelle concentrations (CMCs) typically higher than 1000 ppm (Swisher, 1987), which are too high for effective partition to the grease/water interface and effective grease cleaning under typical dilute wash conditions.

To improve the grease cleaning and sudsing performance of traditional anionic systems, dishwashing detergent formulators have over the years developed several key low-IFT technologies. The best-known such technologies are amine oxide co-surfactant

Table 4 Impact of Amine Oxide (AO) on the CMC of AE_1S Surfactant Mixtures[a]

Surfactant Mixture	Critical Micellar Concentration (CMC, molal)
AE_1S	$1.2\ 10^{-3}$
Amine oxide	$2.1\ 10^{-4}$
AE_1S/AO (1.8:1 Mol ratio)	$4.0\ 10^{-5}$
AE_1S/AO (0.7:1 Mol ratio)	$4.3\ 10^{-5}$
AE_1S/AO (0.28:1 Mol ratio)	$3.1\ 10^{-5}$

[a] Wash water conditions: 0 gpg water hardness and 46°C water temperature.

and divalent cations such as Mg^{2+}. The impact of amine oxide (AO) on the surfactant mixture CMC is illustrated in Table 4. The addition of amine oxide (AO) to AE_1S reduces strongly the CMC of the surfactant system. The surfactant synergism of AES with amine oxide has been discussed in detail by Holland and Rubingh (1992) and Holmberg et al. (2003).

Mg^{2+} divalent ion also helps reduce grease-water IFT and improves significantly the grease removal of hand dishwashing detergents, as discussed by Lai et al. (1997). It is generally believed that divalent ions improve grease cleaning by improving surfactant packing at the grease-water interface to achieve low IFT and to some extent by changing the micelle structures of the surfactant mixture in solution. The impact of Mg^{2+} on the anionic with amine oxide surfactant system can be explained below.

- In absence of Mg^{2+} divalent ion, the amine oxide monomer available in solution is very low, primarily due to the strong interactions between the anionic surfactant and protonated amine oxide in the micelles. Thus only AES anionic surfactant is free in solution and available to partition onto the grease-water interface. The grease removal performance is thus relatively poor without Mg^{2+}.
- With Mg^{2+} divalent ion added to the surfactant mixture, it weakens the interaction between AES and protonated amine oxide inside the surfactant micelles. The level of free amine oxide monomers in solution is thus increased dramatically. Both the anionic surfactant and amine oxide monomer are then available to partition onto grease-water interfaces, resulting in lower IFT and dramatically increased grease removal.

Despite the impact of Mg^{2+} divalent ion on grease removal, it does have a significant drawback. Hand dishwashing detergents with >0.5% Mg^{2+} can have significant storage stability issues under conditions experienced in some countries (e.g., the storage temperature can reach below 0°C in Japan in the winter). To solve this problem, organic diamines have been developed in recent years to replace Mg^{2+} and avoid the low-T storage stability issues (see, e.g., Castro et al., 2000).

Organic diamines work similarly to Mg^{2+} for improving grease cleaning of hand dishwashing detergents. At the pH of the wash solution, the diamines are typically protonated into small organic cations, which weakens the micellar interactions between anionic surfactants and protonated amine oxide. Therefore, organic diamines help to reduce grease-water IFT and improve grease cleaning. Applications of the organic diamines in hand dishwashing detergents have been described extensively in the patent literature over the last 10 years (see patent summary table in Section III.E).

3. *Suds Boosting Polymers*

a. Background. Previous efforts to evaluate suds boosting polymers in hand dishwashing detergents have focused on polymers that could enhance the bulk/film viscosities (e.g., celluloses, guars, acrylamides, polysaccharides, etc) (Lai and Dixit, 1995). Broad-based polymer screening programs (varying backbone, charge, hydrophobicity, etc.) demonstrated the suds boosting benefits of polymers such as hydroxypropyl cellulose, but most of these polymers had several significant compatibility issues with liquid hand dishwashing detergents: (1) no significant benefits under high dilution product usage conditions (typically 0.004 to 0.1% in use), (2) materials are difficult to formulate into product matrix, and (3) poor product dissolution in wash water.

Based on the above findings, technology developers turned their attention to another mechanism of polymer suds stabilization, i.e., using macromolecules to prevent the antifoam effects of greasy soils. This mechanism led to the development of several key suds stabilizing polymers that include weakly charged cationic polymers.

b. Optimization of Cationic Suds Boosting Polymers. A wide range of cationic hydrophobic polymers have been tested for suds stabilization benefits in hand dishwashing detergents (Sivik et al., 2004). The test method used in this evaluation was similar to the foam stability tests described by Lai et al. (1997). Typical test results are shown in Fig. 4. Notice that the cationic polymer did not significantly affect the initial suds volume of the detergent, but suds longevity was significantly extended by using weakly charged hydrophobic polymers.

The suds longevity benefit of the cationic hydrophobic polymers is highly influenced by the charge density on the polymer chain, as discussed by Sivik et al. (2004). This is illustrated by Fig. 5. If the charge density is too high, the cationic hydrophobic polymers would lead to undesirable interactions with anionic surfactants in the product formulation. Based on these data, Bodet et al. (2003) and Sivik et al. (2004) found that the optimum charge density was about 0.15, as shown in Fig. 5.

Over the last 10 years, several key cationic polymeric structures have been reported for optimum suds boosting performance in hand dishwashing detergents. Two of these structures are shown in Table 5. At the pHs of typical dishwashing solutions, the amine

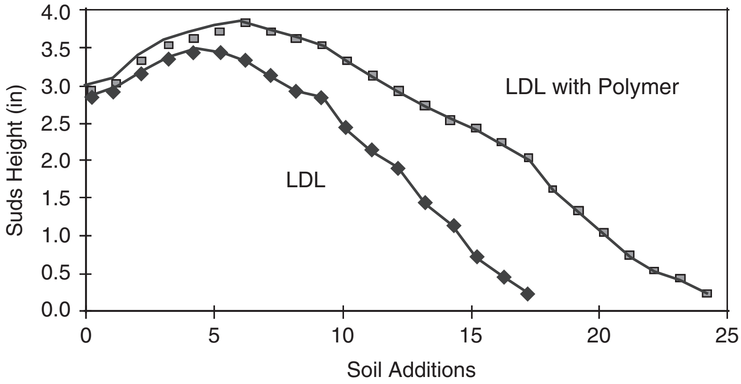


Figure 4 Detergent suds boosting benefits of cationic hydrophobic polymers (LDL is the control detergent formulation).

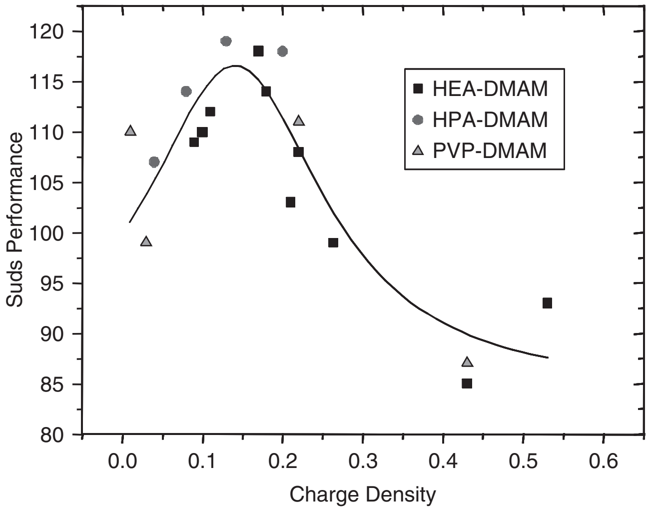
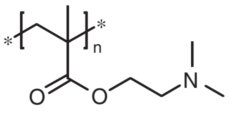
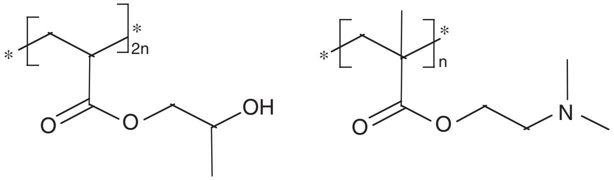


Figure 5 Impact of polymer charge density on suds boosting performance.

Table 5 Key Structures for Cationic Hydrophobic Suds Boosting Hydrophobic Polymers

Poly(dimethylaminoethyl Methacrylate)	**Poly(hydroxypropyl acrylate-*co*-dimethylaminoethyl Methacrylate)**
	

groups on the polymers protonate to introduce cationic charges along the polymer chains. This yields the charge density desired for suds boosting polymers. Applications of these cationic hydrophobic polymers in hand dishwashing detergents have been discussed extensively in existing patent art over the last 5 to 10 years. See, e.g., Kasturi et al. (2003), Bodet et al. (2003), and Sivik et al. (2003).

c. Polymer Suds Stabilization Mechanism. The interactions between cationic hydrophobic suds boosting polymers and grease particles have been discussed by Sivik et al. (2004). There are broadly two types of interactions, as illustrated in Fig. 6. The first type of interaction is electrostatic in nature. Greasy soil particles in a wash solution typically contain fatty acids, which often partition to the interface between greasy soil and water. Under consumer wash conditions, the fatty acids deprotonate, introducing negatives charges at the grease-water interface. These negatively charged fatty acids interact with positive charges on the suds boosting polymer. This results in a tight interaction between the grease particle and the polymer.

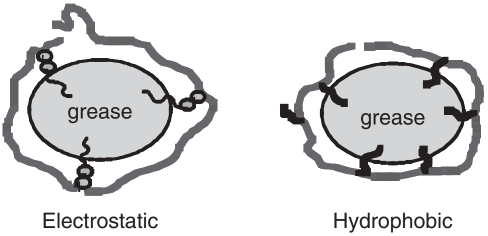


Figure 6 Illustration of interactions of cationic hydrophobic polymers with grease particles.

The second type of grease-polymer interaction is hydrophobic in nature. A large part of the polymer structure is hydrophobic. They can interact with the bulk surface of grease particles via van der Waals forces. This is illustrated in Fig. 6.

To further elucidate the mechanism of polymeric suds boosting, Kasturi and Schafer (1999) examined the impact of Poly(DiMethylAminoethyl Methacrylate), or PolyDMAM, on the grease-water interface and the surface tension of the wash solution. The results are summarized in Fig. 7. Key indication is that PolyDMAM reduces the grease/water IFT significantly at low concentrations (20 ppm in wash solution), but its impact on wash solution surface tension is not significant. This suggests that PolyDMAM has a unique ability to partition onto the grease-water interface, consistent with the grease-polymer interactions illustrated in Fig. 6.

4. *Product Dissolution Aids*

As discussed above, hand dishwashing detergents are typically sold to consumers as a thick and viscous paste to facilitate product dispensing and to achieve product aesthetic benefits. The key requirement for these products is fast dissolution in the wash solution. This is typically achieved by the use of traditional hydrotropes (e.g., sodium cumene sulfonate), as discussed in detail by Lai et al. (1997).

Over the last 10 years, a wide range of hydrophobic polymers have been reported as good dissolution aids in hand dishwashing detergents. For example, Brumbaugh (1999) described using solvent hydrotropes such as alkoxylated glycerides to improve detergent

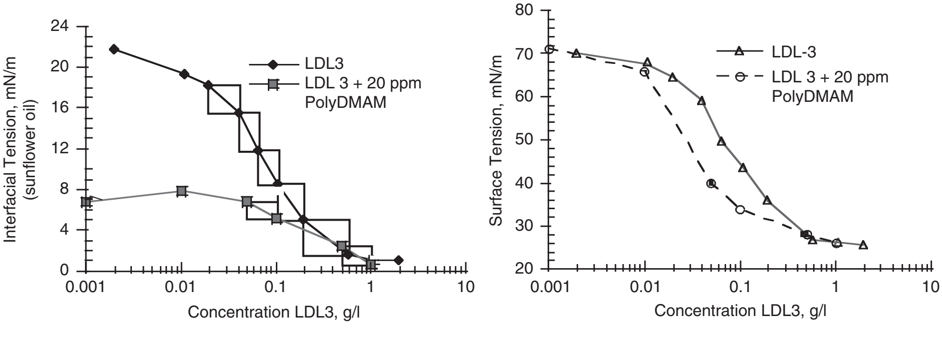


Figure 7 Impact of PolyDMAM on grease-water IFT and wash solution surface tension. The IFT was measured with sunflower oil, and LDL3 was a control product.

dissolution. Clarke et al (2000) described using polymeric glycols of certain molecular weight to improve dissolution of concentrated liquid dishwashing detergents. Similarly, Borgonjon et al. (2002) reported using a broad range of alkylene oxide polymers as dissolution aids in hand dishwashing detergents. These hydrophobic polymers can reduce or eliminate the formation of surfactant liquid crystals in the concentrated detergent product.

5. *Enzymes*

Enzymes have been widely used in detergents and cleaning products (Axelsen et al, 1999). Applications of enzymes in hand dishwashing detergents occurred more recently. Because of their versatile properties, enzymes can be designed to clean a wide range of difficult-to-clean soils, especially starches and baked-on greasy soils. For example, amylolytic enzymes, or amylases, can catalyze the hydrolysis of starch soils. Proteolytic enzymes, or proteases, can catalyze the hydrolysis of peptide bonds in proteins. Lipolytic enzymes, or lipases, can catalyze the hydrolysis of fats or oils. In addition to cleaning, enzymes can also help provide hand care benefits for dishwashing detergents when formulated appropriately. There are many descriptions in the patent literature on using enzymes in hand dishwashing detergents. Foley (1998) described using lipolytic enzyme in combination with amylolytic enzyme for hand dishwashing applications. This combination is especially useful for the removal of baked-on or burnt-on starch and greasy soils in dishwashing. Such soils are known to be particularly difficult to remove in a hand dishwashing process. Mao et al. (1999) described that proteases, when used in a liquid or gel hand dishwashing detergent composition, improve the mildness of the composition and reduce skin dryness experienced by consumers. Kasturi et al. (2004) described using an amylase enzyme additive to soften soils on hard surfaces to improve cleaning.

6. *Bleaches*

Like many other liquid detergents, it's difficult to stabilize traditional bleaches in liquid hand dishwashing detergents. In the last several years, formulators have been able to stabilize hydrogen peroxide in a hand dishwashing detergent context (see Arvanitidou et al., 2003). However, the pH of these products is typically kept at 3 to 4. Products of this low pH are typically poor in grease cleaning.

