RECYCLING USED CLEANERS AND RINSES BY USING OZONE AND ELECTROLYSIS TO SYNTHESIZE SURFACTANTS

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Introduction

Recent worldwide developments have forced industry to look for new and novel ways to reduce the consumption of water and other natural resources while simultaneously reducing the generation of all forms of pollution including waste water and chloro-fluoro-carbons (CFCs). Extensive research and development efforts are under way to find solutions to these complex problems.

Rinse water from various cleaning processes is one of the largest waste streams in existence today. Reverse osmosis (RO)membrane water separation and purification systems have failed to work successfully in most rinse water recycling applications to date. The primary reason for their failure has been the rapid fouling of the membrane surface with oily organic films that substantially reduce the flowrate through the membrane.

We are currently evaluating a new method of solving this fouling problem with the assistance of a process demonstration grant from the U.S. Department of Energy's Innovative Concepts Program. A complete process method of recycling cleaning process rinse waters using RO membranes in combination with a previously disclosed (3, 4) regenerative cleaning solution process would allow users to totally recycle all of their rinse water and cleaning solutions indefinitely. During a prior Innovative Concepts grant, we demonstrated a novel new process that recycles aqueous cleaners by continuously converting the organic soils into useful surfactants. The process uses an advanced oxidation process to partially oxidize organic compounds thereby converting them into usable water soluble organic surfactants. This same conversion process will also make it possible to reuse the rinse water by using RO membranes to split the rinse water from the cleaner. Fouling of the RO membranes will not occur since the membranes will be reconcentrating a regenerated cleaning solution essentially free of oil and grease. As the cleaner is reconcentrated in the RO membrane, it will actually clean the membrane. All of the rinse water and cleaner would be continuously reused.

Background

Chlorinated solvents are rapidly being replaced by aqueous cleaners (1). 1,1,1, Trichloroethane will no longer be manufactured after December 1995. Its price has nearly tripled in just 3 years. New air pollution regulations will severely limit the use of replacement solvents. Waste disposal costs and cradle-to-grave liability have further limited the choice of replacement cleaning methods. A major shift from solvent based to water-based cleaning processes is now underway as a result of these factors.

Increased use of water based cleaning and rinse processes is producing an increase in wastewater treatment requirements. Rinse water must be treated before it can be discharged to remove greases, oils, detergents, heavy metals, and many other compounds that can contribute to water pollution such as phosphates and nitrates. Water-based cleaning solutions are even more difficult to treat than rinse water due to the heavy concentrations of emulsifiers and chelating agents used in their formulas. Several industries such as the plating industry have already invested heavily in treatment systems for wastewater treatment.

Unfortunately these wastewater treatment systems do not eliminate pollution. Instead of air pollution from fugitive solvents or water pollution from untreated wastewater disposal, we are left with sludges that require landfill disposal. Some of these sludges may even be hazardous waste sludges requiring disposal in special landfills. Wastewater treatment and sludge disposal is several times more costly than treatment and disposal of previously used solvents. Water-based cleaning systems are also more costly to operate from an energy and manpower standpoint.

Based on these facts, we can see why industry is actively pursuing new ways of minimizing waste and preventing pollution. The most productive solution to this problem is one that extends the useful life of water-based cleaners, eliminates rinse water requirements or recovers and recycles the cleaner and rinse water. Several methods of extending the useful life of water-based cleaners are on the market today. They include oil skimmers and ultrafiltration systems to name a few. Most of the rinse water recycling systems available at this time are either impractical or far too costly to compete with current treatment and disposal method costs.

The ultimate version of the pollution prevention process is a design where nothing other than the cleaned parts themselves leave the cleaning process. This eliminates the cost of testing the waste to determine if it is hazardous waste and the cost of disposal. The second step is to ensure that the cleaning process operates in such a way that if any waste leaves the system it will be non-hazardous, minimal in volume and can be sold as a by-product. These two concepts taken together constitute the ultimate waste minimization process.

Once we eliminated any concern about disposal of the cleaning solution, we were able to reconsider cleaning formulations that others now avoid due to considerations concerning disposal. Some government jurisdictional areas have outlawed phosphate cleaning compounds. However, this is not a problem if we never intend to dispose of the phosphate cleaner. The next step was to determine why these cleaners stopped cleaning and find ways to reverse the process. In cleaning processes where the same cleaning bath was reused repeatedly, we found two main problems. One was the loss of cleaning solution ingredients dragged out by the parts and the subsequent loss of these cleaning chemicals to the rinse water. The other was bath contamination.

