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Water-Based Cleaning Fundamentals

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W. B. Harding

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Topical Report
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Prepared by W. B. Harding

A basic description of water-based alkaline cleaning is presented. The nature of soils is described. The compositions of conventional cleaning compounds are given with descriptions of the functions of the ingredients. The mechanisms by which soil is removed are explained. The degrees of cleanliness required, along with the influence of the material being cleaned, are discussed. Tests for cleanliness are described.

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SUMMARY

Water-based alkaline cleaners are of renewed interest as replacements for cleaning processes based on the use of halogenated solvents. An understanding of how aqueous processes work is necessary for their effective application to cleaning problems.

Cleaning technology involves the nature of soil, the formulation of cleaners, mechanisms of cleaning, the cleaning processes, the degree of cleanliness required, the object to be cleaned, and tests for verifying cleanliness.

Soils are generally mixtures of organic and inorganic films and particles. Alkaline cleaners remove soils by dissolution of water-soluble soils, conversion of soils into water-soluble substances (neutralization or saponification), emulsification of oils, and deflocculation and suspension of solids. Alkalies are also used to remove hard water ions.

Cleaners normally consist of one or more alkalies and alkaline salts, frequently sodium silicates and sodium phosphates, and one or more surfactants. Many surfactants are available, but most commonly used are sodium alkyl aryl sulfonates and alkyl phenol ethoxylates. Selection of the formulation depends in part on the nature of the article that is to be cleaned; the composition and strength of a cleaner is adjusted so that the article is not harmed.

The cleaning processes used are immersion with and without agitation, spray, tumbling, electrolysis, and ultrasonics.

Cleanliness is not total freedom from foreign material but is freedom from harmful foreign material, that is, material that will interfere with subsequent processing or will prevent the cleaned product from performing its intended function. This is the ultimate test for cleanliness.

In-process tests for cleanliness include examining for complete wetting by water, wiping with a clean white cloth, measuring the degree of spread of a drop of water on the cleaned surface, measuring gloss, examining visually (possibly with a microscope), and applying various instrumental methods.

Additional information about alkaline cleaners can be found in the literature and can be obtained from the suppliers of cleaners and of the constituents of cleaners.

DISCUSSION

SCOPE AND PURPOSE

One objective of this project is a search for a replacement for cleaning processes that employ halogenated solvents.

Many industrial cleaning processes that have been used during the past half century employ halogenated solvents. These solvents are hydrocarbons in which part or all of the hydrogen atoms in the molecule have been replaced with chlorine or with chlorine and fluorine. The first group is referred to as CHCs and the second as CFCs.

The most widely used CHCs are methylene chloride, chloroform, carbon tetrachloride, ethylene dichloride, trichloroethylene, 1,1,1-trichloroethane, and perchloroethane. All are toxic and many or all are carcinogens or suspected carcinogens. They may contribute to the depletion of stratospheric ozone. For these reasons their use is being substantially reduced, and they may be totally phased out of production.

CFCs include refrigerants. The CFC used for cleaning is 1,1,2-trichlorotrifluoroethane (trade names Genesolv D and Freon TF or PCA). It is a mild solvent that removes oils, greases, and rosin fluxes without harming plastic materials. It is also significantly less toxic than the CHCs and is not a suspected carcinogen. However, it, along with the refrigerant forms, is believed to be a serious ozone depleter. Because of this environmentally harmful nature, by international agreement, production of these materials will be totally phased out over a period of years.

Potential replacements for the halogenated solvents are other solvents such as hydrocarbons, terpenes, and moderately high boiling esters. Evaluation of these is part of this project and will be dealt with in other reports.

Water-based alkaline cleaners are also possible replacements and are being evaluated. This report presents the information gathered on the subject of water-based alkaline cleaners in preparation for the evaluations.

ACTIVITY

Introduction

Alkaline water-based cleaners are used in manufacturing processes to clean product. Other important uses are laundering, dishwashing, and custodial cleaning. Only manufacturing uses will be discussed in this study.

It is not expected that users will formulate and mix their own cleaners, although in special cases, this may be appropriate. It is expected, rather, that proprietary cleaners will be used. The information presented here will promote the informed selection and use of these products.

The technology can be divided into the following seven subjects:

1. the nature of soils,
2. the formulation of cleaners,
3. the mechanisms of cleaning,
4. the cleaning process,
5. the degree of cleanliness desired,
6. the surface to be cleaned, and
7. testing for cleanliness.

The Nature of Soils

Soils are mixtures of organic and inorganic films and particles.

