

**THE**  
**Aqueous**  
**Cleaning**  
**Handbook**

**A GUIDE TO CRITICAL-CLEANING  
PROCEDURES, TECHNIQUES, AND VALIDATION**

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*and the*  
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# Foreword

Most cleaning practitioners are familiar with the story: the scientists who developed chlorofluorocarbons (CFCs), first as refrigerants and then as solvents, had struck upon what they thought were safe, inert materials. CFCs would replace petroleum-based chemicals known for their health hazards. CFCs were relatively inexpensive, readily available and most importantly, they worked.

What the researchers did not know was the impact these chlorine-containing substances would have on the ozone layer: that portion of the atmosphere responsible for shielding the earth from some of the solar system's most harmful ultraviolet (UV) rays.

Chlorine (Cl) atoms participate in the destruction of ozone (O<sub>3</sub>) as they randomly make their way into the upper atmosphere. The reaction is catalytic with the potential for one (1) Cl atom to destroy thousands of O<sub>3</sub> molecules. The introduction of hydrochlorofluorocarbons (HCFCs) as secondary replacement chemicals reduced but did not eliminate this danger.

CFCs and HCFCs also increase global warming by interfering with the atmosphere's natural ability to radiate heat away from the planet. This exacerbates the Greenhouse Effect most noticeably impacted by fossil fuel burning.

The international Montreal Protocol treaty and the U.S. Clean Air Act Amendments govern the usage and production of most of these compounds, including VOC (volatile organic

compound) emitters. The U.S. Environmental Protection Agency's (EPA) Significant New Alternatives Policy (SNAP) identifies acceptable substitutes. These laws purposefully devastated organic and chlorinated solvent markets while fostering research and development. Hundreds of companies specializing in surface preparation, cleaning, rinsing, drying and inspection owe their economic feasibility to regulatory drivers.

In addition, the U.S. EPA's Toxic Release Inventory (TRI) provides a powerful tracking tool for looking at the places and the reasons hazardous chemicals are used. This transpired against a back drop of Right-to-Know legislation and chemical accidents culminating, in no small measure, with the inception of Material Safety Data Sheets (MSDSs). The occurrence of the words "test data unavailable" or "unknown" on many of these documents helped set the stage for other environmental initiatives.

Initiatives in northern Europe have begun to reflect the precautionary principle. This is the EH&S equivalent to the Hippocratic medical oath, "First do no harm." The translation: sell no product whose environmental, health and safety concerns have not yet been elucidated.

The principle represents a radical departure from conventional thinking that may be lost on those not directly involved in the chemical industry. Thousands of new chemicals enter the market each year while little is known about the vast majority of existing chemicals. This would no longer be tolerated under a system that demands thorough environmental and health information before exposure (as opposed to after a potential, unknown disaster). Chemical manufacturers would have stronger stewardship responsibilities. Products would take longer to reach the marketplace. And once a substance was deemed safe, who would be liable for any errors that are sure to occur? It remains to be seen whether American society, steeped in litigation, can rise to the occasion.

Testing parameters other than those based on the cancer paradigm need to be determined. The study of chemicals' effects at low concentrations, should be expanded (negative impacts from low-dose exposures include hormone mimickers and endocrine disrupters). The effects of chemical mixtures, individually thought to be benign, bear more investigation.

Methods of extrapolating test data as well as gender and age differentials require review.

Other problems remain. Most government policies focus on chemical handling and use. They do not necessarily take into account a chemical's life cycle or environmental fate. Nor do they fully consider the drain that chemical manufacture can place on natural resources and raw materials. Risks may simply be shifting from the site of usage to the chemical's production plant (or power plant) rather than real progress being made. This is especially worrisome in light of environmental justice issues.

It is no wonder, then, that many industries are rediscovering water (H<sub>2</sub>O) as the ideal cleaning medium, the only universal solvent truly non-toxic to both humans and the environment. Like the CFC and HCFC designers, today's formulators will undoubtedly push aqueous (i.e., water-based) cleaners to the scientific limits of the day. This is no time for intellectual arrogance. Chemical exposures effect workers, consumers and communities. Early partnering with stakeholders may ameliorate the mistakes historically associated with the discovery process.

The constituents and mechanisms of aqueous cleaners must be understood. Surfactants and emulsifiers, alkaline builders and the dependence on water and energy (increasingly precious resources in an over-populated world), all matter to the concerned scientist. One suspects that not all aqueous cleaners are created equal.

There are challenging opportunities for advancement. It is possible to envision the day when manufacturers will no longer be forced to use hazardous materials for surface cleaning in the production of quality goods and services. Furthermore, toxic-free analytical techniques for surface evaluation will be invented that are superior to those now in use.

Based on the cornerstones of pollution prevention and cleaner production,\* pursuit of this vision minimizes or eliminates environmental impacts and health and safety risks linked to many industrial cleaning applications. These objectives support a more sustainable business plan, leading to better job security and overall quality of life.

Alconox, Inc. deserves much credit for its self-imposed mission to educate the public about aqueous cleaning. Readers, prepare to learn well from this Handbook.

— Carole LeBlanc  
Toxics Use Reduction Institute  
University of Massachusetts • Lowell

\*The term *cleaner production* refers to safer, greener, and more sustainable manufacturing methods and materials and *not* the production of chemical cleaners.

# Introduction

Today, the terms precision or critical cleaning include any cleaning process where residue can cause a failure in the function of the surface being cleaned. In general industry, this includes electronic component cleaning and surface preparation of metals prior to coating or bonding. It may also include cleaning applications in industries such as chemicals, food and beverage, pharmaceuticals, and cosmetics where solids and liquids come into contact with plastic, glass, and metal piping and processing equipment.

Current practice for critical cleaning includes the use of volatile solvents, corrosive chemicals, and aqueous detergents. In today's hazard-sensitive workplace, however, many companies are closely examining their use of volatile-solvent and corrosive-chemical cleaners. In that regard, aqueous cleaning represents an economical, environmentally benign alternative. In many cases, aqueous cleaning is also the best available technology and provides a viable long-term solution to environmental issues.

It is important that these cleaners not contain high concentrations of volatile organic compounds or solvents due to their air-pollution and ozone-depletion potential. They should also be formulated to minimize worker hazards yet still deliver critical-cleaning performance in the intended application.

This handbook is designed to help laboratory and plant personnel select aqueous cleaners and systems more wisely

and maximize their cleaning performance. While by no means exhaustive, it represents the culmination of more than 50 years experience with aqueous-cleaning technology by the staff of Alconox, Inc., a leading developer and supplier of aqueous-cleaning detergents.

In its pages you will find handy, easy-to-read summaries of what aqueous cleaning is and how it works—its chemistry and mechanical properties. This handbook also contains critical information on how to select an aqueous cleaner and make the most of the cleaning potential of an aqueous-cleaning system.

To make it easy for you to find important information, cleaning considerations for each industry are also presented.

If you have any questions that are not included in this handbook, please feel free to contact our technical services department at Alconox, Inc. (877-877-2526). In fact, many ideas for new aqueous-cleaning compounds have come from such contact, and you'll find our technical service staff ready and willing to help with your questions or concerns.

Whether you have used aqueous cleaners and systems for some time or are just now considering switching to aqueous cleaning, we hope you find this handbook helpful.

— Alan S. Zisman, M.D.  
Malcolm M. McLaughlin, M.A.  
Alconox, Inc.

# What Is an Aqueous Cleaner?

**A**n aqueous cleaner is a blend of ingredients designed to enhance the cleaning ability of water. Typically an aqueous cleaner contains a surface active agent (surfactant) and builders to help the surfactant. The surfactant acts as a wetting agent to allow the cleaning solutions to penetrate into crevices and around and under soils. The surfactant will usually also act as an emulsifier to help form emulsions with water-insoluble oils. The builders usually react with dissolved metal ions in the water to help stop them from interfering with cleaning. (Chapter Two of this handbook provides a thorough discussion of these ingredients.)

## HISTORY OF CLEANING

Surface cleaning or degreasing can be defined as the removal of residues; contaminants; or soils—unwanted or extraneous material, deposited on or attached to a substrate surface. The purpose may be esthetic, medicinal, social or scientific.

The history of cleaning includes the development and use of four types of cleaning compounds:

- **Soaps**—which use salts of organic acids with cleaning properties such as sodium stearate in hand bar soap that make a surface active agent with wetting and emulsifying properties.
- **Solvents**—which use solvency to remove soils by dissolving them with the solvent to form a homogeneous mixture.
- **Synthetic solvents**—which use manmade fluorocarbon-based compounds such as CFCs, HCFCs, and PFCs.

- **Aqueous cleaners**—which use blends of detergent compounds with surface active agents together with other cleaning chemicals that use detergency to lift soil from a surface by displacing it with surface active materials that have a greater affinity for the surface than for the soil.

**Soaps**—A name stemming from the soapberry, the common name for about 13 species of deciduous or evergreen trees in the soapberry family whose fruit contains a soapy substance called saponin—a natural cleansing agent produced by the reaction of an alkali, typically sodium hydroxide (NaOH) and animal fat or vegetable oil. Its use dates at least from the third millennium BC. (In fact, clay tablets in Mesopotamia contained a recipe for soap that included potash—potassium carbonate—and oil.)

The second-century writings of the Greek physician, Galen, referenced soap as a cleansing, medicinal product that helped to cure skin ailments. Later, the ancient Romans shared their knowledge of soap formulation (*sapo*, the Latin word for soap is still used to describe the saponifiers often added to today's synthetic detergents) and by the Middle Ages commercial soapmaking centers were established in such European countries as France and Spain as well as in England. These early manufacturing methods were crude. Discoveries by Nicholas LeBlanc in the 1800s and a century later by Michel Chevreul made it possible to make predictable soap formulations. Today we have predictable reproducible formulations from batch to batch.

**Solvents**—To understand solvents and their strengths and liabilities as cleaning materials, it's important to understand “solvency”—the ability to dissolve. A solvent is usually a liquid substance that is capable of forming a physical, homogeneous solution. Some materials are soluble in certain other materials in all proportions, while others are soluble only up to a specific percentage and any excess precipitates out of the solution.

Another important aspect of a solvent is its volatility, which is highly related to its boiling point. Solvents that have reasonably low boiling points are more volatile and can be more readily removed from a reaction mixture by distillation

or evaporation. In cleaning substrates, the most common application for industrial solvents is to put dirty solid matter (parts, products, etc.) into the solvent where foreign matter on the surface is dissolved into the solvent. The substrate is then removed from the solvent-dilute-foreign-matter mixture which evaporates and deposits a relatively much smaller amount of foreign matter left over from the dilute mixture—leaving a proportionally clean substrate.

The principle of ‘like dissolves like’ was discovered early in human history by simple observation. In this trial-and-error process some terpenes, natural organic compounds occurring in the essential oils and oleoresins of plants (lemon, orange) and conifers (balsam, pine), were found to have solvating powers. It is very important to match the solvent character of your soil or foreign matter to the type of solvent with which you are cleaning. A given solvent will be “like” some soils and “unlike” other soils where it will not be able to dissolve and clean as well as a solvent with like properties.

**Synthetic Solvents**—Nonaqueous solvent cleaners include chlorocarbons, chlorofluorocarbons (CFCs), and hydrochlorofluorocarbons (HCFCs). Chlorocarbons are carbon-chlorine based solvents. Halocarbons are halogen-carbon compounds (chlorine, fluorine, bromine, and iodine).

The most common examples used in cleaning are carbon tetrachloride, trichlorocarbon (TCA, “trike,” or methylchloroform), and perchloroethylene (PCE, or “Perc”). Chlorofluorocarbons (CFCs) are carbon, fluorine, and chlorine based solvents. The most common example used in cleaning is CFC-113. Hydrofluorochlorocarbons (HCFCs) are modified CFCs with the addition of hydrogen. The HCFCs were developed as less hazardous replacements for CFCs.

The chlorocarbons have good cleaning properties but, unfortunately, have toxic vapors, usually with a narcotic effect. The vapors also contribute to smog formation. Chlorocarbons are volatile organic compounds (VOCs).

The chlorofluorocarbons (CFCs) are less toxic than chlorocarbons, but, unfortunately, their vapors contribute to ozone depletion in the atmosphere which can also contribute to global warming. The CFCs are ozone depleting substances (ODS)



have ozone depleting potential (ODP) and global warming potential (GWP).

Historically, halocarbon chemistry played an important role in the development of solvents and synthetic industrial solvent cleaners. Recently, it has led to the development of aqueous cleaners as a replacement for environmental reasons. Carbon tetrachloride (“carbon tet”) an important, nonflammable solvent for fats and oils, asphalt, rubber, bitumens and gums, initially used as a degreasing and cleaning agent in the dry-cleaning and textile industries—was first produced in Germany in 1839 and marketed as a grease remover. Its vapors, however, are highly toxic. Carbon tetrachloride is also a volatile organic compound (VOC). Evaporating into the atmosphere at ambient conditions, VOCs include almost all synthetic and plant-derived solvents as well as fuels. The calculation of the amount of VOC in a particular product or process is important since ozone, the primary component of smog, is affected by VOC emissions.

In the 1890s, Swarts discovered that the carbon-fluorine bond could be formed with antimony fluoride and the addition of trace quantities of pentavalent antimony, as a fluorine carrier, to form chlorofluorocarbons (CFCs) from chlorocarbons such as carbon tetrachloride. Through his work, carbon tetrachloride also became known as tetrachloromethane, the chemical precursor of CFCs. This discovery led to the development of the first commercial refrigeration systems some thirty years later.

During the following 50 years, continuous reactor processes were developed to control the degree of fluorination of the carbon molecule for the manufacture of refrigerator coolants, some of which exhibited excellent characteristics as a solvent and cleaning agent.

There are a number of carbon-derived cleaning compounds, including hydrocarbons, halocarbons, chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs), hydrofluoroether, and perfluorocarbons (PFCs). While each has its own cleaning advantages, they all have built-in environmental liabilities—CFCs, HCFCs and PFCs are believed to contribute to global warming. Manufacture of ozone-depleting compounds was phased out after a world meeting among industrial and

developing nations to restrict their use and manufacture. This agreement known as the Montreal Protocol on Substances that Deplete the Ozone Layer was signed by 24 countries, including the U.S., on September 16, 1987. Today, more than 160 countries have signed the Protocol.

In addition to the above-mentioned compounds, brominated hydrocarbons, dibromomethane (for example, methylene bromine) are also used for cleaning, although on a much smaller scale. In addition to immersion cleaning, vapor degreasers are often employed with these types of compounds in industrial cleaning. However, their mechanical action can be viewed as secondary because of their excellent solvating properties.

In an effort to continue the use of CFC-related compounds, hydrochlorofluorocarbons (HCFCs) were developed. These are generally less toxic than chlorocarbons, and have less ozone depleting potential than the CFCs. Nonetheless, the HCFCs have sufficient ozone depleting potential and global warming potential to be of concern to end users.

## SEMIAQUEOUS CLEANERS

The acute and chronic toxicological profiles of the aforementioned organic and first-alternative CFC cleaners, coupled with the negative environmental impact of second-generation HCFC substitutes, stimulated the development of new, innovative cleaning techniques and a rebirth of aqueous and semiaqueous cleaning.

Semiaqueous cleaning incorporates the principles of aqueous and organic cleaners. This is accomplished by combining a surfactant with a low-volatility hydrocarbon such as a terpene, in particular limonene and pinene (citrus or pine in origin), to form a cleaning blend. Terpenes are homocyclic hydrocarbons and have a characteristic strong odor; turpentine is an illustrative solvent that is a mixture of terpenes. Semiaqueous cleaning involves cleaning with a solvent or solvent/water mixture followed by rinsing with water as in traditional aqueous cleaning.

Unlike traditional vapor degreasing, however, cleaning with semiaqueous cleaners does not rely on boiling liquids, nor is it restricted to a constant boiling composition. In its

simplest form, semiaqueous cleaning involves using its organic components to dissolve soils and its water component to remove blend-based residues and any other water-soluble soils. Surfactants are used when the water-solubility of the solvent is limited or to improve the emulsifying properties of the cleaner.

## AQUEOUS CLEANERS

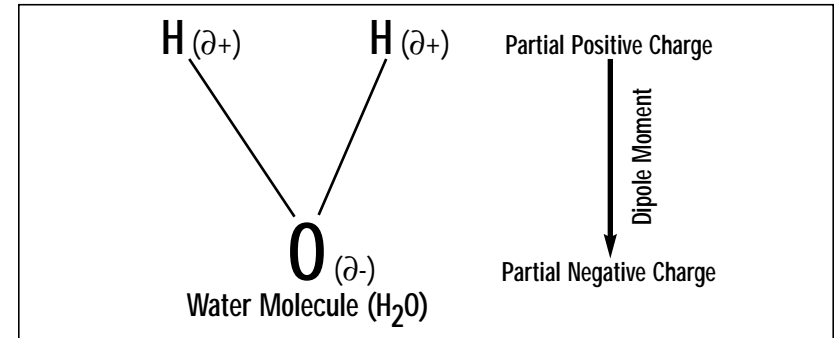
The first aqueous cleaners were soaps as discussed earlier. Detergents, sometimes referred to as synthetic soaps, were first introduced in the 1930s and were found to perform better than soaps in hard-water (mineral-laden) applications because they contained water softeners to effectively treat dissolved magnesium and calcium ions. The development of complex phosphates used to soften water following the Second World War increased the cleaning power of these detergents.

Aqueous cleaners are synthetic detergent cleaning agents used in a water solution. Water, considered by many to be the “universal solvent,” is an important component of aqueous cleaners because it dissolves many types of soils. Water—municipal tapwater, deionized or distilled water depending upon the cleaning application—also functions as a carrying medium for detergent compounds. But, while water is capable of dissolving many inorganic and some organic contaminants, not all residues dissolve readily in water. For this reason, aqueous detergent cleaners are complex mixtures specifically formulated to create greater chemical and mechanical cleaning action.

Water is a polar solvent. Being polar is the characteristic that makes it good at dissolving a wide range of polar residues, contaminants and/or soils. Water has a unique “V” shaped structure with two hydrogen atoms at the top of the “V” and an oxygen at the bottom (see figure 1A). One can think of the oxygen as being a large, dense electron rich atom. This gives the entire water molecule an overall net negative, electron-rich end at the base of the “V” (d-) and an electron-poor positive end (d+) of the molecule towards the hydrogen top of the “V.” This directional net-negative charge towards the base of the “V” is called a dipole moment. Polar molecules such as water have a dipole moment.

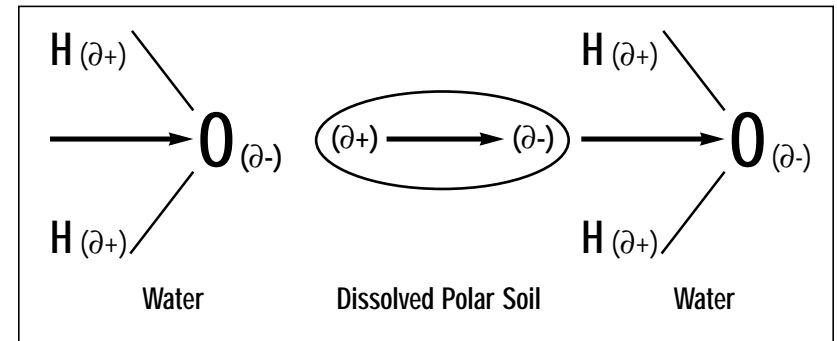
This dipole moment is important because it allows stable solutions of other dissolved polar-soil molecules to become arranged in more thermodynamically stable alternating positive and negative ends of molecules (fig. 1B).

Figure 1A



The electronegativity that attracts electrons toward Oxygen (O) and away from Hydrogen (H) gives water an electrical polarity or dipole moment

Figure 1B



Simplified three body model showing possible stabilized arrangement of polar soil molecule with water molecules with dipole moments arranged negative to positive

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## RESOURCES

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[www.cleantechcentral.com](http://www.cleantechcentral.com)  
[www.colin-houston.com](http://www.colin-houston.com)

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## CHAPTER TWO

# The Chemistry of Aqueous Cleaning

**B**efore reviewing the technologies and processes involved in aqueous cleaning, it is important to understand how aqueous cleaning works and this begins with the cleaner itself.

Aqueous cleaners are typically composed of surfactants for emulsifying, wetting, and penetrating; builders for neutralizing water hardness interference, chelating of inorganic soils, and saponification of natural oils; and additives for corrosion inhibition, anti-redeposition, and rinsing.

## KEY DEFINITIONS OF AQUEOUS-CLEANER INGREDIENTS

**Surfactant**—Short for “surface active agent,” it is an organic molecule with a hydrophobic (water-hating/oil-loving) end and a hydrophilic (water-loving) end. Surfactants are often emulsifiers, wetting agents, and dispersants (see other definitions). The most common surfactant is sodium Linear Alkylbenzene Sulfonate (called LAS for short). The alkylbenzene portion of the molecule is the hydrophobic/oleophilic end of this surfactant and the negatively charged sulfonate molecule is the hydrophilic end of the molecule. Surfactants are typically classified as anionic, nonionic, and cationic. The class of surfactant determines the class of the cleaner.

**Anionic surfactant**—This is a surfactant that has a negatively charged end of the molecule that gives it the hydrophilic part of the molecule. These negatively charged parts of the molecules are usually sulfonates, sulfates, or carboxylates, that are

usually neutralized by positively charged metal cations such as sodium or potassium. Examples include sodium alkylbenzene sulfonates, sodium stearate (a soap), and potassium alcohol sulfates. Anionic surfactants are ionic and are made up of two ions—a positively charged, usually metal, ion and a negatively charged organic ion.

**Nonionic surfactants**—These are surfactants that have no ions. They derive their polarity from having an oxygen-rich portion of the molecule at one end and a large organic molecule at the other end. The oxygen component is usually derived from short polymers of ethylene oxide or propylene oxide. Just as in water chemistry, the oxygen is a dense electron-rich atom that gives the entire molecule a partial net-negative charge which makes the whole molecule polar and able to participate in hydrogen bonding with water (as discussed in the first chapter). Examples of nonionic surfactants are alcohol ethoxylates, nonylphenoxy polyethylenoxy alcohols, and ethylene oxide/propylene oxide block copolymers.

**Cationic surfactants**—These are positively charged molecules usually derived from nitrogen compounds. They are not commonly used as cleaning agents in hard-surface cleaners because of the tendency of the cationic positively charged molecule to be attracted to hard surfaces (that usually have a net-negative charge). Many cationic surfactants have bacteriacidal or other sanitizing properties that are useful in creating disinfectants that leave a cationic disinfectant film on the surface. Cationic surfactants are usually incompatible with anionic surfactants, because they will react with the negatively charged anionic surfactant to form an insoluble or ineffective compound.

**Amphoteric surfactants**—Those surfactants that change their charge with pH. They can be anionic, nonionic, or cationic depending on pH. Usually, any one amphoteric can be any two of the three charge states.

**Dispersant**—This is a cleaner ingredient that helps disperse or suspend solid particles in solution. Dispersants include water-

soluble surfactants or water-soluble polymers (long-chain organic molecules) that are electrostatically attracted to particulates, creating a bridge between the water and the water insoluble solid particulate (in some cases even repelling the solid surface to help lift the particles into suspension).

**Emulsifiers**—These cleaner ingredients help emulsify water-insoluble oils into solution by helping to create a liquid-liquid mixture. Surfactants that use their hydrophobic (water-hating or repelling) or oleophilic (oil-loving) end of their molecule to mix with water-insoluble oils and their hydrophilic (water-loving) end to mix with water create a bridge to emulsify water-insoluble oils into solution. The specific structure of the bridge is called a micelle that can be thought of as a hollow, oil-filled round ball with a skin made of surfactants with their hydrophilic ends facing out in contact with the water solution and the hydrophobic ends facing in to the oil-filled ball. (See Figure)

**Wetting agents**—These are surfactants that lower the surface tension of water and allow the cleaning solution to wet surfaces and penetrate into, under and around soils and surface crevices. They create a bridge between the water and any hydrophobic (water-hating or repelling) surface. You can think of a wetting agent as having one end of the molecule attracted to the surface while pulling the water solution towards the otherwise water-repelling surface, allowing the water solution to be in contact with more of the surface that needs to be cleaned. You might say that wetting agents make water wetter.

**Builders**—These cleaner ingredients react with interfering calcium, magnesium, or iron ions that may be present in the water solution. They stop them from reacting with soils and other detergent ingredients to form water insoluble and difficult-to-clean calcium, magnesium, or iron salts. These metals are present to varying degrees in all water, particularly tap water. Builders are usually alkaline salts, chelating agents, and/or sequestering agents.

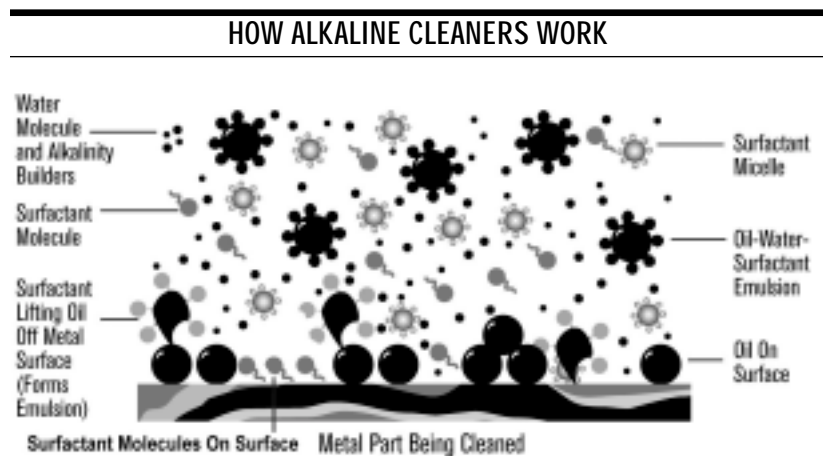
**Alkaline salt builders**—These are inorganic salts such as

sodium carbonate or sodium phosphates. They react with calcium, magnesium, or iron to form water soluble or water dispersible compounds that tie up the calcium, magnesium, and iron.

**Chelating agents**—These are negatively charged or oxygen containing molecules that react with positively charged metal ions to form a stable complex. They have multiple locations in the molecule to react with multiple positive charges that may be present on multivalent metal ions that have more than one positive charge on them. An example of a chelating agent is EDTA, ethylene diamine tetraacetic acid. EDTA has four acetic acid groups giving it a potential for four negatively charged acetates to bond with up to four positively charged sites on metal ions with multiple positive charges, such as calcium which has two (2) positive charges associated with it.

**Sequestering agents**—These are chelating agents (see above) that bind particularly tightly with metal ions and sequester or separate them from reacting with other compounds.

Detergents use both chemical and physical action to clean, which are affected in turn by temperature, time, type of mechanical action, cleaner concentration, and additives. Mechanical action is provided by immersion, spray, or ultrasonics.



Revised from *Precision Cleaning Magazine*, June 1997.

The detergents' chemical action saponifies certain oils, producing water-soluble soap material. The surfactants, used in a cleaning formulation, then work to physically reduce the surface tension of the solution, in the process emulsifying and lifting soils away from the substrate being cleaned. These surfactant molecules can be both free and aggregate forms called micelles, and their ratio is based on the type of surfactant, its concentration, and the temperature of the cleaning formulation. The surfactant lifts oils off the metal surfaces to form a suspended oil-water-surfactant emulsion which is then removed by rinsing.

Typically, immersion cleaning involves submerging parts in a bath and providing air agitation, turbulence, and mechanical brushing or ultrasonics to realize desired levels of cleanliness. In contrast, spray cleaning uses a pressurized wash stream to create even higher soil-removal rates.

Cleaning is then followed by water rinsing. In most aqueous cleaning systems, more water is used in rinsing than in cleaning. Also, rinse water must be purified by a recycling system to a higher level than the detergent solution. Rinse water also requires different separation equipment, since the rinse water is the last solution to touch the surface being cleaned.

The chemical and mechanical action involved in aqueous cleaning is actually a number of processes. These can be described as:

- **Solubilization**—a process whereby the ability of a substance to dissolve in a particular medium is increased
- **Wetting**—the process of lowering surface and interfacial tensions so that the cleaner penetrates small spaces while getting under the soil to lift it from the substrate
- **Emulsification**—the creation of an oil/water mixture by coating oil droplets with surfactant preventing them from recombining and migrating to the surface of a cleaning bath (see previous emulsifier discussion)
- **Deflocculation**—the breaking down of the soil into fine particles and dispersing them through out the cleaning medium in order prevent agglomeration
- **Sequestration**—the introduction of molecules that react with ions such as calcium, magnesium, or heavy metals, in the solution, to prevent the formation of insoluble byproducts (such as soap scum)

- **Saponification**—the alkaline hydrolysis of fat by the reaction of fatty acids with alkalis to form water-soluble soaps

Unlike organic and chlorinated solvents which rely on solvating those residues that happen to be soluble in them, aqueous cleaners may contain a number ingredients that help provide maximum cleaning effectiveness for specific and diverse types of substrates and soils. These ingredients (listed below) reduce surface tension, form emulsions, and/or suspend insoluble particles for removal in the cleaning bath:

- **Surfactants**—As previously defined earlier in the chapter (see key definitions), these are polar molecules that emulsify (create stable liquid-liquid mixtures), disperse (create stable particle-liquid mixtures), wet (allow other cleaning chemicals to contact the hard surface), and penetrate (allow other cleaning chemicals to enter into small cracks and crevices).
- **Builders**—These are inorganic salts that provide alkalinity and buffering capacity common to almost all aqueous cleaners (pH may be alkaline >7, neutral ~7, or acidic <7). Alkalinity may be provided by hydroxides, carbonates, borates, silicates, phosphates, or zeolites (crystalline hydrated aluminosilicates). Builders also soften water or help with saponification or deflocculation.
- **Emulsifiers**—These include substances that can form mixtures of liquids that would ordinarily not mix (e.g., oil and water). Emulsifiers are useful for low soil loading, but their concentration in a detergent limits bath life. Separation of soil and cleaner may be accomplished by making the emulsion unstable by lowering the pH and/or temperature. They are chemically similar to the semi-aqueous cleaners described below.
- **Saponifiers**—They are alkalis that react with fatty acids in oils to form soaps. Chemistry may be mineral (sodium or potassium) or organic-based (such as solutions of ethanol amines).
- **Solvents**—These are aqueous or organic chemistries designed to enhance the removal of oily soils by dissolving them (e.g., glycol ethers, ethylene [Butyl Cellosolve], and propylene compounds).

- **Additives**—They are chemicals that act primarily as contaminant dispersants, anti-redeposition agents, brighteners, viscosity modifiers, antifoaming agents, and corrosion inhibitors or they may have special detergency on a specific soil type. Examples include enzymes, amine compounds, and various polymers.
- **Sequestering agents**—These may be powders or liquids that combine with calcium, magnesium, and other heavy metals in hard water. They form molecules in which these ions are held securely, or sequestered, so that they can no longer react undesirably with other species in solution. Polyphosphates and polyacetates are commonly used.
- **Chelating agents**—They are employed to solubilize hard water salts so that they remain in solution. Produced in both powdered and liquid forms, they do not degrade or lose their potency at elevated temperatures, which make them ideal for aqueous cleaning. However, they can interfere with the ability of other chemicals to remove emulsified oils and dissolved metals from solution, which can lead to waste disposal problems. In addition to EDTA (ethylene diamine tetra acetates), NTA (nitrilo triacetates) are also used.
- **Corrosion inhibiting agents**—They are often added to aqueous cleaners to minimize their effect on metal substrates. They are used for cleaning at high pH and as rust inhibitors to prevent the rusting or oxidation of cleaned parts (or cleaning equipment that is not constructed of stainless steel).
- **Stabilizers**—These are added to extend the shelf life of detergent ingredients and to maintain the uniformity of detergent blends. For example, dilute cleaner solutions may have a tendency to grow microbes. The presence of biocidal additives in a formulation may be indicative of a formulation that is not concentrated (assuming the cleaner is not designed as a biocidal cleaner). In contrast, coupling agents and hydrotropes that are included in detergent formulations are indicative of highly concentrated formulations because these are used to increase the solubility and costability of various active detergent ingredients.

- **Extenders**—These are fillers which are added to detergent that do not improve detergency (and which also tend to increase the packaging and handling costs associated with the cleaner itself). For example, water may be added to a concentrated cleaner, or inert powder may be added to dilute a concentrated powder cleaner. It is occasionally necessary to add a small amount of inert powder, as process aid, to avoid caking of powdered detergent. However, one needs to be careful not to purchase a cleaner that is diluted with excess, cheap inert powder, because it does not improve detergency but does increase packaging and handling costs.

## TYPES OF AQUEOUS CLEANERS

It is important to keep in mind that a cleaner's pH value can have a direct effect on cleaning effectiveness. Technically speaking, pH is the "negative log of the hydrogen ion concentration." This means that the higher the pH, the greater the increase in hydroxide concentration and the faster hydrolysis—the breaking down of a natural fat or oil into a soap—occurs.

Aqueous cleaners are classified according to pH value as being neutral, acidic, or alkaline on a scale of zero to 14, with a pH of 7 being neutral. Thus, a pH value of less than seven is considered acidic, and higher than seven, alkaline.

Certain soils are removed more easily using an acid cleaner; others, by an alkaline one. An acidic solution with a pH of 4.5, for example, would be effective for removing metal oxides or scale prior to pretreatment or painting. And an alkaline (basic) solution with a pH of 13.5 could be formulated to remove carbonaceous soils, heat scale, rust, oil, and grease. Neutral cleaning solutions include alcohols and other water-soluble formulas, and generally contain detergents or other surfactant additives to aid in cleaning. Less foam is generally produced with the use of a neutral cleaning agent. There are also semi-aqueous cleaners which form neutral solutions upon dissolving or emulsifying in water.