Transition metal bleach catalyst is another class of bleaching agents that has been discussed for potential applications in hand dishwashing detergents. For reference, see, e.g., Perkins et al. (2003). Significant technology development is still needed for these bleach catalysts to become practical for hand dishwashing detergents.

D. New Product Forms

Over the last 5 to 10 years, several new product forms have been introduced into the market to aid the consumer's hand dishwashing jobs. These include dish wipes and cleaning implements. No detailed discussions will be provided here as the major detergent ingredients in these new product forms are largely similar to traditional products.

1. *Dish Wipes*

Major hand dishwashing detergent manufacturers have recently introduced dish wipes to consumers. These wipe products can simplify the consumer's dishwashing jobs by combining the detergent and sponge or dish cloth into one. Cleaning ingredients are typically loaded into an inside layer of the dish wipe. Given that the ingredients are loaded on a

INTRODUCTION

Diseases are a constant threat to the health of animals. Surfaces contaminated by feces and body fluids contribute directly and indirectly to the transfer of microorganisms to other animals and locations. Contaminated housing areas, equipment, tools, vehicles, footwear and other fomites all pose risks.

The cleaning and disinfection process – often referred to as C&D – inactivates or destroys these organisms. Decreasing pathogen levels on surfaces reduces the potential for exposure and minimizes disease risks, which protects the health of animals and those working with them. The C&D process should be used routinely for all types of animal settings.

Properly performing C&D processes decreases pathogen levels on surfaces and reduces exposure risks. It also improves the health and well-being of animals, particularly in high density settings.

- C&D is an essential component of biosecurity on farms and in other congregate animal settings (e.g., animal shelter facilities, exhibitions and shows).
- C&D in veterinary clinics is a crucial measure for infection control and preventing disease spread.
- C&D is critical for disease containment and elimination during disease outbreaks and also serves as a layer of protection against novel or emerging diseases.

However, the C&D process is often not done correctly. When efforts are ineffective, the destruction of disease-causing organisms can be inadequate, resulting in exposure to disease agents and further spread of microorganisms.

Successful C&D involves understanding the key principles and steps for the process, choosing the best method, and recognizing any limitations. This document addresses this information as well as factors to consider when setting up a C&D program, common failures in disinfection programs, and how to address health and safety issues.

THE DESTRUCTION OF MICROORGANISMS

BIOCIDE

The general terms “biocide”, “germicide”, or “microbicide” refer to a substance or product that destroys or inhibits the growth or activity of living organisms. This includes disinfectants, sanitizers, antiseptics, and sterilants. **But, these antimicrobial products vary in their ability to destroy microorganisms!**

Designations are often used to convey a specific action of the product against a particular group of microorganisms.

- The suffix –***cide*** or -***cidal*** (e.g. bactericide, virucidal, fungicide, sporicidal, tuberculocidal) reflects a killing action on a particular microorganism class.
- The suffix –***static*** (e.g. bacteriostatic, virostatic, sporostatic) is used if the product only inhibits the growth or replication of the organism.

Depending on the goal for the C&D process, these designations can be critical!

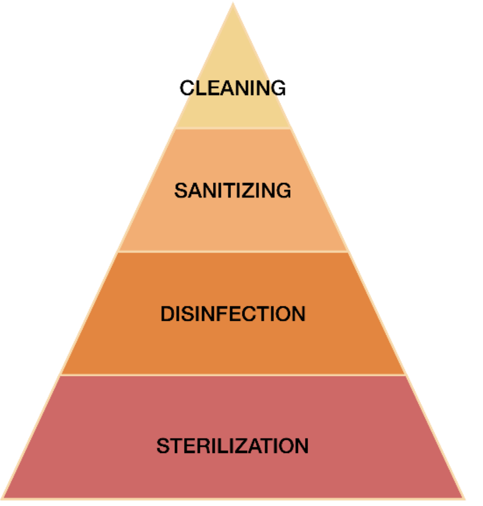
CLEANING, SANITIZING, DISINFECTING – WHAT'S THE DIFFERENCE?

When discussing C&D, it is important to recognize there are different processes that can be used to destroy microorganisms. These terms are often used interchangeably, but their level of destruction varies.

Cleaning involves the *physical removal* of visible contamination from surfaces. **Soaps and detergents** bind to oils, soil and organic material so it can be rinsed away. Some cleaners can disrupt the lipid components (e.g., cell membrane or viral envelope) of certain pathogens.

Sanitizing significantly *reduces bacterial contamination* on surfaces to levels considered safe from a public health standpoint. It does not eliminate all microorganisms. Sanitizers are most commonly used for food contact surfaces.

Disinfection *destroys or irreversibly inactivates most pathogens* (e.g., bacteria, viruses and fungi) *on surfaces (i.e., inanimate objects).** It is generally not effective against bacterial spores. Efficacy will vary with disinfectant product or method.



ALL MICROORGANISMS COMPLETELY DESTROYED

Sterilization *destroys or eliminates all forms of microbial life,* including bacterial spores. This involves the use of higher levels of physical (e.g., extreme heat) or chemical (liquid or gas sterilants) processes and is generally used for medical devices/equipment.

*NOTE: Antiseptics are products applied to the *surface of living organisms or tissues (e.g., skin)* to destroy or inhibit the growth of microorganism.

Some chemical products may act as a sanitizer, a disinfectant, or possibly a sterilant, depending on concentration or contact time used.

For example, the table below shows the required dilutions and contact times for a commonly used hydrogen peroxide disinfectant.

Table 1: Differences in dilution and contact time for an example hydrogen peroxide disinfectant.

Use	Concentrate dilution ratio*	Liquid measurement (concentrate/gallon water)	Contact Time needed*
Sanitizing	1:128	1 oz/gallon	3 minutes
Daily disinfection	1:64	2 oz/gallon	5 minutes
Bactericidal, fungicidal, virucidal	1:16	8 oz/gallon	5 minutes

KEY PRINCIPLES OF C&D

Regardless of the setting or item, there are five key principles to keep in mind for a successful C&D program.

1. **Clean surfaces before disinfection.** Before any disinfection method is used, surfaces have to be cleaned. Cleaning removes dirt, organic matter, (e.g., feces or manure, body fluids), and other debris that can hide organisms during the disinfection process. This material can also inactivate several disinfectants, making disinfection ineffective.

2. **Use the right disinfection product or method for the situation.** Disinfection methods can involve the use of a chemical or physical process. Both disrupt the cell walls or membranes, viral envelopes, or replication processes of microorganisms, resulting in their destruction or inactivation. But, no single product (or process) works for all situations. Products or methods needed for a disease situation will likely be different than those used on a daily basis. Higher concentrations or longer exposure times may be needed to destroy resistant organisms but may increase health and safety risks or damage surfaces.

3. **Read the product label.** In the U.S., products used to destroy microorganisms must be registered with the Environmental Protection Agency (EPA). The information on product labels must include the organisms the product can kill or inactivate, instructions for use (e.g., where the product can be used, the proper concentration for use, the necessary contact times), and any health and safety issues. Always read and follow the label instructions for effective disinfection.

4. **Give it time to work.** Disinfection does not occur immediately. The process needs time to work, and times vary for each product or process. Surfaces must remain wet or exposed for the full contact time for best results. Contact time is critical for success!

5. **Keep everyone safe.** All disinfection methods have health and safety considerations for people, animals or the environment. Read the product label for any safety measures required. Personal protection should be worn when mixing and applying disinfectants. Surfaces should be rinsed before the placement of animals.

BASIC C&D PROCEDURE

In animal settings, C&D should be performed on a regular basis, during, and after infectious disease situations. All surfaces in contact with animals, including the C&D equipment used, should be included.

USE A SYSTEMATIC APPROACH

When performing C&D procedures, use a systematic approach to make sure all areas or items are addressed. Work in small sections. Proceed from the cleanest area to the dirtiest, from the highest level (e.g., ceiling) to the lowest (e.g., floor). Marking tape can be used to indicate where C&D steps have or have not taken place. Disinfect floor drains last.

Regardless of the situation, item, or area, the C&D process follows two distinct phases. Both are needed for optimum results. Without cleaning, disinfection does not work.

- **Cleaning** removes visible organic material that can interfere with the disinfection process.
- **Disinfection** inactivates or destroys most remaining pathogens on inanimate objects.

THE CLEANING STEPS

There are four steps for proper cleaning. The goal is to remove manure, bedding, feed, body fluids, dirt and other debris that can interfere with the disinfection process. This material can hide organisms from the disinfection action. Additionally, disinfectants may react with this material instead of microorganisms, this can reduce the level of active ingredient available to attack microorganisms.

Remove Organic Matter.

Any visible dirt, manure, or other debris should be removed by wiping, brushing, scraping, sweeping, scooping, or other methods. In large production facilities, heavy equipment, such as skid steers or manure scrapers, may be needed to handle large quantities of material. This step is sometimes called dry cleaning. The goal is to remove as much visible debris as possible. **This step may take considerable time and effort, depending on the object, size of the area, or level of contamination. But it is essential for optimum disinfection!**

Wash Surfaces.

Often called wet cleaning, washing the item or area with soap or detergent and water removes material adhered to surfaces. Certain soaps or detergents can destroy some microorganisms.

Mechanical scrubbing or scraping helps to loosen dirt and debris. Areas with deep cracks, pits, pores, or other surface irregularities may require scrubbing with a coarse or wire brush. Presoaking or use of a degreaser may be necessary to remove oils or bodily fluids. Hot water and steam can be effective for cleaning cracks, crevices, and the inside of pipes.

High pressure sprayers may be effective to remove heavy accumulation of urine and feces or for cleaning porous surfaces (e.g., concrete). However, in cases of highly infectious or zoonotic pathogens, high pressure systems should be avoided or used with caution to avoid further dispersal of the pathogen or risk to the applicator.

Rinse.

After washing, it is important to thoroughly rinse surfaces with clean water to remove material and any cleaning product residue. Soaps or detergents can inactivate some disinfectants. Surfaces should be carefully inspected to ensure they are clean. If dirty surfaces or residual oils are seen, rewash the affected areas.

Dry.

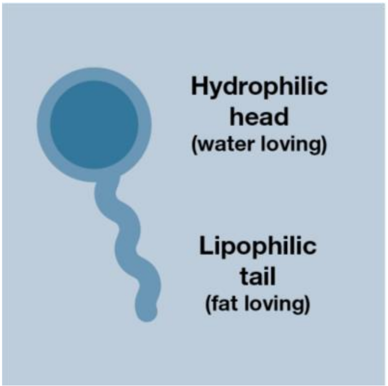
The item or areas should be allowed to dry completely before the disinfection process; excess water, especially on porous surfaces, will unintentionally dilute any disinfectant solution applied. If this is not possible, allow a minimum of 5-10 minutes for water to drip away. Heating the building, circulating the air with blowers or fans, or high-pressure air from a compressor can aid in the removal of excess moisture to speed drying. However, **if highly infectious or zoonotic pathogens are suspected, fans or high-pressure systems should be avoided** to avoid unintended spread of pathogens.

The cleaning step may take considerable time and effort, depending on the object, size of the area, or level of contamination. But it is essential for successful disinfection! It has been estimated that cleaning alone may remove over 90% of bacteria from surfaces. The removal of organic matter helps to ensure that the subsequent disinfection stage has a greater impact on the remaining microorganisms.

Disposal of Debris

Any material removed during the cleaning step should be considered contaminated, and handled and disposed of in a manner that prevents any spread of microorganisms (e.g., burning, burial, or composting). Disposal will need to comply with any federal, state, and local requirements.

How Cleaning Works



Soaps and detergents are surfactants, or **surf**ace **act**ive age**nts**. Surfactant molecules reduce the surface tension of water, which means they increase the ability of water to penetrate, disperse and remove organic material from surfaces. This is accomplished by their bipolar chemical structure. Each molecule has a polar hydrophilic, or water-loving, head and a nonpolar lipophilic, or fat-loving tail.

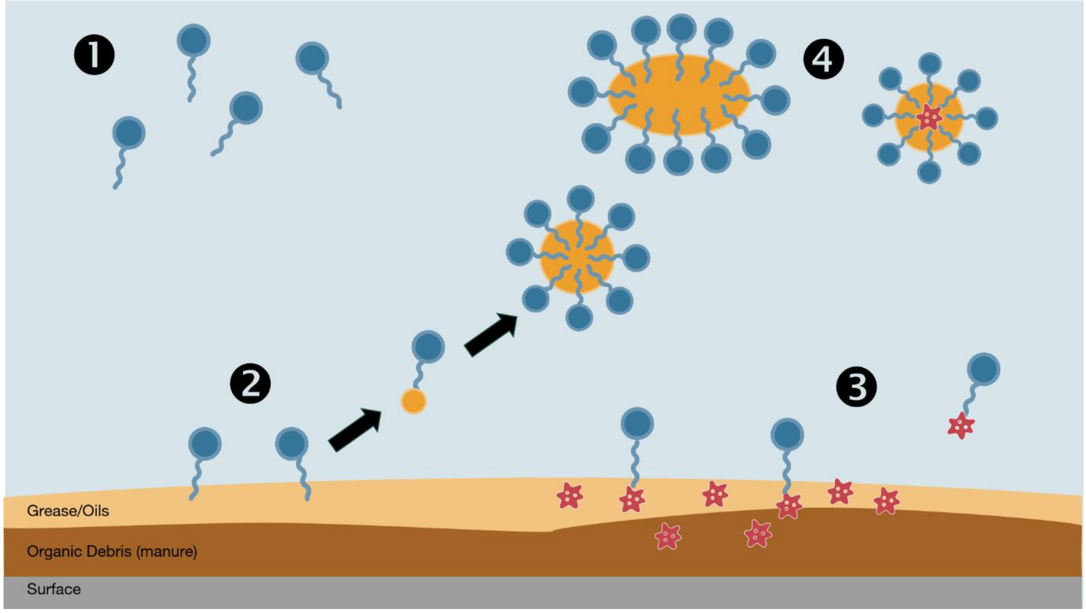
The cleaning process in action (see diagram below)

❶ In solution, the surfactant (detergent) molecules have both water-soluble and oil-soluble properties.

❷ The lipid loving tails attach to oil, grease, dirt, and debris. The hydrophilic heads interact with water molecules.

❸ Surfactant molecules can also attach to other lipid-based substances, such as the cell walls of bacteria or the lipid envelopes of viruses.

❹ As surfaces are scrubbed and debris loosened, it becomes surrounded and trapped by surfactant molecules (i.e., form a micelle), which allows the pieces to be washed away during rinsing.