Organic soils usually are liquid or solid films. Plastic particulates present as fibers and pieces are organic, but their organic nature is less important than their form.

The following are common organic soils.

Mineral Oil	Moderate molecular weight hydrocarbons.
Grease	Mineral oil mixed with a metallic soap.
Fatty Acid	Mixtures of moderate molecular weight aliphatic acids. Although given names of single substances, such as stearic acid, they are mixtures of related materials.
Fat	A mixture of fatty acid triglycerides.
Wax	Esters of high molecular weight aliphatic alcohols and fatty acids.

Insoluble Soap	Metal salts of fatty acids.
Tar	Mixtures of high molecular weight hydrocarbons.
Polymerized Films	Varnish-like films formed by heat during fabrication or aging during storage.
Cutting Oils	May be sulfurized or chlorinated mineral oil or oil-in-water emulsions.
Inks	Layout, mill marks, or temporary information.
Silicone Oils	Can be removed, but presence must be known.

Inorganic soils are solid and may be either films or particulates. Films are reaction products: corrosion, scale, heat-tint, or tarnish. Of these, probably only tarnish can be removed by a conventional alkaline cleaner. The others require special alkaline formulations, acid treatment, mechanical processes such as blasting, or a combination of these; they are not in the scope of this study.

Particulates are minerals (quartz, mica, asbestos, limestone, and many others), glass, metals, abrasives and polishing compounds, carbon smut, and organic fibers and particles.

An important point to be noted in the above lists is that soils are deliberately applied to aid manufacturing or to provide temporary protection, are the result of a fabrication process, or are the result of environmental exposure. The amount and type of soil can be controlled to make cleaning easier and more reliable, to reduce cost, and to reduce the amount of waste to be handled.

Formulation of Cleaners

Water-based cleaners may be as simple as a single surfactant or a single alkaline material. More often, there are two or three surfactants and two or three alkalies and alkaline salts. There may be hydrotropes (see below) and sometimes a solvent.

Cleaners are supplied both as powders and as liquid concentrates, and the formulation will depend in part on the form. In the past, powders were preferred to avoid paying for water. Now, increasing use of automatically controlled processes makes the easily metered liquids preferred.

Surfactants

A surfactant (short for 'surface active agent') provides wetting, emulsification, solubilization, and dispersion. There are thousands of surfactants, but only a handful are used in the alkaline cleaners of interest.

A surfactant is one of four types, depending on whether it ionizes in solution and, if it does ionize, which ion has the surface active properties. The anion is the active part in an anionic surfactant and the cation in a cationic. An amphoteric surfactant switches with the pH of the solution. Nonionic surfactants do not ionize.

For the most part, anionic and nonionic surfactants are the ones used in the cleaners under discussion. Anionics are more effective at removing particles and nonionics at removing oil. Amphoteric surfactants may be in cleaners that are supplied as liquid concentrates to increase the solubility of the other surfactants--a property called "hydrotropy."

The following surfactants are most commonly used in water-based cleaners.

<u>Type</u>	<u>Typical Products</u>
Anionic	
Sodium Dodecyl Benzene Sulfonate	Conoco C-550 Richonate 60B
Sodium Alpha Olefin Sulfonate	Conoco AOS-90F Witconate AOS
Phosphate Ester	Triton H66
Nonionic	
Linear Alcohol Ethoxylate	Neodol 25-12 Tergitol 25-L-7
Branched Alcohol Ethoxylate	Polytergent J-500
Nonyl Phenol Polyethoxylate	Triton N-111 Igepal CO-710
Octyl Phenol Polyethoxylate	Triton X-102 Igepal CA-630

Alkalies and Alkaline Salts

The alkaline constituents are usually one or more of the following.

- Sodium Hydroxide
- Sodium Carbonate
- Sodium Sesquicarbonate
- Sodium Bicarbonate
- Sodium Metasilicate
- Sodium Orthosilicate
- Trisodium Phosphate (TSP, Sodium Orthophosphate)
- Tetrasodium Pyrophosphate (TSPP)
- Sodium Tripolyphosphate (STP)
- Sodium Hexametaphosphate
- Sodium Tetraborate
- Sodium EDTA
- Sodium Gluconate
- Sodium Glucoheptanate
- Sodium Citrate

Potassium compounds are used where their higher solubility is desired.

Sodium hydroxide provides alkalinity for the neutralization of acidic soils and the precipitation of hard water ions. It saponifies fatty acids, dissolves amphoteric metal salts, splits esters, decomposes varnish-like deposits, and provides conductivity when used in electrocleaners. Because of its hazardous properties, sodium hydroxide is being replaced by orthosilicates and orthophosphates.