The first issue in selecting a cleaner on the basis of pH (there are other factors, as we'll see in later chapters) is how fast it needs to work. Most cleaners are alkaline in nature

since hydrolysis—and the chelation and dispersing of soils—typically occurs most effectively at alkaline pH levels. However, the higher the pH the more corrosive the cleaner.

TYPE OF CLEANER	pH RANGE	SOILS REMOVED
Mineral-acid cleaner	0-2	Heavy scales
Mild acid	2-5 1/2	Inorganic salts, water, and soluble metal complexes
Neutral	5 1/2 to 8 1/2	Light oils, small particulates
Mild alkaline	8 1/2-11	Oils, particulates, films
Alkaline	11-12 1/2	Oils, fats, proteins
Corrosive alkaline	12 1/2-14	Heavy grease/soils

Alkaline cleaners work best when the soil can be hydrolyzed. Typically, natural oils and fats, fingerprints, natural greases, some types of food products, and protein residues are soils which belong in this category. The cleaning process should be enclosed to avoid exposure hazards. Workers should use personal protective equipment with handheld sprays.

Time, temperature, and agitation also play important roles in cleaning. But while maximum detergency is achieved at high temperatures with high agitation over long periods of time, the substrate must be robust since corrosion is also a factor.

As a rule of thumb, it is best to use the mildest cleaner possible.

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## RESOURCES

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[www.stepan.com](http://www.stepan.com)  
[www.pilotchemical.com](http://www.pilotchemical.com)  
[www.rhodia-ppd.com](http://www.rhodia-ppd.com)

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## CHAPTER THREE

# Aqueous-Cleaning Processes

In the past, the acronym TACT—Time, Agitation, Chemistry and Temperature—has been used for remembering the essential cleaning variables involved in aqueous cleaning processes. However, it leaves out four very important variables that must be considered for successful cleaning: Rinsing, Drying, Before-cleaning handling, and After-cleaning handling. A more comprehensive acronym that includes these eight important activities is BATH CARD:

### BATHCARD

- |                                     |                                    |
|-------------------------------------|------------------------------------|
| 1. <b>B</b> efore cleaning handling | 5. <b>C</b> leaner                 |
| 2. <b>A</b> gitation                | 6. <b>A</b> fter cleaning handling |
| 3. <b>T</b> ime                     | 7. <b>R</b> inse used              |
| 4. <b>H</b> eat                     | 8. <b>D</b> rying method           |

It is important to understand and control these interrelated cleaning variables in all critical cleaning, but particularly in highly sensitive industrial applications such as medical device manufacturing, metal surface preparation, optics assembly and electronic component manufacturing. Use the variables in BATH CARD to evaluate, diagnose and optimize your cleaning process.

### BEFORE CLEANING

How parts and substrates are handled prior to cleaning can significantly impact the difficulty, or ease, of cleaning. Soils are more difficult to remove if they are:



- Allowed to dry, set up and cross link
- Stored in a dirty environment
- Stored in a humid or corrosive environment.

As a rule, it is important to clean parts as soon as possible after they are soiled. In some instances, it makes sense to take parts directly from a manufacturing process and put them into a soak solution where they may sit for extended periods of time prior to cleaning.

Soiled parts can also be placed in protective packaging, dipped in a protective coating or immersed in oil or grease to maintain their current state and avoid increasing the cleaning burden. Clean storage conditions and proper packing by the supplier make it easier to clean parts and substrates.

## AGITATION

Soaking is a cleaning method that involves no agitation. Other cleaning methods involve some form of agitation which can be performed through manual (cloth, sponge, brush), ultrasonic, flow-through clean-in-place (for pipes, tanks and tubes), spray cleaning (a dishwasher, for example), and high-pressure spray cleaning. In general, increasing agitation means increasing cleaning effectiveness, particularly when trying to remove heavy, bulk soils.

Agitation is a factor in detergent choice. High emulsifying, high foaming cleaners are more effective for cleaning processes with low levels of agitation and longer cleaning time. These include the manual, soak and ultrasonic processes. Likewise, low foaming, high dispersing cleaners are suitable for high-agitation cleaning with short contact time as found in spray washing, parts washing and when using spray CIP systems, etc.

Presoaking generally enhances cleaning, particularly if soils are dried or baked onto the part to be cleaned. As stated above, it is always preferable, to clean as soon as possible after soiling to avoid dried or baked on soils.

Time constraints and volume of parts being cleaned affect choice of an agitation method and with it detergent. When a large number of parts must be cleaned quickly, then a fast, high-agitation method, such as spray washing, with an aggres-

sive detergent is preferable. Likewise, when cleaning fewer parts or batch-continuous quantities of smaller batches rather than the large quantities from continuous manufacturing of parts, ultrasonic soak cleaning with a milder detergent is more appropriate for the wetting and emulsifying mechanisms that work well in ultrasonics.

The cleaning methods referred to above are discussed below in greater depth:

- **Manual cleaning**—typically chosen for small-volume batch cleaning. High levels of cleanliness that can be achieved by manual cleaning. Though, much depends on the consistency of operators performing the cleaning operation. That's why, rigorous operator training and retraining should be arranged. In addition, there is a need for clearly written cleaning procedures and training procedures. It is even a good idea to go so far as to certify operators in different cleaning methods with periodic recertification.
- **Soak cleaning**—usually chosen for cleaning small volumes, of parts, when time is not of the essence. Typically a slow process, soaking is not labor intensive. Care should be taken, however, when cleaning delicate parts. Because soaking involves longer cleaning times, there more opportunity for corrosion to occur. As a result, soaking is best suited for cleaning robust parts.
- **Ultrasonic cleaning**—particularly effective on small parts with blind holes and crevices that are inaccessible by spray cleaning. This process is essentially soak cleaning enhanced by ultrasonic sound energy. It greatly accelerates the speed of cleaning and can greatly improve cleaning in small spaces or crevices. Ultrasound helps disperse and mass transfer the cleaner. It replenishes fresh cleaning solution to surfaces of parts being cleaned. Ultrasonics also accelerates corrosion, so care with substrates and cleaners with suitable inhibitors is required. Ultrasonic cleaning involves more expensive equipment and is typically suitable for larger volume batches and where a higher level of cleaning is required.
- **Clean-in-place by circulation system**—typically used for piping or small tank systems where a spray clean in

place system cannot be used. It is also an appropriate method for cleaning filtration systems in which filters cannot be accessed by spray nozzles.

- **Spray clean-in-place**—typically used in larger tank systems where the increased efficiency, achieved by using less cleaning solution, justifies the cost of the spray system. Spray cleaning of tanks provides more reliable and more complete coverage of the tank. (An immersion cleaning system may not reach the top of a tank and additional manual cleaning may be necessary.)

When choosing a detergent for tank systems, remember that a detergent that performs well for soak cleaning may not perform as well in spray cleaning. Therefore, if you anticipate scaling up a current system to a spray clean-in-place one, consider using a spray-cleaning detergent that performs adequately in soaking operations.

The choice of a cleaning machine depends both on size of batch and size of parts being cleaned. As batch size increases and ultrasonic machine may no longer be efficient. It often makes sense to choose some form of cabinet, under-counter or floor standing washer.

For very high-volume parts washing, a conveyor cleaning system is a suitable option. Parts, placed on a conveyor, are cleaned using spray nozzles as they pass through the system.

Spray cleaning systems are very good for parts and surfaces that are readily accessible. They are not as effective when there are blind holes and small crevices. When cleaning high volumes of parts, where it makes sense to use spray cleaning, investigate spray under immersion.

For cleaning very, large parts, for example, vehicles or very large assemblies (where an operator can physically move around the part), it makes sense to use a power spray wand or handheld pressure spray device to clean part exteriors.

## TIME

In general, the longer the cleaning time, the more thorough the cleaning will be. Many cleaning mechanisms such as emulsifying, dissolving, suspending, and penetrating are time-dependent.

Cleaning time can be accelerated by increased agitation and temperature and by the use of a more aggressive detergent. If none of these variables can be changed—perhaps, because the substrate is too delicate or the proper equipment, unavailable—be prepared for longer cleaning times. While manual cleaning may take minutes: and spray cleaning, seconds: soaking may take hours, possibly overnight, to achieve comparable cleanliness.

There are some instances when long cleaning times may promote substrate corrosion, weakening, or swelling. The optimum cleaning time depends on the specific substrate, temperature, cleaning method, and detergent.

## HEAT

In general, higher-temperature cleaning solutions result in better cleaning. In practice, there is typically an optimum temperature for a given combination of cleaning variables. Many soak, manual, and ultrasonic cleaning methods work best, for example, at 50°C to 55°C. Many spray washing techniques work best at 60°C to 70°C. Waxy or oily soils are more easily cleaned at higher temperatures that are above the melting point of the wax. Particulate soils tend to be more easily removed at slightly lower temperatures where dispersions are not broken down. As a general rule, many cleaning mechanisms follow first order reaction kinetics whereby the cleaning speed doubles with every increase of 10 deg C. Of course, you do not want to use a temperature so high that it damages your substrate.

## CLEANER

The cleaner or detergent used should match to the desired cleaning method, the surface and types of soils being cleaned. For instance, a low-foaming detergent should be used for spray or machine cleaning, a good anti-redeposition detergent for soak and ultrasonic cleaning and a high emulsifying and wetting detergent for manual cleaning. The detergent, temperature, and degree of agitation should be strong enough to remove the soil to the desired level of cleanliness without harming the substrate being cleaned.

It is very important to choose a low-foaming or non-foaming detergent when cleaning in or with a machine that relies on spraying for mechanical agitation. Foam is caused by agitation at an air/solution interface when a foaming agent is present. It may build up and spill over from the machine creating a mess. It will also build up on the substrate and interfere with the mechanical cleaning energy of the spray. Finally, foam may get sucked into recirculation pipes causing problems with pumps in the machine.

Surfactants are often foaming agents. Most aqueous cleaners have surfactants in them. There are three basic types of aqueous cleaners that are suitable for machine washing: cleaners with no surfactant, cleaners with non-foaming surfactants, and cleaners with low or controlled-foam surfactants. There are important differences among these types of cleaners. Remember that foam forms in the presence of an agitated foaming agent where air is present. Many soils are foaming agents. In particular, soap formed by saponifiers, in electronic solder flux cleaning, is a foaming agent. A surfactant-free cleaner will not protect against foam formed by soils. Clean only non-foaming soils with surfactant-free cleaners. A non-foaming cleaner usually has a nonionic polymer surfactant. These surfactants come out of solution at elevated temperatures and form an oil slick on top of the solution. The oil slick is a barrier to air contact preventing foam from forming or being stable. These cleaners will suppress foam from soils. They only work properly if the temperature is hot enough. Find out the minimum temperature at which to use these cleaners.

Finally, there are controlled foam cleaners which usually have limited foam suppressing capabilities. The surfactants themselves do not foam excessively, but they are not able to control much foam resulting from soils.

It is critical that the detergent be scientifically formulated to clean effectively and to rinse away without leaving interfering residues. A scientifically formulated detergent will typically have appropriate surfactant ingredients and non-depositing rinse-aids. The surfactant should have sufficient surface tension lowering properties to assist in proper rinsing. A surface tension below 35 dynes per centimeter for the cleaning solu-

tion, as used, is often sufficient for good rinsing. Non-depositing rinse-aids can help complete a formulation to meet the rinsing requirements of critical cleaning.

In addition, detergents should be manufactured according to appropriate quality-control procedures. In many critical-cleaning applications it is desirable to choose a detergent with a lot number tracking system and with certificates of analysis available from the manufacturer. These certificates document each lot of detergent to assure consistency and quality control and to prevent cleaning failure from inconsistent manufacturing or unannounced formulation changes. It is also desirable to choose a detergent from a manufacturer who maintains quality control of raw materials and who retains samples of each detergent lot to be able to respond to concerns about a particular batch.

The detergent should be widely available and economical to use (for optimum economy, a concentrated detergent is typically used at 1:100 to 2:100 dilutions). The detergent concentrate should be diluted according to the manufacturer's instructions. Typically, warm (about 50°C) or hot (about 60°C) water is used. Ambient temperature water may be acceptable, especially for presoaking. For difficult soils, very hot water should be used (over 65°C), and the recommended detergent concentration doubled.

### **Chemistry Bath-life extension and control**

To avoid potential for cross contamination, only freshly made up cleaning solutions should be used for the highest levels of critical cleaning. For industrial critical cleaning applications, high levels of cleaning can also be achieved with extended bath life. In general, a pH change of 1 unit towards neutral indicates an exhausted cleaning solution. Bath life can be extended by physical filtration of particulates, cooling and settling of sludge and skimming of oils. Bath life can also be extended by adding one half as much detergent, of the initial load, after partially depleting the cleaning life of the bath. With frequent daily use, detergent solutions can rarely be used longer than a week even with these bath life extension techniques. Conductivity, pH and % solids, by refractometer, can be used to control bath detergent concentration.

Free alkalinity titration can be used to control bath life of alkaline cleaners where the soil being cleaned depletes free alkalinity—as is often the case with oily soils. The process:

- Titrate a new solution to determine free alkalinity.
- Titrate the used solution to determine the percent drop in free alkalinity.
- Add more detergent to the bath to bring the free alkalinity back to the level of the new solution. (For example if the initial solution is made up with 100 ml of cleaner concentrate and a 25% drop in free alkalinity is observed, try adding 25 ml of cleaner concentrate to recharge your solution.)

Perform a new free-alkalinity titration to confirm the recharge the first few times this recharging method is used. This is to ensure that the detergent being used is linear with respect to free alkalinity depletion. This form of bath life extension cannot run indefinitely, sludge will eventually form. Fresh solutions must be made up periodically.

Bath lives can also be extended using conductivity. Most cleaners contain conductive salts which can be detected using conductivity. Once the conductivity response of the detergent is determined, the depletion of those conductive salts can be measured.

Many cleaner manufacturers can supply the curves of detergent concentration versus conductivity. By adapting these curves to your conditions and measuring the conductivity, detergent depletion and dilution can be determined. This determination can be used to figure out how much detergent to add to the cleaning solution to restore cleaning performance. Typically, this kind of measure the bath and recharge with detergent process can be done 2-3 times before a new bath is needed.

Keep in mind that, the bath will ultimately reach a point where it forms sludge (or where some other failure occurs). At that point, the bath must be dumped and a complete batch of new cleaner made up. The time to dump the bath, and start over, is generally determined using some sort of cleanliness measurement and defined in terms of number of parts cleaned or time period of bath use. Conductivity does not typically

detect the point of cleaning failure, but only detects concentration of cleaner present, whether depleted or not. The following table gives specific examples of concentration vs. conductivity for several Alconox-brand cleaners. Use this data to derive the concentration of detergent from measured conductivity. Note that, conductivity is temperature dependent. Detergent solutions do not have the same slope as many default settings on temperature-correcting conductivity meters. For best results, allow hot detergent solutions to cool to a consistent temperature for comparison.

**TABLE CONDUCTIVITY (Ms) VS CONCENTRATION OF ALCONOX, INC CLEANERS AT 22 DEG C**

Concentration	Alconox	Alcojet	Terg-a-zyme	Alcotabs	Liquinox	Citranox	Detergent 8 (uS)	Detojet
0.125%	1.136	1.354	1.184	1.011	0.108	0.195	21.00	0.614
0.250%	2.08	2.51	2.21	1.912	0.213	0.327	29.70	1.275
0.500%	3.83	4.6	4.1	3.48	0.402	0.475	41.60	2.58
1.000%	6.99	8.34	7.51	6.36	0.747	0.682	63.30	5.05
2.000%	12.71	15.02	13.65	11.55	1.38	0.987	87.60	9.68
4.000%	22.6	26.6	24.3	20.8	2.63	1.47	106.40	18.17

### **Chemistry, cleaning and corrosion inhibition**

Corrosion, during cleaning, is accelerated by the same variables that accelerate cleaning: heat, aggressive chemicals, time, and agitation. To reduce metal corrosion (in approximate order of importance) use less heat, lower pH detergent, shorter cleaning time and less agitation.

In general, use the mildest pH detergent to limit metal corrosion. Higher pH detergents may have metasilicate corrosion inhibitors making them suitable for cleaning soft metals such as aluminum. In general, to reduce plastic corrosion, use less aggressive cleaners, with less solvent or surfactant character; lower concentrations of cleaners; lower cleaning temperatures; less contact time; and finally, less agitation.

After aqueous cleaning, metal corrosion can occur during rinsing and drying. Corrosion inhibitors can be added to rinse water provided that inhibitor residue does not interfere with clean surfaces. Using hot rinse water (to keep clean surfaces hot) and rapid heat or vacuum drying, speeds drying and minimizes metal corrosion. Forced air drying, drying with a hot oxygen-free gas such as nitrogen and using air knives, that physically remove rinse water, can also minimize corrosion.

When rinsing mild steel with hot water and drying with hot air, “flash rusting” can occur. The corrosion actually occurs during rinsing as a result of dissolved oxygen in the rinse water. In some instances, lowering the water temperature or drying temperature can help avoid corrosion. For instance, in a case where flash rusting on mild steel had been occurring, the rusting was avoided by lowering the temperature of the rinse water from 150°F to 120°F maintaining an ambient air drying system. Flash rusting can also be avoided by using a solvent, such as isopropyl alcohol, to rinse with rather than water. Adding corrosion inhibitors, to rinse water, can also prevent corrosion but the corrosion inhibitor may leave residue during rinsing.

## AFTER CLEANING

How parts are handled and stored, after cleaning, determines whether cleanliness is maintained. Depending on the setting, it may be necessary to make special provisions to establish a clean storage place or storage conditions. It may also be helpful, if not necessary, to determine how long a surface or part will stay clean while stored to decide whether it needs to be re-cleaned prior to use. Cleanliness testing can be done to monitor a surface and determine how long it will remain suitably clean. Humid after-cleaning storage conditions can result in corrosion or condensation that promotes microbial contamination. Obviously a dirty, after-cleaning environment can recontaminate surfaces. Cleanliness can be maintained by as elaborate a process as sterilizing and using sterile packaging, to as simple a process as putting a clean tarp over a piece of equipment that has just been cleaned.

## RINSE

With aqueous cleaning, the last thing to come into contact with the cleaned surface is the rinse water. A thorough rinse will remove soils which have been cleaned from the surface as well as detergent residue. Rinsing is where much of the actual removal of residues from the vicinity of the surface occurs. After the residue/detergent mixture is rinsed away, any conta-

minants, present in the rinse water, may be deposited on the surface when rinse water is evaporated. For many applications, it is possible to rinse with tap water and then do a final purified water rinse to remove tap water residues. For higher level medical device, semiconductor, and electronics cleaning, all rinses should be done using purified water. Rinsing is primarily a mass displacement mechanism and should involve exchanges of water. This is why a running water rinse is typically the most effective rinse.

With soak or ultrasonically agitated rinsing, it is desirable to have two counter-flow cascade rinse tanks dripping “over the tank” to reduce dragout. In all cases, running water or an otherwise agitated rinse is better than a static soak-tank rinse. Higher levels of cleaning may require the exclusive use of deionized or distilled water and in some cases more than three times the volume of rinse water.

In most clean-room, electronic-component and circuit-board cleaning, deionized water is preferred over either tap or distilled water. There is less potential for metallic cation deposition on sensitive electronic components, leaving conductive residues. On metal parts, the use of deionized rinse water reduces the likelihood of depositing calcium, magnesium, or other water spotting salts. For medical device rinsing, distilled or reverse-osmosis grade water is typically used because it contains fewer organic contaminants.

## DRYING

Drying can be done by physically removal of rinse water or by evaporation. Physically removal by wiping, blowing, centrifuging, drying fluids, absorption, or other physical techniques will eliminate the rinse water before it has a chance to evaporate. Such methods prevent precipitating out of any salts or impurities that could form water spots. Water removing drying methods also minimize the risk of corrosion occurring during drying.

Evaporation methods such as air drying, heat drying, and vacuum drying can deposit nonvolatile impurities present in the rinse water and cause water spots. Although vacuum drying does evaporate water and can lead to deposits, in many

cases the deposits themselves evaporate under vacuum drying conditions. Drying can affect residues and corrosion because impurities from rinse water can be deposited during evaporation. Water, particularly high-purity rinse water, can be corrosive to metal substrates during heated and air drying. Physical removal of rinse water, various drying techniques and the addition of corrosion inhibitors (with tolerance for inhibitor residue), to the rinse water, can help minimize such corrosion.

## CONCLUSION

By choosing an appropriate cleaning agitation method, using the right rinsing and drying process, then varying the cleaner, concentration, heat, and time, an optimized aqueous-cleaning system can be achieved. To sustain successful cleaning, control before, and after, cleaning are important considerations. If you think about the variables in BATH CARD (before, agitation, time, heat, chemistry, after, rinse, dry) while evaluating your cleaning process, you will be more successful at diagnosing problems and optimizing your process.

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## RESOURCES

[www.alconox.com](http://www.alconox.com)  
[www.cleansolutions.org](http://www.cleansolutions.org)  
[www.corrosionsource.com](http://www.corrosionsource.com)  
[www.clean.rti.org](http://www.clean.rti.org)

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## CHAPTER FOUR

# Selecting an Aqueous-Cleaning Detergent

The major requirement in the critical cleaning of electronic parts, assemblies, precision parts, and metal surfaces is the absence of residues that interfere with further use or processing of the cleaned surfaces. The cleaning method should be noncorrosive to the component and the detergent chosen should exhibit exceptional free-rinsing qualities.

Critical cleaning requires careful selection of cleaning chemistry and methods to ensure adequate performance without sacrificing either worker safety or benign environmental impact. Current solvent cleaners may have ozone-depleting potential or Clean-Air-Act-Amendment-regulated volatile organic compounds (VOCs). Current corrosive mineral acid or caustic cleaners may present worker exposure hazards and environmental disposal problems. The use of appropriate aqueous cleaners can replace the use of volatile organic and ozone depleting compounds for cleaning. In addition, suitable aqueous cleaners can be milder and easier to dispose of than mineral acid or caustic cleaners.

In practice, it is important to be able to choose from a range of detergents to find one that performs well with the cleaning method and is suitable for the soils and surfaces need to be cleaned. (See Table 4A) Key considerations include:

- **Type of substrate**—A substrate, the surface to be cleaned may be metal (ferrous/nonferrous), glass, plastic,

rubber. Whatever it is, it will affect your choice of detergent. For example, substrates such as magnesium, aluminum, and similar soft metals may be attacked by certain types of chemicals. Stainless steel alloys, on the other hand, often have a high resistance to both acids and alkalies.

- **Type of soil**—What type of soil are you trying to remove—heavy or light, organic or inorganic, oil or particulate matter—this, is perhaps the single most important question to ask when you are selecting an aqueous detergent. Heavy soils typically call for heavy-duty, aggressive detergents, or cleaners, with high concentrations of cleaning ingredients. Highly dispersing cleaners, able to remove bulk quantities of soil without having to react chemically with each individual molecule of soil best suited for cleaning heavy soils.

Light soils require matching detergents. Assume that you are beginning with a surface that is nearly clean. In order to clean this surface critically clean, it is best to identify the type of soil. For example, many organic soils do not dissolve easily in water. It is best to use a highly emulsifying cleaner to clean these oily soils. An inorganic soil again may or may not be water soluble. If it is not water soluble, use a detergent that has a strong chelating agent. Another alternative is to enhance solubility by using an acid cleaner (Acid solubilization mechanisms are discussed in, Chapter Two.) Oils are often effectively cleaned by the same types of cleaners used to remove organic soils. Silicon oils, found in such things as mold release agents, are a special subset of oils that are very difficult to remove. They require a very highly emulsifying cleaner and usually very high temperature.

Finally, particulate soils are best removed using dispersant cleaners that lift them into solution to form suspensions. Very small particulates, for example submicron particulates, need very high wetting, low surface tension cleaners that can lower the distance between surface and solution to submicron increments allowing the cleaning solution to access the submicron particulates when agitation is applied.

- **Part complexity**—Are there severe undercuts, blind holes, or numerous part cavities? If so, higher-powered wetting detergents with low surface tension may be required.
- **Level of cleanliness required**—If the part being cleaned or the manufacturing process does not require exceptionally high technical specifications for cleanliness, harsh, toxic cleaning agents can often be avoided.
- **Manufacturing process**—For example, if a part arrives wet at the cleaning station, an aqueous chemistry may be best.
- **Cleaning efficiency**—As a rule, cleaning efficiency increases with time, temperature, and agitation. Though, each of these factors may affect other important considerations such as foaming, costs, health, or safety.
- **Environmental considerations**—The environmental impact of cleaning operations can often be reduced by selecting the most appropriate aqueous cleaning agent, and an appropriate cleaning and/or recycling system.

TABLE 4A DETERGENT TYPE SELECTION GUIDE

Application Key Concerns	Surface or Soil Cleaned	How Do You Clean?	Recommended Detergent
Metalworking, Precision Manufacturing, and Optics Clean parts, avoid volatile solvents, strong acids, and other hazardous chemicals.	Glass, ceramic, porcelain, stainless steel, plastic, rubber. Oils, chemicals, particulates.	Manual, Ultrasonic, Soak Machine washer, power wash	Mild alkaline Low-foam alkaline
	Aluminum, brass, copper, and other soft metal parts. Oils, chemicals, particulates (acid for oxides, salts, buffing compound).	Manual, Ultrasonic, Soak Parts washer, power wash	Milk alkaline or mild acid Alkaline or acid low-foam
	Inorganics, metallic complexes, trace metals and oxides, scale, salts, metal brightening.	Manual, Ultrasonic, Soak Parts washer, power wash	Mild acid Low-foam mild acid
	Silicone oils, mold-release agents, buffing compounds.	Manual, Ultrasonic, Soak Parts washer, pressure spray	Milk alkaline Low-foam alkaline
	Delicate substrates/neutral for waste.	Manual, Ultrasonic, Soak Machine wash, pressure spray	Neutral pH
Electronics Avoid conductive residues, avoid CFCs, pass cleaning criteria.	Circuit boards, assemblies, screens, parts, conductive residues, resins, rosins, fluxes, particulates, salts.	Manual, Ultrasonic, Soak Machine washer, power spray board and screen washers	Ion-free alkaline
	Ceramic insulators and components.	Manual, Ultrasonic, Soak Parts washers	Milk alkaline Low-foam alkaline

## DETERGENT SELECTION

Today's aqueous critical-cleaning detergents are blended for specific applications—substrate, degree of soil load, and cleaning process—these, are all important considerations when selecting a detergent. Here are a few questions to ask about a detergent brand to ensure that it meets your specific cleaning needs:

- 1. Does it have good detergency on the types of soils that you need to remove?** A broad range of organic and inorganic soils are readily removed by mild-alkaline cleaners that contain a blend of surfactants and sequestering agents. Metallic and inorganic soils are often readily solubilized by acid cleaners. Proteinaceous soils are effectively digested by protease enzyme cleaners.
- 2. Is it free-rinsing? Will it rinse away without leaving interfering detergent residue?** A properly formulated detergent will contain rinse aids to help the rinse water remove the detergent and soil solution. Rinsing is a critical part of high-performance cleaning. The detergent usually loosens all the soil from the surface and then the rinse water sweeps it away. Use a nondepositing nonionic rinse aid. Many rinse aids are cationic positively charged compounds that are attracted to a surface that repel the water; this can leave a surface covered with the water repelling rinse aid.
- 3. Is the detergent recommended for the desired cleaning method?** Use low foam cleaners for high agitation cleaning (pressure spray wash, dishwasher, etc.). Use high foam cleaners for immersion or soaking (manual, ultrasonic, etc.).
- 4. How hazardous is it?** For example, is it highly alkaline or acidic, presenting a personal health hazard? Is it corrosive? Does it present a reactivity hazard with soils? Is it a flammable or volatile solvent? These considerations can be evaluated by reviewing a Material Safety Data Sheet for the agent. Preferably, it should not contain any hazardous ingredients listed on the OSHA standard and Hazardous Substance List 29CFR 1910 subpart Z.

- 5. Can it be disposed of easily?** Any detergent chosen should be readily disposable and biodegradable, containing no RCRA Hazard Classification or EPA Priority
- 6. Is it environmentally friendly?** Considerations include ozone depletion potential and volatile organic compound (VOC) content regulated by the Clean Air Act Amendments. Approval under anticipated future restrictions should be weighed as well.
- 7. How economical is it?** The detergent should be widely available and affordable. For optimal economy, a concentrated detergent is typically used at 1:100 dilutions.

In choosing an appropriate detergent, one must consider the equipment being cleaned, the cleaning method, the degree of cleanliness and residue removal that are necessary and the performance of the detergent. Key questions to ask about selecting a cleaner are:

- **Does it have fillers?** There are a number of ways to tell whether the powder or liquid brand you're considering contains excess fillers or is optimally concentrated.

—**What are the ingredients?**

*Powders:* When selecting a powdered brand, look at the label, technical bulletins, and MSDS to see if it contains any sodium chloride or sodium sulfate compounds which do not perform a useful cleaning function but merely add to volume and weight (and shipping costs).

*Liquids:* With liquid detergents, the most common filler is water. It is important, however, that no more water is used than necessary to ensure a good solution, maintain stability, and prolong shelf life.

—**What is the concentration?**

*Powders:* It is rare that a detergent will require more than a 1 percent solution of detergent to water (1:100) for good detergency. For long bath life, in some cases higher concentrations up to 3 or 4 percent are acceptable.

*Liquids:* Typically, an alkaline cleaner will not require a dilution greater than one percent (1:100). Whereas, a semiaqueous or solvent-containing cleaner may require



a dilution of two percent (2:100) or more. Again, for long bath life, higher concentrations are acceptable.

- **What are the operating costs?** Operating costs for aqueous cleaners are generally low since these cleaners are usually concentrated—typically using only one to five percent of cleaner solution to water. In addition, aqueous cleaning baths last a relatively long time without recycling.

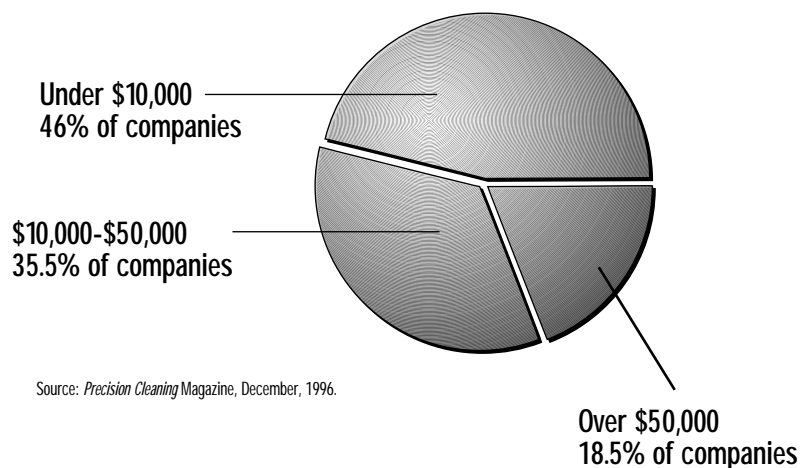
Strong acid cleaners generally require constant system maintenance since their aggressive chemistry can attack tank walls, pump components, and other system parts as well as the materials to be cleaned. (Inhibitors can be used to reduce such attack.) Another disadvantage of strong acid cleaners stems from soil loading—particularly metal loading—which requires frequent decanting and bath dumping, leading to relatively high operating costs compared with alkaline cleaners.

In contrast, alkaline cleaners are often more economical compared to acid chemistries, because they do not cause excessive maintenance problems.

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#### MONEY SPENT ON CLEANING AGENTS PER YEAR

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Source: *Precision Cleaning Magazine*, December, 1996.

## HEALTH/SAFETY CONSIDERATIONS

Human health and safety considerations include detergent toxicity, corrosivity, reactivity, and flammability. These considerations can be evaluated by reviewing a Material Safety Data Sheet for the solvent, chemical, or detergent with which you intend to clean. The detergent(s) you choose for your application preferably should:

- be formulated to minimize health-safety concerns while still offering outstanding cleaning performance
- not contain any hazardous ingredients listed on the OSHA standard and Hazardous Substance List 29CFR 1910 subpart Z
- not have flash points or stability hazards.

Many detergents strong enough to remove fingerprints, can remove oils from skin and, therefore, have the potential to dry out skin and cause “dishpan hands.” This is especially true of detergents designed for machine spray washing which, in order to perform in the limited contact time afforded during spray cleaning, are considered to be aggressive cleaners. Protective neoprene, butyl, rubber, or vinyl gloves are recommended for any extensive manual cleaning operation. In addition, many detergents are potential eye irritants, and should not be used without eye protection. See Chapter Eleven, “Environmental Health and Safety Considerations,” for further discussion.

## ENVIRONMENTAL CONSIDERATIONS

Environmental considerations include concern over volatile solvents with ozone-depleting potential and volatile-organic compound content that is regulated by The Clean Air Act Amendments. Any detergent chosen should be biodegradable and readily disposable, and contain no RCRA Hazard Classification or EPA Priority Pollutants.

Surfactants are not generally viewed as a menace to the environment. Nonetheless, their impact on the environment often receives as much attention as their technical properties and economic aspects. One reason may be that the mental image most people have of foaming streams and rivers, formed over three decades ago, has not faded entirely. This

foam resulted from non or poorly biodegradable surfactants which are no longer used in modern aqueous cleaner formulations.

Then too, public environmental awareness has increased markedly in recent years. Some might say that, environmentalism has transcended its position as a mere social attitude to become a moral imperative. Many of us want to “do the right thing,” environmentally speaking. To this end, regulations are enacted and new products designed and marketed. In the age of environmental marketing and awareness, we form perceptions regarding effects of new products on the environment, often, without complete scientific evidence. More comprehensive consideration of the total cost of environmentally negative practices, can lead to a realization that the most environmental choice can also be the best choice from an economic standpoint. When sustainable, environmental practices and choices of cleaning agents and cleaning techniques are integrated into normal practices without having to be specially labeled as environmental practices, but rather as best practices, they will be most successful.

