N94-30468

2464
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REGENERATING USED AQUEOUS CLEANERS WITH OZONE AND ELECTROLYSIS

Michael P. McGinness
Custom Process Systems & Service Co.
2710 South Shaver Unit 'D'
Pasadena, Texas 77502
(713)-941-0907

ABSTRACT

A new process converts organic oil and grease contaminates in used water based cleaners into synthetic surfactants. This permits the continued use of a cleaning solution long after it would have been dumped using previously known methods. Since the organic soils are converted from contaminates to cleaning compounds the need for frequent bath dumps is totally eliminated.

When cleaning solutions used in aqueous cleaning systems are exhausted and ready for disposal, they will always contain the contaminates removed from the cleaned parts and drag-in from prior cleaning steps. Even when the cleaner is biodegradable these contaminates will frequently cause the waste cleaning solution to be a hazardous waste. Chlorinated solvents are rapidly being replaced by aqueous cleaners to avoid the new ozone-depletion product-labeling law (1). Many industry standard halocarbon based solvents are being completely phased out of production and their prices have nearly tripled. Waste disposal costs and cradle-to-grave liability are also major concerns for industry today.

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 cycle times and decreased energy consumption needed to clean the parts. This results in a more efficient and cost effective cleaning process.

INTRODUCTION

Industrial cleaning processes are currently being re-evaluated and redesigned in order to minimize the amount of waste produced and the resulting cost of waste disposal. Waste disposal costs have soared in recent years. There is increasing pressure from congress, and the public to reduce the amount and the toxicity of all industrial waste streams.

Aqueous cleaning formulations used in spray washers are frequently quoted as being environmentally safe and biodegradable. However, when they are exhausted and ready for disposal they will always contain the contaminates that were removed from the dirty parts. Automotive contaminates include motor oil, transmission fluid, benzene, lead, cadmium and drag in from other cleaning processes which frequently contain phenols, cresols, xylenes and various chlorinated solvents.

In the past, disposing of weak contaminated cleaners and replacing them with fresh cleaners has been the most cost-effective option. Replacing a cleaning bath requires shutting down the cleaning process, draining out the old cleaner, and filling the tank with the new cleaner. Then the old cleaner must be tested and disposed of properly. Testing and disposal costs have soared in recent years.

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(2).

Products are available to separate oils and greases from the cleaning solutions to help increase the life of the cleaning bath. However, these products do not eliminate the eventual need for disposal of the contaminated oil or the spent cleaner. Some facilities have switched to burn off ovens to burn off the oils and greases, followed by dry shot blasting. This option is extremely energy intensive and costly($30,000.00/oven), and is not usable on plastic or aluminum.

Waste generators must determine if their used cleaning wastes are hazardous before disposing of them. A complete lab analysis of just one waste stream can cost from $2,000 to $3,000 and disposal costs for hazardous waste vary from $300.00 to $1,200.00 per barrel. Even when the waste has been properly disposed of the generator remains forever liable for any future problems caused by the waste.

The U.S.Environmental Protection Agency (EPA) now requires hazardous waste generators to certify on their hazardous waste manifests that the amount of hazardous waste produced has been minimized prior to shipping the waste.One current method is to boil the water off and ship the solids. This is one of the most energy intensive and costly methods available. Systems that boil 50 gallons/day can cost over $10,00.00 to purchase. They tend to scale easily reducing their energy efficiency and they do not solve the problem of solids disposal.

Another disposal option is to set up and man a small scale waste water treatment and neutralization system. This option requires trained operators, more chemicals, the energy required to pump and filter the solution prior to discharge, and a permit to discharge the treated waste water. These systems also produce large volumes of wet sludge requiring further treatment prior to disposal.

Chlorinated solvents are rapidly being phased out and replaced by aqueous cleaners in order to avoid the new ozone-depletion product-labeling law (1). This new law requires manufactures to label products which have been cleaned with ozone depleting chemicals as having been manufactured with an ozone depleting chemical. These solvents are being heavily taxed and considering waste disposal costs and cradle to grave liability issues they are no longer cost effective. These market forces are driving industry to replace solvent cleaners with aqueous cleaners.

Past experience has already demonstrated that the advanced oxidation process will oxidize the organic compounds that are frequently dragged in on parts from other processes such as carburetor cleaner (9). 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 as they are introduced, (3,7,9,11) they will not accumulate in the cleaner.

Waste water treatment using ozone is well known and documented in the literature(7). Recent work has been published on advanced oxidation techniques using combinations of oxidizers including hydrogen peroxide, ultraviolet light, and ozone(10). Only one article has been found to date dealing with the use of ozone and electrolysis at the same time (10). 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 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 (4,8,12) 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. The process Patent Number 5,097,556 was issued on March 24,1992. 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 and clean the laundry while the ozone disinfects it. The waste water is then ozonated, filtered and reused again.