Sodium carbonate provides alkalinity reserve. It is a buffer and it softens water by precipitation. It is a carrier for liquid surfactants in dry mixes.

Sodium sesquicarbonate is an equal molar mixture of sodium carbonate and sodium bicarbonate. Sesquicarbonates and bicarbonates yield lower pH solutions than sodium carbonate.

Silicates provide alkalinity, buffering, detergency, surface tension lowering, emulsification of oily soils, deflocculation and dispersion of solid soils, and inhibition of corrosion of product and equipment. They soften water by precipitation. Silicates are absorbed by surfaces and their removal requires thorough rinsing. Even then, enough can remain to interfere with sensitive subsequent processes such as the clear anodizing of aluminum and the phosphating of steel.

Phosphates sequester calcium, magnesium, and iron, preventing them from forming insoluble compounds. Phosphates also provide alkalinity, buffering, deflocculation

and dispersion of solid soils, emulsification of oily soils, synergism with surfactants, and improved rinsing.

Sodium EDTA, gluconate, heptagluconate, and citrate are sequestering agents that tie up calcium, magnesium, iron, and copper ions. Sodium citrate also deflocculates and disperses solid soils.

Miscellaneous Ingredients

Sodium sulfonate salts of benzene, toluene, xylene, and cumene are hydrotropes that may be included to increase the solubility of the surfactants. They have no other function and are being replaced with surfactants that are hydrotropic, such as the phosphate esters already referred to, and amphoteric surfactants based on imidazol.

Ethylene glycol butyl ether and other water-soluble solvents may be added to increase the solubility of oily soils.

Water

The water used is important. It makes up the bulk of the cleaner. Water softening agents are essential if the water is hard. Simpler formulations can be used if soft, reverse osmosis, or deionized water is used. However, if the soils contain polyvalent metallic compounds, the more complex formulations are necessary.

Mechanisms of Cleaning

Forces of attraction bind soil to a surface. The alkaline cleaner breaks the attraction, removes the soil and suspends it so that it can be rinsed away, and leaves behind a surface that is compatible with the function of the cleaned product.

Alkaline cleaners use the following mechanisms to remove soil:

- dissolution,
- wetting,
- emulsification,
- deflocculation,
- dispersion, and
- saponification.

Water-soluble soils are dissolved and flushed away in the rinse. These are salts and also certain organics, for example, sugar.

Because of low interfacial tension imparted by the surfactants, the cleaner will preferentially wet the part surface, undercut and displace oil films, and penetrate aggregated solid soils.

Displaced oil is emulsified into tiny droplets that are suspended in the solution and then are flushed away in the rinse. Cleaners vary in their ability to emulsify; with some, the oil floats to the surface from where it is removed by skimming so that it will not redeposit on the product as it is drawn out of the tank.

Solid soils usually are aggregations of small particles. The cleaner deflocculates the solid mass by penetrating it and breaking the attractive forces that hold the mass together and bind it to the surface. The soil is transformed into small, free particles. The deflocculated solids are dispersed throughout the solution and are flushed away in the rinse.

Saponification, strictly speaking, is the splitting by a strong alkali of fats into glycerine and salts of fatty acids (soap). Although this may be cited as a significant mechanism in cleaning, it actually occurs to only a small degree under the conditions of alkaline cleaning. Saponification is also used to describe the neutralization of fatty acids by an alkali. This does occur in alkaline cleaning to form water-soluble soaps; for example, this is the mechanism for the removal of rosin flux.

Cleaning Processes

The cleaning process consists of bringing the cleaning solution into contact with the soiled product. This may be simple immersion in a quiescent solution. More often, some kind of mechanical action is required: wiping or solution agitation by stirring, tumbling, electrolysis, spray, or ultrasonics. Multiple steps can be employed in which the bulk of the soil is removed in a precleaning stage and the remaining soil is removed in a subsequent stage. The procedure used is a factor in the selection of the cleaner.

Other variables are concentration of cleaner, temperature, and time of treatment.

Degree of Cleanliness

At some point in a discussion of cleaning will be heard, "How clean is clean?" The point is that there is no such thing as a clean surface if "clean" means a surface free of all foreign material. A foreign-material-free surface, even if it can be produced, rapidly acquires a layer of environmental material.

A surface is clean if the foreign material on the surface does not interfere with function or subsequent processing.