Both the issues of health and environmental safety are important and extremely complex. Again, for a more complete description of health, safety and environmental issues, see Chapter Eleven.

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## REFERENCES

Aqueous Cleaning Chemistries, *Precision Cleaning*, December 1996, p. 22.  
Selecting An Aqueous Cleaner by Malcolm McLaughlin, *Precision Cleaning '97 Proceedings*.

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## RESOURCES

[www.alconox.com](http://www.alconox.com)  
[www.cleantechcentral.com](http://www.cleantechcentral.com)  
[www.clean.rti.org](http://www.clean.rti.org)  
[www.cleanersolutions.org](http://www.cleanersolutions.org)

# Testing and Selecting A Detergent and Cleaning System

Testing and selecting an aqueous cleaning system involves a seven-step process:

1. **Identify the key reason** you are developing the system.
2. **Select an evaluation method** to determine whether key cleaning criteria are satisfied.
3. **Select a test cleaning system** that includes a cleaning method, rinse method, and drying method.
4. **Select a test substrate** for cleaning.
5. **Select a test soil and method** for applying the test soil to the test substrate.
6. **Select an aqueous cleaner** for evaluation.
7. **Perform tests** and optimize your selected system.

## IDENTIFY REASONS FOR CHANGING CLEANING SYSTEMS

It is important to identify the key reasons for a new system so that the selection process satisfies all of them. The following table outlines some of the reasons for setting up new systems and the key considerations for each.

**TABLE 5A REASONS FOR NEW CLEANING SYSTEMS AND THEIR CORRESPONDING CONSIDERATIONS**

Reason	Key Considerations
Waste treatment concerns	Estimate quantity and characteristics of discharge, reporting status, hazards, permits needed
Air pollution concerns	Estimate quantity and characteristics of volatile solvents, current and expected regulatory status
Worker safety	Review equipment design and chemical characteristics, flammability, corrosivity, toxicity, need for protective devices, ventilation, thresholds (TLVs), worker training needed
Improved detergency	Review equipment design, rinsing and drying procedures, and cleaner chemical characteristics to see that they fit the type of soil and substrate being cleaned
Improved cleaning speed	Review temperature, agitation, chemistry, and drying conditions
Lower cost	Review recurring costs of chemistry, waste treatment, disposal, safety, regulatory compliance, maintenance, cleaning time labor, utilities, and capital costs
New process	Prioritize and evaluate all of the above, use of existing equipment may be desirable

**Organizational considerations**—Having identified the surface and contaminants to be cleaned, as well as, the reasons for changing to a new process, we must next consider the organizational implications of the new cleaning system. In short, who and what will be affected by the system?

It is important to consider production personnel, supervisors, engineers and members of environmental compliance, purchasing, marketing, public relations, and quality control departments. It is helpful to identify key benefits to each affected group in a manufacturing organization when a new cleaning process is to be adopted. Forming a team of influential representatives from each group, will facilitate the implementation of the new process and enhance the likelihood of its ultimate success.

**Information sources**—In order to help identify options and determine which systems will work best for you, you may wish to consult some of the following resources. These will help narrow your search for optimal cleaning systems and chemistries.

Look for information that addresses your reasons for cleaning and corresponding key considerations.

**TABLE 5B**

Internet	
Alconox detergent selection and use procedures	(www.alconox.com)
CleanTech Central	(www.cleantechcentral.com)
Toxic Use Reduction Institute	(www.cleaningsolutions.org)
Research Triangle Institute	(www.clean.rti.org)
US EPA	(www.epa.gov)
Pollution Prevention Gems	(turi.uml.edu/P2GEMS/)
Finishing	(www.metalfinishing.com)
Waste Reduction	(www.owr.ehnr.state.nc.us/ref/00023.htm)
Environment Canada	(www.ec.gc.ca)
Publications	
<i>Cleantech</i>	(Witter Publishing, 84 Park Ave, Flemington, NJ 08822) 908-788-0343 www.cleantechcentral.com
<i>A2C2</i>	(62 Route 101A, Suite 3, Amherst, NH 03031)
<i>Alconox Guide to Critical Cleaning</i>	(Alconox, Inc. 30 Glenn St., White Plains, NY 10603)
<i>Technical Information Reports TIR 12, TIR 30</i>	(Association for the Advancement of Medical Instrumentation - AAMI, 1110 North Glebe Road, Suite 220, Arlington, VA 22201) 800 332-2264 www.aami.org
<i>NSF White Book Non-food Compounds</i>	(NSF Int'l., 789 N. Dixboro Rd., Ann Arbor, MI 48113) 734-769-8010 www.nsf.org
Conferences	
Cleantech	(National Manufacturing Week, Reed Exhibitions, 383 Main Avenue, Norwalk, CT 06851) 800-840-0678 www.cleantechexpo.com

## SELECT AN EVALUATION METHOD

Once the key reasons for implementing a new cleaning system are identified, methods for evaluating the success of the system must be found. Review available literature on the cleaner being considered for health, safety, and environmental concerns.

Cleaning performance must also be evaluated through test cleaning. First, determine a baseline level of cleanliness and a way of measuring that baseline. (See Chapter Eight for methods to measure cleanliness.) Initially, visual inspection is often sufficient. A relatively simple gravimetric analysis involves weighing a clean substrate before soiling, after soiling, and after cleaning to determine percent soil removal. It is an effective measure of cleaning performance assuming the substrate is impervious to the cleaner. Other reflective analytical techniques require special equipment. Examples include: Optically Stimulated Electron Emission (OSEE) as well as Grazing Angle Fourier Transform Infrared Spectroscopy (FTIR).

Measurement of contact-angle of deionized water on a flat surface is another method of determining cleanliness. In addition, there are a variety of methods that involve extracting soils from the surface and then analyzing the extracts. As a rule of thumb, use the simplest method that will provide suitably sensitive results.

## SELECTING THE TEST CLEANING SYSTEM

In an ideal situation, testing a cleaning system would be done full-scale using actual dirty surfaces. In practice, this is often impossible. Accordingly, a small, bench-scale system which mimics the full-scale system must often be created.

In mimicking the actual cleaning conditions for the process cleaning method, a rinsing and a drying method must be considered. In evaluating a cleaner, it is particularly important to mimic the time, temperature, and agitation that will be available in the scaled-up cleaning process. The following table outlines some mistakes when evaluating a cleaner using a benchtop cleaning system.

TABLE 5C MISTAKES TO AVOID IN EVALUATING A CLEANER AS PART OF CLEANING SYSTEM DEVELOPMENT

Mistake	Result	Correction
Use immersion in small tanks or beakers to test cleaners that will be used in spray cleaning environment	A high emulsifying gentler cleaner will work best, but will fail in the spray agitation system	Use a Water Pik <sup>®</sup> , circulated or the spray system poured cleaning solutions to mimic spray cleaning
Use a higher temperature than will be available in scale-up	A milder cleaner will give adequate cleaning that fails at lower temp	Match temperatures
Clean for a longer time than will be practical when you scale-up	A milder cleaner will give adequate cleaning that fails in shorter time	Only use available cleaning times
Use flat substrates when small crevices and blind holes will be present in scale-up	A system with inadequate agitation will work on flat surfaces that fails on crevices	Use a substrate to mimic the scale-up surface—perhaps take flat plates pressed together
Use a soil that does not represent the real soil	The wrong cleaner may be chosen	Try to use similar soils for testing

When evaluating a cleaner, it is tempting to put the cleaner in a tank or beaker and add some of the dirty parts to determine whether soaking alone will achieve a modest amount of cleaning. (Sometimes people add heat and agitation to enhance cleaning.) This is an acceptable bench test only when developing an immersion-cleaning system. Problems often occur with this approach when the ultimate intent is to use a spray washer or mechanical washer in the scaled-up process. The cleaning mechanisms involved in immersion cleaning can be very different from those involved in spray cleaning. A system that cleans by soaking in a beaker may not work in a spray washing machine.

Effective immersion cleaners rely on kinetically slower mechanisms such as emulsifying, enzymatic hydrolyzing, and dissolving. In contrast, cleaners effective in high-agitation spraying systems, rely on faster cleaning mechanisms such as

acid or alkaline hydrolysis, wetting, penetrating, and dispersing. Spray cleaners must be more aggressive and faster acting since they have but a fraction of a second to do their cleaning before the next droplet of spray sweeps them from the surface. Immersion cleaners may have minutes or hours of contact time.

A cleaner that performs only marginally in an immersion cleaning environment, may perform extremely well in a spray-washer. The reverse is also possible and quite likely.

In particular, high-foaming cleaners that work very well in immersion do not perform well in enclosed spray cabinet washers. There, the foam can create a barrier to the mechanical energy of the spray. In addition, the foam may burst the seals of the cabinet and, possibly, cause cavitation in the circulating pumps.

There is a subtle difference among spray cleaning systems. There are two main types of spray agitation: a high volume/low pressure (laminar flow) method, and a low volume/high pressure (turbulent flow) method. The laminar flow method involves spraying a high volume of cleaning solution over the surface of a substrate, resulting in a flood of solution sheeting or running down the surface to be cleaned. This results in near laminar flow at the surface with a smaller boundary layer that gets some agitation closer to the surface to allow better very small particle and thin film cleaning in the 0.1 to 5 micron range of size or thickness. Larger particles and thicker films are better cleaner by turbulent flow.

In low flow/high pressure turbulent spray washing, the cleaning solution bounces off surfaces with less cascading and sheeting action. Low foaming cleaners are required. These systems do better with heavy soil and large particle removal.

In an effort to shorten cleaning cycles, a successful laminar flow cleaning system may be changed to a turbulent flow one, causing problems with small particles or thin film removal. The system suddenly stops cleaning well. In this case shortening cleaning cycles can be better achieved by raising the temperature. Equally, sometimes a successful turbulent flow system starts to fail when cleaning specifications change and suddenly smaller thinner films need to be change. Switching to a

laminar flow system by lowering pressure and increasing volume with larger nozzles may help.

Again, when performing bench-scale testing for spray cleaning systems it is important to mimic the characteristics of the actual cleaning system. For instance, drench a surface by pouring or gently pumping cleaning solution over a surface in order to mimic high volume/low pressure cleaning. Use a pump and nozzle or Water Pik® to imitate the blasting of a surface which occurs in low volume/high pressure cleaning.

Although ultrasonic cleaning can result in very high localized agitation from cavitation caused by sound waves, the agitation occurs under immersion. Therefore, immersion cleaning mechanisms are still effective. Even spray under immersion can allow for some kinetically slower immersion cleaning mechanisms to work. Though, more movement, in the cleaning solution, occurs during spray under immersion and, thus, kinetically less time is available for slower immersion cleaning mechanisms.

The following table lists bench scale cleaning methods and identifies which full scale methods they correspond to or imitate:

**TABLE 5D TYPICAL BENCH-SCALE CLEANING SYSTEMS AND THE SCALE-UP SYSTEMS THEY MIMIC**

CLEANING METHODS	
Bench-Scale	Full-Scale
Manual cleaning with tool	Manual cleaning with tool
Immersion in a small tank	Immersion in a big tank
Small tank with stirrer	A clean-in-place, agitated big tank
Small ultrasonic tank (be sure to use same frequencies and power densities)	Bigger ultrasonic tank
Gently hosing or pouring	High volume/low pressure washer onto a surface
Power spray onto surface	Low volume/high pressure washer

**Select rinsing and drying conditions**—In any bench-scale cleaning system it is also critical to understand how the rinsing and drying processes can affect cleaning results. In bench-scale cleaning, it may be practical to use copious quantities of running water for rinsing. Often, simply putting cleaned parts under running water at a sink will be both an acceptable and a highly effective rinsing technique. The same level of rinsing, however, must be duplicated in scale-up.

The cleaner loosens all the soils and prepares them to be rinsed away. A running water rinse is far more effective than static dip-tank rinse, or even a slow counterflow cascade tank rinse. Rinsing relies on essentially two types of mechanisms:

- **Mass displacement**—where the rinse water physically replaces the soil/solution mixture.
- **Concentration gradient dissolving**—where the high concentration soil/solution mixture at the surface being cleaned dissolves into the rinse water, creating a uniform low-concentration mixture with a resulting low concentration of soil present near the solution/surface interface.

In a running water rinse system, mass displacement is the dominant rinse mechanism. Whereas, in a static soak-tank rinse, concentration gradient dissolving is the dominant mechanism. When testing bench-scale rinsing, mimic the rinsing that will be used in scale-up. For example, a running water rinse may be effective at bench scale and might allow a less free-rinsing cleaner to perform adequately. However, it may be ineffective or cause failure in scale-up.

It is also desirable to use the same quality of rinse water that will be used in scale-up. If lab-grade deionized water is used for bench-scale rinsing, for example, the same type of water should be available for scale-up. Conversely, it is possible to use tap water rinses in bench-scale testing. Water spots can be avoided by using water removing—as opposed to water evaporating—drying methods. Tap water rinses are often sufficient to show in bench-scale that a cleaning system can remove a particular soil from a surface.

For bench-scale testing first choose a cleaning system and then go on to test the system with a given cleaner. The following table identifies typical rinsing and drying methods used in bench-scale and full scale cleaning systems:

**TABLE 5E BENCH-SCALE RINSING AND DRYING METHODS AND THEIR CORRESPONDING SCALE-UP METHODS**

RINSING METHODS	
Bench-Scale	Scale-Up
Static soak	static soak
Overflowing dip tank	counter flow cascade tanks
Running water	running water or efficient counter flow cascade tank series
DRYING METHODS	
Bench-Scale	Scale-Up
Air dry	Air dry
Oven dry	Hot air dry
Hair dryer	Hot directed forced air
Compressed air nozzle	Air knife
Volatile solvent rinse	Volatile solvent rinse

## SELECT THE TEST SUBSTRATE

Once a cleaning method is selected for testing, the next step in developing a cleaning system is to select a substrate and a soil to clean. Ideally, actual parts or surfaces with actual soils that will be cleaned should be used. Sometimes, of course, this is not possible, in which case similar materials should be employed.

Also, small stainless steel coupons or glass slides are often used for bench-scale cleaning development. For many soils it is not critical what the substrate is, and for many cleaning mechanisms “a surface is a surface”—whether it be glass or metal.

When cleaning plastics, however, the surface considerations are more critical, since some plastics will have particular affinity for organic soils. Also, when removing salts or inorganic soils from metals it is often important to use the exact metal that will be cleaned when a process is scaled-up. The same is true for porous surfaces—such as gold and some ce-ramics—which may require use of the same substrate for bench-scale testing in order to develop a reliable cleaning system.

Similarly, it may be important to use the same surface for testing to be sure that the cleaning system will not corrode or damage the surface. This is especially true for aluminum.

It can be very useful to work with standard clean coupons. There are several suppliers of standard coupons that are more commonly used with corrosion testing, but that can be adapted for use in cleaning testing. Some suppliers include:

**Metal Samples Corrosion Monitoring Systems**

*A Division of Alabama Specialty Products, Inc.*

P.O. Box 8

152 Metal Samples Rd.

Munford, AL 36268

(256) 358-4202

<http://www.alspi.com/msc.htm>

**Metaspec CO**

790 West Mayfield Blvd.

San Antonio, TX 78211

(210) 923-5999

**Q-Panel Lan Products**

800 Canterbury Rd.

Cleveland, OH 44145

(440) 835-8700

<http://www.q-panel.com>

## SELECT A TEST SOIL

It is often more important to pay attention to the soil than the surface during cleaning system development—using the same soil in bench-top testing as in scale-up. Pay careful attention to how dried-on the soil will be in the actual process. A freshly applied soil may be very easy to remove in bench-scale processes, but may become very difficult to remove if it dries on the surface for several hours. (When possible, it is wise to avoid allowing soils to dry onto a surface in the actual cleaning setting.)

If using the exact soils that will be present during actual cleaning is not possible, try to match the characteristics of the soil. Match the particulate sizes, oil viscosities, wax melting points and chemical character (for example, do not use a natural oil to mimic a synthetic or petrochemical oil and vice versa). Try to apply the soil to the surfaces in the same manner and quantity that will be present under actual cleaning conditions. (Soiling the substrate on the heavy side can be helpful in de-signing a robust cleaning system.)

In addition, it may be critical to develop a way of uniformly soiling a surface in order to get significant reproducible

results that are suitable for comparing cleaning systems. One approach is to create a uniform slurry, paste, or solution of the soil, possibly employing a volatile solvent carrier to apply the liquid mixture to surface. Then, using a glass rod with spacers, spread a uniform film of soil onto a coupon to achieve uniform reproducible soil levels.

If the objective is to find a way to absolutely clean a soil—rather than compare cleaning systems—simply smearing or applying some soil to the surface for visual inspection that the soil is present can suffice.

## SELECTING AN AQUEOUS CLEANER

After establishing combinations of cleaning, rinsing, and drying, try a cleaner at different time, temperature, and detergent concentrations to determine if the system will work. Review the information in Chapter Four, on Detergent Selection, to make sure you are testing a cleaner that has a reasonable chance of success. Match the cleaner to the desired cleaning method, soil, and surface being cleaned.

## PERFORM TEST CLEANINGS

It is advisable to perform at least three cleanings using each set of conditions to help minimize anomalous results. For critical-cleaning system development, it is desirable to perform at least six repetitions of each set of conditions.

Whether selecting an aqueous cleaner and cleaning system for a new manufacturing or processing application or switching to an aqueous cleaner, the process is the same. It is a good idea to start by using an “overkill” combination of time, temperature, concentration, and agitation than might typically be required in a bench-test scenario to first prove that the system you are using is capable of delivering the cleanliness required.

**Finding the minimums**—Having proven that the system can work, the next step is to try a combination of what one might guess is slightly less than minimum time, temperature, concentration, and agitation to get some idea of where the system starts to fail. A good, less-than-minimum starting point might be 20% of a conservative recommendation from the cleaner's manufacturer. For example, if a cleaner is recommended for

use at 1% in water, 60°C (140°F) with a 10-minute soak, one might try and see how badly it fails at 0.2%, 40°C (105°F) and a two-minute soak. This provides a sense of the robustness of the cleaning process. One can then choose some combination of time, temperature, and concentration above the minimum based on how poorly the system failed to perform.

Based on these results, try a combination based on a guess of what might be slightly above the minimum requirements. One can then optimize the parameters by successive iterations of cleaning performance testing by going halfway between the last combination of variables that worked (and the last combination that failed) until satisfied that the system has been sufficiently optimized for the specific cleaning needs.

One can also hold one or more variables constant, while optimizing the others. For example, if one needs to be able to clean a batch of parts in two minutes, then vary the temperature and concentration within the two-minute time constraint.

Once you have determined an “overkill” system that works and a “minimal” system that fails, at least in part, an optimum system can be identified. Decide when to stop bench-scale optimizing and when to move on to pilot-scale or full-scale use of the cleaning system.

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**TABLE 5F**

**Typical cleaner test conditions**

**Overkill**

Double the recommended dilution of detergent

Maximum practical temperature

Maximum practical cleaning time

**Minimum**

20% of the recommended detergent dilution

Room temperature

Very short cleaning time

**Optimized**

Recommended dilution

120°F (50°C) for immersion or manual cleaning methods, 140°F (60°C) for spray clean systems

Practical cleaning times

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**REFERENCES**

*Guidebook of Part Cleaning Alternatives*, Karen Thomas Massachusetts Toxics Use Reduction Institute. John LaPlante, Alan Buckley Massachusetts Office of Technical Assistance, March 1997.  
 Developing a System, *from Alconox Cleaning Solutions*, Vol 1, Number 3.

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**RESOURCES**

- [www.alconox.com](http://www.alconox.com)
- [www.clean.rti.org](http://www.clean.rti.org)
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# Industrial Cleaning Applications

**T**oday, new applications for aqueous cleaning are found in a wide range of industries—laboratory science, healthcare, pharmaceuticals, medical device, food-and-beverage processing, metalworking, and precision manufacturing of glass, plastic, and metal components.

This chapter describes key considerations in aqueous cleaning for each of these industries.

## HEALTHCARE

The ultimate goals of healthcare cleaning procedures are to keep instruments and equipment clean and sterile, prolong their working life, minimize cross-contamination, and reduce medical waste. The ideal detergent for cleaning reusable instruments has a neutral pH to prevent corrosion or other surface degradation. Detergents that contain enzymes will remove proteinaceous soils, from blood or body fluids, by soaking and gentle cleaning rather than abrasive scrubbing. This prolongs the working life of the instrument and limits the possibility of cross contamination.

In a healthcare setting, cleaning often means preparing a surface for sterilization. It is crucial to have remove all dirt from the surface to avoid sterilizing the dirt rather than the surface beneath it.

Although healthcare instruments themselves are often made up of robust plastics or stainless steel, the trays that hold them are not. Choose a detergent that will not damage light-weight plastic or aluminum instrument-handling trays.

**TABLE 6A DETERGENT SELECTION GUIDE FOR HEALTHCARE CLEANING**

Application Key Concerns	Articles Cleaned/ Soil Removed	Cleaning Method	Recommended Cleaner
Healthcare/Veterinary Effective preparation for sterilization, longer instrument life. Reduce waste.	Surgical, anaesthetic, and examining instruments and equipment. Catheters and tubes.	Manual, Ultrasonic, Soak	Mild alkaline
		Machine washer, sani-sterilizer	Low-foam alkaline
	Blood, body fluids, tissue on instruments.	Manual, Ultrasonic, Soak	Enzymatic mild alkaline

Healthcare instruments that are cleaned are, generally, examining instruments of one kind or another. Most healthcare instruments that come into contact with blood or body fluids are disposed of eliminating, or substantially reducing, risk of cross-contamination from blood-borne pathogens. Reusable examining and probing instruments (such as endoscopes) that come in contact with blood or body fluids, must be cleaned very carefully.

Cleaning volume varies. For instance, in an individual doctor's office, small groups of instruments are, generally, cleaned in small soak trays and sometimes ultrasonically. Whereas, in hospitals and large medical centers, "control cleaning" occurs. Soiled instruments from the entire facility are grouped in trays and sent to a central cleaning or central sterilization facility. The facility will typically use large batch washer/sterilizers to perform their cleaning.

## PHARMACEUTICAL

Pharmaceutical equipment includes everything from bench scale lab apparatus used for trials to full scale bulk manufacturing equipment. Regardless of scale, all pharmaceutical equipment must meet government standards for cleanliness. These standards are commonly referred to as Good Manufacturing Practice (GMP) and more recently, current Good Manufacturing Practice (cGMP), or more recently still as conforming to Quality Systems (QS). There are additional regulations, established by agencies including the US FDA, the EU (European Union), and the International Conference on Harmonization (ICH), that must be followed. For a discussion of cleaning validation requirements, see chapter 8 on cleaning validation and for examples of standard operating procedures

(SOPs) used in pharmaceutical process equipment cleaning, see Chapter 7 on cleaning procedures.

Residues, found in pharmaceutical cleaning, range from easy to clean water-soluble excipients to difficult to clean petrolatum/metal oxide mixtures. To simplify regulatory compliance, it is desirable to use as few cleaners as possible to remove the entire range of residues encountered. It is also desirable for these cleaners to work in a wide range of cleaning procedures including manual, soak and ultrasonic cleaning, as well as clean-in-place spray systems.

Typically, surfaces to be cleaned are constructed of glass, 316L stainless steel, Teflon, polypropylene, and silicon elastomers used in seals. In some cases, pharmaceutical manufacturers will use disposable seals, pipes and filters to avoid having to validate their cleaning. In some cases, it is safer and more cost effective to use equipment once rather than clean it.

There is no more demanding application for precision cleaning than pharmaceutical manufacturing—where cross-contamination can be costly in lost product and the risk to human and animal health is great.

Today many leading drug companies, as well as medical device manufacturers, are finding that aqueous cleaners provide the kind of scrupulous cleaning required for processing healthcare products. Examples:

- **Capsules and tablets**—Some pharmaceutical ingredients resist going into solution, making tablet presses and dies difficult to clean. Even stubborn, sustained-release product residues come clean quickly with appropriate aqueous cleaners.
- **Suspensions**—Aqueous cleaners also eliminate intensive scrubbing and human contact in cleaning large stainless steel tanks (even 2,000 gal) used in manufacturing liquid suspensions.
- **Intermediates**—Aqueous cleaners are ideal for cleaning glass-lined chemical reactors used in processing pharmaceutical intermediates such as powders, fillers, binding agents, and other chemicals.

**TABLE 6B DETERGENT SELECTION GUIDE FOR PHARMACEUTICAL CLEANING**

Application Key Concerns	Articles Cleaned/ Soil Removed	Cleaning Method	Recommended Cleaner
Pharmaceutical Passing cleaning validation for FDA good manufacturing practices. For stainless steel, glass, plastic, elastomer cleaning.	Titanium dioxide, petrolatum, oils, emulsions, ointments, carbopols, lacquers, zinc oxides, proteins, steroids, alcohols, sugars, and Eudragit* (L/S/L30/D55/NE30D) polymers.	Manual, Ultrasonic, Soak	Mile alkaline
		Machine washer, power wash, CIP	Alkaline surfactant low-foam
	Inorganic residues, salts, metallics, pigments. Eudragit* (E/RL/RS/E100) polymers, amphoteric, coatings, amines, ethers, starches, alkaloids.	Manual, Ultrasonic, Soak	Mild acid
		Machine washer, power wash, CIP	Mild acid
	Protein/ferment residues. R/O, U/F membranes.	Manual, Ultrasonic, Soak	Mild alkaline or enzymatic

\* Eudragit is a ® registered trademark of Roehm GmbH & Co.

In research and development, aqueous cleaners have long been used in cleaning metal, glass, plastic, and polymer components for benchtop labware, as well as, difficult-to-clean pilot processing equipment such as bioreactors and fermentation systems.

**Controlling Pyrogens**—A key consideration, in pharmaceutical process equipment cleaning for parenteral product manufacture, is controlling pyrogens. Pyrogens are endotoxins or cellular debris that can cause fevers when people are internally exposed.

Pyrogens are often controlled using heat. The cleaners Liquinox (Alconox, Inc. catalog number 1201) and Alconox (Alconox, Inc. catalog number 1104) are used to depyrogenate heat sensitive surfaces, as well as, non heat sensitive surfaces. Standard cleaning, of injectables, with a 1% solution of Liquinox at 120 deg F (50 deg C) using manual, soak, or ultrasonic agitation should be followed by a thorough rinse with pyrogen free water also known as Water For Injection (WFI). Post cleaning handling in a pyrogen controlled environment or packaging will provide adequate pyrogen control. Stoppers for injectables are cleaned using Alconox powdered detergent solutions.

An article (Hallie Forcinio, Pyrogen Control, March 2001 Pharmaceutical Technology p.38) made reference to controlling pyrogens with the following:

Pyrogens on packaging materials can be controlled by heating alone or in combination with alkali or strong oxidizing solutions or by washing with detergent (1)...Pharmaceutical makers can render plastic containers pyrogen-free by washing the containers with an alkaline (ie pH 9-10) cleaning agent on a machine integrated with the filling line. When washing is the pyrogen-removal method of choice, any cleaning agent residue must be adequately removed...The favored method of removing pyrogens from stoppers is washing... many stopper makers now offer pre-washed stoppers, which are treated to reduce endotoxin levels by 3 logs. <sup>1</sup>

Liquinox is a detergent often used in pyrogen control. Most laboratories, that do LAL testing for pyrogens, use Liquinox to clean their glassware and testing equipment.

**Stainless Steel Cleaning**—Stainless steel and glass are commonly found substrates that require cleaning. It is worth taking a closer look at some of their surface properties to determine how they effect cleaning and how to optimize the thermodynamics of cleaning by controlling the pH of the cleaning solution.

Much is known about how pH affects aqueous critical cleaning. However, the role pH can play in harnessing electrostatic effects to improve cleaning efficiency is not well known. Since like charges repel, choosing a cleaner of appropriate pH relative to the isoelectric point of the surface and the inverse log of the acid dissociation constant (pKa) of the residue makes cleaning far more efficient (see Table 6C). This is especially true when cleaning residues such as acids, bases, and amphoteric proteins, all of which can have their electrical charges manipulated by pH.

The isoelectric point of a surface is the pH at which the surface's electric charge is neutral with regard to its acid/base and electron donor-acceptor reactions. Moving to a higher or lower pH will shift the effective surface charge or electron density in a negative or positive direction. Examples:

- **Steel**—typically has an isoelectric point of 8.5 associated with the reactivity of the oxygen in the oxides Fe2O3, Fe3O4, and Cr2O3 on the surface of the metal and the hydrates and hydroxides formed in aqueous solutions.

<sup>1</sup> W.A. Jenkins and K R Osborn, *Packaging Drugs and Pharmaceuticals*, Technomic Publishing Co, Lancaster PA, 1993, p 28.

- **Glass**—has an isoelectric point of 2.5 associated with the SiO<sub>2</sub>.

Raising the cleaner solution pH (past the isoelectric point), causes the surface to become more negatively charged. If the residue to be removed also has a negative charge at that pH, then the negative surface will repel the negatively charged residue.

In addition to material surfaces, many residues also change electrical charge as a result of a simple change in their pH. The pKa, of most acids, indicates the pH at which the hydronium ions and conjugate base are present in equal concentrations. Moving higher in pH shifts the equilibrium toward the right, thereby increasing the concentration of the negative conjugate base. Thus, when cleaning acids it is desirable to use a cleaning solution with a pH above the isoelectric point and the pKa of the acid. This results in an increase in the concentration of the negative conjugate base. With a pH above the its isoelectric point, the surface will take on a repelling negative character.

**TABLE 6C RELATIONSHIP OF pKa, CONJUGATE BASE AND HYDRONIUM ION CONCENTRATION**

HA + H <sub>2</sub> O → H <sub>3</sub> O <sup>+</sup> + A <sup>-</sup>			
[HA] = acid concentration	H <sub>2</sub> O = water	H <sub>3</sub> O <sup>+</sup> = hydronium concentration	[A <sup>-</sup> ] = conjugate base concentration
pKa = -log [H <sub>3</sub> O <sup>+</sup> ][A <sup>-</sup> ]/[HA]			

For example, with stearic acid (C<sub>17</sub>H<sub>35</sub>COOH), the conjugate base is the negatively charged stearate ion (C<sub>17</sub>H<sub>35</sub>COO<sup>-</sup>). The pKa is about 5. This means that at a pH of 5 and above, we begin to drive the reaction toward the right, thereby converting stearic acid to negatively charged stearate ion.

Suppose, the stearate ions form a residue on steel and the pH is as high as 8.5 and above. Then, not only do we have negatively charged stearate ions, but also, a negatively charged steel surface with a pH above the isoelectric point. The steel and the stearate ions repel each other, facilitating cleaning.

The reverse holds true for alkaline (basic) residues (see Table 6D). By lowering the pH of the residue below the pKa and the isoelectric point of the surface being cleaned a positive-positive repulsion may be achieved. At the very least, a neutral residue and a positive surface, with no attraction, are created.

**TABLE 6D OPTIMIZING THERMODYNAMIC CLEANING CONDITIONS FOR SURFACE/RESIDUE ELECTROSTATIC REPELSION**

Acidic residues	pH > pKa and isoelectric point of surface
Alkaline or basic residues	pH < pKa and isoelectric point of surface

In all cases, it is important to consider the corrosive effect of pH on the surface being cleaned. Typically, it is desirable to choose a cleaner with a pH that will not etch or corrode the surface—for stainless steel, within the limits of passivation, and for glass, within the limits of etching. The addition of corrosion inhibitors can extend the acceptable pH range.

**Clean-in-place (CIP) Cleaning**—Pharmaceutical operations include R&D, pilot studies and full scale manufacturing. Generally, cleaning techniques and equipment change with the scale of production. Manual and soak cleaning procedures may be adequate when cleaning bench scale equipment. Whereas, Clean-in-Place (CIP) systems are generally more efficient for cleaning large scale manufacturing process equipment. Part of the following discussion, on CIP cleaning, is paraphrased from the website operated by Dale Seiberling—the self proclaimed CIP Evangelist ([www.seiberling4cip.com](http://www.seiberling4cip.com)).

CIP cleaning involves spray or recirculation of the initial flush, wash, and rinse solutions under pressure. Effective cleaning is achieved by adjusting time, temperature and cleaner concentration.

- **Piping Systems** can be effectively cleaned via recirculation of flush, wash, and rinse solutions at flow rates which will produce a velocity of 5 feet per second or more in the largest diameter piping in the CIP circuit.
- **Mixers, tanks and blenders** can be effectively cleaned by distributing flush, wash and rinse solutions on the upper surfaces at pumping rates equivalent to 2.0-2.5 gallons per minute (gpm) per foot of circumference for vertical vessels, or at 0.2-0.3 gpm per square foot of internal surface for horizontal and rectangular tanks.

- **Integrated CIP Design** is a process of cleaning vessels and piping in one pass. Flush, wash and rinse solutions are combined and circulated through the sprays systems. Solutions are returned to the CIP system. This form of CIP cleaning is cost-effective and is minimizes the risk of post CIP recontamination that can occur when lines and vessels are cleaned separately.

A CIP monitoring and control system can be installed to ensure that the CIP system works reliably, rendering the process vessels and piping molecularly spotless after every product run—or a loud alarm will sound. The CIP monitoring and control system can document the system's operation and history, and archive this information for regulatory compliance. To set up a monitoring system, first, circulate and then flush water through the CIP system with the control system monitoring the valves and pressure to assure and record proper operation. Next, proceed to the wash cycle, possibly using conductivity control to measure and record proper addition of cleaner solution. Then, flush out the cleaner solutions and proceed to neutralization and rinsing steps. Final rinses can be circulated to equilibration for rinse water sampling if desired.

**GMP Washing Machines**—Equipment that is disassembled for cleaning, manufacturing tools and bench scale production equipment that can be loaded into racks are often best cleaned in a washer that capable of validated cleaning.