Industry manufactures surfactants and detergents by oxidizing various oils (hydrocarbons) into polar (oxygenated hydrocarbons) water soluble compounds(6). They are manufactured on a very large scale in chemical plants around the world. By converting the oils and greases into detergents as they are dragged into the cleaning solution and the detergents into carbon dioxide and water we will be able to keep the cleaner operating indefinitely.

CONCEPT DESCRIPTION

Custom Process Systems has developed an advanced oxidation process which uses 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 1.1 consists of an external tank and plumbing which accommodates the circulation of an aqueous cleaning solution from the parts 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.

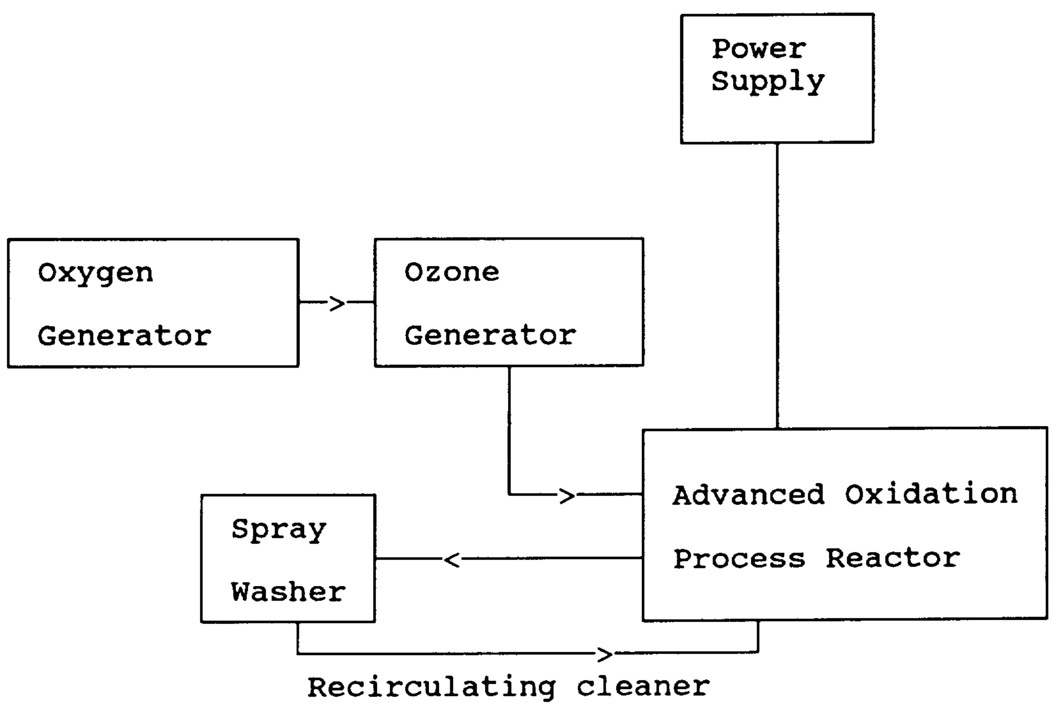

Figure 1. Process flow chart.

The oxidation process converts insoluble organic fatty acids, greases and oils into a variety of soluble surfactants and wetting agents (6). At the same time existing surfactants and organic contaminates are oxidized into carbon dioxide and water (9,11).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. Alternating D.C. current is feed to permanent electrodes immersed in the tank.

The basic concept of the entire process is never to let anything except 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 re-design the cleaning process to operate in such a way that if any waste does leave 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 eliminate the concern about disposal of the cleaner itself we are able to consider cleaning formulations that others avoid due to various environmental considerations. The next step is to determine why these cleaners stop cleaning and find ways to reverse the process. In cleaning processes where the same cleaning bath is reused repeatedly we find two main problems. One is the loss of cleaning solution to drag out by the parts and the subsequent loss of the cleaning chemicals to the rinse water. The other is bath contamination.

The bath contamination has several sources. One is the make up water used to replace water lost to evaporation and drag out. The other is soil cleaned off of the parts themselves. 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 the majority of the cleaning salts recovered and returned to the cleaning bath using various concentration and recovery methods such as reverse osmosis.

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. 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.

KEY EXPERIMENTAL RESULTS

A full scale prototype has been tested on an automotive spray washer that is used to clean engine blocks and heads prior to their being remanufactured. In a recent test a one year old, completely exhausted cleaning bath was restored to 80 % of the performance of the original cleaning bath in less than 8 hours of processing. In a second test, 4-gal. of motor oil were introduced into the same 60-gal cleaning bath. The cleaning solution and oil mixture was then processed for 16 additional hours. Careful evaluation revealed that oxidation of the motor oil had generated enough oxygenated water soluble synthetic surfactants to increase the cleaning performance far beyond the capability of the original cleaner. The cleaning bath was now performing 100% better than the new original formulation. We succeeded in making a better cleaning solution out of a dead-unusable cleaning bath that was loaded with grease and oil.