Good to know: Surfactant classifications

Surfactants vary in chemical structure, particularly the chemical charge of the head portion of the molecule (the hydrophobic tails are often chemically similar). This charge affects the detergency (or cleaning power) and the antimicrobial efficacy of the cleaning product. Most commercial detergents are a combination of anionic (negatively charged) and non-ionic (neutral charge) formulations.

The chemical composition of surfactants (e.g., anionic, cationic) can enhance or interfere with the disinfection process. The cleaning product used must be compatible with the disinfectant selected. Some disinfectant products may be formulated with a detergent component. Cleaning products may also incoporate other chemical components, such as enzymatic agents, such as proteases (which break up proteins), lipases (which break up fats), and amylases (which attack starch), to further aid the cleaning process.

The following table summarizes characteristics of surfactant types and highlights the detergency or antimicrobial efficacy of each.

Table 2. Types and characteristics of various surfactants.

Surfactant Type	Chemical charge (depending on pH of solution)	Detergency (cleaning power)	Antimicrobial efficacy	Examples
Anionic	Negative charge	**+++**	+/-	Soaps, sodium lauryl sulfate
Nonionic	Neutral charge	**+++**	-	Polysorbates
Cationic	Positive charge	+	**+++**	Quaternary ammonium compounds (QAC), such as benzalkonium chloride
Amphoteric	Variable based on pH	++	**+++**	Betaine, alkyl methyl oxide

THE DISINFECTION PROCESS

The second phase of the C&D process is disinfection. This is needed to inactivate or kill remaining microbes, and may involve either physical or chemical processes.

Disinfectant Preparation

Disinfectant selection: The selection of a disinfection method or product will depend on several factors, including the targeted microorganism, the surface or object being treated, environmental conditions and health and safety concerns. Additional information on disinfectant selection is found later in this document.

Read the product label: Always prepare disinfectants according to product label instructions. Products differ in formulation. Some products are ready to use, others require dilution. Fresh solutions are best and should be prepared daily or as specified on the label. Only use EPA-registered products. One U.S. gallon of diluted disinfectant is ordinarily applied to approximately 100-150 square feet (9-14 m^2) of surface area.

Use the proper concentration: The safest, most effective concentration will be listed on the product label. The concentration needed may vary depending on the surface type or target microorganism. Stronger solutions are not always better. Higher concentrations can damage surfaces or lead to health or safety issues. Under-dilution may not be effective against the microorganisms of concern.

Check the amount of active ingredient in stock and prepared solutions: Chemical disinfectants can degrade or lose potency over time. Check the product for an expiration date. Commercial test kits are available for most products to determine if chemical degradation has occurred or if diluted (“use”) solutions contain the necessary amount of active ingredient.

Prepare safely: Prepare disinfectant solutions in a well-ventilated area. Personal protective equipment (e.g., gloves, eye protection) should be worn. Always pour the chemical into water, not water into the concentrate. Some disinfectants can have strong chemical reactions when water is added.

Disinfectant Application

The application of chemical disinfectants most often involve spraying, fogging, misting, wiping, or mop-on methods. Small, portable items can be soaked in a container of disinfectant solution. The application instructions for a particular product will be listed on the label.

Fumigation may be used in some situations, but it is inefficient or ineffective in buildings with ill-fitting doors and windows, or damaged roofs. It also requires higher levels of PPE and often times specific training. The use of fumigation is uncommon except under select circumstances.

As with cleaning, disinfectant application should occur in a systematic manner (e.g., top to bottom, front to back, working in small sections) to ensure all areas are treated adequately. It is essential to pay close attention to corners, deep cracks, crevices, pits, pores, or other surface irregularities. These areas can serve as reservoirs for pathogens. Floor drains should be the last areas disinfected.

Contact Time

Regardless of the disinfection method chosen, it is critical to ensure the full contact time is achieved. **This is a commonly overlooked step, and often leads to disinfection failure!**

The disinfection process is not instantaneous; the process needs time to work. Contact times vary depending on the product or method used, the concentration, the type of surface being treated, and the ambient temperature. Some may require 1-5 minutes, but 10 minutes or more is common; some may require hours, especially for resistant pathogens.

Surfaces must remain exposed (e.g., wet with disinfectant solution) for the full contact time. This can be a challenge during high temperatures. Some chemical disinfectants, particularly alcohols, evaporate quickly. Reapplication may be necessary to ensure the required contact time. Ensure cracks, crevices, and joints remain exposed for the entire contact time.

Rinse Away Disinfectants

After the appropriate contact time has elapsed, all items or areas should be thoroughly rinsed with clean water. Most chemical disinfectants can be harmful to animals and must be rinsed away before the reintroduction of animals. This is especially important around feed and water equipment. Some products can also damage certain surfaces, such as rubber or metals, if not completely rinsed away. However, some products may have residual action and can remain on surfaces to continue to work.

Drying/Down Time

After rinsing, treated areas or items should be dried completely (ideally overnight). Applying disinfectant solutions uniformly over large areas (e.g., ceilings, walls, floors) can be very difficult. Adequate downtime helps to further reduce or eliminate any remaining microorganisms. The area should remain free of any animals or activity during this time.

OTHER C&D CONSIDERATIONS

Biofilms

Biofilms, an invisible, complex aggregation of bacteria, may remain on surfaces. Biofilms are highly resistant to disinfection. The use of detergents, mechanical scrubbing, brushing, and scraping can help remove biofilms.

Personnel Health and Safety

Personal protective equipment (PPE) should always be worn when preparing and applying disinfectants. Recommended PPE for a particular product will be listed on its label. At a minimum, this should include eye protection and gloves. Water-resistant disposable outwear (e.g., coveralls, boots) should be strongly considered. Respiratory protection (e.g., masks, possibly respirators) should be worn when preparing powdered formulations or for products with strong odors. Personnel should always wash their hands after C&D procedures – even if gloves were worn.

One-Step Disinfectant Cleaners

Some disinfectant products may be formulated with a detergent component as a one-step product. Organic matter still needs to be removed for these products. Most are labeled for use on cleaned surfaces, so the cleaning step is still needed. Some require washing of surfaces - **after disinfection** - particularly for situations where animal restocking or exposure will occur.

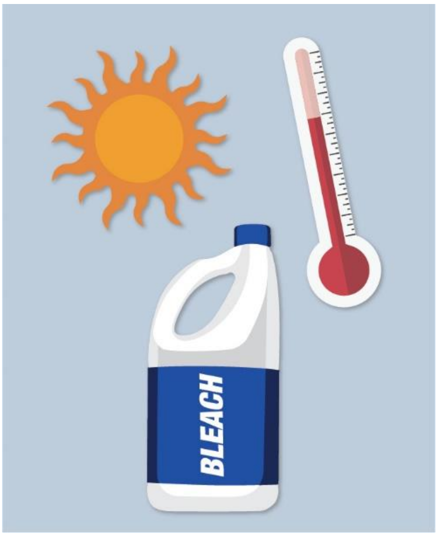
C&D in Cold Temperatures

Many disinfectant products are affected by temperature, and may be ineffective during cold weather conditions. Solutions may also freeze on surfaces when outdoors. Possible solutions for C&D in cold temperatures include heating surfaces or buildings to prevent freezing, using heat blankets around liquid containers, or adding antifreeze agents (e.g., propylene glycol); some disinfectants may be compatible, others are not. Always read the product's label instructions for use in cold conditions.

DON'T FORGET THE C&D EQUIPMENT

After completing the C&D procedure, any equipment used during the process (e.g., shovels, hoses, pressure sprayers, pumps, any heavy equipment or vehicles) should also be properly cleaned and disinfected. Some disinfectants can be corrosive or damaging, and should be rinsed away. Disposable C&D supplies (e.g., paper towels) should be discarded. Any unused disinfectant concentrate or solutions should be properly stored or disposed of in accordance with the label instructions.

DISINFECTION METHODS IN ANIMAL SETTINGS



Disinfection describes the use of a chemical or physical process to inactivate or eliminate microbial organisms *on inanimate objects or surfaces.* These processes destroy or irreversibly inactive most pathogens, but are **generally less** effective against bacterial endospores.

- **Chemical disinfection** involves the use of various chemical classes of products, each with different chemistries, microbial spectrums (or efficacies), and health and safety concerns.
- **Physical disinfection methods** includes drying or desiccation, the application of heat (or thermal inactivation), or the use of irradiation methods (most commonly ultraviolet light).

While an ideal disinfectant is one that is broad spectrum, has low toxicity to humans and animals, is non-corrosive, and is relatively inexpensive. Few products or methods meet all of these criteria.

HOW DISINFECTION WORKS

Disinfection processes target several sites and cause structural and functional damage to various macromolecules (e.g., proteins, lipids, nucleic acids) of microorganisms. This results in the disruption of cell walls or membranes, viral envelopes, or replication processes and destroys or irreversibly inactivates most pathogenic microorganisms.

Biocide Mechanisms of Action

There are four mechanisms of action for this process.

- **Oxidizing mode of action.** Biocides with an oxidizing mode of action remove electrons (oxidation) from a substance -in this case - nucleic acids, lipids, proteins and carbohydrates of microorganisms. Altered structures result in disruption of cell membranes and cell function. Oxidizing agents have a dramatic effect on DNA and RNA, causing strand breakage and disruption of replication, transcription, and translation processes. Oxidizing biocides are widely used and include halogen-based products (e.g., chlorine, iodine) and peroxygen products (hydrogen peroxide, peracetic acid)
- **Cross-linking or coagulating mode of action:** Some biocides primarily act by cross-linking or coagulating the amino acids of proteins, (and sometimes nucleic acids bases) to disrupt the structure and function of many microorganisms. Disinfectants in this category are aldehydes; alkylating agents, such as ethylene oxide; phenols, and alcohols
- **Other structure-disrupting agents:** Several biocides primarily damage lipid membranes. They may directly disrupt membrane proteins or cause increased permeability. The result is leakage of cytoplasm components and cell lysis. Biocides in this category include surfactants (including QACs), biguanides, and organic acids.
- **Transfer of energy:** A final mechanism of biocidal action involves the sudden transfer of energy that results in disruption of structure and function. These processes rapidly denature nucleic acids, lipids, and proteins. They include the application of heat and radiation (e.g., ultraviolet light).

CHEMICAL DISINFECTION

Chemical disinfectants are most commonly used and include a wide range of products classified by the chemical nature of their active ingredients. There are more than 275 different active ingredients used as the primary component of a disinfectant or part of a combination formulation (e.g., products containing multiple active ingredients). Products may be sold as wipes, ready-to-use (RTU) sprays or liquids, or concentrated liquids or powders.

Each chemical class has unique characteristics, microbial spectrums, compatibilities and effectiveness under certain conditions (e.g., presence of organic material, temperature, water hardness) and health impacts and hazards. Therefore, selection of a disinfectant product involves consideration of its specific characteristics and uses.

Most chemical disinfectants readily inactivate vegetative bacteria (gram-positive, gram-negative) and enveloped viruses. Fungal spores and non-enveloped viruses are generally less susceptible. *Mycobacteria*, bacterial endospores, and protozoal oocysts are highly resistant to most disinfectants. Prions, the etiologic agents of bovine spongiform encephalopathy, chronic wasting disease, and scrapie, are exceptionally resistant to chemical inactivation.

Regulation of Chemical Disinfectants

In the United States, chemical disinfectants are regulated by the U.S. Environmental Protection Agency (EPA) through the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA). Chemical disinfectants are considered “antimicrobial pesticides” - or substances used to control, prevent, or destroy harmful microorganisms (e.g., bacteria, viruses, or fungi) on inanimate objects and surfaces.

FIFRA requires a pesticide to be registered (or exempted) before it may be sold or distributed in the United States. Data on its chemistry, efficacy, toxicity to humans, animals and plants, and other parameters must be tested and submitted to the EPA. Labeling information and designations are determined by this data.

Product registration can occur under:

- Section 3 (regular label) or
- Section 18 (emergency exemption)

FIFRA further requires that all label use directions and safety precautions must be followed. The use and application of a registered disinfectant in a manner inconsistent with its labeling may not only result in an ineffective application, but may be a “misuse” of the product and subject to potential enforcement action.

Product labels will list an **EPA Registration Number** to show that the product has been reviewed by the EPA and can be used with minimal risk when the label directions are properly followed. For maximum success in preventing disease spread in a clinic, shelter, or livestock operation, only **EPA registered products should be used.**

While the EPA registers products and approves them for use, it is important to also be familiar with local or state regulations for other restrictions. Individual States (e.g., California) may have additional regulations on permitted products. Contact your local or state environmental agency for more information.

CHEMICAL DISINFECTION CLASSIFICATION BY CHEMICAL CLASS

Disinfectants are classified by their chemical nature. Each class has its unique characteristics, hazards, and efficacy against various microorganisms. Environmental conditions, such as the presence of organic matter, pH or water hardness can also impact the action of a disinfectant. Variations in formulation or combination solutions may have differing characteristics. Before using any chemical disinfectant, **thoroughly read and follow the label instructions**.

The following section provides an overview of characteristics of the primary chemical disinfectant classes (in alphabetical order): acids, alcohols, aldehydes, alkali agents, biguanides, halogen-based compounds (e.g., chlorine, iodine), oxidizing agents, phenols, and quaternary ammonium compounds (QACs).

Disclaimer: The use of trade names does not in any way signify endorsement of a particular product. They are provided only as examples.

For additional product names, consult The National Pesticide Information Retrieval System (NIPRS) –a searchable database of federally active (registered) Section 3 pesticide products.

Tables are available from CFSPH that summarize the key characteristics and antimicrobial spectrums of each chemical class of disinfectants.

- Characteristics of Selected Disinfectants
- Antimicrobial Spectrum of Disinfectants

Acids

Acidic disinfectants include inorganic (e.g., hydrochloric acid, sulfuric acid) and organic (e.g., acetic acid, citric acid) compounds.

The antimicrobial action of acids occurs through the dissociation of free hydrogen ions, which alters the pH of the microorganism’s environment. Acids also destroying the bonds of nucleic acids and precipitate proteins.

Microbial spectrum:
The antimicrobial activity of acids is highly pH dependent. Acids are:

- Generally effective against vegetative bacteria and can be bactericidal when the pH drops below 3.
- Enveloped viruses are particularly sensitive to extremes of pH, and therefore susceptible.
- Fungi may be susceptible with extended contact times (e.g., 30 minutes).
- Acids are not effective against *Mycobacteria* or non-enveloped viruses. One exception is the foot-and-mouth disease (FMD) virus, which is particularly sensitive to acids (e.g., citric acid).
- The efficacy against bacterial spores is variable, but limited, and often requires high concentrations. For example, a 2.5% hydrochloric acid solution is a reasonably effective sporicide that has been used to disinfect animal hides potentially contaminated with anthrax spores before tanning.