**GMP Washer/dryer design**—Within the pharmaceutical industry, there has been, no definitive standard set for mechanical washer/dryers that meet all GMP requirements. The GMP regulations include several specifications (Part 133.4, 1963, and part 211.67, 1978) that provide guidelines for GMP washer/dryer design and construction. Unfortunately, these regs leave many areas open for interpretation. With no clear standard, a great many “lab style” washers have been developed, their limitations, not evident until long after purchase and installation.

There are certain inherent criteria required for washer/dryers used to clean parts, glassware, plasticware and tooling, to achieve GMP compliance in the pharmaceutical industry. Following FDA rationale, the goal is to design cleaning equipment that will “prevent contamination or adulteration of drug products.”

**Structural Flexibility**—The design of the GMP washer has evolved over the past 10 years. Initially, modified laboratory washers were manufactured in common production lines. Later, specific product divisions were established within the most up-to-date manufacturing companies. Complete separation of tooling and superior welder qualifications are now requirements for this group of products. Documentation of quality control monitoring for the entire construction process is provided as a deliverable. The washer/dryer must be able to perform without taking up too much space. Effective placement in the process plant, will allow for easy service and technician access.

The outer shell of the washer, should be constructed of materials of at least 316L to withstand cleaning chemicals used in the clean suite area for easy integration into this area. Service panels should access to the critical components through mechanical chassis or locations that the design of the facility allows. Many times, the washer must adapted to a particular space or room so that the internal components can be easily accessed by the service people, technicians or validation engineers during and after the installation and calibration process. Temperature and monitoring instruments should be easily removed from their ports via tri-clamped connections and have enough coil to be placed on a metrology cart outside of the structure of the washer. This will facilitate calibration and verification during validation.

Freestanding or recessed models must be available to give the facility the product flow characteristics required for their process.

**Chamber Flexibility**—Effective use of the chamber will allow for faster and/or fewer cycles and higher throughput of the washer/dryer during the production day.

Chamber design should allow for minimal water retention. Chamber corners should carry a minimum of a 1” radius and all surfaces should be sloped to the drain. Internal structures of the chamber should feature rounded edges with no threads or entrapment areas. 316L stainless steel finished to a uniform 25 Ra for all surfaces is an appropriate baseline for all surfaces and structures within the chamber.

Care should be taken with respect to the mating of the inventory systems to the hydraulic circuit. There should be no mechanical attachment required for the accessory racks. Spray headers should be positioned at the top and the bottom of the basin to aid in the

cleaning of parts. In keeping with the goals of minimizing utility costs and GMP design and construction, the chamber volume should be sized to match the load configuration required for a specific facility.

Care should also be taken to match the items to be cleaned so that an effective load and unload pattern can be established minimizing operator errors. Multiple level loading configurations will allow for maximum utilization of the chamber space while minimizing the consumption of WFI.

Effective use of Teflon and stainless will allow racks and baskets to mate to the chamber of the washer. (Threaded connections are to be avoided as they are entrapment areas for water and particulate that could lead to cross contamination of the products being cleaned.)

Since loads for GMP cleaning can range from glass to plastic to stainless parts, the design of a loading surface should allow for the weight associated with these components. Two types of doors are typically available:

- **Vertical doors**—These allow for easy access to the items being cleaned but make it difficult to provide a strong seal. In addition, they require the use of loading trolleys which add to the number of accessories in the clean suite. Vertical doors typically have a windows built in that are popular but have no GMP function. (Internal lights required for their use need gaskets that require maintenance. The doors are also prone to leakage and may need service maintenance not always possible during a production run. )
- **Horizontal drop-down doors**—Also easy to access and to load, these doors serve as containment structures. Gaskets, that can be matched to GMP requirements, will allow for complete sealing of the chamber preventing particulate migration into or out of the chamber. In the down position, the door becomes a loading table for operators allowing them easy access to three sides of the rack where components are placed to be cleaned. Heavy parts can be placed on the door so that operators do not have to reach into the chamber of the washer. Teflon wheels on the rack provide a smooth transition into the chamber.

**Component Selection**—Internal components must be compliant with GMP requirements. Sanitary diaphragm valves should be avail-

able for all areas that come into contact with process fluid. Plumbing should utilize orbital welds wherever possible and be finished to a minimum of 25 Ra. Dead legs should be kept to a minimum of 6 pipe diameters. 316L stainless steel should be the material of choice for all metallic areas. Cold rolled steel, copper, and other forms of stainless (except 304L for the frame) should be avoided at all times.

Special attention should be given to the chemical delivery system. This has been an overlooked area in GMP washer design because of the difficulty and expense of finding an effective solution. Delivery systems must allow for precise amounts of additives (caustic detergents and acid based products) and must withstand harsh ingredients to be delivered. Many times, a commercial laundry delivery system is installed only to fail, a few months after qualification, resulting in costly down time at the production facility.

Drying systems should provide complete coverage of all aspects of the load. Additionally, the washer itself should be dried entirely and prepared for the next validated cycle. Non-shedding materials should be used throughout the drying circuit. High temperature rated HEPA filters should be the final point for the air entering the basin or accessories so as to provide for a clean, particulate free drying process. DOP challenge ports should be provided so that the integrity of the HEPAs can be tested regularly. Separate circuits for the basin and the hydraulic unit (including the internal parts for the loading accessories) will provide for the fastest and most effective cycles. This design is inherently more expensive but can be justified quickly.

**Inventory Systems**—While construction of the chamber, chassis, and internal components are important to overall washer performance, inventory is an equally important consideration, frequently overlooked. Most often, manufacturers are criticized for the mating of the inventory system to the chamber and the parts to be cleaned. A complete inventory involves documenting size, weight and specific cleaning requirements for all components to be cleaned. Once this information is assembled, the parts are grouped together in the loads and necessary chamber volume can be calculated. Ergonomic principles should be applied to prevent operator overload, to maximize the parts/run and minimize utility consumption.

**Documentation Requirements**—A documentation package is needed to complete the validation and qualify the cleaning system. The package should contain (as a minimum) the following components:

- User's manual
- Maintenance manual
- Instrument list
- Electrical diagram
- Piping and instrumentation diagram
- Spare parts list
- Exploded view
- Welding report and welder certificate
- Source codes are provided in the form of a written copy, a floppy disc, and a spare E-prom
- Passivation report
- As built drawings
- IQ/OQ documentation

Cleaning components used in a manufacturing environment presents obstacles not found when cleaning glassware or parts used in lab research. Materials of construction, soiling of active pharmaceuticals, load configurations, and regulatory constraints must each be considered when cleaning at production level. However, when properly managed, obstacles can be overcome and a cleaning system implemented. Developing a wash protocol, typically involves the following steps:

- A clear understanding of the items to be cleaned is paramount to the success of a validated system. The operator must load and unload the washer in specific steps so as to maintain the validation of the cycle. Ergonomic principles regarding the load and the rack must be addressed at this point to make additional design and steelwork feasible.
- An understanding of the residues to be removed, is the next step. Determine whether active pharmaceutical residues can be removed within the constraints of available time, temperature, cleaning chemistries and agitation.
- Load patterns must then be addressed. To meet validation requirements, specific components must be cleaned together. This is a challenge requiring designers of inventory systems, for GMP washers, to have complete knowledge of the material make-up and dimensions of the parts being cleaned. Parts can then be arranged on a CAD drawing to determine whether there will be any load/unload problems to overcome. At this point, a clear picture of the cleaning cycle protocol comes into focus.

- The PLC (programmable logic controller) or microprocessor can then be programmed taking into account the established cleaning protocol. System monitoring and data transfer, to other monitoring locations are additional elements of the system design.

By following the steps outlined above, a successful protocol for cleaning pharmaceutical equipment using a GMP washer can be put in place.

## BIOTECHNOLOGY

Cleaning requirements in the biotechnology industry are similar to those in the pharmaceutical industry. Residues resulting from production of biopharmaceuticals and gene-therapy products are often complex mixtures produced during fermentation and cell culture. Cleaners used must remove interfering residues that inhibit culture growth or cause unacceptable batch to batch contamination. As in pharmaceutical process equipment cleaning, disposable single use items may be used for piping, seals, and filters. When pharmaceuticals are manufactured, even at R&D pilot scale for trials, GMP procedures must be followed. The GMP washers described in the preceding section are often used for biopharmaceutical cleaning. See chapter 8 on cleaning validation and Chapter 7 on standard operating procedures, particularly the example given on cleaning fermentation equipment.

## MEDICAL DEVICE MANUFACTURING

Cleaning, during the manufacturing process, prepares medical devices for sterilization and sterile packaging. When selecting a detergent, consider the material composition of the device. Usually medical devices are made of fairly robust materials that can withstand corrosive blood and body fluids. In some instances, one portion of the device is intended to come into contact with skin, blood, or body fluids. Other parts of the device may remain exterior to the human body and be made of less sturdy plastics or aluminum. If less sturdy materials are present, a milder detergent is needed.

Medical devices are usually assembled under fairly clean conditions. As a result, a light-duty cleaner is usually all that is

needed to remove small amounts of light soils.

Good designers avoid creating medical devices with small crevices, cracks, and difficult-to-clean or reach places. Often, medical devices are manufactured in modest quantities, lending themselves to batch-cleaning operations. Ultrasonic cleaning is a common cleaning method used in medical device manufacture. This, and the fact that cleaning operations typically remove only light soils, or small particulates make it important to select extremely free-rinsing detergents suitable for immersion cleaning.

For parenteral medical devices, designed to be implanted inside the body, it is also important to remove all endotoxins or pyrogens from the device surface. Endotoxins or pyrogens are fever-causing cell debris or cell-waste products widely present in the environment. Cleaning pyrogens or endo-toxins requires the use of a high-emulsifying cleaner combined with heat and followed by a rinse with pyrogen-free or endotoxin-free water. This type of water is often called water for injection (WFI). WFI is very high purity water derived from high-purity water filtration systems.

The most common cleaning technique in medical device manufacturing is to use heated ultrasonics followed by suitable purity of water rinsing. Depending on the types of residues, sometimes an alkaline clean is used first to remove all oily residues, followed by a brief rinse to prevent dragout and then an acid cleaner to remove alkaline insoluble inorganic residues. This two step cleaning is then followed by a thorough rinse.

Medical device manufacturing must conform to current Good Manufacturing Practice (cGMP), or as it is now sometimes referred to as Quality Systems (QS). There are additional regulations, established by agencies including the US FDA, the EU (European Union), and the International Conference on Harmonization (ICH), that must be followed. For a discussion of cleaning validation requirements, see chapter 8 on cleaning validation and for examples of standard operating procedures (SOPs) used in cleaning, see Chapter 7 on cleaning procedures.

Some medical devices are manufactured as single-use devices that do not have protocols for cleaning and re-use. There are contract companies that do clean and repackage single-use devices for re-use. By doing this, they are in effect “re-manufacturing” the device and they must validate their cleaning in accordance with good manufacturing practices.

**TABLE 6E DETERGENT SELECTION GUIDE FOR MEDICAL DEVICE CLEANING**

Application Key Concerns	Articles Cleaned/ Soil Removed	Cleaning Method	Recommended Cleaner
Medical Device Passing cleaning validation for FDA good manufacturing practices.	Oils, emulsions, lacquers, zinc oxides, proteins, steroids, alcohols, and sugars.	Manual, Ultrasonic, Soak	Mile alkaline
		Machine washer, power wash, CIP	Alkaline surfactant low-foam
	Inorganic residues, salts, and metallics.	Manual, Ultrasonic, Soak	Mild acid
		Machine washer, power wash, CIP	Mild acid

## LABORATORY CLEANING

Despite increased use of disposable plastics in the laboratory, reusable glass labware is still widely found. This has to do with environmental concerns (recycling issues and disposal problems associated with plastics) and the fact that the vast majority of procedures require glass. In addition, there are instruments and equipment, which must be reused for scientific or economic reasons.

The principal concern for any scientist or technician working is that laboratory glassware, instruments, and equipment be free of interfering residues. These often unseen residues can cause invalid analytical results. For example, they can erroneously accelerate or decelerate rate dependent experiments by causing localized high concentrations of reactants inside micelles. They can inhibit culture growth, cross-contaminate batches, and cause nonreproducible results.

To solve these problems, equipment must be cleaned thoroughly and any interfering residues removed. This requires that an appropriate laboratory detergent be selected and an effective cleaning method used (Table 6F).



**TABLE 6F DETERGENT SELECTION GUIDE FOR LABORATORY CLEANING**

Application Key Concerns	Articles Cleaned/ Soil Removed	Cleaning Method	Recommended Cleaner
Laboratory Reproducible results, no interfering residues, extending equipment life. Keep laboratory accreditation. Laboratory safety.	Glass, metal, plastic labware, ceramics, tissue culture, porcelain, clean rooms, animal cages, bioreactors, tubing, benches, safety equipment.	Manual, Ultrasonic, Soak	Mild alkaline
		Machine, power spray, labware washer, washer-sterilizer, cage-washers	Low-foam alkaline
	Tubes, reusable pipets.	Siphon-type washer-rinsers	Mild alkaline tablet
Microbiology, water lab, and environmental sampling. Phosphate-sensitive labware. EPA procedures. (Acid for water rinse cycle.)	Microbiology, water lab, and environmental sampling. Phosphate-sensitive labware. EPA procedures. (Acid for water rinse cycle.)	Field, Manual, Ultrasonic, Soak	P-free alkaline
		Machine washer, labware washer	Low-foam P-free alkaline Low-foam P-free acid
Radioactive equipment/contaminants.		Manual, Ultrasonic, Soak	Mild alkaline
Stopcock grease.		Machine washer, warewasher	Alkaline low-foam
Trace metals, metal oxides, scale, salts, starches, amines.	Trace metals, metal oxides, scale, salts, starches, amines.	Manual, Ultrasonic, Soak	Mild acid
		Machine washer, warewasher	Low-foam mild acid
Proteinaceous soils, bio-wastes, tissue, blood and other body fluids, fermentation residues.	Proteinaceous soils, bio-wastes, tissue, blood and other body fluids, fermentation residues.	Manual, Ultrasonic, Soak	Enzymatic mild alkaline
		Glassware washer	Low-foam alkaline

p-free=phosphate-free

The following are common laboratory-cleaning procedures, along with guidelines for eliminating interfering residues.

**1. Soaking** is used to clean small items and the insides of larger vessels. It is also recommended as a pretreatment to prevent soils or residues from drying onto labware. A soak tank should be kept at the laboratory bench for immersing used labware until it can be washed. Soaking is also effective for cleaning or pretreating very difficult, dried-on residues. Select a detergent recommended for soaking and follow the manufacturers directions to make up the soak solution. Completely submerge the article to prevent any deposits or etching at the air/solution interface. Soak until soils are removed; this may take several hours. Additional agitation or wiping may be needed to remove difficult soils. A thorough rinse follows.

**2. Manual cleaning**, the most common method found in laboratory cleaning, is used for small batches of labware equipment and benches. To clean manually, wet the article either by immersing it in the detergent solution, or by using a soaked cloth or sponge. For nonabrasive scouring, un-diluted detergent should be poured onto a wet cloth or sponge for scrub-

bing. A cloth, sponge, brush, or pad can be used for cleaning. A thorough rinse follows. Protective gloves and eye protection should be worn if recommended or required.

**3. Ultrasonic cleaning** is used for larger or more frequently cleaned batches of labware.. To clean in an ultrasonic tank, a solution is made up in a separate container, the ultrasonic tank filled, and the machine run for several minutes to degas the solution and allow the heater to reach the correct temperature. Small articles should be placed in racks or baskets; irregularly shaped articles, aligned so that the long axis faces the ultrasonic transducer (usually the bottom). Run the machine for 2-10 minutes until parts are clean. A thorough rinse follows.

**4. Automatic syphon washing** is an effective way to clean reusable pipets. The pipets should be completely submerged in a detergent soak solution as soon as possible after use to pre-soak. This prevents soils from drying onto the pipes. When ready to clean, the pipets are placed in a holder and; an effervescent tablet cleaner is dropped into the autoatic syphon washer; the pipets are placed in a holder over the tablet to hold the tablet at the bottom of the washer so the effervescent bubbles do not float the tablet to the surface during cleaning. Cold or warm water is added at a rate to fill the washer and cover all of the pipets completely at the top of the cycle and allow them to drain thoroughly at the drain part of the cycle. This may take as long as an hour. For analytical use, a final rinse in deionized or distilled water may be required.

**5. Machine washing** is used in laboratories for cleaning large quantities of reusable labware. Follow machine manufacturer's directions for details on correct use. Generally, labware is loaded on racks with open ends facing the spray nozzles. Narrow-necked flasks are placed in the center of the racks, preferably on specially designed spindles with spray nozzles directed into the necks. Keep handling of the labware in the racks to a minimum. Group small articles in baskets to prevent dislodging by spray. Use only low-foaming detergents specifically designed for these machines. Typically, 10 ml of detergent per liter of hot, wash-cycle water (approximately 60°C) is used.

**6. Rinsing** is an often overlooked and very important part of laboratory cleaning. A thorough running water rinse that contacts all surfaces of an article for at least ten seconds per sur-

face may be required. Filling and emptying small vessels with rinse water at least three times is a good rinse procedure. For machine cleaning, there should be at least three rinse cycles after cleaning. Final, or all, rinses in water of suitable purity is necessary for removing tap water residues from analytical labware. A final rinse with deionized or distilled water is used for tissue culture and general analytical ware. Rinse trace organic analytical ware in distilled or organic-free water and trace inorganic analytical ware, in deionized water. Pharmaceutical and clinical research labware may require sterile, pyrogen-free, or injectable water rinsing, depending on the work being done.

Following these procedures diligently, eliminates interfering residues from the surfaces of reusable labware, instruments, or equipment.

## ENVIRONMENTAL AND WATER TESTING

Typically, trace analyses—usually for trace organics—are conducted for pesticides, known carcinogens, and known toxic organic compounds. (The EPA can provide a list of organic compounds that can be tested for.) Other trace analyses focus on inorganic compounds, typically trace metals, which are toxic. Examples include mercury, cadmium and zinc.

**TABLE 6G DETERGENT SELECTION GUIDE FOR ENVIRONMENTAL CLEANING**

Application Key Concerns	Articles Cleaned/ Soil Removed	Cleaning Method	Recommended Cleaner
Environmental Reproducible results, no interfering residues, extending equipment life. Keep laboratory accreditation. Laboratory safety.	Tubes, reusable pipets.	Siphon-type washer-rinsers	Mild alkaline tablet
	Microbiology, water lab, and environmental sampling. Phosphate-sensitive labware. EPA procedures. (Acid for water rinse cycle.)	Field, Manual, Ultrasonic, Soak	P-free alkaline
		Machine washer, labware washer	Low-foam P-free alkaline Low-foam P-free acid
	Radioactive equipment/contaminants.	Manual, Ultrasonic, Soak	Mild alkaline
	Stopcock grease.	Machine washer, warewasher	Alkaline low-foam
Trace metals, metal oxides, scale, salts, starches, amines.	Manual, Ultrasonic, Soak	Mild acid	
	Machine washer, warewasher	Low-foam mild acid	

p-free=phosphate-free

The purpose of the some tests is to determine general water, or soil, quality. In such cases, trace analysis is often performed for toxins. Quantitative analysis is used for drinking water as well as in determining soil quality for farming or gardening.

Cross contamination, from previous soil or water testing, is a key concern when cleaning sampling and handling equipment and glassware. Two procedures which will prevent cross-contamination are as follows:

1. Use a laboratory-grade cleaner with no analyzable ingredients to eliminate the possibility of detergent residue cross-contamination.
2. Perform equipment “blanks” by cleaning glassware or handling and sampling equipment and then testing the glassware or equipment for contaminants. For example, a U.S. Environmental Protection Agency protocol calls for the use of phosphate-free laboratory grade detergents. Phosphate-free cleaners are specified because of the potential risk of cross-contamination from phosphates. Alconox and Liquinox are often used for environmental testing. Although, Alconox does contain phosphates, it has been used for cleaning phosphate analysis labware for many years. When rinsed thoroughly, Alconox does not leave phosphate residues. The makers of Alconox and Liquinox also supply phosphate free laboratory grade cleaners for laboratory dishwashing machines, Solujet liquid and Tergajet powder.

## FOOD AND BEVERAGE PROCESSING

Typically, surfaces found in the food and beverage industries are fairly robust as they must withstand corrosive elements. typical of this industry. For example, meat that contains blood can be fairly corrosive and orange juice is fairly acidic.

**TABLE 6H DETERGENT SELECTION GUIDE FOR FOOD AND BEVERAGE CLEANING**

Application Key Concerns	Articles Cleaned/ Soil Removed	Cleaning Method	Recommended Cleaner
Food and Dairy Avoid interfering residues on food-contact equipment.	Stainless steel, food-contact equipment.	Manual, Ultrasonic, Soak	Mild alkaline
		Machine wash, pressure wash, CIP	Low-foam alkaline
	Oxides, scale, trace metals, salts, milkstone.	Manual, Ultrasonic, Soak	Mild acid
		Machine wash, pressure wash, CIP	Low-foam mild acid
	Filter membranes. Proteins/ biofouling.	Manual, Ultrasonic, Soak	Enzymatic mild alkaline

Good process design avoids cracks and crevices and difficult-to-clean places in food or beverage processing equipment. Manual cleaning is often employed for benches, counters, mixers, extruders, and processing equipment. Cleaners formulated for immersion cleaning are the best choices. High-emulsifying cleaners are needed where there is a significant amount of organic food residue.

In meat or poultry processing plants where proteins are present, an enzyme cleaner is recommended. The types of hard surfaces found in these environments are typically stainless steel or robust plastics such as high density polyethylene, or even ceramic surfaces.

Filtration membranes are unique surfaces found in food or beverage processing plants and are used to filter various process streams of food or beverage products. Filtration membranes are used in juice and decaffeinated coffee processing as well as cheese manufacturing. Such processes often result in highly fouled, difficult-to-clean filter membranes which are often very expensive. Effective cleaning maximizes their useful life and restores their rate of performance (throughput).

Since the foods being filtered are by definition nutritious, membranes are frequently fouled by biocontamination growing on the food and causing a condition known as bio-fouling or bio-film. Bio-film is often effectively removed by an enzyme-based cleaner. Enzyme-based cleaners are also desirable because they can be made with a neutral or near-neutral pH that won't damage the membranes.

Since some membranes are delicate and will be damaged by harsh alkaline or acid cleaners, it is crucial to select a mild detergent.

## GENERAL ELECTRONICS CLEANING

Electronic components are usually made of metal which is conductive and can be easily bonded by soldering. Soldering involves the use of flux an undesirable contaminant. Not only unsightly, it is acidic and can cause corrosion of electronic components.

Electronic components include glass or ceramic insulators. It is important to clean the surfaces of insulators completely to preserve their insulating properties. Oils or other conductive residues or particulates must often be removed.

A special consideration in electronics cleaning involves components that use a vacuum to create an insulator. These include light bulbs and vacuum tubes where residue can “outgas” into the vacuum, degrading it and its performance. This type of cleaning requires A thorough understanding, of the soils present on the part, is required to select an effective detergent.

**TABLE 6I DETERGENT SELECTION GUIDE FOR ELECTRONICS CLEANING**

Application Key Concerns	Articles Cleaned/ Soil Removed	Cleaning Method	Recommended Cleaner
Electronics Avoid conductive residues, avoid CFCs, pass cleaning criteria.	Circuit boards, assemblies, screens, parts, conductive residues, resins, rosins, fluxes, particulates, salts.	Manual, Ultrasonic, Soak Machine washer, power spray board and screen washers	Ion-free alkaline
		Manual, Ultrasonic, Soak Parts washers	Mild alkaline Low-foam alkaline

Additional soils encountered in electronics cleaning are solder flux residues, mold release agents and metal oxides formed on vacuum components. For example, metal oxides may be found on frame holders.

Removal of organic residues usually requires some an emulsifier, whereas removal of metal oxides is generally achieved using an acid cleaner with high chelating or sequestering capacities.

## PC BOARDS

A wide variety of contaminants can remain on the completed assembly surface if they are not properly cleaned. These contaminants can be:

- **Ionic**—These have an ionic charge and are, typically, salts such as sodium, potassium, and chlorides. They are of particular

concern because they are potentially conductive, mobile residues.

- **Polar**—They are contaminants having a dipole moment (a molecule with partially charged, positive or negative ends or poles) In keeping with the principle that “like dissolves like,” these contaminants tend to solvate ionic residues leading to the concerns previously discussed.
- **Nonpolar**— These have no dipole moment and are, generally, organic films with insulating and adhesion interfering properties for bonding or marking.
- **Nonionic**—These are organic compounds that have no ionic charge and are not salts. They may be either polar or nonpolar (as discussed previously).

Salts such as plating salts, etching salts, and activators are typically ionic. Many of the organic species are nonionic. However, organic acids such as the rosin acids and organic acids used as activators are ionic. An organic molecule by definition is one based on the element carbon.

The most detrimental type of contaminant is the ionic type. If not cleaned away, ionic species of contaminants can cause serious problems including leakage currents between traces on boards as well as severe corrosion. The presence of moisture greatly accelerates the activity of ionic species since water solvates the ions and enables them to become mobile. In the presence of an applied voltage across circuit traces and moisture, dendritic growth can occur. This occurs when atoms of the circuit trace migrate outward across the bare laminate until they bridge the circuit width, causing an electrical short.

Mobile ionic species speed up this form of growth. Mobile ionic species are also responsible for corrosion products formed on assembly surfaces. Military contractors are required to apply a conformal coating to protect assembly surfaces from moisture. A conformal coating is, of course, a polymeric material such as an epoxy, polyurethane, or acrylic designed to protect the assembly surface from moisture. In addition, conformal coatings also isolate contaminants and prevent them from migrating or being dislodged during temperature-moisture cycling, high vibration, shock environments, etc.

Nonionic contaminants remaining on the assembly surface can also lead to performance problems. These contaminants can interfere

with electrical bed-of-nails testing (a surface conductivity test) by creating electrical “opens”. They can also lead to adhesion problems if a conformal coating is being applied.

Ionic materials and some hygroscopic nonionic materials under conformal coatings can cause blistering during temperature/humidity cycling. This phenomenon is also called mealing or vesication, and it takes place because no conformal coating is 100% effective against moisture penetration. In fact, the presence of ionic material or hygroscopic material on the surface under the conformal coating actually acts to promote water penetration since such contamination attracts water. Once the contaminant becomes hydrated, it builds up osmotic pressure which causes a lifting of the conformal coating forming the blister or vesicle. This phenomenon is considered detrimental to the finished assembly.

Finally, there is the phenomenon of white residue (WR). White residue is not always white. It can be gray, tan, beige, or amber in color. There are several possible causes. In some instances the assembly butter coat is removed, revealing the glass weave intersections. This is known as measling and can result if too harsh a solvent is used for cleaning. White residue can also occur when activator materials are left behind on the assembly surface. This happens when the solvent used for defluxing has become depleted of alcohol (especially true of solvents based on trichlorotribluoroethane or CFC-113).

Another cause of white residue is solder paste. Solder paste contains materials known as thickening agents (thixotropic agents or rheological modifiers). These materials are difficult to remove during the defluxing operation, especially without using mechanical energy (e.g., sprays). These, thickening agent residues, are prone to form a white residues, especially if exposed to alcohol. Exposure to alcohol can come about either from alcohol in the defluxing solvent or alcohol in an ionic contamination tester.

However, the principal cause of white residue is thermal degradation of rosin. Rosin readily undergoes degradation and polymerization (the molecules bond together to form a much larger molecule). This is especially true when it is heated around 260°C (500° F) or higher. The rosin also interacts with tin and lead salts formed during the fluxing operation by the activator action on the solder oxides. The rosin interaction products are termed tin and lead abietates. The polymerized rosin and/or tin and lead abietates are much more difficult to remove by defluxing solvents because they are less soluble.

Typically, the white residue appears at the end of the defluxing operation after the defluxing solvent has flashed off. Both rosin fluxes and rosin pastes are prone to form this type of white residue. If this type of white residue appears, make sure that it is caused by the flux (or paste) and does not have another cause.

## PRECISION ELECTRONICS

Aqueous cleaning technology meets the high level cleaning requirements found in precision electronics manufacturing of disk drives, semiconductors, and electro-optics. These industries use high purity aqueous cleaners in controlled environment manufacturing settings. The cleaners are made from high purity ingredients and integrate filtration and purification steps in their manufacture. The end-user manufacturers may further filter the cleaners at the point of use. It is not unusual for a high-purity cleaner to be made in a clean environment where it is filtered to 5 microns and then be further filtrated to levels such as 0.2 microns at the point of use. Delivery of finished cleaner that is filtered to 0.2 microns or better requires manufacturing, filtering and packaging in a cleanroom environment.

## PRECISION MANUFACTURING

In many of today's high-tech metalworking applications, surfaces must be prepared by removing debris, oxides, scale, and salts to achieve extraordinary levels of cleanliness. Cosmetic factors can also enhance buyer perceptions—with a bright, oxide-free finish serving as visual indicator of product quality.

Numerous metalworking and metal finishing businesses are finding that aqueous detergents perform as well as or better than solvent cleaners in removing residues without harmful environmental side effects.

Among new, high-tech applications for aqueous cleaners are:

- **Anodized parts**—Anodizers, that produce aluminum substrate caps with anodic coatings for mounting personal computer IC chips, use aqueous cleaners to remove conductive tail-end residues and prevent toxicity and flammability.
- **Computer parts**—A major manufacturer of thermocouples and wafers used in computers and medical devices must clean ceramics and copper paste in heated (150°F) ultrasonic baths prior to nickel plating.

- **Aluminum**—A manufacturer of heat sinks for cooling computer chips in NASA space shuttles uses aqueous detergents to remove oil and organic debris to eliminate any chance of non-condensable gas formation.

In general, precision manufacturing with metals involves preparing the surface for bonding, coating, or exposure to an environment, such as a vacuum or a semiconductor, that is highly sensitive to residues. Therefore, corrosion inhibitors, that leave deposits, are generally inappropriate for precision cleaning. It is also important to make sure that the metal will not be attacked by any materials used in the cleaning, rinsing, or drying process. To clean precision manufacturing equipment use mild cleaners, short contact times and rapid rinsing and drying to minimize the chance for corrosion to occur. It is also critical to be careful using extremely high purity deionized rinse water that can be so “ion hungry” that it is corrosive to the metal substrate being rinsed.

## Plastics

To clean plastics, select a mild, nondamaging, cleaner strong enough to remove the soils that are present. As indicated in the following table, many plastics are resistant to attack by typical mild alkaline aqueous cleaners. For delicate plastics consult the manufacturer for cleaner recommendations or use a specially formulated plastic cleaner.

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### PLASTICS COMPATIBILITY WITH CLEANERS

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Generally acceptable with mild aqueous cleaners

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Polyethylene (LLDPE, LDPE, PE)  
Polypropylene (PP)  
Polyallomer (PA)  
Polymethylpentene (PMP, TPX)  
Fluoroethylenes (FEP, TFE, PFA, ECTFA, ETFE, TEFLON®)  
Polysulfones (PSF)  
Polyvinylchloride (PVC)  
Polystyrene (PS)  
Polyvinyl fluorides (PVDF)  
Polyurethane  
Ethylene Propylene (EPM)  
Buna N rubber  
Nordel®  
Viton®

Noryl®  
Ryton®  
Epoxy

Clean with caution even with mild aqueous cleaners

Polycarbonates (PC)  
Acetal polyoxymethylene (ACL)  
Nylon®  
Polymethylmethacrylate (PMC)

For more delicate plastics, a mild alkaline cleaner can often be used at modest temperatures, low concentration, and short contact times. The most challenging plastic to clean without damage is stressed polycarbonate which is prone to stress cracking when exposed to low surface tension solutions such as solvents and aqueous cleaners. Very dilute cleaner solutions may be needed to clean stressed polycarbonate.

Most plastics are organic in character which makes them attractive to organic film residues. A high emulsifying cleaner is often required to remove organic films from cleaners.

### Glass and Ceramics

Glass and ceramics have excellent insulating, transparency, and dimensional characteristics that make them desirable materials for many high-tech manufacturing applications.

Since these are inorganic matrix materials, they often attract and hold inorganic soils such as salts and ions. Aqueous cleaners with good chelating properties or acidic pH are often effective at removing such inorganic soils. In one application where ceramic crucibles had to be cleaned, mobile ionic residues had to be removed for use in semiconductor manufacturing. To solve this problem, aggressive immersion cleaning using heated ultrasonics with high wetting, high chelating, high emulsifying cleaners has been successful in providing successful cleaning of the ceramic crucibles.

### General Purpose Cleaning

Aqueous cleaners have been widely adopted in solvent-reduction programs for metalworking and parts-washing opera-

tions. Often, the level of cleanliness required is for “appearance only” or to prepare surfaces for painting, bonding or coating. It is critical to choose a detergent that is compatible with the type of parts washer being used.

For example, high-agitation cleaning machines such as bubble/air agitated immersion, spray wand, spray booth and conveyorized spray machines require the use of low-foaming cleaners. In contrast, it is preferable to use high emulsifying, high foaming cleaners when performing circulated, static and ultrasonic immersion cleaning. Less rigorous rinsing is often acceptable. Tap water may be a sufficient rinse and traces of water spots may be acceptable.

For appearance cleaning, however, a “no-rinse” process involving merely wiping the parts or air blowing them may be better when highly dilute cleaner solutions are employed.