The cleaner was heated and operated at 140°F and 200°F. The cleaning solution was feed through the nozzles at 60 pounds of pressure by a 5 HP pump. Since the cleaner was heated a great deal of water was lost to evaporation. The rinse water was reused as make up water to replace the water lost to evaporation.

ECONOMICS AND MARKET POTENTIAL

The economics of the process are based on the following cleaning system cost reductions:

(1) Water is reused.

(2) Cleaner is reused. The need to purchase replacement cleaning chemicals is eliminated.

(3) Waste disposal costs are eliminated.

(4) Since the cleaning performance is constant and does not decline with use, and considering the improved cleaning performance when compared to standard purchased formulas, the cost of power and fuel to operate the cleaning process can be reduced by 50 to 90 %.

The advanced oxidation process varies in cost from $5,000 to $10,000 for the smallest basic system. More complex automated systems or heavy loadings of oil and grease would increase the cost. This is a fraction of the cost of waste water treatment systems. Most water evaporators start at $10,000. Offsite disposal can run anywhere from $.50/gal for waste water to $20/gal for exotic sludges. Replacement cleaning compound can cost several hundred to several thousand of dollars per year.

A typical rebuilding facility could be expected to reduce the amount of (hazardous) waste it generates by 20,000 to 30,000 lbs. per year. Facilities in the more heavily regulated areas like California, where used oil is a listed hazardous waste, should experience a payback in 6 months to one year based just on reduced disposal costs alone.

Eliminating the expense of purchasing new cleaning compounds can save several thousands of dollars per year. This alone could generate a two to three year payback in many cases. The increased efficiency of the cleaning process will result in reduced cycle times, heating costs and a substantial increase in productivity. The reduced heating costs alone can produce a six month payback. The increased productivity can result in an expansion of cleaning capacity without incurring the capital expense of purchasing additional cleaning equipment.

Considering all of these benefits at the same time indicates that most aqueous cleaning systems could be retrofitted with this process and expect a six month to one year payback. A recent marketing study by D'Ruiz(2) 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. According to another survey(5) there are over 300,000 separate shops of various types that do some level of automotive engine repair work. 60,000 of them are engine remanufacturers. There are over 19,000 automobile transmission rebuilders as well.

Other potential markets also exist such as cleanup of hazardous waste or superfund sites, cleanup of process waste water in a number of industries, detoxification of waste water prior to biological waste water treatment, treatment in combination with processes such as reverse osmosis prior to water reuse, treatment of cooling water in cooling towers, and cleanup or disinfection of medical waste just to name a few. Another possible application would be nuclear decontamination. A mixed radioactive organic waste cleaning solution could be decontaminated and continuously reused to clean hazmat uniforms, respirators or other radiation contaminated equipment thereby reducing the volume of radioactive waste needing disposal.

Although it is not the subject of this paper, it has not escaped our attention that by carefully manipulating various process parameters such as PH, temperature, voltage, electrode type, and electrode surface area, in combination with various membrane separation techniques, it will be possible to modify the hydrophilic and lipophilic nature of various compounds. This means that it will be possible to carefully neutralize the hazardous or dangerous properties of numerous wastes and convert them into useful compounds and materials. Some of these materials may turn out to have new properties that could lead to useful technological spin offs that could be useful in the fields of energy production, industrial manufacturing, electronics, pharmacuticals and agriculture.

SUMMARY

This new technology eliminates the need for frequent bath dumps required by many cleaning processes. Many cleaning processes require frequent bath replacement due to build-ups of oily contaminates which reduce the performance of the cleaning bath to unacceptable levels. By converting these contaminates into cleaners the problem is eliminated. The need for waste treatment and disposal is eliminated thereby eliminating the original environmental impact of the cleaning process (waste cleaner disposal). By increasing the efficiency of the cleaning process by nearly 100% we reduce the need for fuel to heat and operate the process and the pollution that results from that fuel consumption is prevented.

FUTURE DEVELOPMENT NEEDS

This process is ready for limited introduction into the market place. A large variety of cleaning formulas, cleaning processes, soils, contaminates and part compositions are in use today. Because of this variety of process conditions that exist we are currently looking for a select group of clients who wish to try this process out on their cleaning lines as part of their waste minimization and/or pollution prevention plans and strategies for compliance with federally mandated requirements to prevent and minimize waste. We are also looking for clients who need or wish to go to closed loop systems otherwise known as zero discharge. This process can make zero discharge a reality. We are also looking for cleaning systems manufactures who wish to license this technology for sale as an integral part of their cleaning processes.

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