There are several sources of bath contamination. One is the make-up water used to replace water lost to evaporation and drag-out. Tap water is contaminated with a variety of mineral salts and organic matter. Calcium and iron are frequent problems. The other source is soil cleaned off of the parts themselves. This soil can contain just about any contaminate imaginable. The water used for make up can be filtered and deionized prior to use. If the cleaning process is heated the rinse water can be deionized and filtered prior to use and after use as rinse water it can be reused as make up water for the cleaning bath to replace the water lost to evaporation. This also allows us to recover the cleaning chemicals that were previously lost to the rinse water. Even if the cleaning process is not heated, a triple dead deionized rinse system can be used and in some cases the majority of the cleaning salts recovered and returned to the cleaning bath using various concentration and recovery techniques such as RO or evaporative distillation and concentration.

The current industry practice is to dispose of the cleaning bath once it is contaminated with oil and grease or to skim the oil and grease off in an attempt to extend the life of the bath before eventually disposing of both. Some facilities are using ultrafiltration systems to partially separate water and cleaning compounds from oil and grease. They do not eliminate the disposal problems, they only delay it. Replacing a cleaning bath requires shutting down the cleaning process, draining the old cleaner out, and filling the tank up with the new cleaner. The old cleaner must be tested to determine if it is hazardous then stored in storage containers and finally disposed of. Even if the material is not a hazardous waste disposal can still be a very costly and time consuming task.

Although many have tried to recycle and reuse rinse water from these cleaning processes, most of them have meet with early membrane failure or produced larger waste cleaning solution problems when they cleaned the membranes to restore their flow. In general, they have found recycling rinse water to be too costly compared to treatment and disposal. The most frequent problems are organic contaminates that blind off and foul RO membranes as well as the dynamic changes in the concentrations and types of contaminates that make systems design work such a nightmare.

As previously disclosed, a new process (patent pending) has been developed that converts organic oil and grease contaminates in used water-based cleaners into synthetic surfactants, wetting agents, and emulsifiers. This permits the continued use of a cleaning solution long after it would have been dumped using previously known methods. Since the oily organic soils are converted from contaminates to water-soluble cleaning compounds, the need for frequent cleaning solution bath dumps is totally eliminated.

This new process reduces the amount of water and chemicals needed to maintain the cleaning process. The cost of waste disposal is eliminated because the water and cleaning compounds are reused. Energy savings result by eliminating the need for energy currently used to produce and deliver fresh water and chemicals as well as the energy used to treat and destroy the waste from the existing cleaning processes. This process also allows the cleaning bath to be maintained at the peak performance of a new bath, resulting in decreased cleaning cycle times and decreased energy consumption needed to clean the parts. This results in a more efficient and cost-effective cleaning process.

Concept Description

Custom Process Systems has developed an advanced oxidation process (patent pending) that uses a combination of ozone and electrolysis to oxidize the oils and greases, which are dragged into used cleaning solutions, into polar water-soluble surfactants that can be used in the same cleaning process. The process shown in Figure 1 consists of an external tank and plumbing that accommodates the circulation of an aqueous cleaning solution from the parts washer to the advanced oxidation reactor tank and back to the washer. The solution in the tank is treated with an advanced oxidation process utilizing ozone and electrolysis. Figure 2 is a flow diagram of the recyclable rinse water/dilute recyclable cleaning solution mixture, separation, recovery and recycling process as it relates to the original cleaning process and cleaning solution work station.

The advanced oxidation process converts insoluble organic fatty acids, greases and oils into a variety of soluble surfactants and wetting agents (2). At the same time, existing surfactants and organic contaminates are oxidized into carbon dioxide and water (5, 6). The process is designed to generate its own cleaning surfactants directly from the oils and greases cleaned off of the prior batch of soiled parts. The only waste produced by the process is a very small amount of precipitated inorganic solids. These solids can easily be rendered non-hazardous or even be recycled should they contain heavy metals such as lead.

The process includes a pressure swing adsorption oxygen generator that feeds dry high-purity oxygen to a corona discharge ozone generator. The oxygen and ozone are generated and used as needed. Electric current is feed to permanent electrodes immersed in the tank.