TABLE 6J DETERGENT SELECTION GUIDE FOR PRECISION MANUFACTURING

Application Key Concerns	Articles Cleaned/ Soil Removed	Cleaning Method	Recommended Cleaner
Precision Manufacturing Clean parts, avoid volatile solvents, strong acids, and other hazardous chemicals.	Glass, ceramic, porcelain, stainless steel, plastic, rubber. Oils, chemicals, particulates.	Manual, Ultrasonic, Soak	Mild alkaline
		Machine washer, power wash	Low-foam alkaline
	Aluminum, brass, copper, and other soft metal parts. Oils, chemicals, particulates (acid for oxides, salts, buffing compound).	Manual, Ultrasonic, Soak	Mild alkaline or mild acid
		Parts washer, power wash	Alkaline or acid low-foam
	Inorganics, metallic complexes, trace metals and oxides, scale, salts, metal brightening.	Manual, Ultrasonic, Soak	Mild acid
		Parts washer, power wash	Low-foam mild acid
		Manual, Ultrasonic, Soak	Mild alkaline
	Silicone oils, mold-release agents, buffing compounds.	Parts washer, pressure spray	Low-foam alkaline
	Delicate substrates/neutral for waste.	Manual, Ultrasonic, Soak Machine wash, pressure spray	Neutral pH

### OPTICS

Aqueous detergents are also used to clean equipment during the manufacture of scientific, as well as, consumer optics such as contact lenses. For example, one manufacturer uses machining oils and heavy waxes to grind and polish its scientific optics to exacting tolerances. The oils and waxes must be

removed from the surfaces of finished products. The company's technicians have found that an alkaline detergent—normally used in lab washers and ultrasonic cleaning systems—was ideal for removing such wax. (They use a separate, pH-neutral cleaner to brighten the copper and copper alloys that surround these optics.)

On the consumer-product side, contact lens manufacturers also use pH-neutral aqueous cleaners. A wax is used to secure silicon/acrylic copolymer lenses to collets for machine formation of the all-important base curve layer which ensures proper fit and wearer comfort. The wax must be removed when the process is complete. Neutral aqueous detergents in ultrasonics were effective at removing the compounds used in grinding rigid gas permeable (RGP) contact lenses.

**TABLE 6K DETERGENT SELECTION GUIDE FOR OPTICS CLEANING**

Application Key Concerns	Articles Cleaned/ Soil Removed	Cleaning Method	Recommended Cleaner
Optics Clean parts, avoid volatile solvents, strong acids, and other hazardous chemicals.	Glass, ceramic, porcelain, stainless steel, plastic, rubber. Oils, chemicals, particulates.	Manual, Ultrasonic, Soak	Mild alkaline
		Machine washer, power wash	Low-foam alkaline
	Silicone oils, mold-release agents, buffing compounds.	Manual, Ultrasonic, Soak	Mild alkaline
		Parts washer, pressure spray	Low-foam alkaline
Delicate substrates/neutral for waste.		Manual, Ultrasonic, Soak Machine wash, pressure spray	Neutral pH

## COSMETICS

Cosmetic manufacturing involves many oils, pigments, emollients, and “waterproof” ingredients. Some of the most difficult to clean are titanium dioxide cremes and silicon oil emollients. Aqueous cleaning detergents are ideal cleaners for silicon, titanium dioxide, and other hard-to-clean residues generated in cosmetics processing. As with pharmaceutical processing, all residues, that could contaminate products and cause eye or skin irritation, must be removed. Silicon emollients can be removed using very high temperatures above 75°C (170°F) and double-strength solutions of a high emulsifying cleaner in a total immersion cleaning systems. Removal of titanium dioxide cremes also, generally, requires very high temperatures and high emulsifying cleaners with excellent dispersants.

**TABLE 6L DETERGENT SELECTION GUIDE FOR COSMETICS CLEANING**

Application Key Concerns	Articles Cleaned/ Soil Removed	Cleaning Method	Recommended Cleaner
Cosmetic Manufacturing Passing cleaning validation for FDA good manufacturing practices. For stainless steel, glass, plastic, elastomer cleaning.	Titanium dioxide, petrolatum, oils, emulsions, ointments, carbopols, lacquers, zinc oxides, proteins, steroids, alcohols, sugars, and Eudragit* (L/S/L30/D55/NE30D) polymers.	Manual, Ultrasonic, Soak	Mild alkaline
		Machine washer, power wash, CIP	Alkaline surfactant low-foam
	Inorganic residues, salts, metallics, pigments. Eudragit* (E/RL/RS/E100) polymers, amphoteric, coatings, amines, ethers, starches, alkaloids.	Manual, Ultrasonic, Soak	Mild acid
		Machine washer, power wash, CIP	Mild acid

\* Eudragit is a ® registered trademark of Roehm GmbH & Co.

## NUCLEAR

Few industries use more exotic alloys, or have more stringent quality-control requirements in manufacturing, than precision manufacturing of nuclear equipment. Components such as guide tubes, end fittings, coil springs, grids, and fasteners used in fuel assemblies for reactor cavities must be absolutely free of oils or other contaminants.

One major manufacturer of nuclear fuel assemblies has found that large parts such as 12-foot guide tubes can be effectively cleaned by manual soaking in a 1:100 dilution of a pH-neutral aqueous detergent and hot tapwater.

In reactor cavity cleaning, a specialty chelate-free aqueous cleaner has been used successfully during outage procedures at commercial nuclear-power plants. It has also been used successfully for radiological decontamination of floors, walls, tools, personal safety equipment, and components made of metal and plastic in auxiliary buildings—permitting release of cleaned items from controlled areas.

When cleaning on-site, be sure to avoid detergents containing chelating agents as they can bond chemically to radioisotopes. Also avoid detergents containing fluorides, chlorides, or sulfur ingredients which might cause surface corrosion or intergranular stress corrosion of stainless components.

**TABLE 6M DETERGENT SELECTION GUIDE FOR NUCLEAR CLEANING**

Application Key Concerns	Articles Cleaned/ Soil Removed	Cleaning Method	Recommended Cleaner
Nuclear Plants Dcontaminate radioisotopes without causing difficult to treat chelated waste.	Maintenance equipment and containment surfaces.	Manual, soak, power wash	Alkaline chelate free

**CHEMICAL AND OTHER FLUID PROCESSING**

The three primary areas of concern in chemical and fluid processing cleaning are:

- **Cleaning chemical process equipment**—most notably water or other high-purity chemical delivery systems
- **Oxygen/gas delivery systems**—where pipes and tanks must be kept extremely clean
- **Waste treatment systems**—particularly those involving the use of filter membranes

Clean-in-place cleaning is generally used to clean piping systems. A cleaning solution is circulated through the pipes and then rinsed thoroughly with an appropriate rinsewater until the desired level of cleanliness is achieved.

This is quite similar to cleaning done with oxygen delivery piping systems. In an oxygen delivery piping system it is crucial to remove residues that could oxidize, creating flammable or explosive conditions.

Waste-treatment filtration generally involves working with small to medium sized, in-plant systems. Fats, oils, greases, or process oils from manufacturing processes must be separated from waste water to achieve acceptable plant discharge. If this separation is done by a filtration system, use a high-emulsifying and/or a high-dispersing detergent to clean and rejuvenate the filter membranes. Often a high-emulsifying cleaner is used first to remove the oils and greases, followed by an acid cleaner to remove particulates such as organic soils and silt.

**TABLE 6N DETERGENT SELECTION GUIDE FOR CHEMICAL AND FLUID PROCESSING**

Application Key Concerns	Articles Cleaned/ Soil Removed	Cleaning Method	Recommended Cleaner
Chemical and Fluid Processing For stainless steel, glass lined and plastic pipes and tanks.	Petrolatum, oils, emulsions, ointments, carbopols, lacquers, zinc oxides, proteins, steroids, alcohols, and sugars.	Manual, Ultrasonic, Soak Machine washer, power wash, CIP	Mild alkaline Alkaline surfactant low-foam
	Inorganic residues, salts, metallics, pigments, amphoterics, coatings, amines, ethers, starches, alkaloids.	Manual, Ultrasonic, Soak Machine washer, power wash, CIP	Mild acid Mild acid
	Protein/ferment residues. R/O, U/F membranes.	Manual, Ultrasonic, Soak	Mild alkaline or enzymatic

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**RESOURCES**

www.alconox.com  
 cleantechcentral.com  
 www.metalfinishing.com  
 www.seiberling4cip.com



# Standard Operating Procedures

**A** A large part of successful cleaning depends on having sound, reproducible procedures also known as Standard Operating Procedures or SOPs. These help when training operators to clean consistently. In general, a good SOP includes a list of the materials and people involved in the cleaning procedure. It identifies the surface or part to be cleaned and addresses the eight cleaning variables which impact cleaning effectiveness as was discussed in Chapter 3 on Aqueous Cleaning Processes. To refresh your memory, we proposed an acronym composed of the first letter of each variable forming the word "BATHCARD" to help you remember what variables need to be controlled and specified in an SOP:

- 1) **B**efore—methods of handling surfaces or parts prior to cleaning.
- 2) **A**gitation—the type of movement used to enhance cleaning
- 3) **T**ime—duration of cleaning cycle
- 4) **H**eat—temperature of cleaning solution
- 5) **C**hemistry—the chemical composition and concentration of the cleaning solution
- 6) **A**fter—postcleaning handling
- 7) **R**inse—rinsing conditions
- 8) **D**rying—method of drying

Below are examples of SOPs for manual cleaning, ultrasonic cleaning, machine washer cleaning, and large-tank cleaning. In some cases, these SOPs were written for specific combinations of detergent concentrations and cleaning tem-

peratures temperatures for specific soils. As a result, you may need to adapt those SOPs for any new applications you might be developing. However, they do give you an idea of what to include in SOPs for several cleaning applications.

Wherever cleaning solutions are re-used in baths or sumps, determine the following: control parameters (such as pH, conductivity, refractive index/dissolved solids, or titration amounts), equipment to be used, (such as conductivity meters, pH meters or refractometers, or titration equipment), the person, or persons responsible for monitoring the baths, type of report or logbook entry to be made, trigger points and alert levels, when and what actions are to be taken in response to these levels and finally, the conditions under which the bath is to be dumped and a fresh bath made up.

## MANUAL PARTS OR MANUAL SURFACE CLEANING SOP

- 1. List parts or surfaces to be cleaned.** State the maximum number of parts or surface area that the process is designed to clean. Describe any training or certification requirements for those who will perform the cleaning operation
- 2. List materials to be used for cleaning.**
  - a. Detergent—provide full name, manufacturer, manufacturer part number, distributor/supplier, and internal part number as appropriate
  - b. Water of suitable purity—determine whether tap water, deionized water, distilled water or water-for-injection as is appropriate
  - c. Brush, absorbent cloth or sponge—whatever is used
  - d. Container of suitable size for the detergent solution—define container
  - e. Any baskets for handling small parts, if used
  - f. Any rinsing containers, if used
  - g. Any drying equipment, if used
  - h. Any required protective equipment, gloves, eye protection, clothing etc.
- 3. List any requirements for handling prior to cleaning.**

**Typical requirements might be:**

  - a. Parts to be cleaned within 4 hours of being processed to remove grime—if you knew that the grime had a tenden-

- cy to dry onto the parts and become more difficult to clean, or
- b. Tank to be cleaned within 3 days of last use—if you had validated that the tank could be successfully allowed to sit dirty for 3 days and still be cleaned by this manual procedure, or
- c. Do not remove parts from shipping containers until they are about to be cleaned—if you know that unpacking the parts increases the risk of new contaminants, or
- d. Handle all parts with finger cots to avoid adding fingerprints to surfaces – if you do not want to add any new fingerprints to a surface where you are using a cleaning process that is only designed to remove particulates, or
- e. Presoak the parts in a specific detergent solution, for a specific time at a specific temperature prior to cleaning. For example: Presoak parts completely immersed in 1% Terg-a-zyme detergent (1.25 ounces Terg-a-zyme in 1 gallon of water) at 120 deg F for 20 minutes prior to cleaning—if you know your parts have dried on protein soils that are difficult to clean without presoaking.

**4. Provide directions for making up the detergent solution following the manufacturer's instructions.** Address degree or water purity required, container size and suitable temperature. For example: Mix 1.25 ounces of Alconox powdered detergent in 1 gallon of 120 deg. F hot tap water in a 2.5 gallon bucket. Use cleaning solution within 15 minutes before the temperature drops below 120 deg. F.

**5. Provide manual cleaning instructions such as:**

- a. Wet part or surface with solution by
  - i. Dunking the part in the solution, or
  - ii. Wiping the part with a solution soaked brush, absorbent cloth or sponge
- b. Clean by scrubbing with the brush, absorbent cloth or sponge. Define any particular cleaning or scrubbing actions required such as: brush all surfaces vigorously, but particularly be sure to use brush vigorously on the inside of the port for at least 30 seconds.

**6. Itemize rinse procedures.** Examples might be:

- a. Place parts in basket and run them under running tap water for 20 seconds while moving basket to assure all

- parts are exposed to running water, or
- b. Hose down all surfaces with running water assuring that all parts of surface are rinsed for at least 10 seconds, or
- c. Dip part in bucket of rinse water for initial rinse, dip in second bucket of rinse water for second rinse, and then place under running water at the sink for 10 seconds as a final rinse.

**7. Describe drying procedure.** For example:

- a. Place parts on rack and allow to air dry, or
- b. Place parts on tray and place in 210 deg. F drying oven for 40 minutes, or
- c. Open all ports in tank and allow tank to air dry

**8. List any post cleaning handling procedures** Examples are:

- a. Inspection actions to be taken, for example: take 10 parts from the batch and inspect for particulates and visible smudges with a 10X magnifying glass. Record results in batch record. Reject entire lot if there are any failures. Or,
- b. Mark tank with “clean tags” recording time, date, and operator who performed cleaning. The next day after the tank has dried, close the ports to keep out dust. Or,
- c. Dispose of used detergent solution down the drain.

An example of a manual cleaning SOP written for cleaning of a bench top fermentation reactor appears below and follows the guidelines provided. This example was adapted from “Fundamentals of Fermentation: Techniques For Benchtop Fermentors Part I - E. coli” which was prepared by the R & D Lab, New Brunswick Scientific Co., Inc.

**1. Scope**

- a. For cleaning bench top fermentation reactors
- b. Operator training a qualification required

**2. Materials**

- a. Liquinox Detergent (Alconox, Inc. catalog number 1201)
- b. Water
- c. Kimwipes®
- d. pH 7 buffer
- e. chemical resistant gloves
- f. glycerine

- g. sponge
- h. non-abrassive pad

**3. Precleaning requirements and procedures:**

- a. When the fermentation run is complete, carefully shut the process down. First, turn all operating settings for agitation, temperature, dissolved oxygen (D.O.) level, pH, and gas feed, from their current control modes (e.g. PID, D.O., Base) to the off mode. Also close the manual air valve on the right side of the unit. If a supplemental oxygen feed was used, close the gas tank valve and the lines leading from it to the unit. If a recirculating chiller is in use, shut it off when the temperature control is shut off. Clamp off feed lines from any addition bottles that prior to detaching them from the vessel, and then be remove them.
- b. The next step is to disconnect the vessel from the unit. The temperature probe must be removed from the thermowell. Remove the motor and place the protective cap over the agitation shaft. Always disconnect incoming lines water lines prior to the outgoing lines. The air line must be disconnected from the sparger. Disconnect the pH and D.O. probes from the unit and replace their protective caps. The D.O. probe is easy to remove. Simply unscrew the thread and gently pull it out. It should be rinsed off immediately and then wiped dry gently. Always remember to avoid touching the membrane tip. Some runs will result in an accumulation of biomaterial on the probe and it may be necessary to wipe the probe down more vigorously, but, in no case should the tip be touched. After the D.O. probe is cleaned, visually inspect the tip for damage. The probe should then be stored in a clean area so as to protect the sensitive tip. Removing the pH probe is usually not as difficult a process as inserting it because the shaft will be wet and should be relatively easy to remove as a result. However, the danger of probe breakage is still very real and extreme care must be taken when removing it. Use two hands keeping one hand at the top of the port to act as a guide and ensure proper removal. A gentle pace is required. If at any point in this process

the probe jams, it is essential to avoid trying to force it. It may be necessary to reinsert it part of the way and apply a lubricant such as glycerin to the shaft and port in order to effect the probes' removal. In extreme cases it may be necessary to remove the headplate with the probe still inside so that you can approach the problem from both ends. In this case, it is critical to remove the headplate very carefully. (We recommend that you have a spare probe available at all times, in case of breakage.) Once the pH probe has been removed, wash it off immediately with warm water. If biomaterial has accumulated on the probe, use a sponge (or an equivalent that will not scratch glass) and gentle pressure to clean the surface. The very tip of the probe should be handled with extreme care and a Kimwipe® should be used gently to dry it off after washing. The probe should be stored with the tip immersed in either electrolyte or pH 7 buffer. This electrolyte/buffer can be reused, but it should always be inspected prior to each use for precipitation or contamination.

#### **4. Manual cleaning, rinsing and drying description**

- a. Now that the vessel is detached from the unit, it can be cleaned. To do this, remove any remaining cotton and/or foil covering the ports. The rubber bulb on the sampler should be removed and rinsed separately. The glass wool can also be removed. The sampling tube is detached and washed separately. The valve on the sampling port and clamps on all tubing connected to ports will need to be open for proper washing. (Note that the media will need to be removed prior to unclamping any tubing that is below the liquid level, as is the case with a side harvest line). The headplate should be detached by loosening and then removing the clamps that hold it to the rest of the vessel. Those clamps may require rinsing. The remaining culture broth should be sterilized or emptied into a bucket and disinfected by using bleach or other accepted disinfectant prior to disposal. Note that some media may be incompatible with this procedure, in which case the media can be placed into another container for sterilization prior to disposal. The

headplate should be washed thoroughly with warm water and then deionized (DI) water. It may be necessary to scrub accumulations of biomaterial off. A pad that won't scratch the steel is required for this. The agitation shaft, thermowell, harvest and sparger tubes and short beveled tips of the interior portion of the base-type addition ports will often require special attention. All tubes and shafts must be cleaned. Note that there may be some residual base or acid left in those lines, so extreme caution is required. Use of chemically-resistant gloves is strongly recommended. It is often necessary to hand wipe surfaces with a paper towel in order to remove all traces of small particulate debris.

- b. The same procedure is used to wash the bottom portion of the vessel and the headplate. Note that the sides of the vessel, particularly the parts that were adjacent to the baffle, and side ports (plugged or unplugged) may require special attention.
- c. The vessel can now be cleaned by washing with detergent, or by using a cleaning solution. If the vessel is to be sterilized, all standard precautions must be taken. Note that for this purpose, the vessel does not need to be sealed except for those previously cited valves and tubing which run under the liquid level. It will be necessary to use water in the vessel. We recommend the use of DI water, and the fill should be at least as high as your standard level for a run. Unless you have already specifically wiped the residual grease off the top of the glass cylinder, there should be enough grease that will make a good seal with the headplate so that the headplate can be clamped to the lower portion of the vessel. Note that, it is best to fasten these clamps with slight tension to avoid vessel damage. Use as little pressure as possible. The advantage to sterilization is that not only are residual viable organisms killed, but residual debris will loosen and be removed easily by washing after the vessel has cooled. If a cleaning solution is required, use a 1% dilution of Liquinox cleaning solution (Alconox, Inc. catalog number 1201). Or, if you are using the vessel for consecutive runs with the same media, rinsing with warm tap

water and DI water may suffice. If water will run over a vessel surface that has grease on it, remove the grease by wiping the surface with a wet paper towel.

- d. In cases where the vessel must be decontaminated prior to cleaning, add water so that the liquid level reaches the maximum working volume of the vessel. This will help prevent biological materials from adhering.
- e. Allow vessel to air dry after thorough rinsing

#### **5. Post cleaning procedure**

- a. Store vessel in a clean area.
- b. Inspect visually prior rinsing and sterilization for next use.

### **ULTRASONIC CLEANING SOP**

**1. List parts to be cleaned.** Indicate the maximum number of parts per batch. Define any training or certification requirements needed to perform this cleaning operation.

**2. List materials to be used.**

- a. Detergent—provide full name, manufacturer, manufacturer part number, distributor/supplier, and internal part number as appropriate
- b. Water of suitable purity—indicate whether tap water, deionized water, distilled water or water-for-injection as is appropriate
- c. Ultrasonic cleaning tank—define size, frequency, configuration, manufacturer, and identifying specifications
- d. Any baskets for handling small parts, if used
- e. Any rinsing containers or equipment
- f. Any drying equipment, if used
- g. Any required protective equipment, gloves, eye protection, clothing etc.

**3. List any requirements for handling prior to cleaning.**

Typical requirements may include:

- a. Degas solution for 10 minutes to remove dissolved gasses that will dissipate cavitation energy and decrease cleaning performance, or
- b. Turn on heaters and preheat the tank to 120 deg. F (50 deg. C) or,
- c. Parts to be cleaned within 4 hours of being processed to remove grime – if you knew that the grime had a tenden-

cy to dry onto the parts and become more difficult to clean, or

- d. Do not remove parts from shipping containers until ready to clean them – if you know that unpacking the parts increases the risk of new contaminants, or
- e. Handle all parts with finger cots to avoid adding fingerprints to surfaces – if you do not want to add any new fingerprints to a surface where you are using a cleaning process that is only designed to remove particulates, or
- f. Presoak the parts in a specific detergent solution for a specific length of time at a specific temperature prior to cleaning. For example: Presoak parts completely immersed in 1% Terg-a-zyme detergent (1.25 ounces Terg-a-zyme in 1 gallon of water) at 120 deg. F for 20 minutes prior to cleaning – if you know your parts have dried on protein soils that are difficult to clean without presoaking

**4. Provide instructions for making up the detergent solution following manufacturer's directions.** Address degree of water purity required, container size and suitable temperature. For example: Mix 1.25 ounces of Alconox powdered detergent in 1 gallon of 120 deg. F (50 deg. C) hot tap water which will fill tank to within 1 inch of the top. Another example: Fill the tank within 1 inch of top and turn on heaters. Make up 1% Alconox solution in a beaker (20 g Alconox in 200 ml water in a 250 ml beaker). Place the beaker of Alconox solution in a beaker tray immersing it in the heated water. Fill 3 other beakers with deionized water for rinsing and place them in the beaker tray.

**5. Provide step by step cleaning instructions:**

- a. Include directions for part placement in cleaning device. Never place parts or receptacles directly on the bottom of the unit. It can cause the unit to fail because the parts will reflect the ultrasonic energy back into the transducer. Always allow at least one inch between the tank bottom and the beaker or receptacle for adequate cavitation. Keep solution within one inch of the top of the unit when a beaker or tray is in place.
- b. Describe the use of a holder. If using a tray or basket to lower the parts into the solution, it is better to use a

holder that is of open construction, either an open mesh basket or an insert tray, that is adequately perforated for drainage. This also permits free access of the sound waves to the parts.

- c. Clean the parts in the solution by
  - i. Placing them in basket and immersing them in the ultrasonic tank for 10 minutes
  - ii. After 10 minutes lift basket and allow it to drip off for 1 minute to reduce dragout
  - iii. Cover ultrasonic tank after removing and draining basket

**6. Itemize rinse procedures.** For example:

- a. Place basket containing parts under running tap water for 20 seconds while moving basket to assure all parts are exposed to the water.
- b. Do a final rinse by immersing in a second ultrasonic tank filled with deionized water for a final rinse. (Change rinse water when it reaches 50 Kohms resistance.)

**7. Describe drying procedure.** For example:

- a. Place parts on rack and allow to air dry, or
- b. Place parts on tray and place in 210 deg. F drying oven for 40 minutes,

**8. List any post cleaning handling procedures.** Examples are:

- a. Define any inspection actions, for example: take 10 parts from the batch and inspect for particulates and visible smudges with a 10X magnifying glass. Record results in batch record. Reject entire lot for recleaning if there are any failures. Or,
- b. Dispose of used detergent solution down the drain.

An example of an ultrasonic cleaning procedure adapted from a manufacturer of small stainless steel and aluminum parts is:

**1. Scope**

- a. For the cleaning of small stainless steel and aluminum parts
- b. To be carried out by trained and qualified operators

**2. List of Materials**

- a. Alcojet powdered detergent (Alconox, Inc. catalog number 1450)
  - b. Drain rack with mounting pins to mount connectors on for cleaning operation
  - c. Ultrasonic cleaning tanks
  - d. Ultrasonic rinsing tanks
  - e. Air knife, filtered hot air dryers
  - f. Deionized water
  - g. Drying ovens
  - h. 10X magnifying glass
  - i. alkaline resistant rubber gloves
3. Flow chart showing handling, cleaning, rinsing, drying, control and post cleaning handling (see chart on following pages).

**ALUMINUM FOIL ULTRASONIC CLEANER TEST PROCEDURE**

When cleaning using ultrasonics, it is a good idea to test the performance of your ultrasonic washer. Use the following aluminum foil test adapted from a Brooks Airforce Base procedure ([http://www.brooks.af.mil/dis/ic\\_guidelines/attach2.htm](http://www.brooks.af.mil/dis/ic_guidelines/attach2.htm)) as a guide.

1. Prepare an aluminum foil sample. Obtain a roll of standard lightweight household aluminum foil. Unroll a rectangular piece of foil measuring approximately the length (long dimension) of the tank by one inch greater than the depth. For example: A tank with dimensions of 9 inches long by 5 inches wide by 4 inches deep would require a foil sample measuring 9 inches by 5 inches. Use scissors to cut the foil. Do not tear.
2. Prepare a fresh cleaning solution according to the manufacturer's instructions and fill the ultrasonic tank to one inch of the brim.
3. If heaters are supplied with the cleaner, turn them off for the remainder of the test. If the unit has a HI/LO switch use the highest setting.
4. Before placing the foil in the tank, turn the ultrasonic cleaner on for five (5) minutes using the timer located on the machine. If the timer is analog, be sure to turn it to 20 min-

## CLEANING PROCESS FLOW FOR PARTS

STEP NUMBER	STEP DESCRIPTION	CHEMICAL USED	WATER USED	AGITATION	TIME (MIN.)	BATH CHANGE NO PARTS.	CONTROLS/ PARAMETERS
	Incoming DI water						Resistivity
							pH
	Incoming Inspect						Visual
	Material input						Qty/load
1	Initial Presoak	Alcojet		Manually	3 min	100K	Concentration
	Rinse(water jet)		Water	Manually	1min		
2	1st Ultrasonic Clean	Alcojet	DI water	Ultrasonic	5±1min	100k	Concentration
				(40KHZ)			pH
	Rinse(water jet)		DI Water	Manually	1 min		Pressure
3	2nd Ultrasonic Clean	Alcojet	DI water	Ultrasonic	5±1min	100k	Concentration
				(40KHZ)			pH
	Rinse(water jet)		DI Water	Manually	1 min		Pressure
	Rinse(DI water jet)		DI Water	Manually	1min		Resistivity
8	DI rinse (immersion)		DI water	Air	5min		Resistivity
9	Final DI rinse (immersion)		DI water	Ultrasonic	2min		Resistivity
				(40KHZ)			
11	Spin initial dry			Machine	2 min		
12	Dryer			Hot air	10min		
13	Oven Dry			Hot air	45min	Every Lot	
	Outgoing inspect						Visual
	Performance test		DI water		4 h	Every Lot	Visual
	Packing	Plastic tray/bag					As Required
	Storage						As Required

ALERT LEVEL: 1. INFORM SUPERVISOR OR QC/ENGINEERING/PRODUCT MANAGER

## CLEANING PROCESS FLOW FOR PARTS

Specified Limits	Temperature (Degree C)	Check Frequency	By	Control Chart	Check/ Equipment	Trigger Points	Alert Level	Trigger Actions
>2 Megohms	R/ T	Once/Day	Technician	Trend	Cond meter	<5Megohms	1	Change DI column
5.5-8.0		Once/Day	Technician	Trend	pH meter	Out of spec	1	
As required		All	IOC tech	Insp report	10 x Glass	1% failure	1	Inform Customer
500pcs/holder								
1%	R/ T							
	R/ T							
3%	60-70				Control Box	65±5		Concentration
10.4-11.4		Once/Day	Technician	log bk	pH meter	Out of spec	1	Increase/Dilute
2-4kg/c	R/ T							
3%	60-70				Control Box	64±5		Concentration
10.4-11.4		Once/Day	Technician	log bk	pH meter	Out of spec	1	Increase/Dilute
2-4kg/c	R/ T							
>2 Megohms	R/ T							
>2 Megohms	R/ T							
> 2 Megohms								
	55+5	Once/Day	Technician		Control Box	50-60		
			Technician		Spin Machine		1	
	90±10_		Technician		Control Box	95±5	1	Check temp probe
	150±10_		Technician		Control Box	150±5	1	Check temp probe
0.1% fail			QC tech	Insp report	Microscope10		1	Sorting 100
Corrosion	95+5_	3pcs/lot	Technician	Insp report	Visual	No Corrosion	1	Rework

utes, then back to 5 minutes for maximum time accuracy. Digital timers can be set directly.

5. Place the foil sample, prepared in Step 1, into the tank in a vertical position. The long dimension, of the sample, should be positioned parallel to the long side of the tank. The foil should extend downward, but should not touch the tank bottom.
6. Hold the foil, approximately centered front to back, as steady as possible. Turn the ultrasonic cleaner on for exactly 20 seconds.
7. Turn the cleaner off and remove the foil sample. Shake the foil sample to remove any water droplets and allow it to air dry. Be careful not to wrinkle the foil.
8. If the unit is functioning properly, the entire foil surface will be uniformly “peppered” (covered with a tiny pebbling effect). If areas greater than one inch square show no pebbling, there may be a problem with the unit. Retest with new foil to substantiate the failure. If both samples fail, return the unit, along with the latest foil record, to your service center, or to the manufacturer, for repair. Retain foil samples for reference. If future tests show marked changes over time, you may need to service your unit. Always, include foil samples when you send the unit in for service.

## CLEAN-OUT-OF-PLACE IN RACK LOADED SPRAY-IN-AIR WASHER

Standard Operating Procedures for the wash cycle in a machine washer, which does not include the scope and list of materials is:

1. Precleaning, required only to remove bulk ingredients, can be accomplished by a thorough rinsing. Handle the items you are cleaning according to manufacturers recommendations. Follow your company’s safety regulations when handling and transporting items.
2. Chemical composition and concentration of cleaners is specific to the soils and residues to be removed. A GMP Washer utilizes precise dosing pumps to deliver chemicals to the wash chamber which contains a fixed volume of water. The dosing time will determine the amount of chemical delivered to the chamber.

3. GMP wash temperatures are programmed by the user up to 95 degrees Centigrade.
4. Adequate exposure time, of cleaning chemistry at setpoint temperature, will ensure proper cleaning. GMP Washers validate exposure time through continual monitoring.
5. Purified Water rinsing (i.e. WFI, USP) ensures removal of all cleaning chemicals at the end of the wash cycle. Measure conductivity measurement of final rinse water to validate rinsing efficiency.
6. On Drying models, a drying step with temperatures up to 110 deg. C. can be performed. All drying air is HEPA filtered.
7. Postcleaning handling, of washed items, must follow internal company procedures that assure cGMP compliance.

POSSIBLE SETTINGS FOR WASHER CYCLES		
Function	Possibility	Prog. 11
PREWASH 1 PERIOD	0 to 30 min	
PREWASH 1 TEMPERATURE	up to to 95° C	
PREWASH 1 DETERGENT	0 to 6 min	
PREWASH 2 PERIOD	0 to 30 min	
PREWASH 2 TEMPERATURE	up to to 95° C	
PREWASH 2 DETERGENT	0 to 6 min	
PREWASH 3 PERIOD	0 to 30 min	
PREWASH 3 TEMPERATURE	up to to 95° C	
PREWASH 3 DETERGENT	0 to 6 min	
WASH PERIOD	0 to 30 min	
WASH TEMPERATURE	up to to 95° C	
WASH DETERGENT	0 to 6 min	



Function	Possibility	Prog. 11
W.F.I RINSE 1	0 to 9	
ACID RINSE PERIOD	0 to 30 min	
ACID INTAKE	0 to 6 min	
W.F.I RINSE 2	0 to 9	
COLD W.F.I RINSE 1	0 to 30 min	
COLD W.F.I RINSE 2	0 to 30 min	
COLD W.F.I RINSE 3	0 to 30 min	
COLD W.F.I RINSE 4	0 to 30 min	
HOT W.F.I RINSE	0 to 30 min	
HOT W.F.I TEMPERATURE	up to to 95° C	

During the inspection and qualification of the GMP Washer, verification of the effectiveness of the inventory system, as described above, must be demonstrated. Testing protocols must be established. An example is as follows:

One test protocol for establishing GMP washer operation that can be used can be done by the riboflavin U.V test:

Soil the parts with a Riboflavin solution.

Let them dry for 2 hours and then soil them again.

Let them dry overnight.

Perform a wash cycle that does not include drying.

After cycle, the wet parts are checked with an U.V lamp.

Does Riboflavin remain?

Test 1 Yes / No

Test 2 Yes / No

Glassware Test 1: Yes/No

Test 2: Yes/No

Test 3: Yes/No

After the system has been inspected and verified, operators must be trained to load/unload the racks is an efficient manner.

## CLEAN-IN-PLACE ULTRAFILTRATION BRINE WATER FILTER SYSTEM CLEANING

### 1. Scope

- To clean a large ultrafiltration brine water filter system
- Operators must be trained and qualified

### 2. Materials

- Good quality chlorine-free tap water (total dissolved solids less than 5,000 mg/l)
- 316 stainless steel mix tank sized appropriately to the system (minimum of 3 minute retention time during circulation) with an exhaust fan, mixer, cooling coil, and temperature indicator
- 316 stainless steel centrifuge pump sized for appropriate flow rates
- 10 micron cartridge prefilter
- Flow meters
- Suitable flexible piping, sampling ports and port connectors
- Terg-a-zyme (Alconox Inc. catalog number 1350) enzyme cleaner

### 3. Pre cleaning conditions

- Filter system suffering from biofouling and/or inorganic particulate build-up

### 4. Cleaning, rinsing and drying description

- In large systems, isolate the 1 block of filter elements to be cleaned, allowing the rest of the blocks to operate normally.
- Flush filter element block with water once through (10 gallons for a typical 4 inch diameter filter element unit – different sized units would take proportionally more or less water).
- In the mix tank, dissolve enough Terg-a-zyme to make a 0.5% solution taking into account the volume of the tanks and filter element blocks (2.5 gallons for a 4 inch system).