Specific acid compounds:

- **Acetic acid** is usually sold as glacial acetic acid (95% acetic acid) which is then diluted with water to make a working solution concentration of 5%. Household vinegar is a 4-5% solution of acetic acid (by volume). Acetic acid is typically applied by spraying, misting or immersing an item in a diluted solution. Acetic acid has poor activity in organic material. Acetic acid has been routinely used by the USDA (under a FIFRA quarantine exemption) to wipe down the coats of horses arriving from FMD virus positive countries.

- **Citric acid** has been used alone or as an additive to detergents in other countries to inactivate the foot-and-mouth disease (FMD) virus. In October 2012, the EPA approved the use of citric acid (under a FIFRA quarantine exemption) to control FMD and African swine fever in the U.S. The rate of application was amended in May 2013.
- **Other acids:** Some acidic compounds (e.g., formic, citric, lactic, malic, glutaric, and propionic acids) are added to anionic detergent or other disinfectant formulations to enhance antimicrobial properties. Strong inorganic acids (e.g., hydrochloric acid, sulfuric acid) have been used to disinfect farm buildings, but are typically too hazardous for use as a disinfectant.

Characteristics of acids:
Acids are generally slow acting, especially against viruses. They can be highly corrosive to metal surfaces (e.g., galvanized) and concrete. Acid efficacy can be affected by the presence of organic matter, pH, and water hardness.

Uses:
Some acids are EPA-registered as pesticides or exempted under FIFRA, while others are not. (NAHEMS FAD PReP 2014) Acids have a defined but limited use as disinfectants.

- Inorganic acids, such as nitric, hydrochloric, sulphuric, phosphoric, are often used as cleaners (e.g., anionic detergents) to remove lime scale or milk stone.
- Organic acids, such as citric, lactic, mallic, glutanic, propionic, are often incorporated into disinfectant formulations to enhance antimicrobial properties (e.g. viruses, fungi).
- Acetic acid has been routinely used by the USDA (under a FIFRA quarantine exemption) to wipe down the coats of horses arriving from FMD virus positive countries.
- Citric acid has been used alone or as an additive to detergents to inactivate the FMD virus. A FIFRA emergency exemption was approved by the EPA in October 2012, for the use of citric acid to control FMD and African swine fever in the U.S.
- A 2.5% hydrochloric acid solution is a reasonably effective sporicide that has been used to disinfect animal hides potentially contaminated with anthrax spores before tanning.

Health and safety:
While typical dilutions are considered non-toxic and non-irritating, concentrated solutions of acids can cause chemical burns, and can be toxic at high concentrations in the air. During preparation, acids should ***always*** be poured into water (not the water into the acid) to avoid violent boiling or splashing of concentrated acid. Personnel should wear eye protection and rubber gloves when mixing, applying, and rinsing acidic disinfectants. Acids may result in potential aquatic hazards, if released into the environment, due to their low pH levels.

Alcohols

The most commonly used alcohol-based disinfectants are ethyl alcohol (i.e., ethanol) and isopropyl alcohol (i.e., isopropanol).

Their hydroxyl functional group (-OH) interacts with the membrane proteins and lipids of microorganisms resulting in disorganization, membrane damage, and lysis. These products also alter the pH of the environment. Some alcohols are EPA-registered as “antimicrobial pesticides” under FIFRA, while others are not.

Microbial spectrum:
Alcohols are considered fast-acting, broad-spectrum antimicrobial agents.

- Alcohols are capable of killing most bacteria within five minutes of exposure. They are also effective against acid-fast bacteria (e.g., *Mycobacteria*). Fungi can be susceptible at prolonged contact times.
- Virucidal activity varies with the product. Ethanol is considered virucidal, while isopropanol is not effective against non-enveloped viruses, especially small, non-enveloped viruses.
- Alcohols alone are not effective against spores, but may potentiate the sporicidal effect of some halogen-based products (e.g., iodines).

Uses:
Alcohols are used for surface disinfection, as topical antiseptics and hand sanitizing lotions. They are often incorporated into disinfectant formulations for increased efficacy, and have been used in combinations with phenols, quaternary ammonium compounds and chlorhexidine. Alcohols may be used to disinfect small areas or items (e.g., cell phones, keyboards, stethoscopes); however, they evaporate rapidly making extended exposure time difficult.

Characteristics of alcohols:
The activity of alcohols is limited in the presence of organic matter. Surfaces must be cleaned before application. This class of disinfectants can damage to rubber and plastic with frequent or extended use.

Health and safety:
Alcohols can be very irritating to injured skin. Alcohols are highly flammable; products must be stored in a cool, well-ventilated area and used with caution.

Noteworthy: The presence of water is necessary for alcohol efficacy; therefore, concentrations of 60-90% are recommended. Most rubbing alcohol (i.e., isopropanol) is 70% and hand sanitizers are typically 62%. Higher concentrations (95%) are actually less effective because some degree of water is required for efficacy (to denature proteins).

Aldehydes

Aldehyde disinfectants [R-CHO] include formaldehyde, glutaraldehyde, and ortho-phthalaldehyde (OPA). These alkylating agents denature proteins and disrupt nucleic acids causing irreversible inhibition of microorganism enzyme activity.

Microbial spectrum:
Aldehydes are highly effective, broad spectrum disinfectants. They are slow-acting but very effective against bacteria and enveloped viruses and somewhat effective against non-enveloped viruses, bacterial spores, and acid-fast bacteria. High concentrations of formaldehyde can destroy all microorganisms, including spores, (sterilization) and has been used extensively to inactivate viruses.

Uses:

Aldehydes are highly irritating, and acutely toxic to humans or animals with contact or inhalation. Formaldehyde is a known carcinogen. The use of aldehydes is limited to certain applications, and requires caution and higher levels of personal protective equipment and training.

Characteristics of aldehydes:

Aldehyde disinfectants are non-corrosive to metals, rubber, plastic, and cement. Health and safety concerns limit the use of these products to specific situations or warrant increased personal protection measures.

Health and safety:

Aldehydes are highly irritating and toxic to humans or animals by contact or inhalation. Solutions can cause irreversible eye damage and skin burns. They are harmful if absorbed through the skin and fatal if swallowed. Prolonged or frequent repeated skin contact may cause allergic reactions in some individuals.

Appropriate personal protective equipment, (e.g., fluid-resistant gloves and clothing, and eye/face protection) must be worn when using all aldehyde products. Fumigation measures require specialized equipment and training. When used as a mist or gas, respiratory protection is warranted.

Formaldehyde has been identified as a potential carcinogen. Occupational Safety and Health Administration (OSHA) standards limit the exposure time for personnel working with formaldehyde (29 CFR 1910.1048). The pungent fumes can be irritating to mucous membranes, contact can cause skin irritation, and ingestion can be fatal. Personal protective equipment must always be worn when working with this compound, and application must be confined to areas which are air-tight and completely sealed to prevent gas escape.

Specific aldehyde compounds:

Formaldehyde

- ***Formaldehyde*** can exist as a gas or liquid. A solution of 4-8% formaldehyde in water is considered an intermediate to high-level disinfectant. Its use is limited due to health and safety concerns. It has been used as a surface disinfectant and a fumigant to decontaminate rooms, buildings, wooden surfaces, bricks, electronic devices and mechanical equipment (e.g., hatchery equipment). When permitted under an exemption, gaseous formaldehyde may be used to decontaminate air spaces and equipment that must be kept dry (e.g., electronic devices or equipment).
- Formaldehyde combines readily with proteins, so efficacy is decreased by the presence of organic matter. The efficacy of formaldehyde is dependent on relative humidity and temperature; optimum conditions are humidity close to 70% and temperature close to 57°F (14°C).

Glutaraldehyde

- ***Glutaraldehyde*** is EPA-registered as a disinfectant in over 300 products at various concentrations. Many products containing glutaraldehyde are a combination glutaraldehyde/quaternary ammonium product; examples include Synergize® (Neogen) and Virocid® (CID LINES).
- Glutaraldehyde has been widely used for high level disinfection of medical (e.g., endoscopes) and thermosensitive equipment. A 2% concentration is used for high-level disinfection. It can also act as a sterilant with prolonged contact times. Efficacy is also increased by greater temperatures.
- Glutaraldehyde is considered more efficacious in the presence of organic matter, soaps and hard water than formaldehyde; however, its activity is affected by pH and temperature.
- The product remains chemically stable at acidic pH levels, but is more “active” at alkaline (pH 7 or greater) levels; however, pH over 9 can result in decomposition of the product.

- Although it can be less acutely toxic than formaldehyde, exposure can cause skin and mucous membrane irritation, epistaxis, and possibly asthma. Glutaraldehyde is considered noncorrosive and usually does not damage rubber or plastics; however, it may be mildly corrosive to metals.

Ortho-phthalaldehyde (OPA)

Ortho-phthalaldehyde (OPA) is a high-level disinfectant used for reprocessing reusable heat-sensitive semi-critical medical devices such as endoscopic, respiratory therapy, and anesthesia equipment. An example product is Cidex®

Alkalis

Alkali agents include products such as sodium hydroxide, sodium carbonate, and calcium oxide.

Their antimicrobial action involves the dissociation of hydroxyl ions (–OH), which alters the environmental pH. These products also have saponifying (soap) action on fats and the lipid envelope of the outermost membrane, which also contributes to the cleaning process.

Microbial spectrum:

Alkalis have good microbicidal properties, especially at high concentrations and at high temperatures. The range of microorganisms varies with agent and are described below.

Uses:

The use of alkalis is limited for routine use; however, they are commonly incorporated into cleaning products. Alkalis have been used to disinfect livestock- or poultry-production areas, including pens, yards, buildings, and effluent waste pits and sewage collection areas, since they can maintain effectiveness even with high concentrations of organic matter.

Characteristics of the class:

The activity of alkali compounds is slow but can be increased by raising the temperature. The activity of these products is optimum at pH greater than 9; however, a pH above 12.0 may be needed for resistant bacterial pathogens (e.g., *Mycobacterium*).

Alkalis are very corrosive to metals (especially aluminum) and painted or varnished surfaces; they will not harm bare wood. Health and safety concerns limit the use of these products to specific situations or warrant increased personal protection measures.

Health and safety:

Alkalis are very caustic. Personal protective equipment (e.g., rubber gloves, boots, raincoat or apron, goggles) is essential when preparing or applying any of these agents. Exposure can cause severe skin burns. Dust from these products may cause severe burning of the eyes and mucous membranes or respiratory tract if inhaled. They can also cause burns on the footpads of animals and hoof drying and cracking.

Specific alkali compounds:

- ***Sodium hydroxide [NaOH] (i.e., lye, caustic soda, soda ash)*** is a commonly used strong alkali which has been applied extensively for cleaning and disinfection in various industries (e.g., slaughter houses, dairy industry). It has been used to disinfect buildings. Only two products are registered by EPA and neither is for agricultural uses. Only USDA-APHIS has an exemption to use this chemical to inactivate foreign animal disease agents. It is considered an effective FMD disinfectant.

Sodium hydroxide is highly caustic and can damage metals, especially aluminum and derived alloys. Protective clothing, rubber gloves, and safety glasses should be worn when mixing and applying the chemical. **Never pour water into lye!** A violent chemical reaction can occur, and high heat will be generated (which can melt plastic containers). **Sodium hydroxide solutions should ALWAYS be prepared by carefully adding the lye into water.**

- ***Sodium carbonate*** [Na_2CO_3] (soda ash, washing soda) is a very good cleaning agent and has been used in a hot solution (180°F) for disinfecting buildings, which have housed animals with FMD. It is more effective as a cleanser than a disinfectant since it lacks efficacy against some bacteria and most viruses. A 4% solution has been listed as an approved chemical for the FMD virus. It has poor activity in the presence of organic material and can be deactivated by hard water. It can be irritating and requires protective clothing and is harmful to aquatic life. Only four products containing this active ingredient are EPA-registered, and the maximum concentration of active ingredient in one product is 3%. Only USDA-APHIS has an exemption for use of this chemical to inactivate FAD agents. A 4% solution has been used for washing vehicles and cleaning the hooves of horses being imported into the United States. This product can cause irritation during application and is harmful to aquatic life.
- ***Calcium oxide (quicklime)*** when mixed with water becomes lime wash, which is sometimes spread on the ground following depopulation of infected premise and has been used to retard putrefaction of buried carcasses after depopulation. It has biocidal effects on some bacteria and viruses. It is not very effective against the FMD virus. Only one product containing calcium oxide is EPA-registered, and that is labeled for treatment of medical wastes.
- **Calcium hydroxide** [CaOH] (i.e., air-slaked lime) is reasonably effective against many non-spore-forming organisms. No end-use products containing calcium hydroxide are currently EPA-registered, so the following uses are not registered at this time. When mixed with water, it forms hydroxyl ions (–OH) and liberates heat [$CaO + H_2O = Ca(OH)_2 + HEAT$]. Although it is not sporicidal, it has been used to disinfect premises. A 20% suspension is commonly used as whitewash.
- ***Ammonium hydroxide*** is an effective disinfectant against coccidia oocysts however strong solutions emit intense and pungent fumes.[5] This substance is not considered effective against most bacteria, therefore additional methods of disinfection should follow the use of this compound.

Note: Quicklime (calcium oxide) is produced by burning limestone. If water is added to quicklime, slaked lime is produced. If lime is exposed to the air, air-slaked lime (calcium hydroxide) is formed.

Biguanides

Biguanides are cationic compounds (e.g., surfactants) and are detrimental to microorganisms by reacting with the negatively charged groups on cell membranes which alters permeability. Chlorhexidine (e.g., Nolvasan®, Virosan®) is one of the most widely used biguanides.

Uses: Biguanides are most often used as a skin antiseptic and for preoperative skin preparation. It has also been used as an effective cattle teat dip. Two chlorhexidine products are EPA-registered for use on farm premises. They have been formulated in conjunction with quaternary ammonium compounds.

Microbial spectrum: Biguanides have a very effective bactericidal action, but are generally more effective against gram-positive species. Some bacteria (e.g., *Pseudomonas*) may be resistant. Effectiveness against viruses and fungi is variable. These products are not sporicidal or tuberculocidal (e.g., Mycobacteria).

