

**CLOSED LOOP RECYCLING OF AQUEOUS CLEANING SYSTEM RINSE
WATERS USING REVERSE OSMOSIS, OZONE AND ELECTROLYSIS**

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ABSTRACT

Recent world wide 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 CFC's (Chloro-flouro-carbons). Extensive R & D 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 (R.O.) membrane water separation and purification systems have failed to work successfully in most rinse water recycling applications to date. A primary reason for their failure has been the rapid fouling of the membrane surface with oily organic films that substantially reduce the flow rate through the membrane.

We proposed to solve the fouling problem and demonstrate a method of recycling cleaning process rinse waters using reverse osmosis membranes. The proposed process would allow users to totally recycle all of their rinse water and their cleaning solutions indefinitely.

Under a prior INCON grant we demonstrated a novel new method of recycling aqueous cleaners by the oxidative conversion of the organic soils into useful surfactants. We had reason to believe that this conversion process would also make it possible to reuse the rinse water by using reverse osmosis membranes to split the rinse water from the cleaner. We believed that fouling of the reverse osmosis membranes would not occur since concentration of the used cleaner contaminate in the rinse water would progressively clean the dirty side of the R.O. membrane. All of the rinse water and cleaner would be continuously reused.

INTRODUCTION

Increased use of water based cleaning and rinse processes is producing an increase in waste water 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 waste water treatment.

Unfortunately these waste water treatment systems do not eliminate pollution. Instead of air pollution from fugitive solvents or water pollution from untreated waste water 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. Waste water 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 will be 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 ultra-filtration 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.

One of the current popular ways of dealing with this problem is to boil the water off and ship the solids. It is popular due to its simplicity. It does not require a chemist or engineer to operate and it is easy to understand its operating principles. Buyers prefer low tech solutions like these and are buying large quantities of atmospheric evaporators. Unfortunately this is a very energy intensive and costly proposition. Systems that boil 50 gallons per day can cost over \$10,000.00 to purchase. They tend to scale easily reducing their energy efficiency and they do not solve the problem of solids disposal. Boiling off water as a waste disposal method is one of the most costly methods available in terms of energy usage. Evaporative disposal (boiling) of waste water can cost \$300/ 1000 gallons unless energy recovery methods are used. Energy recovery system prices start at \$30,000.00, a price that is out of the reach of most small manufacturers. These systems also vaporize any volatile hydrocarbons in the waste water. Some of them have started grease fires as the concentration of oil and grease accumulated.

Another option is to set up and man a small scale waste water treatment and neutralization system. This requires trained operators, more chemicals, the energy required to pump and filter the solution prior to discharge, and a permit from the local, state or federal authority to discharge the treated waste water. Waste water treatment systems also produce large volumes of wet sludge which require further treatment and disposal. Sludges produced by evaporators or waste water treatment systems can be more costly to dispose of than direct deep well (injection) disposal of the untreated liquids.

A complete process method of recycling cleaning process rinse waters using reverse osmosis membranes in combination with a previously disclosed 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 useable water soluble organic surfactants. This same conversion process should also make it possible to reuse the rinse water by using reverse osmosis membranes to split the rinse water from the cleaner. Fouling of the reverse osmosis membranes should not occur since the membranes would be reconcentrating a regenerated cleaning solution essentially free of oil and grease. As the cleaner is reconcentrated in the R.O. membrane it should actually clean the membrane. All of the rinse water and cleaner would be continuously reused.

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 insure 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 re-used 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 reverse osmosis 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 ultra-filtration systems to partially separate water and cleaning compounds from oil and grease (Kronmiller, Succ.). 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 encountered are organic contaminates, including Biofouling (Paul), that blind off and foul R.O. membranes. The dynamic changes in the concentrations and types of contaminates that enter these processes also contribute to fouling. When various inorganic compounds are reconcentrated in the R.O. membranes they can reach a solubility limit and precipitate as scale in the pores of the membrane (Kronmiller, Succ.). This scaling process can sometimes be irreversible. Iron, calcium, magnesium , sulphate, ortho-phosphate and silica are the most common inorganic scale forming compounds (Cherynan p.173,182-3), (Kronmiller, Memb.).

The advantages of modifying the cleaning formula, adding the Advanced Oxidation Ozone/Electrolysis Process Reactor and reverse osmosis 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 cost and cycle times.
- (c) Reduces the amount of hazardous and solid waste produced.
- (d) Recycles and reuses the rinse water and cleaning solution.

CHEMISTRY

Water based cleaning and degreasing chemistry is based on the principle that non-polar compounds are essentially insoluble in polar compounds. Removing non-polar contaminants 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 (Drew, p.55).

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 which 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 water phase.

DESCRIPTION OF THE CONCEPT

The process consists of an external tank and plumbing which accommodates the circulation of an aqueous cleaning solution from the spray washer to the tank and back to the washer. The solution in the tank is treated with an advanced oxidation process utilizing ozone and electrolysis.

The oxidation process converts insoluble organic fatty acids, greases and oils into a variety of soluble surfactants and wetting agents (Kirk-Othimer) . At the same time existing surfactants and organic contaminants are oxidized into carbon dioxide (Rice, Takahashi).