- d. Turn on mixer to dissolve detergent.
- e. Circulate the cleaning solution through the filter block. Send the first 20% of the solution to drain via the brine return valve. Circulate the rest of the cleaning solution at 4.5 gallons/min at 345-1035 Kpa pressure for a 4 inch system. Use the chiller to maintain the temperature below 35 deg. C.
- f. The cleaning progress can be monitored by observing the color of the effluent. Circulate continuously or alternate circulate and soak cycles for 15 minute each. Circulate for at least 2 hours for a 4 inch system. Continue until the return effluent is no longer badly discolored.
- g. When cleaning is completed, stop recirculation and drain mix tank to waste. Flush residual cleaner with feed water at 4.5 gallons per minute (for 4 inch systems) at 345-518 Kpa pressure (for 4 inch systems) sending both brine and product side to drain. Collect sample of effluent in a small jar, cover, shake and observe foam indicating the presence of detergent. Rinse jar between uses. Continue flushing until no foam is observed in the shaken sample jar.

### 5. Post cleaning handling

- a. Perform post treatment procedures and return block to normal operations. Check pressure and performance to determine whether further treatment with a citric cleaner such as Citranox (Alconox, Inc. catalog number 1815) is needed to reduce particulate and inorganic scale buildup

## CLEAN-IN-PLACE LARGE TANK FILL, SOAK AND AGITATE CLEANING

### 1. Scope

- a. To clean a large stainless steel tank to remove a blended material that contains a thick high melting wax.
- b. Operators must be trained and qualified

### 2. Materials

- a. Detergent
- b. Brush
- c. Bucket
- d. Recirculation pump

- e. Hot water hose

### 3. Precleaning conditions

- a. Tank with waxy residue shall be cleaned within 24 hours.
- b. Tank ports should be kept closed while in holding.

### 4. Cleaning, rinsing and drying

- a. Fill tank full with hot plant water.
- b. Add detergent recommended for the type of residue in the tank (see note).
- c. Turn on mixer wipers to agitate.
- d. Turn on tank heaters to raise temperature above 95 deg C (see note).
- e. Turn on pumps and connect pipes to recirculate through any lines that need to be cleaned. Note: pumps should be operated with sufficient head pressure or at a slow enough speed to avoid cavitation from foam.
- f. Run for 4 hours. Depending on how well sealed the tank is, you may need to add make-up solution to compensate for evaporation during the 4 hours.
- g. Open top and, using a brush dipped in hot solution, manually scrub the unexposed top sections of the tank that were not immersed by the cleaner.
- h. Drain the tank
- i. Fill the tank with hot plant water that had been heated to 95 deg C. Keep the agitation and any recirculation pump turned on for 10 minutes.
- j. Use a hose, with hot water, to rinse the top part of the tank above the immersion line
- k. Drain the tank
- l. Visually inspect the interior of the tank and clean any known problem areas with a hot bucket of detergent solution and a brush.
- m. Rinse the tank thoroughly with hose, of hot plant water, or a spray ball apparatus with hot plant water.
- n. Drain the tank.
- o. Allow tank to air dry with ports open

### 5. Post cleaning conditions

- a. Tag the tank as clean with a date to allow control for clean hold times.
- b. Record cleaning in equipment log, including date, time, and operator.

Note that, as experience is gained with specific soils and tanks, you may need to adjust cleaning time. The cleaning regimen, described above, was designed to remove a wax, which melts at approximately 90 deg C. You will not need this much heat to remove most soils and residues. For example, many waxes melt at 75 deg C. Adapt this procedure by lowering temperatures as appropriate.

The SOPs, that appear above, are examples which may be adapted for other cleaning situations. There are many varieties of cleaning machines including: vibratory washers, oscillating washers, reel-to-reel washers, spray cabinet washers, and a range of other industrial washers. Each requires a different SOP. The machine manufacturer can help you understand how to operate the washer correctly. Use the above examples as guides and your own experience to formulate a successful SOP.

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#### REFERENCES

- DuPont Company Bulletin 507 "Cleaning Procedures" p 1-4 (1982)  
Durkee, JB, *The Parts Cleaning Handbook*, Gardner Publications, Cincinnati, 1994  
Dollard, R M Keeping Validation Current: Elements of an Effective Change Control Program, Philadelphia. presented at Cleaning Validation and Cleaning Processes Jan 14-15 Philadelphia, PA (2002)  
James Fry, Private communication regarding Lancer Washers May 2002

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#### RESOURCES

- [www.alconox.com](http://www.alconox.com)  
[www.lancer.com](http://www.lancer.com)  
<http://www.brooks.af.mil/dis/icguidelines/attach2.htm>

# Cleaning Validation

**A** cleaning validation is a documented guarantee that cleaning can be performed reliably and repeatedly to meet a predetermined level of cleanliness. It involves testing for acceptable residues on manufacturing surfaces. Cleaning validation is becoming a requirement in the pharmaceutical industry and other industries that adhere to Good Manufacturing Practice (GMP) and quality Systems Regulations (QSR). Other industries include bio-pharmaceutical, bulk-pharmaceutical, medical-device, cosmeceutical and clinical-diagnostic manufacturing. The validation is specific to detergent and method used for cleaning.

A cleaning validation generally consists of three parts: Installation Qualification (IQ), Operational Qualification (OQ), and Performance Qualification (PQ) of manufacturing equipment and operations. The validation includes a final report and a set of written procedures that, when followed, will maintain a validated state. It is performed on those critical cleaning steps that effect the quality or safety of the final device or product. It is done when a cleaning process cannot be fully verified. In some low volume, high value medical device manufacturing, it is more practical to verify cleaning on 100% of devices made. In most pharmaceutical or large volume medical device manufacturing, verification is not practical and cleaning validation is generally done.

To perform a cleaning validation, begin with a validation "master plan". The master plan generally dictates what needs to be included in the final report. A typical report might include the following sections:

- Objective
- Responsibilities of validation committee members
- Equipment/products/ procedures
- Test acceptance limits
- Analytical methods
- Sampling procedures and recovery
- Cleaning process design
- Data analysis
- Assumptions
- Change control/maintenance
- References

The objective of the validation might be to ensure product, worker, and environmental safety while controlling the risk of cross contamination. The individuals or departments involved in carrying out the validation, also known as the “validation committee”, will have clearly defined responsibilities. A typical committee might include the following:

- **Validation Specialist**—writes, coordinates validation
- **Manufacturing**—writes SOPs, provides training
- **Quality Assurance/Quality Control**—approves, carries out analytical methods
- **Engineering**—informs of changes, provides equipment data
- **R&D**—performs recovery studies, validates methods, transfers methods, selects new cleaners

Since August, 2002, cleaning validation in the US, has come under the jurisdiction of the FDA and must comply with their standards. There is a risk based approach which emphasizes quality systems inspections. In pharmaceutical manufacturing, the quality subsystems inspected by the FDA under The Drug Manufacturing Inspection Program (US FDA Center for Drug Evaluation and Research CDER 7356.002) include: production systems; facilities and equipment systems; packaging and labeling systems; materials systems; and laboratory control systems. In medical device manufacturing, the subsystems or departments inspected under the Quality System Inspection Technique (US FDA Center for Device and Radiological Health CDRH August 1999) include: corrective

and preventive action systems; production and process control; equipment and facility controls; records, document and change controls; material controls; and design controls.

## PHARMACEUTICAL CLEANING VALIDATION

To simplify the validation process, assembling an equipment matrix, that defines all shared and dedicated equipment, is suggested. It is possible to identify and document a “worst case,” or most difficult, to clean equipment and perform a complete validation. This will represent the (documented) easier to clean equipment.

By the same token, a matrix of residues can be assembled. Group residues into classes each cleaned under a particular set of conditions. Then, determine which is most difficult to clean. Once a worst-case residue, or residue class, is identified, a matrix of cleaning procedures be assembled. This will limit the number of procedures and help standardize those procedures improving efficiency of implementation and training.

It is important to validate a worst case scenario and to justify your choice. Worst case is typically based on several factors including: product solubility in cleaner or detergent, toxicity of the products or degredants being cleaned, dose sizes and normal therapeutic dose size (smaller may be more critical to validate, hardest to clean equipment/residue, and worst interactions with the next batch to be cleaned.

Cleaning validation for a specific cleaner involves testing for acceptable residues on pharmaceutical manufacturing or medical device surfaces. This includes:

- Identifying residues,
- Selecting a residue detection method,
- Selecting a sampling method,
- Setting residue acceptance criteria,
- Validating residue detection methods
- Conducting recovery studies, and finally
- Writing procedures and training operators.

This procedure is used to document acceptable residues three or more times and then a rational monitoring program, to maintain a validated state, can be put in place. If changing any part of the cleaning procedure including the cleaner, you

must revalidate. To do this first clean the new way, collect data and then clean the old way before using any equipment. Follow these steps until the new procedure is fully validated.

**Identifying residue**—in a pharmaceutical manufacturing environment means determining and documenting any possible residues that could be left on parts or surfaces as a result of the cleaning process. This includes: cleaners, primary ingredients, excipients, decomposition products, and preservatives.

**Selecting a residue detection method**—for cleaners, may involve choosing a specific method or a non-specific method. Specific methods test for a specific ingredient and include: high-performance liquid chromatography (HPLC), ion selective electrodes, flame photometry, derivative UV spectroscopy, enzymatic detection and titration. Non-specific methods test for, the presence of a blend of ingredients, such as: total organic carbon, pH, and conductivity. The FDA prefers specific methods, but will accept non-specific methods with adequate rationale for their use. For investigating failures or action levels, a specific method is usually preferable. (A later section of this chapter lists references to several methods for each cleaner brand.)

**Selecting a sampling method**—for cleaners, involves choosing between rinse water sampling, swabbing surfaces, coupon sampling and placebo sampling.

Rinse water sampling involves taking a sample of an equilibrated post-final rinse that has been recirculated over all surfaces. Rinse samples should be correlated to a direct measuring technique such as swabbing.

Swabbing uses a swab, or wipe, moistened with high purity water (WFI), that is drawn over a defined area using a systematic, multi-pass technique always moving from clean to dirty areas to avoid recontamination. A typical swabbing pattern might begin with ten side by side vertical strokes, followed by ten horizontal strokes and then ten strokes with the flip side of the swab in each diagonal direction. You then cut off the head of the swab and place it in the pre-cleaned TOC vial. For TOC analysis very clean low background swabs or wipes and sample vials such should be used. The Texwipe

large Alpha Swab 714A and 761 have been used successfully. These are available in kits with clean sample containers. For UV testing, Texwipe TX 762 swabs have been used in conjunction with running a swab blank to set the zero level on the UV-visible analyzer.

Quartz glass fiber filter papers have also been used successfully. Coupon sampling involves the use of a coupon or an removable piece of actual pipe that is dipped into high purity water to extract residues for analysis (see p. 48 suppliers).

Placebo testing is done using placebo products and analyzing for residues from the previous batch.

**Setting residue acceptance criteria**—in pharmaceutical and medical device manufacturing requires identifying potential residues including the active drug, excipients, degradation products, cleaning agents, bioburden and endotoxins. To determine acceptable levels of each residue, take into account how the residue will affect the next product to contact that surface, or equipment, during production. Residue levels must maintain pharmacological safety and stability while avoiding toxicity and contamination of the next product being produced. Limits are typically set for visual, chemical, and microbiological residues.

The cleaning agent limits are generally covered under chemical limits. Chemical limits can be expressed as a maximum concentration in the next product (ug/ml), amount per surface area (ug/cm<sup>2</sup>), amount in a swab sample (ug or ug/ml), maximum carryover in a train (mg or g) or concentration in equilibrated rinse water (ug/ml). You should have a calculated safety based acceptance limit. In addition, you may want to have a lower internal action level, and a lower process control level based on actual manufacturing and measuring experience.

Cleaning agent safety based limits are typically calculated from a safety factor of an acceptable daily intake (ADI), a (1/1000 or more) reduction of an LD50, preferably by the same route of administration or reproductive hazard levels. If the calculated limit is equal to or greater than a 10 ppm carryover, to the next batch, then the safety based limit can be set to the more stringent 10 ppm carryover level.

Calculated safety based limit in mg/cm<sup>2</sup> or mg/ml of cleaner residue on a just cleaned equipment:

$$\text{Limit (mg/cm}^2 \text{ or L)} = [\text{ADI carryover, see below (mg) X Smallest Next Batch (kg)}] / [\text{Size of Shared Equipment (cm}^2 \text{ or L) X Biggest Daily Dose or of Next Batch (kg)}]$$

$$\text{ADI carryover (mg)} = [\text{LD50 by administration route (mg/kg) X body weight (kg) X (1/ 10,000 or 1/1000*)}]$$

\*a conversion safety factor, see p. 114

Comparison calculation of limit based on no more than 10 ppm carryover:

$$\text{Limit (mg/cm}^2) = [10 \text{ mg residue on just cleaned surface X Next Batch Size (kg or L)}] / [1 \text{ kg of L of next product X Size (cm}^2 \text{ or L) shared equipment}]$$

Note that, for many residues, a visual detection limit can be validated on the order of 1-4 ug/cm<sup>2</sup>. It is possible that the visually clean criteria will be the most stringent criteria.

For example, for a cleaner with a rat oral LD50 of over 5 g/kg, the ADI calculation using a 70 kg person and a safety factor of 1000 gives a result of 350mg (5 g/kg x 70 kg / 1000 ). In a 2000 kg mixer where the next smallest batch of 1000 kg, the area of the mixer and equipment used in the next batch is 100,000 m<sup>2</sup> and the daily dose of the next product is 0.005 kg: the calculated residual acceptance criteria is 700 mg/cm<sup>2</sup> (350 mg x1000 kg/(100,000 cm<sup>2</sup> x 0.005 kg). By comparison, the 10 ppm in next batch limit gives an acceptance criteria of 100 ug/cm<sup>2</sup> (10 mg x 1000 kg/(1 kg x 100,000 cm<sup>2</sup>) x 1000ug/mg. In this case, it is likely that you will be able to demonstrate the ability to detect visually to 4 ug/cm<sup>2</sup>. Because you need a visually clean surface, your most stringent acceptance criteria will be the visual limit.

Note that in this example you are trying to avoid more than 350 mg of residue in a daily dose of the next product. In the case of small final filling equipment such as filling needles for vials or tablet punches and dies, you may need to do separate residue studies on the filling needles or punches. This will ensure that not enough residue remained, on that particular equipment, to contaminate the first few bottles or tablets of the next batch with a residue of 350 mg/daily dose.

If the safety based limit in this example is set at 100 ug/cm<sup>2</sup>, it can be expressed as a rinse water concentration of 100 mg/L in a post final rinse using 100 L of rinse water recirculated to equilibrium (0.1 mg/cm<sup>2</sup> x 100,000 cm<sup>2</sup>/100 L). The same limit could be expressed as 6.25 ug/ml or ppm total organic carbon (TOC) in a sample for a residue that is 10% TOC by weight in a 20 ml swab sample from a 25 cm<sup>2</sup> swab area where 50% recovery has been established [(25 cm<sup>2</sup> x 100 ug/cm<sup>2</sup>) x 50% recovery] x 10% TOC/20 ml. The same safety limit can be expressed several different ways.

**Validating methods and implementing recovery studies**—involves validating your residue detection method by establishing accuracy, precision, linearity, reproducibility, selectivity, specificity (if it is a specific method), limits of detection, limits of quantitation, and ruggedness of the analytical residue detection method. Recovery studies involve the use of the sampling and detection methods on known spiked surfaces at representative levels. Typically, spikes are set at 50%, 100% and 150% of the acceptable limit and at lower than expected actual levels. This helps show linearity with documented % recovery as analyzed. It can also help determine the limits of detection and quantitation. Ideally, the expected values and limits should be multiples of the limits of quantitation. The % recovery is used to correlate amount detected with amount of assumed surface residue found acceptable. For example if 100 ug of residue was spiked on the surface and only 90 ug was detected after swabbing, extracting and analyzing, then there was 90% recovery. When used in a cleaning validation, any results would have to be adjusted by this recovery factor. In this example, a result of 90 ug per swabbed area would have to be interpreted as actually being 100 ug per swabbed area to adjust for the 90% recovery.

This is a good time to consider wipe and rinse sample storage conditions as well time frame for sample analysis. A rinseability profile, showing complete rinsing of an individual detergent ingredient, should be done when the solubility of that ingredient or its rinseability after drying is in doubt. If your analytical detection method is only sensitive to one ingredient in the detergent, document that all ingredients rinse at the same rate or that the ingredient that you are testing for is

the last to rinse away. If you cannot demonstrate either of these, provide a rationale that explains why you believe one or both to be true.

For example, a surface active agent, or surfactant, is a good candidate to represent the entire detergent formulation. A scientific rationale can be made for this. Because a surfactant, is attracted to the solution-surface interface, it is likely to be the last ingredient to rinse away. However, this is only true if the other detergent ingredients are significantly water soluble at the rinse concentrations. In fact, in the cases where all detergent ingredients are at least somewhat water soluble, have solubility greater than 10,000 ppm, they should all rinse at similar rates when tested using detergent spiked coupons in sequential rinses.

To test by this method, dip coupons in rinse water, then analyze water for the detergent ingredients. In this crude form or testing, expect no detectable difference in rinse rate for somewhat water soluble ingredients at typical cleaning concentrations within the solubility limit of the detergent ingredients. This can be verified by comparing rinse rate for a specific ingredient analyzed by a specific method with rinse rate for a non-specific method such as TOC.

In some cases, bioburden/endotoxin levels may need to be validated. As this takes longer, it is recommended that this process be done separately from the validation of the cleaning process so.

## MEDICAL DEVICE CLEANING VALIDATION

In the medical device manufacturing industry, cleaning validation is generally performed by examining the finished device rather than the process equipment used to manufacture the device. Concerns vary, across the industry, dependent on class of medical device being validated. Devices are classified according to the nature of patient contact. Re-usable examining devices, with incidental patient contact, might tested for protein and endotoxin (pyrogen) contamination. Whereas, implantable medical devices, with years of potential internal patient contact, might also be tested for biocompatibility and proper device function. In small volume medical device manufacturing and re-use, verification tests may be performed as

deemed appropriate by hazard analysis. Such tests might show 3-log reduction of bioburden, levels of less than 10 colony forming units CFU/device, less than 20 endotoxin units EU/device and chemical residues shown to be below limits affecting biocompatibility or toxicity. Where verification cannot be done, in a re-usable device, a validation study involving spiking with protein soils and bioburden, to show 3-log reduction, might be done. For an implantable device, validation studies demonstrating proper device function and biocompatibility would be done. Studies for biocompatibility might include: cytotoxicity, sensitization, irritation, systemic toxicity, chronic toxicity, genotoxicity, and hemocompatibility testing, depending on the class of the device.

As in pharmaceutical cleaning validation, residue acceptance criteria must be set. Residues might include process fluids, polishing compounds, mold releases, bioburden, endotoxins, cleaning agents and any degradation or interaction products. Acceptance criteria are set based on potential for the residue to effect biocompatibility, toxicity, or functionality of the finished device. Where historical data, on particulate contamination, from existing successful manufacturing processes exists, it can be used to set acceptance limits for particulate levels. This will serve as a general control and facilitate cleaning consistency. For existing devices with a history of acceptable performance, the mean level of residue plus three standard deviations can be used for particulates and other types of residues. For a new device, a series of residue spiking biocompatibility studies at different levels can be done to determine the failure point. A lower level, possibly half the failure point, could be used to perform an analysis demonstrating that device performance was not effected and toxicity levels were not exceeded. When testing a new device, you can determine the expected level of residue, spike the device at a suitably higher level of residue and then evaluate for biocompatibility and functionality. If it passes, then that is where to set the limit. With cleaning agents and process fluids, consider systemic toxicity based limits. These can be derived if systemic toxicity is known. If not, estimate the acceptable daily intake (ADI) from LD50 (lethal dose for 50% of the population by compatible route of exposure depending on device) and a con-

version factor using the equation that follows:

$$\text{Acceptable Daily Intake} = \text{LD50 (mg/kg)} \times \text{body weight (kg)} / \text{conversion factor}$$

Conversion factors will vary from 100 to 100,000 depending on the type of device and duration of exposure. Higher risk devices have higher conversion factors. A more thorough discussion of conversion factors can be found in:

1. Kramer, van den Ham, Slob, and Pieters, "Conversion Factors Estimating Indicative Chronic No-Observed-Adverse-Effect Levels from Short Term Toxicity Data," *Regulatory Toxicology and Pharmacology*, 23, 249-255 (1996).
2. Conine, Naumann, and Hecker, "Setting Health-Based Residue Limits for Contaminants in Pharmaceuticals and Medical Devices," *Quality Assurance: Good Practice, Regulation and Law*, 1 (3), 171-180 (1992).
3. Layton, Mallon, Rosenblatt and Small, "Deriving Allowable Daily Intakes for Systemic Toxicants Lacking Chronic Toxicity Data," *Regulatory Toxicology and Pharmacology*, 7, 96-112 (1987).

According to the equation above,,acceptable residue per square centimeter will depend on the size and quantity of devices being used. Consider the following example. A cleaner has an LD50 of greater than 500 mg/kg. Acceptance criteria is to be set for a device with less than one week of patient exposure. A safety factor of 10,000 is appropriate and the resulting limit should not exceed acute biocompatibility limits such as irritation. The calculation for a 70 kg adult would be:

$$\text{ADI/Device} = 500 \text{ mg/kg} \times 70 \text{ kg} / 10,000 = 3.5 \text{ mg/device}$$

The size of the device is then be factored into the calculation. If the device had a surface area of 100 square cm, then the surface residue limit for that detergent would be 35 micrograms per square cm (3.5 mg/device / 100 square cm). Of course, a process requirement of visually clean might very well be more stringent. In this example, we are working with a fairly non-toxic detergent, a fairly short contact time medical device and the resulting safety-based limit is fairly high. When working with more toxic residues on devices with greater

exposure risk, such as implantable devices, conversion factors would be higher and acceptance limits lower. In such cases visibly clean levels might not stringent enough.

Writing procedures and training operators—are necessary components of cleaning validation in both medical device and pharmaceutical industries. Written procedures should include the following: assigned responsibilities; protective clothing requirements; equipment disassembly and monitoring procedures; documentation requirements; labeling instructions, for in process and cleaned equipment, that include cleaning expiration date, post cleaning inspection procedures, storage conditions and inspection requirements before next use. The operators must then be trained and certified in the procedures. Appropriate retraining should also take place. Whether performing a medical device or pharmaceutical cleaning validation, you will need a validated analytical method for detecting detergent residue. Table 8A, below, taken from the Alconox Cleaning Validation References, for cleaners made by Alconox, Inc., lists a variety of residue detection methods that can be used for those cleaners (see A-J).

**TABLE 8A: DIRECTORY OF CLEANER RESIDUE DETECTION METHODS FOR EACH ALCONOX DETERGENT**

	A. Anionic Surfactant HPLC, Titrate, Kit	B. Nonionic Surfactant by HPLC	C. Direct UV/Vis	D. Phosphate by Titration	E. Enzyme by Assay	F. Organic Carbon by TOC	G. Conductivity	H. Citric Acid by HPLC, Assay, Deriv. UV/Vis	I. Potassium by Flame or IC	J. Glycol Ether by GC
ALCONOX®	•	•	•		•	•				
LIQUINOX®	•	•	•			•	•	•		
TERGAZYME®	•		•	•	•	•				
ALCOJET®				•		•				
ALCOTABS®	•		•			•	•			
DETOJET®				•		•		•		
DETERGENT 8®						•			•	
CITRANOX®	•	•	•			•	•	•		
LUMINOX®						•			•	
CITRAJET®						•	•			



As discussed in the section on validating methods, different analytical methods will require different validation procedures. The FDA, the International Conference on Harmonization (ICH) and European Union (EU) all, have defined validation requirements for analytical methods used in manufacturing pharmaceuticals. The United States Pharmacopoeia (USP) provides method validation guidelines in Chapter 1225. Residue detection methods can vary from non-specific methods such as total organic carbon (TOC) to selective ones. Selective methods have been shown to be specific, at a 95% confidence level, under the specified conditions of use without significant bias or interference from impurities, degraded, excipients or other ingredients. Generally, the FDA prefers the use of selective methods that have been shown to be specific, particularly for investigations of instances where results outside an action limit or particularly an acceptance limit were found.

Non-specific methods such as TOC are commonly used where the limits of detection and quantitation are well below residue acceptance limits. TOC also detects virtually all organic residues, which, in a way, make it a superior method for showing overall cleanliness. The following table reviews method validation requirements:

**TABLE 8B: ANALYTICAL METHODS VALIDATION CONDITIONS**

Method	Accuracy	Precision (Repeatability)	Linearity	Reproducibility	Selectivity	Specificity	LOD	LOQ	Ruggedness
HPLC	X	X	X	X	X	X	X	X	X
GC	X	X	X	X	X	X	X	X	X
TLC	X	X	X	X	X	X	X	X	X
IC	X	X		X	X	X	X	X	X
Wet Methods	X	X	X	X	X	X	X	X	X
UV-vis	X	X	X	X	X	X	X	X	X
TOC	X	X	X	X			X	X	X

HPLC- high performance liquid chromatography, GC – gas chromatography, TLC – thin layer chromatography, IC ion chromatography, UV-vis – ultraviolet visible spectroscopy, TOC- total organic carbon, Wet methods- titrations/assays

In the final report, the next section would deal with cleaning process design. It should include references to standard operating procedures and how they were evaluated. Next,

include a section of data analysis that provides statistical justification for conclusions reached. A defined procedure for changing a validated process is necessary. It should describe approval and review processes required when making specific changes. Provisions for emergency changes should be made. There should also be a list of assumptions made, to be reviewed, whenever anything is changed (eg. hardest to clean or most toxic).

Include a review of validated processes during the annual product review (APR). Use it as an opportunity to determine whether all the minor changes made, since the previous review, do not amount to significant changes that exceed the assumptions made and require a revalidation. Typically, a revalidation is required when the cleaner is changed. It may be appropriate to continue an old cleaning operation while phasing in a new one. Monitor the new process to prove that it produces the same validated results as the old one.

The final section of the validation report should provide the references to any standard methods, journal articles, or government documents used.

In selecting an aqueous cleaner for GMP manufacturing, where a cleaning validation is required, consider both the efficacy of the cleaner and the ability of the cleaner manufacturer to support validation efforts.

What to look for from a cleaner manufacturer:

- Lot traceability of the cleaners
- Certificates of Analysis for the cleaners
- Consistent manufacturing
- Ingredient disclosures under confidentiality
- Cooperation with audits and quality questionnaires
- Ingredient toxicity data
- Ingredient reactivity information to help determine degradations and interactions
- Cleaner shelf life information
- Residue detection method information
- Residue sampling information
- Acceptance limits information
- Recovery information
- Residue detection methods validation information
- Assistance with written cleaning procedures

If you have specific questions regarding validating Alconox detergents, please), contact Malcolm McLaughlin at 914-948-4040, ext. 160, or write [mmclaughlin@alconox.com](mailto:mmclaughlin@alconox.com).

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- Association for the Advancement of Medical Instrumentation AAMI TIR12:1994, Designing, testing and labeling reusable medical devices for reprocessing in health care facilities: A guide for device manufacturers
- Association for the Advancement of Medical Instrumentation AAMI TIR30: 2003, A compendium of processes, materials, test methods, and acceptance criteria for cleaning reusable medical devices.
- Drug Manufacturing Inspection Program (US FDA Center for Drug Evaluation and Research CDER 7356.002)

- Quality System Inspection Technique (US FDA Center for Device and Radiological Health CDRH August 1999)
- Code of Federal Regulations, Title 21 (21 CFR) Part 210 Current Good Manufacturing Practice in Manufacturing, processing, packing, or holding of drugs; general; Part 211 Current Good Manufacturing Practice for Finished Pharmaceuticals Part 820 Quality System Regulation; Part 803 Medical Device Reporting; Part 806 Medical Device Corrections and Removals; and Part 821 Medical Device Tracking
- The Global Harmonization Task Force GHTF/SG3/N99-10:2004 (Edition 2) "Quality Management Systems – Process Validation Guidance," (2004)
- European Union Directive 91/356/EEC – EC Guidance to GMP for Medicinal Products
- UK Medicines Control Agency, Rules and Guidance for Pharmaceutical Manufacturers and Distributors 2002,

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## RESOURCES

- [www.alconox.com](http://www.alconox.com)  
[www.ivthome.com](http://www.ivthome.com)  
[www.cleaningvalidation.com](http://www.cleaningvalidation.com)  
[www.fda.gov](http://www.fda.gov)  
[www.fdainfo.com](http://www.fdainfo.com)

# Wastewater Treatment and Cleaner Recycling

**W**astewater must be treated to reduce contamination prior to environmental discharge. Contaminants may include: insoluble oils, emulsified oils, other dissolved organics, suspended solids, and dissolved inorganic solids such as chlorides, nitrates, phosphates, and metals. Treatment requirements vary from state to state, and municipality to municipality. Most local governing authorities specify acceptable criteria for pH, biological oxygen demand (BOD), and chemical oxygen demand (COD). Criteria will be noted on your discharge permit.

A typical wastewater treatment system involves several steps. The first, pretreatment, reduces the volume of solids and wastewater.

## TYPES OF CONTAMINANTS

- **Solids**—Use acid conditions to breakup of the oil-water emulsion. The water layer is pumped into a chamber, where a polymer flocculent is added. The wastewater is then pumped into a clarifier, where much of the oil condenses into a floc and settles to the bottom of the chamber.

Flocculated solids are transferred to a filter press, where they are dried in preparation for disposal. The supernatant liquid is pumped into a process tank where the pH is raised in order to promote precipitate metals. A polymer is added resulting in flocculation of the metals.

- **Oils**—Removal of trace quantities of floating oil in a cleaning bath, improves cleaner performance and extends bath life. Further, by filtering out any particulates or fines, oils collected may be evaluated for reuse, rather than disposal.

Traditional mechanical separation of oil from wastewater involves the use of skimmers, tank overflow, and decanting methods. Such out-of-process, post-production, end-of-pipe wastewater treatment approaches tend to perform less efficiently in a continuous manufacturing operation and contribute to disposal problems

## EQUIPMENT OPTIONS

- **Evaporators**—Evaporation is commonly used to reduce the volume of water for further treatment. The contaminants concentrate at the bottom, as sludge, and the water is transferred to a holding tank. There, it is allowed to cool to room temperature. The water is either discharged to drain (with the necessary permits and approvals in place) or further treated.
- **Separators**—Gravity separation of nonemulsified oil in wastewater can occur in the clarification tank. The influent and effluent flow rates are optimized to allow efficient separation of the lighter oil layer from the water. An inclined plate can be used to direct the flow of the oil layer away from the wastewater.

A current method of oil-water separation applies Bernoulli's principle, whereby the wastewater is split into two laminar flows. Oil is continuously collected and concentrated in a second chamber, which is separated by a baffle from the primary chamber and a reduced-pressure area below. The reduced pressure directs the flow of water down, away from the second chamber.

Oil is recovered from the top of the concentrated layer, when it reaches a designated thickness. High-quality, reusable oil is recovered this way.

- **Activated carbon**—Suspended organic materials can be removed from the waste stream using an activated carbon filter. An extensive pore network, enables the filter to absorb material many times its own weight.

However, activated carbon is used for organic materials only. Metal contaminants and other inorganic materials will remain dissolved or suspended in the wastewater. An activated carbon filter can be used as one of the last stages before discharge or recycling to assure cleanliness. Filters can be arranged in series or parallel. A parallel arrangement allows for change-out of one filter while the others remain operational.

- **UV Systems**—Ultraviolet (UV) light is an effective means of destroying biological organisms. A UV-oxidation system can be used, as needed, to reduce the BOD of wastewater.

## SELECTION CONSIDERATIONS

Following are basic guidelines for selection of a wastewater treatment system:

- **Treatment options** should be studied by an engineer to assess process alternatives. The system should be optimized for proper flow rates, filter capacities, throughputs, etc.
- **Design, maintenance, and operations** should allow for downtime.
- **Capital and operating costs** may justify the recycling of wastewater in a closed-loop system.

## CLEANER RECYCLING

When legislation began to limit the use of ozone-depleting compounds, many companies chose aqueous cleaning as an alternative to solvent degreasing.

In the early transitional days, many process and manufacturing engineers were concerned that aqueous processes would reduce part quality and throughput, create additional waste and wastewater treatment problems and increase costs.

Alternatives to aqueous cleaning systems include "drop-in" semi-aqueous or solvent-based cleaning systems. These options are not without their own problems including employee health risk from exposure to chemicals, worker discomfort from chemical odor and flammability.

One public lab where solvent replacement work has been done is the Toxics Use Reduction Institute at the University of

Massachusetts at Lowell. The Institute has demonstrated the effectiveness of aqueous cleaning in industrial settings. Aqueous cleaning provided a sound alternative to vapor degreasing in as many as four out of five applications that the Institute reviewed on a laboratory scale for industry clients.

Modern closed-loop aqueous cleaning systems remove contaminants from both the cleaning bath and rinse water. When compared with solvent cleaning systems, they are relatively inexpensive to install.

Recycling can help reduce or eliminate liquid waste by trading dilute liquid waste for more easily disposed solid waste in the form of spent filters or concentrated sludge. Recycling can also help reduce detergent consumption in order to clean more parts per pound or gallon. It may also save time by increasing throughput while reducing system set-up procedures.