The system may be started up with a special cleaning formulation that can vary with the application. In certain applications titration and addition of very small amounts of additives may be desirable through out the year. This new process eliminates the typical solid and hazardous waste problems associated with aqueous cleaning processes. Furthermore, it drastically improves the life expectancy and capacity of RO units used to regenerate rinse water while returning the concentrate back to the cleaner for reuse. It also drastically improves the cleaning performance of the cleaning solution over time since the user is in effect always cleaning parts with a brand new cleaning solution.

The advantages of modifying the cleaning formula, adding the Advanced Oxidation Ozone/Electrolysis Process Reactor and RO rinse water recovery to a water based cleaning process are as follows:

a. The process consistently produces cleaner parts by producing a superior cleaning solution.

b. The process maintains the cleaning solution at its peak strength at all times reducing operating costs and cleaning cycle times.

c. Reduces or eliminates the amount of hazardous and solid waste produced.

d. Recycles and reuses the rinse water and cleaning solution.

The process is unique in its method and ability to total recycle and reuse the cleaning solution and rinse water in a cleaning process. The process converts the contaminates accumulated in the cleaning process into cleaners thereby eliminating the need to dispose of used cleaner, used rinse water or the contaminates cleaned off of the parts themselves. The process produces a superior cleaning solution that reduces cleaning cycle times and operating expenses by maintaining the cleaning solution at its peak strength. The process cleans the RO membrane while the membrane is simultaneously separating contaminated rinse water from recyclable reusable cleaning solution.

Some of the industries that are expected to benefit from this new technology are:

a. Manufacturing — new parts, parts washers and paint lines

b. Electroplaters

c. Machine shops — parts washers

d. General automotive repair

e. Vehicle washing

f. Food industry — process tank washing

g. Trucking — tank washing

h. Petrochemical industry — process tank and pipe washing/ flush

i. Labs — glass wear washing

j. Industrial hygiene — respiratory washers

k. Medical industry — surgical instrument washing

Chemistry

Water-based cleaning and degreasing chemistry is based on the principle that non-polar liquids are essentially insoluble in polar liquids. Removing non-polar contaminates and dissolving them into the polar solvent water requires a compound that is polar on one side and non-polar on the other. This double property is what allows surfactants to couple water and oil molecules together in the cleaning and emulsification process. Polar solvent activity is the result of hydrogen bonding. Hydrogen bonding is exhibited by most compounds that contain oxygen and nitrogen in the structure.

The advanced oxidation process described above provides a means of adding oxygen atoms to non-polar compounds including hydrocarbons such as those found in grease and oil. By adding these oxygen atoms in a controlled manner parts of the hydrocarbon molecule's structure can be modified to form a polar site on a previously non-polar molecule. Since these hydrocarbon molecules are typically very large the polar site is a localized phenomena that attracts water only to the polar site and repels non-polar compounds from the site. The non-polar areas of the same molecule attract other non-polar molecules. Thus the newly created polar/non-polar surfactant molecule will couple polar and non-polar compounds together. The more surfactant molecules you generate the more non-polar (oil) compounds you can dissolve in the polar water phase.

References

1. D'Ruiz, Carl D. "Aqueous Cleaning as an Alternative to CFC Chlorinated Solvent-Based Cleaning", Noyes Publications (1991).
2. *Kirk-Othomer Concise Encyclopedia of Chemical Technology*, Martin Grayson Ed., John Wiley and Sons, New York, N.Y. (1985).
3. McGinness, Mike P. "Minimizing Waste in Automotive Spray Washers using Ozone and Electrolysis", *Proceedings of Waste Stream and Utilization Innovative Concepts — An Experimental Technology Exchange*, Austin, Texas, Lee, V.E., Ed., Vol. 2, pp. 3.1-3.7, Pacific Northwest Laboratory, Richland, Wash., PNL-SA-22193 Vol.2 (April 22-23, 1993).
4. McGinness, Mike P. "Regenerating Used Aqueous Cleaners with Ozone and Electrolysis", *Proceedings of The Fourth National Technology Conference and Exposition*, Anaheim, Calif., Vol. 1, pp. 241-247, NASA Conference Publication #3249, Technology Utilization Foundation, N.Y. (Dec. 7-9, 1993).
5. Rice, Rip G.; Browning, Myron E. "Ozone for Industrial Water and Waste Water Treatment, a Literature Survey", EPA-600/2-80-060 (1980).
6. Takahashi, N.; Katshuki, O. "Decomposition of Ethylene Glycol by the Combined Use of Ozone Oxidation and Electrolytic Methods", *Ozone Science and Engineering 12(2)*, p.115-131 (1990).