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 would be 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 which feeds dry high purity oxygen to a corona discharge ozone generator. The oxygen and ozone are generated and used as needed. A low voltage D.C. current is feed to permanent electrodes immersed in the tank.

Industry manufactures surfactants by oxidizing various oils (hydrocarbons) into polar (oxygenated hydrocarbons) water soluble compounds (Kirk-Othomer).They are manufactured on a very large scale in chemical plants around the world (Kirk-Othomer). By converting the oils and

greases into surfactants as they are dragged into the cleaning solution we are able to keep the cleaner operating indefinitely. In the past it has been more cost effective to dispose of weak contaminated cleaners and replace them with fresh cleaners.

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.

Most cleaning system users are looking for ways to extend the life of their cleaning solutions. Mechanical filters, oil skimmers and special oil releasing cleaning formulas are becoming quite common. None of these methods has eliminated the need for continued frequent disposal of used cleaning solutions. Solvent based cleaners can be distilled and reused. However, they tend to be flammable, sources of air pollution, odorous, or depleters of the ozone layer. There is a major shift underway from hazardous solvent based cleaners to aqueous based cleaning products (D'Ruiz).

KEY EXPERIMENTAL RESULTS

In an early field trial a one year old cleaning bath that was heavily contaminated with oil and grease was restored in less than two days to 80 % of its original strength. In an accelerated test used motor oil was introduced directly into the same bath at a 5% concentration. The bath was restored to it's original performance in less than two 8 hr days of treatment. After 36 hours of treatment the bath formed an emulsion cleaner that outperformed the original cleaning formula by a ratio of two to one.

We already know from past experience (Rice) that the advanced oxidation process will oxidize the organic compounds that are frequently dragged in on parts from other processes such as carburetor cleaner. These compounds include phenol, benzene, creosols, xylenes, chlorinated hydrocarbons and various paint solvents. Most of these compounds are now on the EPA's new "TCLP" hazardous waste list. Waste cleaners frequently leach more than the limit of these organic compounds and are therefore considered to be hazardous wastes. Since the advanced oxidation process destroys these compounds (Huang, Takahashi) as they are introduced they will not accumulate in the cleaner.

Waste water treatment using ozone is well known and documented in the literature (Rice). Recent work has been published on advanced oxidation techniques using combinations of oxidizers including hydrogen peroxide, ultraviolet light, and ozone (Takahashi). Only one article has been found to date dealing with the use of ozone and electrolysis at the same time (Takahashi). This article suggests that any compound that can first be oxidized by either process into formaldehyde or glycolic acid can be further oxidized to carbon dioxide by the simultaneous exposure to both ozone and electrolysis. Neither ozone nor electrolysis accomplish this alone. Ultraviolet light is highly dependent on the clarity of the fluid being treated and therefor is not a candidate for this type of process since the cleaning solutions are highly opaque.

Recent work in Florida (Tri-o-clean product bulletin.) has demonstrated the feasibility of cleaning

laundry with ozonated water on a large scale. The process has eliminated the use of chemical cleaning compounds and heat in a major laundry facility. They do use some liquid bleach to aid in stain removal. Their success has been well documented.

The laundry systems success is due to a chemical reaction between ozone and the unsaturated hydrocarbons (soil in the fabric) which form soluble surfactants that emulsify, clean and disinfect the laundry. The waste water is then ozonated, filtered and reused again. Spray washers in the automotive industry have several characteristics similar to those of a cloths washing machines. They typically use heat, agitation and cleaning chemicals to remove dirt, soil, grime, grease, oil, and carbon. . However, the automotive industry is faced with other problems. Removal of rust, scale, paint and burned on carbon and varnish are frequently required while laundries are more concerned with disinfecting the laundry.

Preliminary lab tests using synthetic rinse water samples indicated that organic fouling of R.O. membranes was only one of the problems that needed to addressed. A more significant problem turned out to be the PH change of the cleaner as it was rinsed from the parts and diluted with water. As the PH drops colloidal silica begins to form and precipitate. According to Bergna (pg. 543) , the solubility of amorphous silica is constant from a PH of 4 to 9. Above the PH of 9 the solubility of silicates increases. Most alkaline cleaning compounds in use today operate at a PH of 12.5 and include a substantial amount of sodium metasilicate in the formula. The silicate adds alkalinity and PH buffering capacity to the formulas. Some cleaning action of alkaline detergents can be attributed to saponification of fatty acids used in grease and lubricant formula's. Additives such as silicates also sequester troublesome cations such as magnesium and calcium thereby acting as deflocculating agents (Shaw, p.167), (Bergna, p. 599). It is also used as a corrosion inhibitor for reactive metals such as aluminum (Bergna, p.598).