The first place to install recycling equipment is in the rinse water portion of the cleaning system. In sequential tank cleaning, use a series of countercurrent cascading rinse tanks to accomplish this. Water from each tank will be reused successively. Because water use is limited, this system is easy to use and inexpensive. Still, it ensures that the final rinse stages contain the cleanest water.

It is easier to recycle the detergent solution separately from the rinse water because the equipment used is merely separating soils, not creating high-purity water. For that you would need to use activated carbon, deionizing resins or reverse-osmosis. To treat cleaning solutions, use one or more of the following procedures:

- **Physical filtration**—uses gravity or low-pressure pump cartridges at one to 100 micron levels of filtration to remove suspended particulates.
- **Microfiltration**—uses low-pressure pumps, dead-end, or cross-flow filter membranes to realize 0.1 to 1.0 micron levels of particulate filtration (used to break and remove very fine suspensions of particulates).
- **Physical separation**—includes cooling and skimming, settling and emulsion breakup. Cooling solutions allow emulsions and suspensions to break. Settling allows water-insoluble materials to separate by density; heavy

sludge, generally settling to the bottom when a suspension breaks. In emulsion breakup, light oils will generally rise to the surface and the overflow can be physically skimmed off with oleophilic wicks or cycling bands of oleophilic material, leaving reusable cleaning solution.

- **Solution recharge**—is the process of adding fresh detergent to extend the life of an exhausted detergent solution. For example, add 50 percent of the original dose of detergent to the used solution. The concentration of useable detergent will then be sufficiently raised to a level where effective cleaning will occur.
- **Ultrafiltration**—is a process in which multiplex membrane filters are packaged into a variety of cartridge configurations and integrated into the cleaning process. A feed solution is pumped through the filter cartridge and split into a permeate or filtrate (material retained by the membrane) and retentate (fluid retained by the membrane). The soil-free permeate stream is then recycled back into the parts washer.

## FILTER SELECTION

Advances in membrane technology and evolution of systems with greater temperature and chemical stability have made possible the development of many types of filters for ultrafiltration. For example, extremely hydrophilic (water-absorbing and oil-repellent) polymeric membranes have been developed. These, resist fouling by free oils, emulsions, and other hydrophobic solutes to maintain efficient filtration rates over extended periods.

Filters can be either symmetric, with fairly uniform pore diameters throughout the membrane, or asymmetric, consisting of a thin “selective” layer over a thick, porous substructure.

Membrane selection is critical to the effectiveness of any recycling system. Before deciding on a system, users should ask the following questions:

- **Surface chemistry**—Has the membrane been engineered for easy cleaning or to resist fouling by free-floating and emulsified oils?
- **Stability**—Is it physically and chemically stable when exposed to a broad range of pH and aggressive chemicals?

- **Pore size**—Has it been designed to ensure complete passage of all cleaner components while sufficiently retaining the oils?
- **Temperature tolerance**—What is the membrane's temperature tolerance?

While not required for all aqueous cleaning, membrane-based filtration can be particularly helpful in achieving steady conditions, desirable for maintaining quality control in high-production applications. Detergents must be selected for their compatibility with specific membranes used, and vice versa.

### CLOSING THE LOOP ON AQUEOUS CLEANING AND RINSING

There are a number of methods for removing contaminants from aqueous-cleaner solutions. The size of the contaminants affects the choice of method. Particulates may be removed using settling tanks, chip baskets, media filtration, or canister filters. Oils are collected using skimmers and coalescers. Most of the remaining contaminants can be removed using micro- and ultrafiltration. Generally, the rinse water and the cleaner solution are recycled separately.

Cleaners are recycled using physical filters, oil separators, ultrafiltration, and microfiltration. The pore sizes of microfiltration membranes range from 0.1 to 1.0 microns, while those of ultrafiltration membranes range from 0.0005 to 0.1 microns.

Ultrafiltration membrane pore sizes are also specified by molecular weight cutoffs (MWCOs). Contaminants with a diameter greater than the membrane's MWCO are thus filtered out. Keep in mind that both micro- and ultrafiltration are pressure-driven processes. Neither will reject salts, which can adversely affect performance and make disposal necessary. Therefore, it is important to monitor the salt content of both the recycled bath and the rinse water used.

Rinse water must be purified separately. Rinsing recycle systems can be designed to provide water that will leave parts clean enough to meet standard requirements. In addition to particle, micro- and ultrafiltration, these recycling systems may also use reverse osmosis (RO) in conjunction with microfiltration to protect the filter membrane. Activated carbon may

be used for the removal of the majority of organic contaminants. Ion exchange is another type of system that uses specially designed resins to capture cations and anions such as chlorine, heavy metals, calcium, and magnesium. Since these types of cations and anions may be considered hazardous waste, they must be shipped back to suppliers for regeneration.

### MONITORING AND CONTROLLING CLEANING BATHS

The cleaning bath should be monitored to determine when the solution can be recharged with detergent and when it is spent, mandating a fresh batch. There are numerous sophisticated analytical chemistry techniques, such as FTIR (fourier transform infrared spectroscopy, HPLC (high pressure liquid chromatography), COD (chemical oxygen demand) and TOC (total organic carbon), for analyzing recycled cleaner. Free alkalinity and total alkalinity are additional tests for cleaning baths. Free Alkalinity is the measurement of unreacted builder in the cleaner; whereas, Total alkalinity, includes the measurement of total alkalinity, as well as, the alkalinity lost in the cleaning process from sludge formation or hydrolysis of animal or vegetable-based oils. Neither free alkalinity nor total alkalinity tests include the measurement of the level of surfactants, which makes them inappropriate for procedures that remove soil.

Some very simple, yet effective, techniques can be used to monitor bath life, including:

- **Conductivity**—When you are using detergents with high ionic content, measurement of the ionic content of the cleaning solution, using electrodes connected to a conductivity meter, helps determine when to add more detergent to the cleaning solution. Detergents high in salt content, for example, potassium hydroxide or sodium metasilicate, generally, have high ionic content. Conductivity will drop as soils react with the salts. This is not a useful technique for monitoring high emulsifying cleaners that rely heavily on surfactants.
- **Refractometry**—This is the indirect measure of the concentration of dissolved components which influence the refractive index of a sample of solution. The measurement may be taken using a simple handheld refractome-

ter. Refractometry can also be used to monitor the build up of soils and concentration of a solution as a result of water evaporation.

Empirical observations of cleaning solutions may be compared with recorded measurements to determine appropriate times to recharge or discard solutions. For example:

- **Foam Height**—The foam height and foam stability, in a sample of cleaning solution in a vigorously-agitated, stoppered test tube will decrease as oils accumulate. When foam height decreases, recharge or discard cleaning solutions. Observations must be made at consistent temperatures.
- **pH**—This is the measurement of the acidity or alkalinity of a solution on a scale of 0–14. It is expressed as the negative log of the hydrogen ion concentration, which is measured using electrodes dipped in the solution connected to a pH meter. Note that pH paper should not be used with surfactant-containing cleaners, because they commonly hamper accurate reading. A given brand of detergent will have a typical pH. If the soils are acidic, inorganic, or saponifiable natural oils, the pH will drop as the cleaning solution is used up. Typically, when pH drops 0.5 pH units, the detergent should be recharged. Then the solution can be used to exhaustion as it drops one full pH unit.

The technique chosen to monitor bath life will depend on the both the type of detergent you are using and the soil or residue you are removing. For example, when cleaning with an ionic detergent, use conductivity to monitor dilution, dragout, and loss of detergent. Whereas, when using a high-emulsifying or dispersing detergent to remove oils or particulate soils, refractometry is an effective means of measurement and control. Foam height observation is most effective when cleaners contain foaming surfactants that rely on emulsification to remove oily soils. When using an alkaline cleaner to remove a soil that is either acidic or neutralizing in character (as most soils are), pH can be used as a control measure.

**TABLE 9A BASIC BATH MONITORING AND CONTROL TECHNIQUE SELECTION BASED ON TYPE OF DETERGENT USED**

Conductivity	Ionic cleaner removing nonionic soil such as a high alkaline cleaner used for degreasing
Refractometry	High emulsifying and dispersing cleaner used on mixed particulate and oily soil
Foam height	High-foaming cleaner used to clean oily soils
pH decrease	Alkaline cleaner used to clean acidic or hydrolyzable soils that react with the cleaner (most soils are acidic or hydrolyzable)
pH increase	Acidic cleaner used to clean an alkaline or neutral soil

### ECONOMIC FACTORS

Where detergent recycling is concerned, it is possible to be penny-wise and pound-foolish. It may not be worth risking inadequate, or even uncontrolled, cleaning simply to get every last penny of performance from a detergent solution. The cost of installing recycling and reuse equipment and procedures must be weighed against the cost of disposal and solution use. The value of the parts being cleaned, the increased risk of cleaning failure with each new part cleaned and the chance of cleaner exhaustion or soil redeposition must all be considered. The question, “Is it cheaper and/or more efficient to send partially used cleaner to drain and make up a fresh batch?” must be answered.

When working with nonhazardous or easily treated detergents and wastes, it is generally cheaper and more efficient to send the bath to drain and make fresh solution; with difficult to treat hazardous wastes, recycling may be a more economic option. Where regulatory compliance costs are prohibitive or no drain is available, it is better to recycle.

Another factor to consider is the volume of your cleaning system. In high-volume, high-performance cleaning applications with quality control inspection or low fault-tolerance parts such as electronic components and optical parts, recycling may well be worth it. But in low-volume, extreme-cleaning performance applications such as pharmaceutical process equipment, medical devices and high-priced, soil-sensitive

equipment, recycling the detergent may not be cost effective.

Before considering recycling as an option, determine whether the EPA needs to be involved. Complete a SARA (Superfund Authorization and Reauthorization Act) report stating the quantity of any chemical found either in the soil or detergent discharge.

Fully review the following parameters:

- **Toxicity**—by TCLP (Toxicity Characteristic Leaching Procedure)
- **Corrosivity**—pH below 2 or higher than 12.5
- **Ignitability**—flash point below 60°C (140°F) ignitable

Also look at compressed gases and oxidizers, as well as, reactivity of the waste stream to determine whether RCRA regulations apply. Refer to 40 CFR 261.21-.24, as well as, any applicable state and local discharge regulations.

## PROVEN TECHNOLOGIES

There are suppliers of closed-loop aqueous-cleaning systems designed to increase process efficiency by decreasing waste generation. Implementing such systems should not be based solely on short-term economic concerns, but must include a careful review of environmental and regulatory considerations. The benefits of sophisticated closed-loop systems must be weighed against the costs of maintaining those systems. For example, membrane systems need periodic cleaning or may need to be replaced. In the long run, recycling may be more economical than playing catch-up with evolving regulations surrounding industrial parts cleaning.

Take note that, manufacturers already using aqueous-cleaning solutions don't need a closed-loop system to begin recycling today. In fact, recycling can be as simple as making up a large soak tank for continuous use throughout the manufacturing process. Time and money are saved merely by recycling wash-tank water through a skimmer, then recharging it with detergent at midweek intervals. This prevents downtime during draining, refilling, recharging and reheating the tank

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## RESOURCES

[www.alconox.com](http://www.alconox.com)



# Measuring Cleanliness

Depending upon method selected, cleanliness can be detected to varying degrees or levels. Cleanliness can be detected to levels as low as 0.01 grams per square centimeter using the following methods:

- Visual inspection
- Low power microscope inspection
- Wiping and visual inspecting
- Water break tests
- Atomizer tests
- Nonvolatile residue inspection
- Surface UV Fluorescence detection
- Tape test.

The next level of cleanliness measurement, detects soils of 0.01 to .001 grams per square centimeter (sq/cm), a level suitable for aerospace, electrical, automotive and many surface preparation applications. This level of detection can be achieved through Millipore filter measurement techniques such as:

- Optical microscopy
- Extraction
- Oil evaporation
- Oil soluble fluorescence
- Gravimetric analysis
- Surface Energy tests
- Contact angle measurement
- Particle counting.

Finally, the highest level of cleanliness measurement, below 1 microgram per square centimeter, is suitable for use in semiconductor, disk drive, and medical device applications.

Techniques that are used for this level of precise cleanliness measurement include:

- Carbon coulometry
- Electron spectroscopy for chemical analysis (ESCA)
- Fourier transform infrared (FTIR)
- Gas chromatography/mass spectrophotometry (GC/MS)
- Ion chromatography (IC)
- Optically stimulated electronic emissions (OSEE)
- Particle counting, scanning electron microscopy (SEM)
- Secondary ion mass spectroscopy (SIMS).

Measuring techniques appropriate to each of the three levels of cleanliness are summarized below.

### CLEANLINESS DETECTION AT 0.01 GRAMS PER SQ. CM

- **Visual inspection**—is best used to detect residues of contrasting color or texture. Good lighting can enhance visual inspection. Magnification and fiber optic lighting, which throws light across a surface, improve detection.
- **Low-power microscope inspection**—is a quick and efficient way to verify cleanliness of residual oils and greases, flux residues, particles and surfaces.
- **Wiping**—with a white wipe provides a contrasting surface with which to detect dark residues (the white glove test).
- **Water-break test**—uses running water, allowing it to form a sheet, across the surface. Breaks in the water indicate the presence of hydrophobic (water-fearing) residues. (See “The Hydrophobic Surface Film by the Water Break Test,” ASTM Method F 22-65—found at [www.astm.org](http://www.astm.org).) The water break test is a fairly crude test which is suitable for detecting films of process oils and heavy fingerprints. It does not readily detect non-hydrophobic residues. This test is often used for parts washing and may not be suitable for precision cleaning applications.
- **Atomizer test**—a variation of the water-break test, involves a gently sprayed water mist. Any areas, where water repulsion occurs, indicate the presence of a hydrophobic soil. The atomizer test is slightly more sen-

sitive to hydrophobic soils than the water break test in which the kinetic energy of the flowing water may overcome a hydrophobic residue. In contrast, the atomizer test allows you to see a small droplet of water being repelled by a hydrophobic contaminant.

- **Nonvolatile Residue Inspection (NVR)**—involves extraction of soil from a dirty surface into a solvent. The solvent is then evaporated onto a coupon of known weight. After the solvent is evaporated off the coupon, any residue will be deposited on the coupon. The coupon is then re-weighed and any weight increase detected is attributed to the nonvolatile residue. Many solvents can be used for this purpose. It is important to use a solvent that can dissolve the soil being detected. (Isopropyl alcohol, methylene chloride, acetone and other solvents have been used for this purpose.)
- **Surface Ultraviolet (UV) Florescence**—Many organic and some inorganic contaminants will fluoresce under UV light. Shining a UV light on the surface makes residues more visible, particularly in a slightly darkened or dark room. The higher the intensity of the light used, the lower the level of contaminants easily detected. Note, however, that the typical black light found in novelty or specialty gift stores may not be strong enough to cause much residue to fluoresce. More powerful UV lights, available from scientific supply houses or industrial suppliers, will provide far better results. The test is performed by shining the light on the surface and observing an easily seen, fluorescent—typically a yellow, orange or green, sometimes red—color which glows under the light.
- **Tape Test**—The Tape Test, a simple method aiding visual inspection, is well suited for testing the cleanliness of smooth metal and plastic parts. It involves attaching transparent adhesive tape to the surface being measured, firmly pressing it down, carefully removing it and then placing it on a sheet of clean white paper. Visually comparing the sample with an adjacent piece of white paper, is a fast, easy way to monitor particulates and sometimes even film residues.

## CLEANLINESS DETECTION AT 0.01 TO .001 GRAMS PER SQ. CM

- **Millipore Filter Measurement**—The Millipore Test—also known as the “patch” test—involves spraying samples of parts with filtered hexane, isopropyl alcohol, or trichlorethylene at pressures of 60 to 80 psi through a 1.2-micron filter membrane inside a jet nozzle. The spray is collected, vacuum-filtered onto a clean filter membrane and examined under a microscope for any particle-per-micron contaminants. (The membrane can also be weighed to determine total contaminants in milligrams.)
- **Optical Microscopy**—High-power compound microscopes can also be used (typically on circuit boards), however, these are more delicate and more expensive than simple, low-power microscopes and generally require greater operator skill and training.
- **Extraction**—This is a particularly useful method for detecting detergent residues. Solvent-soaked glass filter paper, or a high purity swab is used to wipe surface. Residue is then extracted, or digested from the filter paper or swab and a trace analysis performed on that extract. The procedure can be quantitative if a known area is wiped.

Extraction methods can be highly sensitive to a wide range of possible soils and residues. However, it is important that an appropriate solvent must be used to extract any soils. When performing trace analysis for detergent residues it is advisable to use water as the solvent. (The sensitivity of an extraction test depends on the method of trace analysis.)

The most frequently used types of trace analysis are UV visible spectrophotometry, total organic carbon (TOC) analysis, high performance liquid chromatography (HPLC), atomic absorption (AA) of inorganic residues, and liquid chromatography (LC). (These techniques are discussed separately in this chapter under ‘Detection below 1 microgram per sq. cm.’)

- **Oil Evaporation**—When working with filmy residues, a

few drops of organic solvent can be deposited on the surface, then removed via pipette and placed on a watch glass. If any filmy residues are present, a characteristic ring of organic-material deposits will appear.

- **Oil Soluble Fluorescence**—This process involves immersing a part in a fluorescent oil soluble penetrant dye and then observing the part under fluorescent light. If any dye penetrates or adheres to the part, oil is present. This method is outlined in ASTM F601-98 “Standard Practice for Fluorescent Penetrant Inspection of Metallic Surgical Implants.” Of course, cleaning procedures need to be established to remove the dye after testing.
- **Gravimetric Analysis**—Small parts of known weight, can be weighed after cleaning. Any excess weight detected represents the amount of soil present.

If the part returns to its original weight, after cleaning one can conclude the part is considered clean. Gravimetric analysis is also quite useful as a screening tool in lab cleaning. When a coupon is weighed before soiling, after soiling with an artificial soil, and then weighed again after cleaning the percent of soil removed can be derived.

- **Surface energy**—Any hard, flat material has a characteristic surface energy. As a result, a deposit of a known volume of pure liquid (typically deionized water) will form a droplet of predictable size. Measuring droplet size will determine surface cleanliness. Generally, hydrophobic soils create smaller droplets; hydrophilic soils, larger ones. The surface-energy test is far more sensitive than the atomizer or water-break test and has the advantage of detecting both hydrophilic and hydrophobic soils. The problem with the surface energy test is that it only tests the surface directly underneath the droplet that you are measuring. If measuring a small surface area, characteristic of a larger one, this can be an excellent and highly sensitive method. If a part is full of cracks, crevices and holes, the surfaces that are accessible for measurement may not contain the same soils that are hidden in the cracks, crevices, or blind holes. (For a complete descrip-

tion of this technique see “More on water-drop surface energy test,” following this section.)

- **Contact angle measurement**—A variation of surface energy testing, contact angle measurement is the measure of the relationship of the surface energy of a surface and the interfacial tension of the liquid on the surface, whereby the liquid droplet will have a characteristic contact angle between the surface and the edge of the droplet when the droplet stabilizes on the surface. This method can be used to determine cleanliness because the properties of various contaminated surfaces are reflected by different contact angles. Contact-angle measurement is especially suited to manufacturing operations such as wire bonding on PCBs or the application of thin films on quartz glass as these operations require nondestructive cleanliness testing. Vapors, such as vacuum or diffusion pump oils, resulting from the operation itself; various process chemicals; and even human perspiration, are all contaminants that can be detected by changes in the contact angle. (For a full description of this measurement technique see “More on Contact Angle Measurement Methods,” below.)
- **In-situ Particle Counting (ISPM)**—Part cleanliness becomes critically important as mechanical, optical, and electronic parts shrink in size and formerly inconsequential particles grow in significance. High-technology cleaning techniques, such as ultrasonic bath cleaning are widely used in today’s precision industrial applications. In-situ particle monitoring (ISPM) provides is a tool for observing particle removal in ultrasonic bath cleaning at work in real time. This helps to adjust and optimize the cleaning process quickly and easily. Once cleaning is optimized, ISPM can be used to monitor bath performance as well as filtration recycle performance. ISPM measures particle counts directly during both ultrasonic wash and rinse baths.

## AN EXAMPLE OF IN-SITU PARTICLE MONITORING

John Hunt’s work for Pacific Scientific Instruments in Grants Pass, OR demonstrates the use of In-situ particle monitoring. To select the best cleaning agent and determine the correct concentration, Hunt began by depositing known types and amounts of particle contamination on glass slide test coupons. Several cleaning agents were tested for, effectiveness by monitoring the rate of particle removal from soiled plates in the bath. To do this, bath water was recycled through a filtration loop and particles detected just before filtration and removal from the recycle loop. Hunt studied the effectiveness of several detergents at various concentrations on various particle sizes. The particle removal was observed in the bath for each detergent concentration when the soiled glass plate was added to the bath. The number of particles/ml/minute was determined by integrating the area under the particle size counting curves for a given length of time for each particle size monitored at each concentration of each detergent. By evaluating this information, the best detergent, concentration, and cleaning time can be determined for a given particle size.

When determining optimal detergent concentration, be sure to allow bubble activity to subside after adding more detergent but before placing the soiled plate in the bath. Typically, you will see an initial spike of particles coming off the plate when it is added to the bath. Particles continue to come off over time but the rate slows. Generally, after 10 or 15 minutes no more particles are observed. This information can also be used to optimize cleaning time. During actual cleaning, parts should be removed from the bath when particle counts have dropped back to baseline

## MORE ON WATER DROP SURFACE ENERGY TEST

Surface energy can be indirectly detected by measuring the size of a droplet of known volume sitting on a surface. Using a volumetric pipette a drop of typically 0.2 ml of water is placed carefully onto a surface being investigated. The droplet size is measured with a micrometer. If the droplet is circular, determine area by calculating  $\pi r^2$  Note that any machining or scoring will distort droplets. Multiplying length times width may be a safer way to calculate area. Whichever method you

choose, do not vary area calculations within a set of tests. Typically a surface with a hydrophobic oily residue film will repel the water and cause the droplets to be smaller than those observed on a clean surface.

This method works well when testing glass and metal surfaces. It is better for detecting films than particulates on smooth surfaces. If the surface is scratched during cleaning, the droplet size will become smaller causing a false “after” reading in a before and after test. If a volumetric pipette is not available, use an eyedropper to deposit drops and a scale sensitive to 0.001 grams, to measure droplet weight. The ratio of droplet weight to area can be used to detect changes in surface energy. Again, a rise in this ratio occurs when comparing a dirty surface to a clean one. It is useful to work with a known clean surface to observe droplet size behavior and known soiled surfaces to confirm that the residue will give the expected decrease in droplet size caused by the presence of an oily film. Note that if the film is hydrophilic, unlike most oily films that are hydrophobic, then the droplet size will increase, not decrease. Either way, by working with known clean and dirty substrates you can empirically observe the expected change..

As with other cleanliness verification techniques, special tips for contact angle measurement, if practiced, will increase the repeatability and validity of the measurement results. The following tips from Precision Cleaning magazine, (Oct. 97 p. 23) will help you achieve accurate results:

- Use gloves when handling the samples to be measured. Organics, such as finger oils, cosmetics, and other contaminants, will skew the contact angle results.
- Note the nature of the droplet after applying it to the surface. Wait until the droplet has ceased its advancement and no more change in lateral movement has occurred. Measure this time interval, making sure that you wait this period of time after every measurement. Retain consistent time intervals between the placement of the droplet and its measurement.
- Use medical-grade, ultra-purified deionized water from a laboratory supply house for a consistent measuring liquid. This will limit the number of measurement variables.

- Use test liquids of larger surface tension than the solid's surface energy in order to obtain easy-to-read results.
- Neutralize the effects of static charges on substrates. Substrates that are electrostatically charged can skew contact angle readings up to 5 degrees.
- Accurately control liquid droplets so that they are repeatedly deposited onto the sample. Gently move the sample to the liquid droplet formed at the end of the syringe/dispenser in order to minimize gravitational effects.
- In the case of very high contact angles, it difficult to attach the droplet, from the needle, to the solid sample. Use a Teflon-coated needle of a higher gauge (smaller inner diameter).
- In case of very low contact angles, use the highest possible needle gauge (smallest inner diameter needle) for controlling very small droplet volumes onto the sample.

## MORE ON CONTACT-ANGLE MEASURING METHODS

Accepted methods of measuring contact angles to determine surface characteristics include the inverted bubble, Wilhelmy Plate, and sessile drop techniques. The latter is the most widely practiced quality control technique, as it is relatively quick and requires minimal investment of time and money.

In the sessile drop technique, the specimen to be measured is loaded onto a specimen holder. A liquid droplet 3 to 4 mm in diameter is carefully deposited onto the substrate surface. A tangent line is drawn at the three-phase interface point in order to determine the contact angle. Alternately, a line is drawn from the three-phase interface point through the apex. This angle turns out to be equal to 1/2 of the tangent angle and is reproducible by different operators.

A “real world” example helps illustrate the use of the contact angle measuring technique to determine the existence of impurities on a surface.

LCD (Liquid Crystal Display) panel surfaces contaminated with organic matter are less accepting of a variety of films, including metals and protective layers, resulting in poor manufacturing yields. Sources of such contaminants include the vapor of process materials, chemicals, and human perspira-

tion. Very thin organic contaminants several monolayers in thickness (greater than 10 angstroms) can be evaluated using the contact angle technique. It is generally agreed that the wetting behavior involves only the last layer or two atoms on either side of a solid's interface. The water contact angle correlates the "cleanliness" of the surface to the adhesion of the copper deposited onto the surface of the LCD.

Water contact angles can be used in many situations to determine contamination levels, predict cleanliness and adhesive bond strengths, and monitor cleaning operations. Whether you are checking the moisture effects on silicon wafers or LCD quartz panel glass metal adhesion, all that is needed is an understanding of the basic theory involved and proper measurement techniques.

#### DETECTION BELOW 1 MICROGRAM PER SQ. CM

- **Carbon Coulometry**—This technique uses in-situ direct oxidation of surface carbon to carbon dioxide (CO<sub>2</sub>), followed by automatic CO<sub>2</sub> coulometric detection. (For a more complete description of in-situ monitoring, see the "In-Situ Particulate Monitoring" section of this chapter above.)
- **Electron Spectroscopy for Chemical Analysis (ESCA)**—ESCA is an extremely surface-sensitive technique, which uses the photoelectric effect, to detect elements and determine elemental composition. Electrons are ejected from a solid surface by irradiating the surface with an x-ray monobeam. The emitted photoelectrons have a kinetic energy equal to the x-ray less the binding energy of the electron. The measured kinetic energy of the electrons can therefore be converted to binding energies, enabling element identification.
- **Fourier transform infrared spectroscopy (FTIR)**—FTIR spectroscopy is used for structural characterization of organic and inorganic molecules in solids, liquids, gases, and on surfaces. Spectrometers record the interaction of light energy in the form of infrared radiation with an experimental sample, measuring the frequencies at which the sample absorbs the radiation and the intensities of the absorption. To determine the chemical com-

position of a sample, use an extraction method or a surface scanning machine and then compare the unknown spectra from your sample to the standard frequency at which specific molecules are known to absorb infra-red light. Most FTIR machines have standard libraries of known molecules for comparison purposes. Even if you do not get an exact match, information about the type of chemical present can be derived by looking for telltale frequencies of absorbance for typical functional groups.

- **Gas Chromatography/Mass Spectrophotometry (GC/MS)**—GC/MS is used to identify surface contamination by extracting contaminants into a solvent and analyzing them. Organic compounds are then separated via GC and identified, by molecular weight, using MS.
- **Ion Chromatography (IC)**—Ion Chromatography is a form of liquid chromatography of aqueous samples used to determine ionic contamination on critical components. Columns containing ion-exchange resins are used to separate the atomic or molecular sample ions based on their partition ratios of how attracted to the column vs how attracted to the carrier those ions are as they pass through the columns. It is the only technique that can provide quantitative analysis of anions at the part-per-billion (ppb) level of an extract that has been swabbed or wiped from a surface and extracted into solution for analysis.
- **Optically Stimulated Electronic Emissions**—When high-energy UV light hits a surface, electrons are emitted, and the reflected current can be measured. A clean surface will give the highest return current, so any drop in current represents contamination. This method is good for determining low levels of contamination (both ionic and nonionic). However, while optically stimulated electronic emissions can detect contamination, they cannot identify the contaminants.
- **Scanning Electron Microscopy (SEM)**—By scanning high energy electrons across a specimen, SEM enables study of the composition and morphology of biological and physical materials. When high energy primary electrons impact the specimen they are deflected or scat-

tered. Those that are deflected at an angle greater than 90° can reenter the vacuum above the specimen and make up the backscatter signal. The proportion of primary electrons collected as backscatter electrons (bse) increases as a function of the atomic number of the sample specimen, revealing its chemistry. Forward scattering primary electrons, those that are deflected at an angle of 90° or less, travel through the specimen while losing energy. The atomic electrons gain the lost energy, allowing them to escape from their atoms. Those that are very close to the surface (within the escape depth) may have sufficient energy to escape from the sample surface back into the vacuum as secondary electrons (SE). An incline surface exposes a larger area to the electron beam and thus allows more electrons into the escape depth. Production of secondary electrons is attributed to high incident angles between the specimen and electron probe. The resulting SE image reflects the surface topography of the specimen.

- **Secondary Ion Mass Spectroscopy (SIMS)**—SIMS is an extremely sensitive surface analytical technique. It is used for chemical determination of surface constituents, both elemental and molecular, as well as ppb concentrations of impurities in semiconductors and metals. The material under investigation is bombarded with primary ions which, upon impact, cause the release of secondary ions from the sample's surface. The secondary ions can be identified by their mass, which is determined by measuring their travel time from surface to analyzer.

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## RESOURCES

www.alconox.com  
www.astp.com  
www.photoemission.com  
www.pmeasuring.com

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## CHAPTER 11

# Environmental Health and Safety Considerations

**A**queous Aqueous cleaners, by definition, use water for cleaning and rinsing. This has both advantages and disadvantages. Water is an inherently environmentally sound and substantially safe chemical to work with. It is a recyclable natural resource. Yet, as populations grow, clean surface water will become increasingly scarce. Water can also be a transport medium for various polluting or hazardous chemicals that may derive from the use of aqueous cleaning in specific instances.

One way to look at the environmental health and safety of a cleaning process is to consider:

- How hazardous is the cleaning process?
- How hazardous is the effluent resulting from the cleaning process?
- How sustainable—in terms of energy and resources—is the process?

All critical cleaning falls within a safety continuum. At one end are the polluting, hazardous processes; at the other, those that are to clean and safe processes; clean, safe, sustainable and produce little waste. Aqueous cleaning may fall anywhere along this continuum.

Of course, some aqueous cleaners do contain hazardous ingredients that may be used to clean hazardous soils, which may produce hazardous and polluting waste. But by the same



token, industrial cleaning may involve the use of an aqueous cleaner with no hazardous ingredients used to clean the same hazardous soil, resulting in a clean and relatively safe process.

Improvement in safety can be achieved by eliminating the source of the hazardous soil in the process. Going a step further, waste can be reduced by integrating soil recycling, cleaning solution recycling and/or rinse water recycling into the cleaning process. It is possible to design a so-called “zero-discharge” system with no fluid effluent, limited volatile effluent and reduced solid waste by recycling cleaning and rinsing solutions using filters. In order to move toward a clean, safe and sustainable process, however, one would need to eliminate the hazardous soil and replace it with a nonhazardous biodegradable soil. Then, after the water used in the cleaning and rinsing process has been recycled sufficiently, for energy efficiency, the now nonhazardous soil in the effluent would not pose no environment threat. Any water released could safely be incorporated into the natural water cycle (surface water evaporates to form clouds, which later precipitate as rain, and return as surface water).

It is, generally much more difficult to clean safely and sustainably using nonaqueous cleaning methods. Many nonaqueous cleaners are themselves health hazards, water pollutants, or air pollutants. Certainly not all nonaqueous cleaners are hazards and/or pollutants, but most lack a basic natural means, such as the water-cycle, of purifying and/or recycling key ingredients. Of course, this is an oversimplification. Given enough time, almost anything can complete a natural cycle of synthesis and decay. However, here, we are considering processes achievable in the course of a human lifetime.

One might argue that the carbon cycle, the nitrogen cycle, the oxygen cycle and other elemental cycles are involved in the decomposition and purification of ingredients used in nonaqueous cleaners. In fact, some of these cycles are also involved in the purification of ingredients found in aqueous cleaners but to a lesser degree. All of the cycles, noted above, involve multiple chemical transformations. They are slow processes in which chemicals may remain in one state for many years before degrading to a purer form. For example, during the nitrogen cycle, nitrogen remains in the air typically

for years. Likewise, carbon takes the form of geological carbonates for extensive periods of time during the course of the carbon cycle, in some cases for millenia. Oxygen also remains tied up in in the form of geological carbonates. These elements simply do not cycle rapidly, to a pure state, the way water does.

## ENVIRONMENTAL ISSUES IN AQUEOUS CLEANING

Generally, the environmental issues involved in aqueous cleaning have to do with the ingredients used and their ultimate discharge into the environment. Taking a larger view, it is also important to consider the energy and resources consumed in making and using the cleaner.

There are several important factors concerning discharge of spent cleaning solutions into the environment: biodegradability, aquatic toxicity and eutrophication acceleration. Early detergent formulations contained poorly biodegradable surfactants that often caused foaming of lake and river surfaces after spent solutions were discharged to drain. All modern detergent formulations use biodegradable surfactants that do no buildup or persist in the environment causing foaming problems.

Aquatic toxicity can come from very high or very low pH or from toxic ingredients. Where extreme pH cleaning is required, it is advisable to neutralize or discharge spent solutions in small enough quantities to avoid problems. The surfactants in aqueous cleaners may be a source of aquatic toxicity. The use of biodegradable surfactants and the discharge of limited quantities of cleaning solutions generally results in safe concentrations of surfactants on water surfaces. Older, more highly toxic surfactants are rarely used in aqueous-cleaner formulations.