Characteristics of the class:
Biguanides are easily inactivated by anionic soaps and detergents, hard water and organic matter and are pH sensitive, only functioning in the range of pH 5-7. These products are toxic to fish and should not be discharged into the environment.

Health and Safety:
As antiseptics, these products are generally safe for skin contact. Biguanides are toxic to fish and should not be discharged into the environment.

Halogens

Halogen-based compounds include chlorine (e.g., sodium hypochlorite/bleach, chlorine dioxide) or iodine-containing agents. They are strong oxidizing agents and commonly used disinfectants in animal settings. The antimicrobial impact of halogens is due to their electronegative nature (i.e., free chlorine or iodine) which denatures proteins.

Microbial spectrum:
When used on clean surfaces, halogen-based compounds are broad-spectrum, with efficacy against bacteria, most viruses, *Mycobacteria*, and fungi; they can be sporicidal at high concentrations. Efficacy can be rapid, but is related to the concentration level of free halogen ions. For example, the low concentrations (2 to 500 ppm) of chlorine compounds are active against vegetative bacteria, fungi and most viruses. Rapid sporicidal action can be obtained around 2500 ppm, however this concentration is very corrosive so should be limited in its use.

Characteristics of halogens:
Halogens are considered low in cost and easy to use. Halogens rapidly lose their efficacy in the presence of organic material. These products must only be applied to thoroughly cleaned surfaces. Fresh solutions should always be used. Sunlight (i.e., UV light), high temperature, pH and some metals can also inactivate halogen products. Solutions are not active at temperatures above 110°F or at pH levels greater than 9. They are generally compatible with soaps and detergents and are not affected by water hardness. Chlorine-containing compounds are very corrosive to rubber, fabrics, and some metals; concentrated solutions can etch or erode concrete surfaces over time. Iodine containing products can stain surfaces.

Health and safety:
Halogens products are generally considered to be low in toxicity; however, high concentrations of hypochlorites are irritating to the mucous membranes, eyes, and skin, and can cause damage to the footpads of animals. **Halogens, especially those containing chlorine, should never be mixed with strong acids or ammonia - toxic chlorine gas can form**. Halogens are highly toxic to aquatic animals; discharge into watersheds or waterways must be avoided. If this is not possible, efforts should be taken to neutralize the halogen solution with sodium thiosulfate.

Specific halogen compounds:

Chlorine containing compounds: Hypochlorites are one of the most widely used chlorine-containing disinfectants. They are sold in liquid form (e.g., sodium hypochlorite - household bleach) or as a solid (e.g., calcium hypochlorite - a swimming pool chemical). There are hundreds of EPA-registered antimicrobial pesticide products containing sodium or calcium hypochlorite as the active ingredient

- When using bleach, it is important to determine the stock concentration the product being used, as this will affect dilution ratios. Regular strength household bleach is a 5.25-6% aqueous solution of sodium hypochlorite (52,500-60,000 ppm available chlorine). Concentrated or "germicidal" bleach formulations are 8.25% sodium hypochlorite (82,500 ppm available chlorine).
- Sanitizing and disinfecting concentrations vary from 50 to 5,000 parts per million (ppm). A 1:32 (bleach:water) dilution is generally used for routine disinfection purposes. A 1:10 dilution may be used for outbreak situations, but this is a very strong solution and should be used on a limited basis. For example, this concentration has been used at anthrax clean-up sites under a crisis exemption.

Table 3. Bleach dilutions.

% standard bleach solution (5.25% sodium hypochlorite)	**0.025% bleach solution**	**0.05% bleach solution**	**0.1% bleach solution**	**0.16% bleach solution**	**0.5% bleach solution**
ppm available chlorine	~250 ppm	~500 ppm	~1,000 ppm	~1,562 ppm	~5,000 ppm
Use	Sanitizing	Disinfection	Disinfection	Disinfection	Strong solution, use on limited basis
Dilution (bleach:water)	1:200	1:100	1:50	1:32	1:10
Amount of standard bleach (5.25%) in 1 gallon of water	5 teaspoons 1.5 Tbsp	2-1/2 Tbsp. (1/6 cup)	2 Tbsp 1/3 cup	1/2 cup (4 fl. oz.)	1-1/2 cups (12 fl. oz.)

1 tablespoon = 3 teaspoons = 1/16 cup = 1/2 fluid ounce
Note: Always add bleach to water

A useful chlorine dilution calculator is available from Public Health Ontario.

Iodine-containing compounds: The most commonly used iodine-containing compounds for disinfection purposes are iodophors, complexes of iodine with a solubilizing agent which sustains slow release of free iodine. Povidone-iodine (i.e., polyvinylpyrrolidone) is one such example.

Iodophors are broad-spectrum disinfectants. They are bactericidal, mycobactericidal, and generally virucidal (may be less effective against non-enveloped viruses compared to chlorine-containing compounds). Several iodine-based disinfectants are EPA-registered. Concentrated Iodine-containing solutions can be irritating to the skin and may also stain clothes and damage rubber and some metals.

Peroxygen Compounds

Peroxygen disinfectants are another class of broad-spectrum, rapidly-acting oxidizing agents, that are commonly used in animal settings. Examples include hydrogen peroxide containing products (e.g., Accel® (also sold as Rescue or Intervention), peracetic acid, and peroxymonosulfates (e.g., Virkon ™ S). There are also several combination products (e.g., OxyCide™, a hydrogen peroxide + peracetic acid formulation). They function by denaturing the proteins and lipids of microorganisms leading to membrane disorganization.

Microbial spectrum:
Peroxygen compounds vary in their microbiocidal range (see specific peroxygen compounds for descriptions).

Characteristics of peroxygen compounds:
Peroxygens are considered effective on hard surfaces and equipment. These products may have some efficacy in the presence of organic material.

Health and safety:
In their diluted form, these agents are considered relatively low toxicity, but concentrates may be irritating to the mucous membranes, eyes and skin and damage clothing. These products are considered environmentally friendly, and has increased safety as it decomposes to oxygen and water.

Specific peroxygen compounds:
Hydrogen peroxide [H_2O_2] is rapid acting. Solutions of 5-20% are considered bactericidal, virucidal (for enveloped viruses), fungicidal, and sporicidal (at the higher concentrations). Non-enveloped viruses may be resistant, and its effectiveness against spores, and acid-fast bacteria (e.g., *Mycobacteria)* is limited. [Note: Household (over-the-counter) hydrogen peroxide consists of a 3-10% solution; industrial concentration hydrogen peroxide is a 30% or greater solution.] Over 100 antimicrobial pesticide products containing hydrogen peroxide are EPA-registered. Hydrogen peroxide solutions alone are generally unstable and can break down quickly, so fresh solutions should be used.

Accelerated hydrogen peroxide products (e.g., Accel Rescue/ Intervention) incorporate additional compounds, such as stabilizers to minimize the degradation after mixing and surfactants to enhance the cleaning ability.

Peracetic acid [$CH_3C(O)OOH$] (peroxyacetic acid) (e.g. OxySept™ 333, OxyCide, Oxonia Active™) is a strong oxidizing agent and is a formulation of hydrogen peroxide and acetic acid. It is considered bactericidal, fungicidal, sporicidal and virucidal. It is also effective against mycobacteria and algae and has some activity in the presence of organic material. Over 50 antimicrobial pesticide products containing peracetic acid are EPA-registered. Peracetic acid in its pure form is extremely shock sensitive and explosive; modern stabilized products are generally mixtures of low levels of peracetic acid (0.25%), hydrogen peroxide, and/or acetic acid to reduce this risk. Solutions may corrode soft metals such as copper or brass, as well as steel and galvanized iron. It can also react with natural and synthetic rubber, releasing potential carcinogens.

Peroxymonosulfate-based products (e.g., Virkon S, Viroxide) are broad-spectrum products with some efficacy in the presence of organic material. One example is Virkon™S, a buffered potassium peroxymonosulfate and sodium chloride formulation. This product is typically used at a 1% solution, which has a pH of 2.6, so it should not be used on skin. In general, the prepared solutions are considered to have low human toxicity; however, preparation of the powdered form can cause mucous membrane irritation. Face and eye protection should be worn. Virkon® S has been shown to be effective for direct misting of hard to reach surfaces and for footbath solutions. Prepared solutions are unstable once diluted (a 1% solution degrades to half-strength in six days. Product ingredient decomposition and degradation are considered comparatively harmless to the environment. It can be corrosive to steel, iron and concrete.

Phenols

Phenols [C_6H_5OH] are among the oldest established disinfectants and include compounds derived from coal-tar or synthetic formulations or various homologues (e.g., cresols, xylenols and ethylphenols). These compounds can have a strong pine-tar odor and usually turn milky when added to water. A commonly used phenol compound is orthophenylphenol. Over 90 antimicrobial pesticide products containing orthophenylphenol are EPA-registered. Examples include PhenoTek 128 (ABC Compounding Company, Inc.), Tek Trol II (2-benzyl-4-chlorophenol, o-phenylphenol).

Phenols function by denaturing cellular proteins and inactivating membrane-bound enzymes. This disrupts cell wall permeability and causes molecular instability of microorganisms.

Microbial spectrum:
Phenols are typically formulated with soap (anionic) solutions to enhance their penetrative power. The antimicrobial activity depends on the formulation. In general, phenolics are broad-spectrum, and considered effective against many bacteria, mycobacteria, fungi, and enveloped viruses. Their efficacy against non-enveloped viruses is variable. They have minimal sporicidal activity. One of the substituted phenols, 2-phenylphenol, is particularly effective against *Mycobacterium* species and was extensively used during the U.S. campaign against *Mycobacterium bovis*.

Characteristics of phenols:
Phenols are stable at concentrated and use dilutions. They have a high tolerance of organic load and hard water. Some products may have residual activity after drying. Phenols are temperature sensitive and should be applied at a temperature of 60°F or greater. If the environmental temperature is below 60°F, heating the solution to 120°F (49° C) or higher can help ensure proper temperature during necessary contact time. Nonionic and cationic surfactants (e.g., quats) can reduce the activity of phenolic products. Phenols are readily absorbed by porous materials and can damage rubber and plastics.

Health and safety:
Phenols are readily absorbed through the skin and can cause severe burns at high concentrations. Skin and eye irritations have also occurred. These compounds can have a strong pine-tar odor that can be irritating to the respiratory tract. Phenols are fatal if swallowed.

Concentrations over 2% are highly toxic to all animals, especially cats (e.g., systemic toxicosis) and pigs (e.g., dermal contact lesions). Surfaces should be thoroughly rinsed prior to restocking of animals. There are environmental concerns when disposing of these compounds, so containment efforts may be warranted.

Quaternary Ammonium Compounds

Quaternary ammonium compounds (QAC, (sometimes referred to as “quats”) are a diverse group of cationic surfactants normally used for routine cleaning of noncritical surfaces. Hundreds of antimicrobial pesticide products containing QACs are EPA-registered.

There are several “generations” of products that vary in composition and performance. Later generations are typically more germicidal, less foaming, more tolerant of organic loads and anionic soaps and detergents. Active ingredients for each generation are listed below. Example QAC products include KennelSol®, Virex®, Lysol®; benzalkonium chloride is one of the most widely used.

QACs function by irreversibly binding to the negatively charged phospholipids in bacterial cell membranes and denaturing membrane proteins impairing permeability.

Table 4. Common active ingredients for various quaternary ammonium compound generations.

Generation	Active Ingredient Examples
First generation	Benzalkonium chloride ADBAC: alkyl dimethyl benzyl ammonium chloride
Second generation	ADEBAC: alkyl dimethyl ethylbenzyl ammonium chloride
Third generation	ADBAC + ADEBAC
Fourth generation	DDAC: alkyl dimethyl ammonium chloride (or dodecyl dimethyl ammonium chloride, dioctyl dimethyl ammonium chloride)
Fifth generation	DDAC +ADBAC

Microbial spectrum:
The antimicrobial spectrum of most QACs is generally limited. They are good against gram-positive bacteria. The can have limited efficacy against gram-negative bacteria, viruses and fungi. They are not generally mycobactericidal or virucidal for non-enveloped viruses. They are ineffective against spores.

Characteristics of quaternary ammonium compounds:
QACs are stable in storage, non-staining, and non-corrosive. Higher concentrations can be corrosive to metals. These products are affected by pH, and are more active at neutral to slightly basic pH but lose activity at pH less than 3.5. They can also have reduced activity in hard water conditions and are easily inactivated by organic material and anionic detergents (this may vary with the "generation"). Some products may have a bacteriostatic residual effect, keeping surfaces bacteriostatic for a brief time. Surfaces that will come into contact with food must be rinsed to ensure that there are no traces of chemical disinfectants that could contaminate the food.

Although uncommon, incorrect use or working at sub-lethal concentrations can lead to the emergence of tolerant microorganisms that make it necessary to increase the dose and/or combine different types of biocides. [Langsrud 2003]

Health and safety:
When used at recommended dilutions, QAC are generally non-toxic. Higher concentrations can cause irritation of the skin, eyes, and respiratory tract, including oral and skin ulcerations, pneumonia and possibly rarely, death. Quats are highly toxic if ingested, so areas or items disinfected with these products should be rinsed thoroughly after an appropriate contact time and before animal use. These products are toxic to aquatic animals, particularly fish, so runoff into external water sources should be avoided.

PHYSICAL DISINFECTION

Disinfection can also include several physical methods, such as drying or desiccation, the application of heat, and the use of ultraviolet irradiation, and may be used in some circumstances in animal settings.

Drying (Desiccation)

Water is a critical component for the metabolism and survival of microorganisms. The loss of water (i.e., desiccation or dehydration) can inhibit the activity and growth, and possibly kill some microorganisms. However, a number of pathogens, such as parvovirus, calicivirus, many food-borne pathogens (such as *Salmonella*), bacterial endospores and protozoal oocysts can survive and be persistent in the environment. The effectiveness of drying varies and is influenced by environmental conditions such as moisture, pH, and surface type, so the drying process is most often used in combination with other disinfection methods, and is an important last step in the C&D protocol.

Heat (Thermal Inactivation)

The use of heat is one of the oldest physical methods against microorganisms, and can be a fairly reliable method of sterilization. The process causes irreversible structural and functional damage (e.g., DNA disruption (breaks), protein denaturation, oxidative damage, and loss of membrane integrity) to microorganisms.

Heat can be applied under moist or dry conditions. Dry heat applications include burning or direct flaming, or hot air, such as baking. Moist heat can be effectively applied through steam, boiling, pasteurization, or autoclaving (i.e., steam under pressure). Moist heat applications are generally more effective and require less time than dry heat.