Other problems encountered in the use of R.O. membranes include the precipitation of calcium, magnesium, and iron carbonates, sulfates and hydroxides. The solubility of the organic soaps also decreases (Meyers, p.323) with lower PH's thereby increasing the availability of organics that can foul the membrane. Biofouling is also a major concern where rinse water contains all the nutrients needed to support biofilm formation. Carbon, nitrogen, phosphate and sulfate are almost always readily available in alkaline cleaner rinses to feed biological growth. Cellulose acetate membranes require chlorinated feeds in order to inhibit biological activity since bacteria can eat the membrane material resulting in permanent loss of membrane integrity. Newer thin film composite membranes do not require chlorinated feeds but can become fouled with biomass if not prevented.

Raising the PH of the feedwater to the membrane was considered as a way of overcoming the PH / silica solubility problem. Unfortunately the PH drops across the membrane forming a PH gradient across the membrane wall as it produces clean water. This results in silica precipitation in the membrane itself. This in effect results in filling the pores of the membrane with what is essentially concrete (calcium silicate). This results in irreversible damage to the membrane.

Apparently the manufacturers of R.O. membranes have been dealing with all of the above contaminates on a small scale as they occurred in various feed water streams. However, they were

unaware of the fact that most alkaline aqueous cleaners contain silicates in their formulas. They contain silicates in their formulas at concentrations that are orders of magnitude greater than those normally dealt with in the typical R.O. installation. To date most alkaline cleaner compound manufacturers have had little reason to design alkaline cleaning compounds that are free of silicates.

Pretreatment to remove precipitated materials is not sufficient to avoid early catastrophic failure of the R.O. membrane. Substitution with a suitable substitute for sodium metasilicate would solve one of the problems encountered. However, as water is produced across the membrane the feed water is concentrated resulting in the formation of additional precipitants (such as calcium sulfate) due to the concentration and formation of supersaturated solutions. Therefore pre-treatment would need to include an additive that would prevent the further precipitation of scale forming compounds as they were concentrated in the R.O. membrane. This same additive would need to be antibacterial in nature and be compatible with the advanced oxidation cleaner recycling process if the concentrated rinse feed is to be returned to the alkaline cleaner.

One possible solution to the problem encountered in the tests that is being considered for further tests is the use of a silica free alkaline cleaner where the cleaner itself is processed through the R.O. membrane. Most of the osmotic back pressure encountered in operating R.O. membranes results from the ionic concentration of the feed solution (Cheryan). The use of nonionic surfactants would not increase the operating (pumping) costs of an R.O. system. The high operating PH would severely limit the inorganic, organic and bio-fouling potential in the R.O. membrane. Finally the rinse water could be filtered to remove precipitated scale forming salts prior to returning the used rinse water to the cleaner bath. The use of a silica free alkaline cleaner would limit the market since silica is the primary corrosion inhibiting additive used to make alkaline cleaners safe on metals such as aluminum.

ECONOMICS AND MARKET POTENTIAL

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

In order to be successful we need to work closely with the end users of the cleaning system to insure that their cleaning needs have been met. We will also need to work closely with the cleaning system manufacturers since they are our best potential customer. The end user does not buy a tank, heater, pump, and plumbing from several sources and assemble a cleaning system. They buy the entire system ready to use from one company. The easiest way to market this product would be to sell or license its installation on cleaning systems manufactured by any one or more of a number of existing cleaning systems manufacturers.

Initially we could market some of these systems direct to customers with existing cleaning equipment. Then when we were satisfied with the systems performance in a particular application we could begin selling it as an integral part of new systems through existing cleaning system manufacturers for that particular application. This would be far more cost effective than try to set up to manufacture and market our own complete cleaning systems. It would also speed up introduction of the product into the market place.

A recent marketing study by D'Ruiz indicates that the aqueous cleaning systems market is in a major growth stage. 147,000 aqueous cleaning systems are projected to be sold in the next ten years just to replace chlorinated solvent cleaning systems.

Because of the potential volume this market represents and the lack of market entry barriers we feel that it is the best market for us to concentrate on at this time. Other potential markets do exist but they have market barriers that would have to be addressed before they could be targeted. Cleanup of hazardous waste and superfund sites, cleanup of process waste water in a number of industries, detoxification of waste water prior to biological waste water treatment, and cleanup or disinfection of medical waste are just a few.

FUTURE DEVELOPMENT NEEDS

This concept was developed from an extensive prior study and marketing analysis of the cleaning process industries. There is a major existing market for this process. We have already determined and evaluated several potential market entry points. The next major objective is to evaluate possible pretreatment steps needed to keep scale forming compounds such as silicates from precipitating in the R.O. membranes. These pretreatment steps should not produce new waste streams and should allow the recovery and reuse of silicates in the aqueous cleaner after being reconcentrated. Any additives used to prevent scaling in the R.O. membrane should be reusable and compatible with the aqueous cleaner as well as the advanced oxidation process. Compatibility with the materials being cleaned must also be maintained.

Another alternative would be to find a suitable corrosion inhibiting cleaner additive with properties similar to those of sodium metasilicate that would be a suitable replacement in alkaline cleaning formulas. This would be combined with the use of the alkaline cleaner itself as the feed to the R.O. membrane to produce clean rinse water. The used rinse water would be filtered and returned to the alkaline cleaner holding vessel.

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