Eutrophication involves cleaners that contain phosphates. Phosphorus is an essential nutrient for algae. When significant amounts of phosphorus are discharged into surface water, vigorous algae blooms may result. The algae die and settle to the bottom filling lakes and ponds with silt and organic matter more rapidly than normal. Although eutrophication is a normal, natural process, the acceleration of this process by phosphates is undesirable. The main source of phosphorous in sur-

face waters is agricultural run-off from farming. There are no national regulations restricting the use of phosphates in cleaners, however, many states and municipalities have enacted legislation that restricts the use of phosphates in household cleaners. There are currently no restrictions on the use of phosphate containing cleaners in industrial cleaning applications.

## **SAFETY ISSUES IN AQUEOUS CLEANING**

Worker safety issues, for aqueous cleaners, involve skin exposure, eye exposure, ingestion, inhalation, and chronic systemic exposure. Consult the label and material safety data sheet on the cleaner for warnings and safety precautions.

When cleaning by hand, it is always good practice to wear protective gloves. Even the mildest cleaners can sometimes cause “dishpan-hands”. Gloves also provide protection and comfort when working, by hand, with hot solutions. In fact, many highly acidic or alkaline cleaners require the use of chemical-resistant gloves for worker safety.

Eye exposure is also a concern with many aqueous cleaners. Eye tissue is particularly vulnerable to attack by chemically active aqueous solutions. Accordingly, it is also considered good industrial practice to wear safety glasses or other eye protection when working with aqueous-cleaning solutions. Particularly hazardous aqueous cleaners should have warnings and recommended eye protection on the label.

In addition, there may be inhalation hazards with some aqueous cleaners. Because aqueous cleaners generally do not have volatile solvent ingredients, it is somewhat unusual to find the need for respiratory protection with such cleaners. However, it is considered good industrial practice to have some respiratory protection when working with sprays and mists in open-spray cleaning. Any special ventilation required should be noted on the material safety data sheet. Some semi-aqueous cleaners may contain volatile solvents that require special ventilation and possibly even flammability controls.

While it is relatively unusual for an aqueous cleaner to contain any carcinogenic ingredients, the cleaner’s material safety data sheet should disclose any long-term chronic exposure concerns relating to carcinogenicity.

Physical safety issues with aqueous cleaners, generally, concern storage and handling to avoid any hazardous reactions with other industrial chemicals. Good industrial practice usually involves storing acid and alkaline chemicals separately to avoid any reactions between them in the event of accidental spills. Some aqueous cleaners contain bleaches or other oxidizing agents that should be stored away from reactive chemicals that might undergo hazardous oxidation reactions. As previously mentioned, most completely aqueous cleaners are not flammable. However, some aqueous cleaners contain ingredients that form hazardous chemicals when burned. (It is considered good practice to wear respiratory protection when fighting any fire involving industrial chemicals.)

## **PRACTICAL REGULATORY REVIEW**

In today’s manufacturing environment, it is possible to use safe, clean, reduced waste cleaning processes that are ultimately sustainable. At the very least, use processes that comply with current environmental and health safety regulations.

The first step in evaluating the environmental health and safety of an aqueous cleaner is to secure the material safety data sheet and technical bulletins for the cleaners you plan to test or use, and to assemble as much information as you can about the soils you will be removing. A review of this information should disclose important environmental and health hazards as well as regulations.

When performing an initial review of regulations for an aqueous cleaner, it is important to consider Occupational Safety and Health Administration (OSHA) regulations, National Pollutant Discharge Elimination System (NPDES) discharge permits, Department of Environmental Protection (DEP) sewer connection/extension permits, and any Resource Conservation and Reclamation Act (RCRA) hazardous waste class or Clean Water Act regulations. State and local environmental regulations should also be considered.

It is wise to conduct a full scale environmental audit no matter what type of cleaning system you are using. Such an audit may result in changes in the way you currently manufacture and clean. In fact, after conducting a full-scale environmental audit many companies turn to aqueous cleaning to

achieve regulatory compliance easily and safely. A program of regular re-auditing can assure continued regulatory compliance.

Compared to hazardous nonaqueous and semiaqueous cleaners—particularly, those containing ozone-depleting fluorocarbon solvents, carcinogenic organic solvents, and/or flammable components—aqueous cleaners are good choices for safe, environmentally sound cleaning. By choosing high quality, environmentally sound aqueous cleaners, most cleaning problems can be solved without endangering workers or the environment.

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#### ADDITIONAL READING

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#### RESOURCES

[www.alconox.com](http://www.alconox.com)  
[www.epa.gov](http://www.epa.gov)  
[www.osha.gov](http://www.osha.gov)

# Appendix

- I List of Abbreviations
- II Cleaner Types from Alconox, Inc.
- III Detergent Selection Guide
- IV Glossary of Essential Terms
- V Application Case Histories
- VI Index

## APPENDIX I

### LIST OF ABBREVIATIONS

BOD	Biological Oxygen Demand
CFC	Choloro Fluoro Carbon
CIP	Clean in Place
COD	Chemical Oxygen Demand
DEP	Department of Environmental Protection
EH&S	Environmental Health & Safety
EPA	Environmental Protection Agency
FT-IR	Fourrier Transform Infra Red
GWP	Global Warming Potential
LAS	Linear Alkylbenzene Sulfonate
LCD	Liquid Crystal Display
MSDS	Material Safety Data Sheet
NPDES	National Pollution Discharge Elimination Systems
ODP	Ozone Depleting Potential
ODS	Ozone Depleting Substance
OSHA	Occupational Safety and Health Administration
RCRA	Resource Conversation and Reclamation Act
SARA	Superfund Authorization and Reauthorization Act
SNAP	Significant New Alternatives Policy
TCVLP	Toxic Chemical Leaching Properties
UV	Ultra Violet
VOC	Volatile Organic Compound

## APPENDIX II

### CLEANER TYPES FROM ALCONOX, INC.

30 Glenn St., White Plains, NY 10603, ph 877-877-2526, email [cleaning@alconox.com](mailto:cleaning@alconox.com), [www.alconox.com](http://www.alconox.com)

Cleaner Type	Cleaning Methods Used	Brand
High emulsifying, mild alkaline	manual, soak, ultrasonic, circulate CIP	ALCONOX® powder LIQUINOX® liquid
Acid cleaner	manual, soak, ultrasonic, circulate CIP	CITRANOX® liquid
Low-foaming, alkaline	machine washer, pressure spray, spray CIP	ALCOJET® powder
Low-foaming, high alkaline	machine washer, pressure spray, spray CIP	DETOJET® liquid
Ion-free, low-foaming	machine washer, pressure spray, spray CIP, manual, soak, ultrasonic, circulate CIP	DETERGENT 8® liquid
Mild alkaline tablet	siphon tube and pipete washer	ALCOTABS® tablet
Neutral, low-foaming	machine washer, pressure spray, spray CIP, manual, soak, ultrasonic, circulate CIP	LUMINOX® liquid
Enzyme cleaner	manual, soak, ultrasonic, circulate CIP	TERGAZYME® powder
Low-foaming, acidic	machine washer, pressure spray, spray	CITRAJET® liquid

DETERGENT SELECTION GUIDE

Application Key Concerns	Articles Cleaned/ Soil Removed	Cleaning Method	Recommended Cleaner Powder	Recommended Cleaner Liquid	
Healthcare/Veterinary Effective preparation for sterilizable, larger instru- ment life. Reduce waste.	Surgical, anesthetic, and examining instruments and equipment. Catheters and tubes.	Manual, Ultrasonic, Soak	ALCONOX	LIQUIDOX	
	Blood, body fluids, tissue im- plantments.	Machine washer, tap-sterilizer	ALCOJET	DET-O-JET	
Pharmaceutical/Medical Device/Biotechnology Passing clearance validation for FDA good manufacturing practices. For stainless steel, glass, plastic, elastomer cleaning.	Titanium dioxide, petrolatum, oils, emulsions, stain- ings, dyes/pigments, waxes, zinc oxides, proteins, stereols, alcohols, sugars and Euthragl® (LUSI,3005)PE-300) polymers.	Manual, Ultrasonic, Soak	ALCONOX	LIQUIDOX	
	Inorganic residues, salts, metallics, pigments, Euthragl® (LUSI,RS,ET150) polymers, amphoterics, coatings, amines, ethers, starches, alcohols. Protein/enzyme residues, PEO, BIP membranes.	Manual, Ultrasonic, Soak Machine washer, power wash, CIP	ALCONOX ALCOJET	LIQUIDOX SOLUJET	
Laboratory/Environmental Adequable results, no interfering residues, extend- ing equipment life. Keep lab- oratory accreditation. Laboratory safety.	Glass, metal, plastic labware, ceramics, tissue cul- ture, porcelain, clean rooms, animal cages, disinfect- ant, tubing, benches, safety equipment.	Machine, power spray, labware wash- er, washer-sterilizer, tap-washers	ALCOJET	LIQUIDOX (p-free) DET-O-JET SOLUJET (p-free)	
	Tubes, reusable pipets.	Siphon-type washer-rinsers	ALCONOX (p-free)		
	Microbiology, water lab, and environmental sam- pling. Phosphate-sensitive labware. EPA proce- dures. (acid for rinse cycle.)	Font, Manual, Ultrasonic, Soak Machine washer, labware washer	TERGAJET	LIQUIDOX SOLUJET-base CITRAJET-acid	
	Radioactive equipment/contaminants, Stereoink grease.	Manual, Ultrasonic, Soak Machine washer, varnisher	ALCONOX	LIQUIDOX SOLUJET	
	Trace metals, metal oxides, scale, salts, starches, amines.	Manual, Ultrasonic, Soak Machine washer, varnisher	ALCONOX	LIQUIDOX CITRAJET	
	Proteinaceous soils, bio-washes, tissues, blood and other body fluids, irreversible residues.	Manual, Ultrasonic, Soak Glassware washer	TERGAZYME	SOLUJET	
	Manufacturing, Precision Manufacturing, and Capex Clean parts, avoid volatile solvents, strong acids, and other hazardous chemicals.	Glass, ceramic, porcelain, stainless steel, plastic, rubber, die, chemicals, particulates.	Manual, Ultrasonic, Soak Machine washer, power wash	ALCONOX ALCOJET	LIQUIDOX DET-O-JET
		Aluminum, brass, copper and other soft metal parts. Oil, chemicals, particulates (acid for oxides, scale, buffing compounds).	Manual, Ultrasonic, Soak Parts washer, power wash	ALCONOX ALCOJET	LIQUIDOX-base CITRAMIX-acid SOLUJET-base CITRAJET-acid
		Inorganics, metallic complexes, trace metals and oxides, scale, salts, metal brightening.	Manual, Ultrasonic, Soak Parts washer, power wash	ALCONOX	CITRAMIX CITRAJET
		Silicone oils, mold-release agents, buffing com- pounds.	Manual, Ultrasonic, Soak Parts washer, pressure spray	ALCONOX	CITRAMIX SOLUJET
Delicate substrates/heads for waste.		Manual, Ultrasonic, Soak Machine wash, pressure spray	ALCONOX	LIQUIDOX (Semi-SP)	
Electronics Anodic conductive residues, zinc/CDCs, pass cleaning criteria.		Circuit boards, assemblies, screws, parts, conduc- tive residues, resins, rosin, fluxes, particulates, salts.	Manual, Ultrasonic, Soak Machine washer, power spray board and screen washers	ALCONOX	DETERGENT 9
	Ceramic insulators and components.	Manual, Ultrasonic, Soak Parts washers	ALCONOX	LIQUIDOX SOLUJET	
	Food and Dairy Acid interfering residues on food-contact equipment.	Stainless steel, food-contact equipment.	Manual, Ultrasonic, Soak Machine wash, pressure wash, CIP	ALCONOX ALCOJET	LIQUIDOX DET-O-JET
Oxides, scale, trace metals, salts, milkstone.		Manual, Ultrasonic, Soak Machine wash, pressure wash, CIP	ALCONOX	CITRAMIX CITRAJET	
Filter membranes, Protein/boiling.		Manual, Ultrasonic, Soak	TERGAZYME		
Cosmetics Acid cross-contamination.	Product contact surfaces (pails for pigments and salts).	Manual, Ultrasonic, Soak Parts washers, power spray	ALCONOX ALCOJET	LIQUIDOX-base CITRAMIX-acid SOLUJET-base CITRAJET-acid	
	Nuclear Acid waste interference	Reactor cavities, pipes, tools, protective equipment.	Manual, Soak, Spray	DETERGENT 9	

p-free -phosphate free  
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# Glossary of Essential Terms

**483**—warning letter, from the FDA, threatening to close a manufac-  
turing site unless an adequate response is made..

**Acid cleaner**—an aqueous cleaner that has a pH significantly below  
7, typically below a pH of 5.5. Acid cleaners contain acids and often  
other cleaning ingredients such as surfactants. Acid cleaners use a  
mechanisms known as "acid solubilization" (see other definitions)  
inwhich an acid reacts with a soil molecule to create a water solu-  
ble molecule, and "acid hydrolysis" (see other definitions) inwhich  
an acid reacts with a soil molecule and breaks it into a smaller  
water soluble soil.

**Alkaline cleaner**—a water based cleaner that contains alkaline  
ingredients that significantly raise pH. A cleaner with a pH of  
8.5–11 can be considered a mild alkaline cleaner. A cleaner with a  
pH of 11–12.5 is at least an unqualified alkaline cleaner. A cleaner  
with a pH above 12.5 would be a high alkaline and corrosive clean-  
er. Alkalinity fosters saponification(see other definitions), solubi-  
lization (see other definitions) of alkaline soluble soils and hydroly-  
sis (see other definitions).

**Anionic surfactant**—a cleaner ingredient that is a surface active  
agent (see other definitions) with a negative charge on the organic  
portion of the molecule. The charge on the surfactant determines  
the charge of the cleaner or detergent. An anionic detergent con-  
tains an anionic surfactant or surfactants. Anionic surfactants can  
be and usually are emulsifiers (see other definitions) and disper-  
sants(see other definitions). Typical anionic surfactants include  
organic sulfates, sulfonates and carboxylates. The most common  
anionic surfactant is sodium dodecylbenzene sulfonate.

**API**—active pharmaceutical ingredient.

**Aqueous cleaner**—a blend of water soluble chemicals designed to  
remove soils into the cleaner solution.

**APR**—annual product review. Part of quality systems review of a  
product.

**Bed-of-nails testing**—a test for conductive residues on a surface by  
touching the surface such as a circuit board to a bed of nails that  
are connected to conductivity detectors to see if any conductivity  
happens on the surface.

**Bioburden**—microbes on the surface.

**Builder**—a cleaner ingredient that enhances the cleaning ability of the surfactants in at least one, and usually a combination of the following ways: using chelation, sequestration or binding to soften water, prevents hard water or metal ions from reacting with surfactants and soils; enhances the surface tension lowering property of surfactants; adds alkalinity; buffers cleaners to maintain alkalinity; emulsifies oils; disperses particulates; inhibits redeposition of soils; breaks up clumps of particles by deflocculation; saponifies soils; provides corrosion inhibition; and improves the handling, flowing, and storage characteristics of the cleaner. A typical builder is sodium polyphosphate.

**CFR**—code of Federal regulations.

**cGMP**—current good manufacturing practice.

**Cavitation**—the creation of a tiny "bubble" of a vacuum in the bath of an ultrasonic tank caused by the "trough" in the sound waves going thru the solutions. These tiny bubbles are constantly forming and collapsing as sound is pumped through the tank. The act of collapsing is the source of mechanical cleaning energy in an ultrasonic cleaning tank.

**Chelating**—the binding that occurs with metal ions by a chelating agent (see definition below)

**Chelating Agent**—a cleaner ingredient that is a chemical with at least two sites on each molecule available to bind with metal ions in a water based solution and form a ring compound. Typical examples of chelating agents include sodium polyphosphates and ethylene diamine tetra acetic acid (EDTA). Many chelating agents are also sequestering agents (see other definitions).

**Chromatography**—a method of separating ingredients in a mixture and identifying them by the length of time they take to pass through a system when they are injected at the top of a chromatography column along with a carrier solution using a detector at the base of the column to detect when they come out.

**CIP**—clean in place. A process used to clean manufacturing equipment in-place without disassembling the equipment. Often this is done by circulating cleaning solutions through pipes and spraying using spray-balls or nozzles to clean the insides of tanks.

**Cleaner**—a chemical or blend of chemicals designed to clean. These may be solvents, acids, bases, detergents, and/or water based blends.

**Corrosion**—is the damage caused on a substrate (typically a metal) by reacting with the environment around the substrate. A common form of corrosion is the reaction of ferrous metals with dissolved oxygen in water to form reddish-brown iron oxide - rusting.

**Coupling agents**—are cleaner ingredients that are added to improve the solubility of other desirable cleaner ingredients. They allow more concentrated cleaners to be made than would otherwise be possible based on the inherent solubility of the other ingredients.

**Degreaser**—a cleaner that is designed to remove oils and greases. These are typically heavy duty cleaners. Unlike light duty fine

cleaners that are designed to remove low levels or trace amounts of oil and leave surfaces measurably or analytically clean, degreaser are designed to remove gross amounts of oil and grease and leave surfaces measurably clean. Most degreasers are either high alkaline aqueous cleaners or solvent based cleaners.

**Detergent**—a blend of ingredients intended for cleaning that include at minimum a surfactant (see other definitions) to provide emulsifying or dispersing properties and a builder (see other definitions) to inhibit water hardness from the precipitation of calcium and magnesium salts. In the industry, the word detergent is often used to mean surfactant.

**Dispersant**—a cleaner ingredient that reacts with water insoluble particulates. A dispersant overcomes the electrostatic attraction of a particulate to a hard surface and creates a liquid solid mixture in the form of a suspension. A typical dispersant is sodium polyphosphate.

**Dissolve**—to clean using a cleaning fluid to form a stable mixture containing individual soil molecules. In aqueous cleaning, the use of water to dissolve water soluble soils is an example of this mechanism.

**Emulsifier**—a cleaner ingredient that lowers the interfacial tension between immiscible liquids such as oil and water allowing them to mix. Typically, an emulsifier forms a micelle, a small droplet of oil surrounded by the emulsifier. The emulsifier is in contact with the water and the surrounded droplet, the micelle, is dissolved in the water. Emulsifiers are surfactants (see other definitions).

**Ester**—is a molecule made up of an organic acid joined to an alcohol. These types of molecules are natural oils that are found in fingerprints or natural lubricants. Some synthetic lubricants are also esters.

**Eutrophication**—the enrichment of a water body with nutrients (such as nitrogen or phosphorus either from natural or manmade sources), resulting in excessive growth of phytoplankton, algae, or vascular plants, leading to depletion of oxygen and silting up of the body of water.

**Excipients**—fillers, non-active pharmaceutical ingredients.

**Flocculation**—The combination, agglomeration, aggregation or coagulation of suspended particles in such a way that they form small clumps or tufts (called floc).

**Free-rinsing**—the ability to easily be rinsed away from a surface using rinse water. Cleaners and detergents that are completely water soluble, have low surface tension, and do not tend to react to form insoluble molecules with typical residues or ions commonly found in water will typically be free-rinsing.

**GC**—gas chromatography

**HPLC**—high performance liquid chromatography.

**Hydrolyze**—to break a molecule apart using acid (H+) and hydroxyl ions (OH-) from water (H<sub>2</sub>O). This occurs when a fat or oil is hydrolyzed to make soap, as in saponification (see other definitions) or when an enzyme breaks down a protein.

**Hydrotrope**—a cleaner ingredient that improves the solubility and stabilizes another desired detergent ingredient in water. Their use allows for more concentrated aqueous cleaners.

**Hydrophylic**—"water loving." A molecule or part of a molecule that is more thermodynamically stable in contact with a polar environment such as water.

**IC**—ion chromatography. (see chromatography definition)

**ICH**—International Conference on Harmonization.

**Ion-free cleaner**—a cleaner that has no metal ion ingredients. Typically an ion-free cleaner will contain nonionic surfactants and other ingredients that are not metallic salts. An ion-free cleaner does not contain sodium or other metal salts. Note that a nonionic cleaner is not necessarily ion-free. A nonionic cleaner merely has no ionic charge on the surfactant in the cleaner. A nonionic cleaner can and usually does have builders or other inorganic salt ingredients that would contain ions.

**IQ**—installation qualification. The documentation that a device is installed properly according to its specification.

**Laminar flow**—In fluid flow, a smooth flow in which no crossflow of fluid particles occur between adjacent streamlines; hence, a flow conceived as made up of layers - commonly distinguished from turbulent flow.

**LOD**—limit of detection (approximately signal to noise  $S/N = 3$ ), the limit at which an analytical detection method can detect a residue being analyzed for

**LOQ**—limit of quantitation (approximately signal to noise  $S/N = 10$ ), the limit at which an analytical detection method can detect and quantify the amount of a residue being analyzed for.

**Micelle**—is a sub-microscopic aggregate of molecules. In the context of cleaners, these molecules are surfactants usually arranged in sphere or rod shapes with their hydrophilic ends facing outward into the water solution and hydrophobic ends facing the inside of the aggregate. Micelles can hold hydrophobic oil molecules at their centers to create stable emulsions.

**Neutral cleaner**—a cleaner that has a pH near 7, typically ranging from 5.5 to 8.5. These cleaners tend to use mechanisms such as emulsifying and dissolving rather than the more aggressive chemical attacks on soils, possible with acid or alkaline cleaners.

**Nonionic cleaner**—a cleaner that contains nonionic surfactants. The term does not mean an ion-free cleaner. A nonionic cleaner may easily contain nonionic surfactants blended with many ionic builders that are sodium salts or other metal ion salts. (see ion-free cleaner).

**Nonionic surfactant**—a cleaner ingredient that is a surface active agent (see other definitions) that has a no charge on the organic portion of the molecule. The charge on the surfactant determines the charge of the cleaner or detergent. A nonionic detergent contains nonionic surfactants but is not necessarily ion free (see other definitions). A nonionic detergent may contain many ionic salts. It is the surfactant alone, that has no electrical charge (is nonionic).

Nonionic surfactants can be and usually are emulsifiers (see other definitions) and dispersants (see other definitions). Typical nonionic surfactants include organic ethoxylates. The most common nonionic surfactants are alcohol ethoxylates and alkylphenol ethoxylates.

**Oleophilic**—"oil loving." A molecule or part of a molecule that is more thermodynamically stable when in contact with oily, less polar surfaces such as oils. As distinguished from hydrophilic (see definition)

**OQ**—operational qualification. The documentation that a device is operating correctly according to its specification.

**pH**—a measure of how acidic or basic a solution is. It is the inverse log of the hydrogen ion concentration in water. In practical terms, pH 7 is neutral, below 7 is acidic and above 7 is basic or alkaline.

**ppb**—parts per billion (ug/liter, microgram/liter).

**ppm**—parts per million (mg/liter, milligram/liter).

**Outgas**—the act of a residue evaporating into a vacuum from a contaminated surface that is exposed to a vacuum.

**Parenteral**—Outside the digestive tract. This term refers to intravenous, subcutaneous and other nonoral modes of administering medications, devices and therapies.

**Polar**—the property of a molecule that has a significant electrical dipole moment which is a direction of charge resulting from a concentration of negatively charged electrons at one end of the molecule.

**PQ**—performance qualification. The documentation that a device is performing properly according to its specification.

**RAL**—residue acceptance limits.

**Saponifier**—a cleaner ingredient that reacts with a poorly soluble natural oil ester, or resin ester such as rosin to split the ester or resin into a more soluble salt of an acid (soap). In the case of many compounds this converts a water insoluble oil or resin into a water soluble soap that in turn acts as an emulsifier to emulsify any unreacted oil or resin and assist with cleaning. Typical saponifiers are potassium hydroxide and sodium hydroxide.

**Semiaqueous cleaner**—a chemical, or blend of chemicals or solvents, used for cleaning, that relies on a water rinse. Usually, a solvent or blend of water soluble solvents, these cleaners are used straight, without water, and then followed by a water rinse, or they may be blended with water during use.

**Sequestering agent**—a cleaner ingredient that is a chelating agent (see other definitions) that reacts with metal ions in a water based cleaner. The sequestering agent binds with the metal ions tightly, preventing them from reacting with other chemicals or soils. Sodium polyphosphate is a typical sequestering agent.

**Soap**—the salt of an acid. A typical example is the sodium salt of stearic acid (sodium stearate) formed from sodium hydroxide (a saponifier—see other definitions) and glycerol tristearate (natural animal fat). Soap is a surfactant (see other definitions) generally

having good emulsifying properties for the oils or fats from which it was derived by the process of saponification, ie. sodium stearate (a soap) would be good at emulsifying glycerol tristearate (a natural animal fat). However, soap can react with calcium or magnesium ions in "hard" water to form calcium or magnesium salts that are insoluble in water and precipitate out as soap scum or film. For this reason, soaps are not very free-rinsing cleaners.

**Solubilizing**—a cleaning mechanism that involves dissolving a soil into a single aqueous phase that relies on a "like dissolves like" principle. In an aqueous cleaner the water acts as a polar solvent to help solubilize polar soils. The main cleaning mechanism of solvent based cleaners is solubilizing or dissolving.

**Solvent cleaner**—a cleaner, containing one or more organic chemicals, that can dissolve soils. Typically solvent cleaners contain volatile organic compounds. Fluorocarbon based freon cleaners are solvent cleaners. The cleaning process using solvent cleaners lacks a water continuous phase and there is, generally, no water present in the formulations of solvent cleaners. This is distinguished from semi-aqueous cleaners that are blends of water and solvents, or solvents that can be rinsed and dissolved with water.

**Solvate**—the action of solubilizing (see definition above).

**SOP**—standard operating procedure.

**Surface tension**—a force running parallel to a surface and resulting from the attraction of surface molecules toward those below the surface. This tension minimizes surface area of solution.

**Substrate**—a surface or part that is being acted on, for example being cleaned.

**Surface active agent**—or surfactant, an ingredient found in most aqueous cleaners, is a chemical active at solution/surface interface. In the cleaning context, the surface acting agent lowers the surface (interfacial) tension at liquid/gas, liquid/liquid, and liquid/solid interfaces. The structure of surface active agents, used in aqueous cleaners, is usually oblong. One end of the molecule is hydrophobic ("water hating" ) and the other, hydrophilic ("water loving"). The hydrophilic end of the molecule is attracted to and remains stable in water; while the hydrophobic end is attracted to air, particulate, oil or surface and away from water where it is less stable. This means that a surface active agent can act as a wetting agent helping a cleaner wet a surface or penetrate into small cracks and crevices where it can perform. A surface active agent reacts with a particle as a dispersant, and can also act as an emulsifier for oil. Surface active agents are either anionic, nonionic, cationic, or amphoteric (see other definitions).

**Surfactant**—see surface active agent.

**Titrate**—wet chemistry test used to detect an amount of something by measuring how much of the unknown reacts with a known reagent to determine how much of the unknown is present..

**TOC**—total organic carbon analysis.

**UV-vis**—ultraviolet or visible spectroscopy.

**Water Continuous Phase**—a water based solution that has water continuously in contact throughout the solution, the water may be surrounding oil or micelles, but it is continuously connected around those pockets, rather than the water being separated into pockets of water within an oily solution (an oil continuous phase).

**Wetting agent**—a surfactant (see definition) that lowers the surface tension of water to allow it to more broadly contact a surface and penetrate into cracks. Without the presence of a wetting agent in the water, water will bead up on a given surface, with a wetting agent, the solution will spread out and form a broader bead.



# Application Case Histories

## 1. OPTICAL WAX

### MORE HEAT FOR FASTER CLEANING

An optical lens manufacturer had been using ALCONOX powdered detergent in a heated ultrasonic bath to remove a wax from lenses during manufacturing. As production increased, this system was unable to clean fast enough. By increasing the temperature, adequate cleaning performance and speed were achieved.

	Initial Problem	Solution
Time	10 min	5 min
Temp	60 deg C	70 deg C
Agitation	ultrasonic	ultrasonic
Chemistry	1% ALCONOX	1% ALCONOX
Rinse	deionized water	deionized water
Dry	air	air
Problem	cleans too slowly	cleans adequately

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## 2. PRECISION MANUFACTURING PROCESS OILS

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### HIGHER CONCENTRATION INCREASES BATH LIFE

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For many years, a metal valve manufacturer had been using LIQUI-NOX, liquid detergent, in an immersion tank, to remove process oil from metal valves. The cleaning solution was made up and depleted in one shift. Over time, production increased and with it the number valves and quantity of process oil. The manufacturer observed that the cleaning solution was less effective at the end of the shift. By increasing the concentration of detergent, he was able to increase the cleaning capacity of the solution and thereby extend the bath life to meet his needs.

---

	Initial Problem	Solution
Time	20 min	20 min
Temp	50 deg C	50 deg C
Agitation	soak	soak
Chemistry	1% LIQUINOX	1.5% LIQUINOX
Rinse	deionized water	deionized water
Dry	air	air
Problem	tank did not last long enough	bath life extended

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## 3. PHARMACEUTICAL TABLET COATING EQUIPMENT

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### SOIL CHANGE CAN REQUIRE CLEANER CHANGE

---

A pharmaceutical company had been using a typical high alkaline cleaner for manual cleaning of tablet coating equipment. This worked fine with their standard tablet coatings. When the company started to make tablets with enteric coatings, they observed that their standard cleaner could not get their coating equipment even visually clean. By changing to an acid cleaner, that was effective on the water insoluble inorganic salts used in the enteric coating, they were able to get their equipment clean.

---

	Initial Problem	Solution
Time	10 min	10 min
Temp	50 deg C	50 deg C
Agitation	manual	manual
Chemistry	1% High Alkaline	2% CITRANOX
Rinse	deionized water	deionized water
Dry	air	air
Problem	system could not clean enteric coating on tablet coating equipment	system cleaned enteric coating on tablet coating equipment

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#### 4. ARCHITECTURAL GLASS MANUFACTURER SEES SPOTS WHEN SETTING UP MANUFACTURING IN A SITE WITH HARD WATER

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##### DEIONIZED WATER STOPS WATER SPOTS

---

An architectural glass manufacturer had one plant where DETOJET cleaner was used to clean glass prior to coating. The tap water, at this plant, was soft with little dissolved calcium or magnesium. Sheets of glass were cleaned effectively using a conveyor spray system with tap water rinsing prior to air knife drying. When a new plant was set up, water spots were a problem. The local water used at the new plant was hard containing a great deal of dissolved calcium and magnesium. By switching to a deionized water rinse at the new plant and by beefing up the air knives, spotting was eliminated

---

	Initial Problem	Solution
Time	10 s/ft	10 s/ft
Temp	55 deg C	55 deg C
Agitation	spray	spray
Chemistry	1/2% DETOJET	1/2% DETOJET
Rinse	hard tap water	deionized water
Dry	air knife	air
Problem	water spots	no water spots

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#### 5. WASTE TREATMENT FILTERS

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##### ENZYME CLEANER CURES BIOFOULED FILTERS

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A small scale in-house waste treatment filtration system was used to remove oils from a waste stream at a manufacturing plant. Typically, the filter membranes were cleaned with a high alkaline cleaner at high heat. Eventually, bio-fouling began to occur in the filter and the resulting proteinaceous soils would crosslink and become tenacious when exposed to the hot alkaline cleaning solution. As a result, filter flow rates and pressures did not recover after cleaning. By cleaning the filters with TERG-A-ZYME, an enzyme cleaner, at moderate temperatures, normal flow rates and pressures were restored.

---

	Initial Problem	Solution
Time	1 hour	1 hour
Temp	55 deg C	55 deg C
Agitation	circulate	circulate
Chemistry	high alkaline	1/2% TERGAZYME
Rinse	tap water	tap water
Dry	none needed	none needed
Problem	fouled filter membranes	fouled membranes cleaned

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## 6. WINE TASTING GLASSES

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### ELIMINATING DETERGENT FRAGRANCE RESIDUES

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In his book *BORDEAUX*, the world renowned wine critic Robert Parker observed "I can't begin to tell you how many dinner parties I have attended where the wonderful, cedary, blackcurrant bouquet of 15 or 20-year-old Pauillac was flawed by the smell of dishwasher detergents..." In fact, the human nose is very sensitive to fragrances found in many detergents. A major supplier of wine tasting glasses was able to satisfy the needs of his discerning clientele by suggesting that they use free-rinsing, fragrance-free LIQUI-NOX cleaner instead of the non-free-rinsing, fragrance containing household detergents they had been using.

---

	Initial Problem	Solution
Time	30 sec	30 sec
Temp	50 deg C	50 deg C
Agitation	manual	manual
Chemistry	dish detergent	1% LIQUINOX
Rinse	tap water	tap water
Dry	air	air
Problem	fragrance residues on wineglasses interfered with wine bouquet	no interfering fragrance deposit on glasses

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## 7. LABORATORY PIPETS FAIL TO DELIVER

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### INCREASED AGITATION IMPROVES CLEANING

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An analytical laboratory had been using volumetric pipets to measure volumes of analytical reagents precisely. When they calibrated their pipets they found that their old ones were not as reliable as brand new ones. The problem was traced to incomplete cleaning. The old cleaning process involved soaking the pipets in a static soak bath and then rinsing them in a siphon pipet rinser before air drying. By adding ALCOTABS tablets to the siphon pipet rinser, the detergent became more highly concentrated and residues that had been loosened during soaking were easily removed. After the ALCOTAB had completely dissolved in the siphon rinser, rinse water continued to flow and rinsing was completed.

---

	Initial Problem	Solution
Time	8 hours	8 hours
Temp	ambient	ambient
Agitation	soak	soak followed by circulate
Chemistry	lab detergent	lab detergent plus ALCOTABS
Rinse	DI water	DI water
Dry	air	air
Problem	soaking alone could not remove all reagent residues in pipets	addition of ALCOTABS works to remove all reagent residues in pipets

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