- Steam under pressure (e.g., autoclaving) is the most efficient since it can achieve temperatures above the boiling point of water, which may be necessary when dealing with thermally resistant bacterial spores.
- Dry heat applications involve incineration (i.e., direct flaming) or hot air (i.e., baking). In addition to temperature impacts, the loss of water loss of water content inhibits bacterial activity and growth and can result in the destruction of some bacteria in seconds. Heat baking transport trailers has been used as a measure to reduce the transmission of swine pathogens (van Kessel 2020, 2021; Dee 2005).
- Pasteurization - the application of heat to food or liquid items (e.g., milk, cheese) – uses heat at designated temperatures for an established amount of time (e.g., 145°F (63°C) for 30 minutes), to destroy pathogenic organisms. Pasteurization does not kill all microorganisms, but may be one process needed during an animal health emergency situation if the dumping of milk from affected animals is necessary.

Most microorganisms can be destroyed at temperatures greater than 158°F. Destruction is generally more rapid as temperature increases, and thermal inactivation can be a reliable method of sterilization. some pathogens (e.g., *Bacillus anthracis* endospores) are exceptionally thermostable and can require temperatures of 250°F or more for destruction.

However, the thermal inactivation process is gradual. It takes time for the process to have its effect. The time required for microbial death is inversely related to the temperature and directly related to the number of microorganisms. Microbes are generally killed more rapidly as temperature increases.

Considerations when using heat disinfection methods

- The object being heat disinfected must be able to withstand the temperature used. Heat disinfection works best for metal, glass, and fabrics; direct flaming has been used for concrete.
- The presence of organic material can impede heat disinfection processes. Surfaces need to be cleaned first.
- Temperature and exposure times need to be measured and monitored to ensure the targeted goal is achieved. Equipment, such as thermometers or monitoring equipment, should be periodically checked for accuracy.
- If the method is used for large areas (e.g., barns, vehicle bays), thermometers should be placed in various locations to ensure all areas reach the desired temperature.

Example 1: Dry Heat

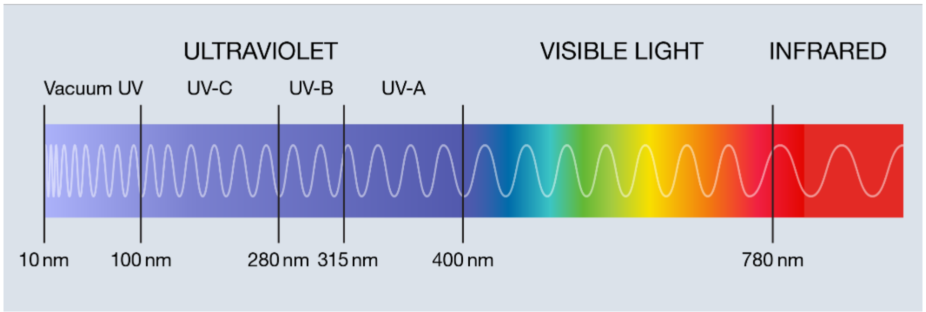
One example of the use of dry heat in animal settings is the heat baking of transport trailers. Thermo-Assisted Drying and Decontamination (TADD) systems use a natural gas or LP heater in combination with high-volume, high-velocity fans to heat and dry livestock trailers quickly. Chemical disinfection is not required. The temperature and time required to inactivate pathogens varies, but TADD systems are generally an effective and time-saving disinfection method compared to washing, chemical disinfection, and drying overnight.

Example 2: Dry Heat

During the 2014-2015 HPAI outbreak response in the U.S. the heat treatment of poultry houses was a key method used for virus elimination. The process involved dry cleaning and the heating of poultry buildings to an established temperature over a set period of days. Barns/houses required heating between 100°F and 120°F for a total of 7 days; with at least 3 consecutive days (of the 7 days) of heating continuously to within this temperature range. This method was found to be a cost effective and accepted method of disinfection/virus elimination for the emergency response. Heat treatment may not be appropriate in all situations.

Ultraviolet Radiation

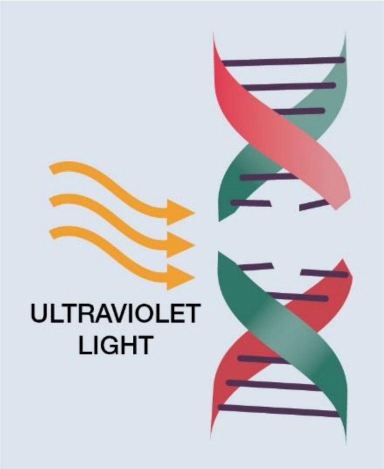
Another physical disinfection method used to destroy microorganisms involves non-ionizing radiation – in particular ultraviolet light (UV). This is most commonly applied by exposure to direct sunlight (solar radiation), but the use of mercury vapor lamps or ultraviolet light chambers or pass-through boxes are becoming more frequent.



UV light is a form of non-ionizing (low energy) radiation, with wavelengths between 100-400 nanometers (nm). The most effective biocidal wavelengths ("germicidal" range) fall within the UV-C range of 200-280 nanometers; this spectrum has biocidal effects on bacteria and can inactivate single-stranded RNA viruses on surfaces. [Ruston 2021, Cutler 2011]

The electromagnetic energy of UV light is invisible to humans. However, it damages or alters essential cell components, particularly nucleic acids (e.g., cellular DNA), through a photochemical reaction. This can have a detrimental effect on a number of microorganisms and may be a practical, supplemental method for inactivating viruses, mycoplasma, bacteria and fungi, particularly those that are airborne.

To be destroyed, microorganisms must be directly exposed to the UV-C beam. The required dose (e.g., length of exposure) varies by pathogen. Bacterial spores can be resistant, and require 10 times the exposure time as the vegetative forms of the organisms.



UVC radiation has been found useful for the control of airborne pathogens in enclosed areas, such as surgical sites, medical settings, or shelter environments. It has been used for air-handling units and ventilation systems, as well as for water disinfection.

UV light has a very limited capability to penetrate water, soil or organic material. A recent study [Ruston, 2021] found that while the top layer of an earthen manure storage (lagoon) exposed to direct sunlight was found to contain low levels of porcine epidemic diarrhea virus (PEDV), high amounts of infectious virus remained at increased depths. Therefore, the use of UV-C radiation is limited for surfaces, and like other disinfection methods, cleaning should occur prior to disinfection. Additionally, delivering the inactivating dose in a uniform and consistent manner can be a significant challenge.

UVC light can be used for on-farm disinfection of small items like lunch boxes, cell phones, tools, and medications. Most applications are designed as a pass-through chamber, where items move from the dirty side (entryway or hallway) to the clean side (office or break room). Items are cleaned and placed within the chamber on wire shelves with space in between them or treatment. To be effective, UVC chambers must be properly constructed and maintained. All individuals using the chamber must be trained.

Considerations when using ultraviolet light disinfection methods

- Ultraviolet light produces primarily a surface effect. It does not penetrate even a thin layer of dirt or debris. When used to inactivate airborne microorganisms, UV light efficacy can be affected by temperature and relative humidity. When used for water, the layers exposed to the light must be very thin.
- Irregular or porous surfaces, such as cardboard, cloth, cracks, or crevices, can shield microorganisms from the incident beam. Items should not be stacked on top of each other or block one another from exposure to the UV-C beams. Care should be taken to ensure there is space between items, so all surfaces can be exposed.

OTHER PHYSICAL METHODS OF MICROBIAL REDUCTION

Filtration: While not a true disinfection method, filtration can be used to physically remove microorganisms from gasses and fluids. For example, high-efficiency particulate air (HEPA) microfilters (≥0.3µm) use biologically inert material to prevent or retard the passage of microorganisms based on their size. This process enhances the safety of discharged air and has been used in some capacity in swine production. [Dee 2012]

Freezing: Freezing is a type of environmental stress for microbes, but it is not a reliable method of disinfection. While cold temperatures may inhibit or kill some pathogens, others can tolerate or may even adapted for it. For example, *Listeria monocytogenes*, can reproduce and survive in refrigerated foods.

CONSIDERATIONS WHEN SELECTING A DISINFECTION PROCESS

Selecting an appropriate disinfectant (or disinfection method) is an essential component of any C&D program. No single disinfectant is adequate for all situations. There are a number of factors to be considered since they can impact efficacy, possibly cause failure of the disinfection procedures, or result in hazards or injury to personnel or animals. Selection will depend on the microorganism(s) suspected, availability, the characteristics of a specific disinfectant or process, environmental factors and safety issues.

MICROORGANISM CONSIDERATIONS

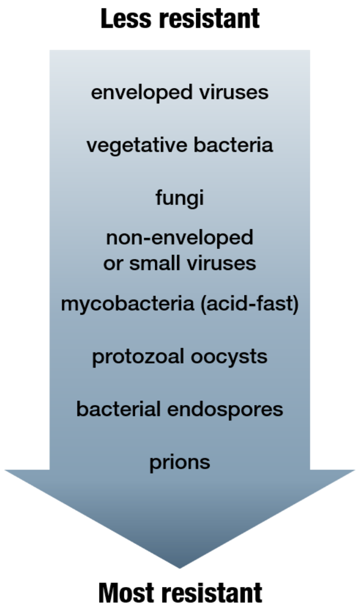
Selection of a disinfectant begins with the identification of the target microorganism. It is easier to select a product or protocol for a single microorganism, although this is not always possible in everyday practice. If the organism has not been identified, or a disinfectant is needed for a wide range of organisms, a broad-spectrum approach should be utilized.

Resistance and Susceptibility

Microorganisms vary in their ability to survive or persist in the environment as well as their susceptibility to disinfection. It is important to not only be aware of the suspect or confirmed pathogen involved but also its ability to persist in the environment, its routes of transmission as well as its susceptibility to disinfection.

Bacteria: Most vegetative bacteria (e.g., gram-positive, gram-negative) are readily inactivated by disinfectants. Some, such as *Pseudomonas aeruginosa* and *Coxiella burnetii*, can have greater resistance to disinfection. *Mycobacteria* and other acid-fast bacteria and bacterial endospores are highly resistant to disinfection, often requiring specific products, increased concentrations, or prolonged contact times.

General Microbial Resistance to Chemical Disinfectants



Fungi: The vegetative stage of fungal organisms are susceptible to most disinfectants; however, fungal spores are usually quite resistant.

Viruses: Virus susceptibility is generally related to the presence or absence of a lipid envelope and size.

- **Enveloped viruses** (e.g., coronaviruses, herpesviruses, orthomyxoviruses, paramyxoviruses, retroviruses) are generally the most susceptible due to their lipophilic nature.
- The lack of envelope for **non-enveloped or naked viruses** (e.g., adenoviruses, picornaviruses, reoviruses, rotaviruses) makes these pathogens more hydrophilic, resulting in increased resistance.
- **Small, non-enveloped viruses** (e.g., parvoviruses, picornaviruses, or caliciviruses) demonstrate even greater resistance due to their size and lack of an envelope.

Prions, the etiologic agents of bovine spongiform encephalopathy, scrapie, and chronic wasting disease, are exceptionally resistant to chemical inactivation.

Tables to review animal virus families by type (enveloped or non-enveloped) and by size can be found on the CFSPH Disinfection webpage. An *Antimicrobial Spectrum of Disinfectants* table, that shows general susceptibilities to disinfectant chemical classes can also be found on the webpage.

Other Resistance Mechanisms

Biofilms

Although cleaning may appear to remove all debris, biofilms - an invisible, complex aggregation of bacteria - may remain on surfaces. Some bacteria (e.g., *Staphylococcus aureus, Staphylococcus epidermidis* and *Pseudomonas aeruginosa*) can create biofilms, which enhances their ability to persist in the environment and avoid the action of disinfectants. This action is often triggered in response to variety of environmental stresses, such as UV radiation, desiccation, extreme pH or temperatures - many of the same methods used for disinfection purposes. Biofilms are highly resistant to disinfection. The use of detergents, mechanical scrubbing, brushing, and scraping can help remove biofilms.

Repair mechanisms
Some bacteria have the ability to counter the effects of the disinfection process (e.g. nucleic acid repair).

Number and location of microorganisms
The location of microorganisms can also pose challenges disinfection. While smooth, non-porous surfaces are generally easy to clean and disinfect, items with complex structures, multiple pieces, crevices, or joints can present challenges during the disinfection process. Additionally, the larger the number of organisms present, the greater the quantity of germicide and time will be needed.

DISINFECTANT CONSIDERATIONS

The effectiveness of a particular disinfection product or method depends on its composition and the conditions under which it is used.

An ideal disinfectant is one that is broad spectrum, works in any environment and is non-toxic, non-irritating, non-corrosive and relatively inexpensive. Unfortunately, no disinfectant is ideal. Therefore, careful consideration of the characteristics of a disinfectant (or disinfection method) is essential to select the most useful, effective and cost-efficient product.

Chemical Class

As previously discussed, chemical disinfectant classes vary in their effectiveness against pathogens. Each class varies in its mechanism of action, microbial spectrum, as well as advantages and disadvantages for use, including safety issues. Combination products may have synergistic properties that expand its microbial spectrum. Read the product label (e.g., kill claims) before use so an effective product is selected.

Disinfectant Concentration.

Use of the proper concentration of a disinfectant is important to achieve the best results for each situation. Some products will have different dilutions depending on the desired use of the product (i.e., -*static* versus –*cidal* action; sanitizing vs. disinfection action). While using higher concentrations can be more efficacious, routine use may be limited by the degree of risk to personnel, surfaces or equipment, and cost of the chemical. However, over-dilution of a product will cause the disinfectant to be ineffective against the targeted microorganism(s). The product label will list the best concentration to use for each situation. Consider any standing water or other water sources (i.e., rainfall) as a potential dilution source for a disinfectant.

Application Method.

Disinfectants can be applied in a variety of ways including wiping, brushing, spraying, misting, soaking, fumigating, etc. Application methods should follow instructions described on the label should be used. If application results in insufficient coverage of surfaces, it can lead to ineffective efforts.

Contact Time.

Contact time is critical! Disinfectant products and methods need time to have their effect. This will vary depending on the product or method selected. For example, 70% isopropyl alcohol can destroy *Mycobacterium tuberculosis* in 5 minutes, whereas 3% phenol requires 2-3 hours. Poor application or evaporation during high temperatures will impact sufficient contact times. The minimum contact time needed will be provided on the product label. Surfaces must remain wet (for chemical disinfectants) or exposed (for physical methods) for the full contact time. Some chemicals may have residual activity (i.e., QAC) while others may evaporate quickly (i.e., alcohols), especially with high temperatures.