Cleaning processes remove soil, that is, harmful foreign material. Processes that go beyond this are wasteful. In a way, cleaning was simpler a generation ago before

sensitive surface analysis instruments such as Auger and ESCA were developed. Foreign material was there, but it was difficult to detect, much less measure. Emphasis was on performance. If it worked, the surface was clean. Now, with the ability to detect extremely small quantities, precious time may be spent worrying about the significance of an analysis and trying to eliminate the detected foreign material. Modern tools should be used, but the goal--a product that is clean enough for the intended purpose--must be kept in sight.

The Surface To Be Cleaned

The cleaner must not harm the product.

Ferrous and many magnesium alloys are resistant to strong alkalis and can be cleaned with solutions high in these materials. These solutions can tarnish copper alloys and remove zinc from brass, so somewhat milder alkaline cleaners are used for them.

Because aluminum is rapidly attacked by strong alkalis, aluminum cleaners are less alkaline and usually contain silicates, which adsorb onto the surface and inhibit the attack. Thorough rinsing, possibly a dip in a nitric-hydrofluoric acid solution, is required to remove it. Some aluminum cleaners are formulated to produce a slight etch for more effective cleaning, to produce a pleasing appearance, to hide superficial defects, or to provide a more active surface for a subsequent operation such as plating, anodizing, and chromating.

Zinc is more sensitive to alkali attack than aluminum and requires even milder solutions, lower operating temperatures, and reduced cleaning times.

Plated parts can be deceiving. Plating is inherently microporous and the underlying metal may be exposed through the pores. The cleaner must be compatible with the substrate metal as well as the plating.

Anodic coatings on aluminum are highly corrosion resistant but may be attacked by strong alkaline cleaners.

The beneficial properties of chromate coatings on aluminum and on cadmium and zinc plating depend on the integrity of the film and soluble chromate salts in the film. High temperatures (above 160°F) will damage the film. Water-based treatment may leach chromate.

Ultrasonic cleaning can damage polished surfaces. A process may produce a superficial etch that is not apparent on normal finishes but that will destroy a highly polished finish.

Testing for Cleanliness

The ultimate test for cleanliness is the performance of the product either in subsequent processing or in service. However, there are tests for in-process monitoring of the cleaning. Several are described in the references.¹⁻⁹ The following are some simple tests.

The water-break test probably is the most widely used. The cleaned product is observed as it emerges from the final rinse. If the water breaks up into drops and partially wetted areas, the product is not clean. Clean product will retain a continuous water film. This is based on the fact that water will not wet an oily surface, even when the oil is present in molecular quantities; but it will wet an oil-free surface. The test assumes that the material from which the product is made is hydrophilic--the case with metals, ceramics, and certain plastics--and that if soil is present, it includes oil. Thorough rinsing is necessary because residual cleaner may promote the wetting of a soiled surface.

Wipe with a clean white cloth and examine the cloth for stains.

A drop of water of known volume placed on a horizontal surface will spread to a degree that depends in part on the cleanliness of the surface. The spread can be measured and compared to the known spread on a clean surface.

Gloss measurements are made of painted surfaces. Optical examination is used for wafers. Other techniques involve radioactive tracers, fluorescence, determination of residual carbon, evaporation rate of an applied solvent drop, and electrostatic charge decay.

Sources of Information

There are several sources of general information about cleaners and cleaning in the references. Suppliers of commercial cleaners and of the ingredients used in cleaners can also be good sources.

A potentially important source of a commercial cleaner formulation is the Manufacturer's Safety Data Sheet. A supplier may be quite forthcoming in describing his product. Another may claim proprietary secrets and reveal little. There probably are no trade secrets in the business, at least as far as the mainstream suppliers are concerned. They use essentially the same formulations and know what each other is supplying.

Knowing a cleaner's formulation is useful. It can save time by avoiding the testing of several cleaners that are essentially the same. For example, one supplier markets several cleaners for use in ultrasonic cleaning. The Manufacturer's Safety Data Sheets show that some are the same even though they have different names and are described as being formulated for different applications.

It is important to know the formulation of a cleaner so that its waste can be properly handled. It may be prudent to insist upon knowing the formulation even if the vendor claims proprietary secrets.

ACCOMPLISHMENTS

This report summarizes much of the technology of water-based alkaline cleaners and should provide the reader with a sound foundation for additional studies. Alkaline cleaners are shown to be versatile, low-cost products that remove a variety of soils using a variety of mechanisms.

This study has furthered the understanding of the mechanisms of cleaning and illuminated the various ingredients of cleaners that contribute to the cleaning processes. These understandings simplify development studies and further the ability to operate an efficient and effective cleaning process.

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