Stability and Storage.

The efficacy of a disinfectant product can also be affected by its stability after preparation as well as its shelf life. Use of an expired product or one with reduced active ingredients may be ineffective. Some disinfectants will degrade over time, especially when stored for long periods. Others can be inactivated by heat or light, or lose stability quickly after preparation. Many disinfectant products have test kits available to allow for assessment of the concentration of active ingredients. Disinfectant product labels may list the shelf life of the concentrated product. To maximize stability and shelf life, products should be stored in a dark, cool location and preferably in stock concentrations.

Safety Precautions.

Most disinfectants can cause irritation to eyes, skin and/or the respiratory tract, therefore, the safety of all personnel should be considered. Training on proper storage, mixing and application procedures is essential. Personal protective equipment (PPE), such as gloves, masks and eye protection, should be worn during the mixing or application of disinfectants. All chemical disinfectant have a Material Safety Data Sheets (MSDS) listing the stability, hazards and personal protection needed, as well as first aid information. This information should be available to all personnel. A 3-ring binder containing this information in one easily accessible location may be useful.

Expense.

Economic considerations are always important when selecting a disinfectant. Disinfection is generally a cost-effective means of reducing pathogenic organisms. Disinfectants vary in cost, contact time and dilution. **Costs should always be calculated on a per gallon of use/dilution rather than the cost of concentrate**. For example, consider a QAC concentrate that costs $68.00 per gallon (128 oz.). The dilution required is 0.5 ounces concentrate per gallon of water, which will cover approximately 100-150 square feet (10-15 m^2). The cost to disinfect a 500 (5*100) square foot room would be calculated as:

- Concentrate needed to cover the area: 0.5 oz per gallon x 5 gallons to cover the 500 sq. foot area = 2.5 oz concentrate needed to cover the 500 sq. foot area
- Concentrate cost per oz = $68.00/128 oz (i.e., gallon) concentrate = $0.53 per oz.
- $0.53 per oz x 2.5 oz (needed for 500 sq. foot area) = $1.33

Human Factor – Ease of use

Another important consideration is ease of use. How easy or hard is the product to apply? Does the product have an offensive odor? Is a long surface contact time, and possible reapplication required? These factors can impact the level of compliance personnel may have during a C&D procedure, and should be considered.

ENVIRONMENTAL CONSIDERATIONS

Environmental conditions can have a profound effect on disinfection success. This includes factors such as the organic load, the type of surface, temperature, water hardness, pH or the presence of other chemicals.

Organic Load (Heavy Soiling)

The presence of organic matter (e.g., soil, manure, body fluids, bedding) is one of the most important environmental factors to influence disinfection activity!

Organic matter provides a physical barrier that protects microorganisms from contact with the disinfectant. Additionally, debris and organic material can neutralize many disinfectants (e.g., chlorine, QACs), reducing the level of active ingredient available to attack microorganisms. Ultraviolet light applications, including direct sunlight, have limited penetration below the surface of organic matter. Some disinfectants, such as phenols or glutaraldehyde, are less affected by organic matter, and may need to be considered when the complete removal of organic debris is difficult. However, these products are not effective for heavy loads of organic material, so surfaces should still be cleaned first.

Surface Type

Surfaces in animal settings can be quite diverse. They may include various metals, glass, rubber, plastic, concrete, wood, or fabric or woven material (e.g., clothes, nets, and ropes). The type of material or complexity of an item can factor into disinfection efficacy.

Disinfectants are labeled for use on hard, non-porous surfaces (e.g., glass or stainless steel). Surfaces that are porous, cracked, or pitted (e.g., wood, concrete) or that have complex structure, such as hinges, bends, or crevices can be challenging to disinfect effectively. Some chemical disinfectants can be incompatible with or corrosive to certain materials or surface types.

Some products have been developed for use on porous surfaces, but generally require much longer contact times or higher concentrations. Alternative or supplemental disinfection methods, such as gaseous or vaporous sterilant products or physical disinfection methods (e.g., drying, ultraviolet light) should be used for treating porous surfaces. Flame guns (i.e., application of heat) may be a useful alternative if the item can withstand the high temperature.

Temperature

Temperature is another important environmental factor that can affect disinfectant efficacy. Considerations should include both the ambient temperature as well as that of the disinfectant solution. The exposure temperature is particularly important if you will be disinfecting outdoors (e.g., vehicles).

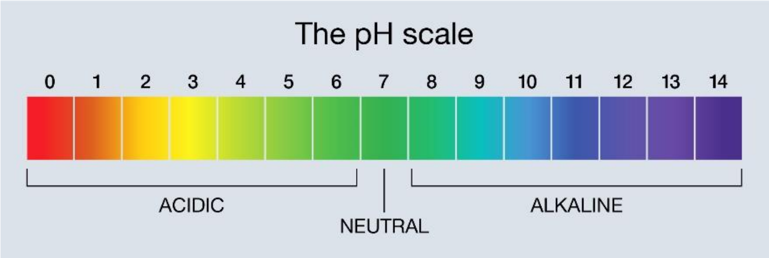
Most chemical disinfectants work best at temperatures above 68°F (20°C). Lower temperatures can reduce disinfectant efficacy or solutions may freeze in these conditions. Some disinfectant products are compatible with the addition of ethylene glycol to prevent freezing. Read the product label for appropriate instructions. Caution should be used, since antifreeze solutions can be highly toxic. The runoff of any solutions containing the chemical should be contained or avoided when possible.

Conversely, while elevated temperatures can aid in microorganism destruction, it can also accelerate the decomposition or evaporation of a disinfectant, thereby reducing the ability to achieve the necessary contact time, thereby affecting efficacy. Heat may also damage items being disinfected.

pH

pH extremes can be detrimental to microorganisms, however environments that are very acidic or very alkaline can alter the effectiveness of some disinfectants. pH changes in the environment may be caused by organic material, water composition (e.g., water hardness ions), or from other chemical products used. These conditions may change the degree of ionization or dissociation of the active ingredient of a chemical disinfectant or the stability of a solution. Examples include phenolics, hypochlorite, and iodine compounds.

This can affect efficacy. Some disinfectants have optimum pH ranges at which they work best. For example: The efficacy of glutaraldehyde is best at a pH greater than 7. Quaternary ammonium compounds have the greatest efficacy at a pH of 9-10.

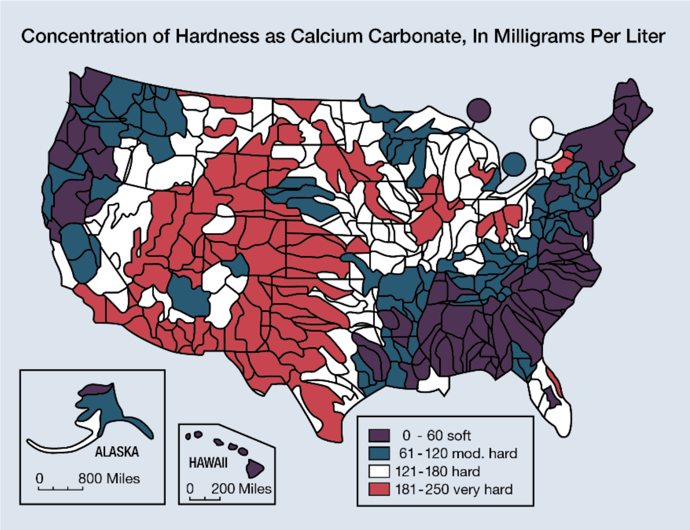


Presence of Other Chemicals

Another confounding factor that can impact disinfectant efficacy is the presence of other chemicals. While some disinfectant products contain cleaning or surfactant components to potentiate their effect, others can be inactivated by the residue when present. For example, iodine-based agents are inactivated by quaternary ammonium compounds, while phenols are commonly formulated with soaps to increase their penetrative ability.

Water Hardness

A factor not always considered influencing disinfectant activity is the hardness of water. Water hardness is determined by the amount of dissolved minerals, primarily calcium (Ca^{2+}) and magnesium (Mg^{2+}) ions, in a water source. The presence of these ions can form complexes with cleaning and disinfection products, leading to inactivation, reduced efficacy, or residue buildup. This impact is particularly important for quaternary ammonium compounds, iodophors, and phenols. Many products have chelating agents, such as EDTA, to help bind these ions. Acids, such as acetic acid, can aid in dissolving mineral particles.



Water hardness varies throughout the United States (see map above). Commercial test kits to measure water hardness are available. Water harness classifications (in mg/L calcium carbonate) are listed below:

- 0 to 60 mg/L – soft;
- 61 to 120 mg/L - moderately hard;
- 121 to 180 mg/L – hard;
- greater than 180 mg/L - very hard

Relative Humidity

When using gaseous disinfectants, activity is influenced by the relative humidity of the environment. Relative humidity also influences the efficacy of ultraviolet light methods. Moisture content can affect the ability of the gaseous product to reach intended surfaces. For example, formaldehyde fumigation requires a relative humidity in excess of 70% for effectiveness.

DISINFECTANT PRODUCT LABELS–FINDING INFORMATION YOU NEED

Disinfectant product labels contain important information on the proper use and hazards of a chemical. This information is often overlooked, but understanding this information is essential for developing an effective disinfection protocol.

The product label tells important information, such as:

- What microorganisms the product is effective against
- The product's effectiveness under certain conditions (e.g., water hardness, presence of organic material)
- How to mix and apply the solution
- The necessary contact time the solution will need
- Any health and safety concerns
- Other considerations, such as storage and disposal or environmental impacts, flammability or corrosiveness

This information will vary among products, so it is always important to read the product label before use.

It is a violation of federal law to use a product in a manner inconsistent with its labeling.

EPA REGISTRATION NUMBER

Chemical disinfectants in the United States are registered and regulated by the U.S. Environmental Protection Agency (EPA). Products intended for the control, prevention, and destruction of pathogenic microorganisms on inanimate objects and surfaces are classified as "antimicrobial pesticides" under the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA). This includes sanitizers, disinfectants, and some sterilants.

Any pesticide sold or distributed in the United States must be registered. Prior to registration and marketing of the chemical, the product's chemistry, efficacy, toxicity to humans, animals and plants, and other parameters must be tested and submitted for EPA review and approval.

- Most products are registered under FIFRA Section 3, Regular label.
- Some products can be registered under FIFRA Section 18, Emergency Use Exemptions. These are discussed in greater detail in Lesson 10: C&D During Disease Outbreaks.

All EPA-registered pesticides must have an EPA registration number listed on the label., which consists of a company identification number and a product number (e.g., 123-45). The EPA Registration Number indicates the product has been reviewed by the EPA and can be used with minimal risk when the label directions are properly followed. The number is not an endorsement or guarantee of product effectiveness.

Finding EPA-registered Products: The product label for any EPA-registered disinfectant may be retrieved by entering the registration number in the EPA's Pesticide Product Label System (PPLS) search engine. **Try it out! Enter the EPA-registration number of a product you currently use to obtain its product label and registration information.**

PRODUCT INFORMATION

Product Type

Chemical disinfectant products can be labeled as a cleaner, deodorizer, sanitizer, disinfectant, fungicide, virucide, tuberculocide, for hospital, institutional and industrial use, agricultural premises and equipment, veterinary use, etc.

Effectiveness Under Certain Conditions

The testing conditions used (e.g., efficacy in simulated organic load or hard water conditions) are provided. All disinfectants are tested in a manner that simulates the product's effectiveness under field conditions. These parameters are hard water conditions (e.g, up to 400 ppm hardness ($CaCO_3$) in the presence of 5% serum contamination). If a product has been tested under additional conditions, this will be indicated on the label.

CHEMICAL INGREDIENTS

Active Ingredients

The individual active ingredients contained in the product are listed as percentages and include the chemicals responsible for the control of the microorganisms. This information can be used to determine chemical class categories.

Table 5. Examples of active ingredients for various chemical classes of disinfectants

Chemical Class	Example Active Ingredients
Acids	Acetic acid, citric acid
Alcohols	Ethanol, isopropanol
Aldehydes	Glutaraldehyde, formaldehyde
Alkalis	Sodium hydroxide, calcium hydroxide, ammonium hydroxide, sodium carbonate, and calcium oxide
Chlorine-containing compounds	Sodium hypochlorite, calcium hypochlorite, chlorine dioxide
Peroxygen compounds	Hydrogen peroxide, peracetic acid, potassium peroxymonosulfate
Phenols	Orthophenylphenol, 2-phenylphenol
Quaternary Ammonium Compounds	Benzalkonium chloride, alkyl dimethyl ammonium chloride, alkyl didecyl dimethyl ammonium chloride, and dialkyl dimethyl ammonium chloride

Note: Some disinfectants can have a combination of chemical classes.

Inert Ingredients

Inactive ingredients are often lumped into one statement and include items such as soaps or detergents, dyes or coloring agents, perfumes, and water.

PRODUCT LABEL KILL CLAIMS (MICROBIAL SPECTRUM)

Review product label claims before choosing a disinfectant. Label claims list the microorganism (e.g., bacteria, viruses, protozoa) the product has been shown to be effective against when used according to label directions. Label claims must be supported by efficacy testing. Tests used are standardized and conducted under laboratory conditions that mimic field conditions.

Basic Efficacy Testing

EPA registers three types of disinfectant products based on efficacy data submitted using three specific test microorganisms:

- A **limited** efficacy disinfectant only has efficacy against one specific microorganism group, this is either the Gram-positive bacteria, *Staphylococcus aureus* or the Gram-negative bacteria, *Salmonella enterica*. The label must specify the group against which the product is effective.
- A **general or broad-spectrum** disinfectant is effective against both gram-positive and gram-negative bacteria. This claim must be supported by efficacy testing against *S. aureus* and *S. enterica*.
- A **hospital** designation is a general or broad-spectrum disinfectant that is also effective against the nosocomial bacterial pathogen, *Pseudomonas aeruginosa*

** Pseudomonas aeruginosa may be substituted for Salmonella enterica*

Additional Organisms

Efficacy claims against additional organisms (e.g., viruses, fungi) must be supported by established standardized testing for each particular organism. All data must be reviewed by EPA before it can be added to a product label.

In some instances, surrogate organisms may be allowed for certain claims. For example, *Mycobacterium bovis* is used as a surrogate for human *Mycobacterium tuberculosis* to determine tuberculocidal claims. Feline calicivirus is used as a surrogate for norovirus (i.e., small non-enveloped viruses). Testing for sporicidal claims use spores of *Bacillus subtilis* and *Clostridium sporogenes* or *B. anthracis.* Claims against biofilms must attain a minimum mean six log reduction of *Pseudomonas aeruginosa* or *Staphylococcus aureus* biofilms.

To learn more, see the EPA's Efficacy Requirements for Antimicrobial Pesticides and the EPA Product Performance Test Guidelines (OCSPP 810.2000).

Emerging or Novel Pathogens

What about emerging pathogens, particularly viruses? Many instances have occurred in recent years - Ebola virus, Mpox virus, rabbit hemorrhagic disease virus. These novel or emerging pathogens were unpredictable and are often not found on disinfectant product labels. Prior to 2019, labels did not include SARS-CoV-2. The EPA has a process where a company can apply for an emerging viral pathogen claim. In general, claims for harder-to-kill viruses may be allowed for acceptable emerging claims after review by the EPA.

The EPA and CDC divides viruses into three viral subgroups based on their relative resistance to inactivation by typical disinfectant products: small non-enveloped, large non-enveloped, and enveloped viruses.

- **Small, Non-Enveloped Viruses (<50 nm):** Considered highly resistant to inactivation by disinfection due to their very resistant protein capsid. Includes the families of Picornaviridae, Parvoviridae, Caliciviridae, Astroviridae, Polyomaviridae

- **Large, Non-Enveloped Viruses: (50-100 nm):** Considered less resistant to inactivation by disinfection compared to small, non-enveloped viruses, based on their larger size. Includes the families of Adenoviridae, Reoviridae, Papillomaviridae
- **Enveloped Viruses:** Considered the least resistant to inactivation by disinfection due to the presence of a lipid envelope, which is easily compromised by most disinfectants. Includes the families of Arenaviridae, Bornaviridae, Bunyaviridae, Coronaviridae, Filoviridae, Flaviviridae, Hepadnaviridae, Herpesviridae, Orthomyxoviridae, Paramyxoviridae, Poxviridae, Retroviridae, Rhabdoviridae, Togaviridae

Using this approach, antimicrobial products that can kill a small, non-enveloped virus should be able to kill any large, non-enveloped virus or any enveloped virus. Similarly, a product that can kill a large, non-enveloped virus should be able to kill any enveloped virus.

For more information see: selected EPA-registered disinfectants and antimicrobial products registered with EPA for claims against common pathogens and the EPA Emerging Viral Pathogen Program Guidance.

Emergency Exemptions

What about highly contagious foreign animal diseases? While some companies have conducted testing for some FAD organisms (FMD, ASF), other diseases may not be tested.

In the event of a FAD outbreak, when a particular pathogen is not be listed on the product label of an EPA-registered disinfectant, an exemption (Section 18 of FIFRA) may be authorized by EPA to allow Federal Agencies or States to use unregistered pesticides or the “off-label” uses of a registered pesticide for a limited time.

USDA-APHIS and EPA have been preparing for such an event, and have developed listings of approved disinfectants with both FIFRA Section 3 (i.e., a regular label) or exempted under FIFRA Section 18 (i.e., emergency use label) for use against select foreign animal diseases.

For more information on emergency exemptions:

--USDA-APHIS: Potential EPA-registered disinfectants to use against the causative agents of selected foreign animal diseases in farm settings

--EPA: Pesticide Emergency Exemptions

--Code of Federal Regulations Title 40, part 166. Exemption of Federal and State agencies for use of pesticides under emergency conditions

DIRECTIONS FOR USE

The use directions for the product are stated on the label. This may include housing areas, vehicles, equipment, footwear, etc. All disinfectants are labeled for hard, non-porous surfaces; some may be labeled for food or non-food contact surfaces, wood or concrete. Different concentrations, contact times, or application methods may be needed depending on the surface or area being disinfected.

- **Where to Use:** Registered use locations are listed and may include hard, non-porous surfaces, food or non-food contact surfaces, boot or shoe wash, vehicles, wood or concrete.

- **How to Use:** Formulations may be ready to use (RTU) or concentrated and require dilution or mixing. Mixing or dilution directions will be on the label. The application method (e.g., spray, wipe, soak) to for the product will also be noted on the label.
- **Storage and disposal:** Instructions for storing the product and for disposing of any unused pesticide and the pesticide container will be listed.
- **Compatibilities:** The label will also include considerations such as optimum temperatures, organic matter, and other factors that may affect the product's efficacy.
- **Specific Uses:** Instructions for specific uses such as boot baths, vehicles, or food-contact surfaces will be provided.

HEALTH AND SAFETY INFORMATION ON THE PRODUCT LABEL

A critical area of the product label is the Health and Safety section. All chemical disinfectants have safety concerns. Precautionary statements, hazards to humans, animals, or the environment, protective equipment that should be worn, first aid and medical treatment information will be provided. This information should be read and understood by anyone using the product.

Hazards/Precautionary Statement

Most disinfectants will have a Hazards/Precautionary Statement. Specific "signal words" are used to indicate the degree of hazard. Descriptors used (from least harmful to most harmful) are:

- "Caution",
- "Warning",
- "Danger" and
- "Danger-Poison".

Most contain "Keep out of Reach of Children" Statement, which may extend to dangers for animals.

Additional Health and Safety Information

- **PPE:** The product label – either in the health and safety information section or the Directions for Use section will outline **personal protective gear** that should be worn when mixing and applying the product.
- The **first aid** section will contain instructions for handing various routes of exposure (e.g., accidental swallowing, inhalation or skin contact with the product).
- A **"Notes to Physicians"** section may be listed with specific medical information needed by medical professionals in the case of poisoning.
- **Physical or chemical hazards**, such as flammability, corrosiveness, or explosive characteristics will be stated, with guidance on precautions to take.
- **Environmental hazards** are listed and address risks to birds, mammals, fish, aquatic invertebrates and estuarine organisms, and pollinating insects.

HEALTH AND SAFETY DURING C&D

Ensuring the health and safety of people, animals, and the environment during C&D procedures is essential. All disinfection methods have some level of hazard associated with their use. Careful attention should always be paid to warning and safety statements printed on the product label. Personnel training, personal protective measures and safety precautions should always be taken.

CHEMICAL HAZARDS

All chemical disinfectants can have some level of hazard if not used appropriately. Exposures may occur during preparation of a product or when applying solutions. During preparation, exposure to concentrated solutions can occur if the product is spilled or if splashes occur while pouring. During application, sprays or misting of solutions can expose the eyes, skin, or the respiratory tract.

Health effects may occur acutely or develop after prolonged or extended exposures. Effects can range from mild irritation to severe damage of the skin, eyes, or respiratory tract. Impacts to people and possibly animals may include:

- Irritation to the eyes, skin, mucous membranes, or respiratory tract
- Allergic reactions, such as allergic dermatitis or asthma attacks
- Irreversible eye damage
- Chemical burns from corrosive chemicals, especially concentrates
- Respiratory distress, if inhaled
- Some chemical classes of disinfectants (e.g., formaldehyde) are considered potential carcinogens.
- All are toxic if ingested

Product labels should always be read for any health and safety risks and the recommended protection measures. All chemical disinfectants also have a Material Safety Data Sheet (MSDS) listing the stability, hazards, and personal protection needed, as well as first aid information. This information must be kept on site and be available to all personnel handling disinfectants. A 3-ring binder containing this information in one easily accessible location is recommended.

PHYSICAL HAZARDS

In addition to potential chemical exposures and injuries, various physical hazards are also a concern during C&D duties. The following highlights some of these risks:

- Cutaneous burns when using hot water, steam, flame, or other heat disinfection methods.
- Direct exposure to high levels of UV light can damage the skin or eyes.
- Skin punctures or injury from water jets are possible when using high pressure sprayers.
- Respiratory irritation may occur from the generation of dust during the cleaning phase.
- Musculoskeletal injuries may occur following a slip, trip or fall working in wet, slippery conditions.
- Tripping hazards from hoses or other C&D equipment will be in the work area.
- PPE worn can limit a person’s range of motion and vision, predisposing them to falls and it can also quickly lead to overheating.
- Electrical shock can be a risk when electrical equipment is not turned off.

Table 6. Summary of some of the health risks for the chemical classes of disinfectants.

Chemical Class	Hazards to People, Animals, or the Environment
Acids	Corrosive - can damage skin and lungs; high concentrations can cause chemical burns; may be toxic in the air at high concentrations
Alcohols	Flammable and should be stored away from heat sources
Aldehydes	Aldehydes are highly irritating and toxic to animals and humans through contact or inhalation. Formaldehyde has been identified as a potential carcinogen. Occupational Safety and Health Administration (OSHA) standards limit the exposure time for personnel. Glutaraldehyde is less acutely toxic than formaldehyde, but exposure can cause acute and chronic skin and mucous membrane irritation, epistaxis, and possibly asthma.
Alkalis	Very caustic - exposure can cause severe skin burns, burns on the footpads of animals and hoof drying and cracking. Dust from these products may cause severe burning of the eyes and mucous membranes or respiratory tract if inhaled. Lye is highly reactive with water.
Biguanides	Can cause minimal skin irritation or allergic reactions. Toxic to fish; avoid discharge into the environment
Chlorine compounds	High concentrations are irritating to the mucous membranes, eyes, and skin, and can cause damage to the footpads of animals. Toxic gas can be formed when mixed with strong acids or ammonia Highly toxic to aquatic animals; avoid discharge into the environment
Peroxygens	Concentrated products can be irritating to the mucous membranes, eyes, and skin. Powdered concentrates can cause mucous membrane irritation. Face and eye protection should be worn.
Phenols	Readily absorbed through the skin; high concentrations can cause severe burns; skin and eye irritation Odor can be irritating to the respiratory tract Fatal if swallowed Concentrations over 2% are highly toxic to all animals, especially cats and pigs Highly toxic to aquatic animals; avoid discharge into the environment
Quaternary ammonium compounds	High concentrations can cause irritation of the skin, eyes, and respiratory tract, including oral and skin ulcerations, pneumonia, and possibly (rarely) death Highly toxic if ingested Toxic to aquatic animals, particularly fish; avoid discharge into the environment

BIOLOGICAL RISKS

Consideration should also be given to any potential biological risks. Some disease situations may involve C&D to contain zoonotic pathogens. Since this activity will occur in some of the most contaminated areas (e.g., animal housing areas), personnel need to be cautious to avoid exposures through inhalation, ingestion, or direct contact on skin, eyes or mucous membranes. Cleaning activities such as sweeping and scraping, or washing, particularly with high powered sprayers, or drying activities using blowers may disturb and further disseminate pathogens. When dealing with a potentially zoonotic disease, use careful dry and wet cleaning methods and wear personal protective equipment (PPE).

PROTECTING PEOPLE

Health hazards and exposure risks can be minimized through training, safety precautions, and personal protective measures.

Read the Label

Warnings and safety information is printed on the product label. This will include, any hazards to humans, animals, or the environment; protective equipment that should be worn; the necessary first aid and medical treatment information; and any hazards, such as flammability, corrosiveness, or explosive characteristics

The recommended precaution measures listed on the label should always be followed.

Safety Data Sheets

All chemical disinfectants have a Safety Data Sheet (SDS) listing the stability, hazards, and personal protection needed, as well as first aid information. This information must be kept on site and be available to all personnel handling disinfectants. A 3-ring binder containing this information in one easily accessible location is recommended.

Personnel Training

Ensure all personnel have training on the proper handling, preparation and application of chemical disinfectants. They should be aware of any hazards from the products being used, and the protective measures necessary. They should follow all product label safety precautions and wear appropriate PPE (e.g., gloves, goggles), as required. Be sure personnel know what PPE is needed and how to don and doff (put on and take off) the equipment properly.

Personal Protective Equipment (PPE)

Personal protective equipment should always be worn when handling, mixing and applying disinfectants.

At a minimum this should include waterproof gloves, protection for exposed skin (e.g., coveralls, long sleeves), and eye/face protection (e.g., goggles, face shield). Masks or respirators may be needed for some products. They should also be worn for situations involving significant amounts of dust generation or zoonotic disease potential.

Additional personal protective equipment, such as waterproof or chemical-resistant suits (including both pants and jackets with hoods), waterproof aprons, or respirators may be necessary for some situations (e.g., formaldehyde or acidic disinfectants).

Handwashing

Personnel should always wash their hands after handling, mixing or applying disinfectant solutions and before eating, drinking, or other possible exposure risk activities.

PROTECTING ANIMALS

Animals can be at risk to the same chemical and physical hazards previously described. Animals are also more prone to incidental ingestion or chemical exposures on feet or skin. Efforts to eliminate health issues for animals need to be addressed.

- Disinfectants should not be applied directly to animals unless labeled for such use.
- Most disinfectants cannot be used when animals are present.
- All disinfectants are toxic if ingested and must be rinsed away before animals are introduced to the area. This is especially critical for feeding and watering equipment.
- Some products can damage the foot pads or hooves of animals.
- Some disinfectant products recommend cleaning and rinsing ***after the disinfection phase*** for animal contact areas, feeders and waterers.

PROTECTING THE ENVIRONMENT

Protecting the environment during C&D procedures is also critical. Many chemical disinfectants are toxic or ecological hazards for aquatic organisms and plants. Runoff should be avoided or controlled to prevent entry into waterways, such as lakes, streams, ponds or wetlands. The use of berms and pumps to collect wastewater may be necessary. Products that are biodegradable or safer for the environment should be considered.

SUMMARY

The prevention of disease in animal settings involves effective cleaning and disinfection of contaminated surfaces. Properly performed C&D decreases pathogen levels on surfaces and reduces exposure risks. Successful C&D involves remembering and understanding the key principles and steps for the process, choosing the best method, and recognizing any limitations.

KEY PRINCIPLES OF C&D

Regardless of the setting, item or area, ensure the five key C&D principles.

1. Clean surfaces before disinfection.
2. Use the right disinfection product for the situation.
3. Read the product label.
4. Give it time to work.
5. Keep everyone safe.

Keep in mind these common failures of C&D success.

- The target pathogen is resistant to the disinfection process or product used.
- The surface type (e.g., porous, cracked) allowed the pathogen to persist in the environment.
- Surfaces were inadequately cleaned prior to disinfection.
- An ineffective disinfectant concentration was used.
- The product or process was not used (applied) correctly.
- The necessary contact time was not observed.
- Environmental factors such as organic load, temperature, pH or water hardness are impacting the selected disinfectant or method.

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