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Surfactant/Supercritical Fluid Cleaning of Contaminated Substrates

Progress Report

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Abstract

CFC's and halogenated hydrocarbon solvents have been the solvents of choice to degrease and otherwise clean precision metal parts to allow proper function. Recent regulations have, however, rendered most of these solvents unacceptable for these purposes. New processes which are being used or which have been proposed to replace these solvents usually either fail to remove water soluble contaminants or produce significant aqueous wastes which must then be disposed of.

In this work, a new method for cleaning surfaces will be investigated. Solubility of typical contaminants such as lubricating greases and phosphatizing bath residues will be studied in several surfactant/supercritical fluid solutions. The effect of temperature, pressure, and the composition of the cleaning mixture on the solubility of oily, polar, and ionic contaminants will be investigated. A reverse micellar solution in a supercritical light hydrocarbon solvent will be used to clean samples of industrial wastes.

A reverse micellar solution is one where water is dissolved into a non-polar solvent with the aid of a surfactant. The solution will be capable of dissolving both water-soluble contaminants and oil soluble contaminants. Once the contaminants have been dissolved into the solution they will be separated from the light hydrocarbon and precipitated by a relatively small pressure drop and the supercritical solvent will be available for recycle for reuse.

The process will be compared to the efficacy of supercritical CO₂ cleaning by attempting to clean the same types of substrates and machining wastes with the same contaminants using supercritical CO₂. It is anticipated that the supercritical CO₂ process will not be capable of removing ionic residues.

Work Accomplished

The original timeline was based on an assumed starting date at the beginning of August. The grant actually began October 24, so the timeline was revised accordingly. The original and revised timelines are appended to this section.

The project consists of five phases, which overlap in time. Most of these phases have multiple sub-tasks. As shown in the timelines, Phase 1 and part of Phase 2 were to be completed during the first year of the project.

Phase 1: Equipment Construction In this phase, an apparatus was built for conducting the experiments of Phases 2, 3 and 4.

Task 1.1 was the design and specification of the equipment. Physical dimensions of each component of the apparatus were decided. Additional considerations in the design were:

Safety All equipment must meet process pressure requirements. Emergency pressure relief is provided by an in-line rupture disk to protect against overpressuring. All surfaces that may contact other chemicals during the experiments must be compatible with those chemicals. A PID temperature controller was installed to control the temperature since uncontrolled heating could lead to significant increases in pressures within the experimental apparatus. To minimize fire hazards, the experiment was placed in a fume hood and, wherever possible, electrical connections were made outside the hood.

Simplicity The preliminary design presented in the original proposal was reviewed to determine if it could be modified to eliminate valves or pieces of equipment. The physical layout was determined with an eye towards minimizing the necessary length of connecting tubing as well as providing maximum flexibility for the experiments.

Task 1.2 was the ordering and acquisition of the necessary equipment. Necessary tools for assembling and testing the equipment were also ordered. Considerations in selection and ordering of the equipment were:

Capability All equipment must be capable of performing the desired functions.

Cost Equipment costs must fall within the budget allocation. One piece of used equipment, an ISCO syringe pump, was available which meets the safety and performance requirements. The funds saved by purchasing this pump were redirected to purchase other equipment such as an analytical balance. The balance will allow the students working with the PI to make all necessary weighings in the laboratory rather than in a lab in another building each time material must be weighed out.

Task 1.3 was the assembly of the equipment. As the ordered equipment arrives, it was assembled by the PI and assisting students. By assisting in this portion of the project, the students are learning the techniques of proper construction of high pressure processing apparatuses.

Task 1.4 was pressure testing the equipment. The first pressure tests were conducted with water to verify that the system can reach and sustain the required pressures without mechanical failure or fracture of tubing and vessel walls. A second round of pressure testing was conducted with pressurized gas to find and eliminate gas leaks.

Phase 2: Solubility Studies In this phase, the solubility behavior of representative contaminants will be studied as a function of temperature and pressure.

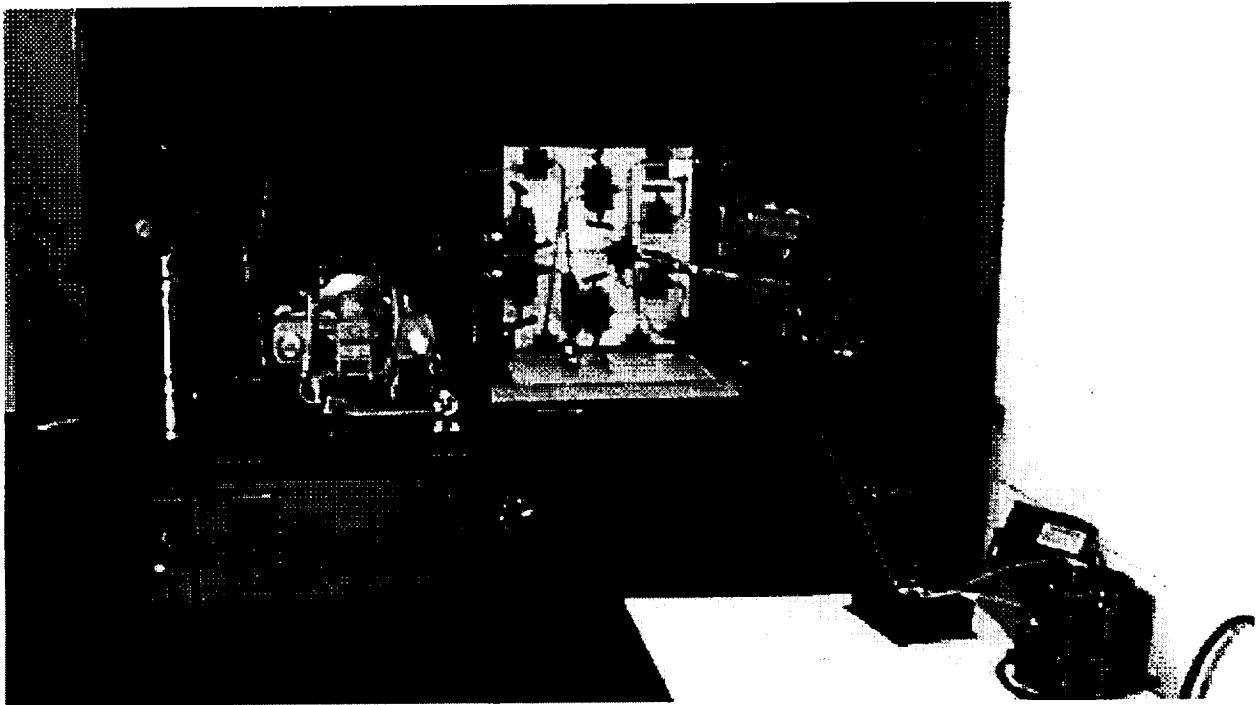
Task 2.1 is ordering and acquisition of supplies. The supplies including most of the chemicals, gas cylinders, sample collection containers, and other supplies necessary for the studies. Supplies for Phase 3 will also be ordered during the experiments of this phase, as the optimum conditions are determined.

Task 2.2 will be conducting the solubility experiments as detailed in the discussion of the experimental method of the original proposal.

Task 2.3 will be the analysis of the solubility data. The analysis will focus on the solubility of the compounds used in **Task 2.2** as a function of the surfactant used, surfactant concentration, and system pressure and temperature. The actual solubility values will be based on the total solute collected divided by the amount of gas collected from the sample loop. Since multiple samples will be taken at each condition, the data will also be evaluated for the statistical mean and variance to estimate the error range of the data.

10/24/96 – 08/15/97

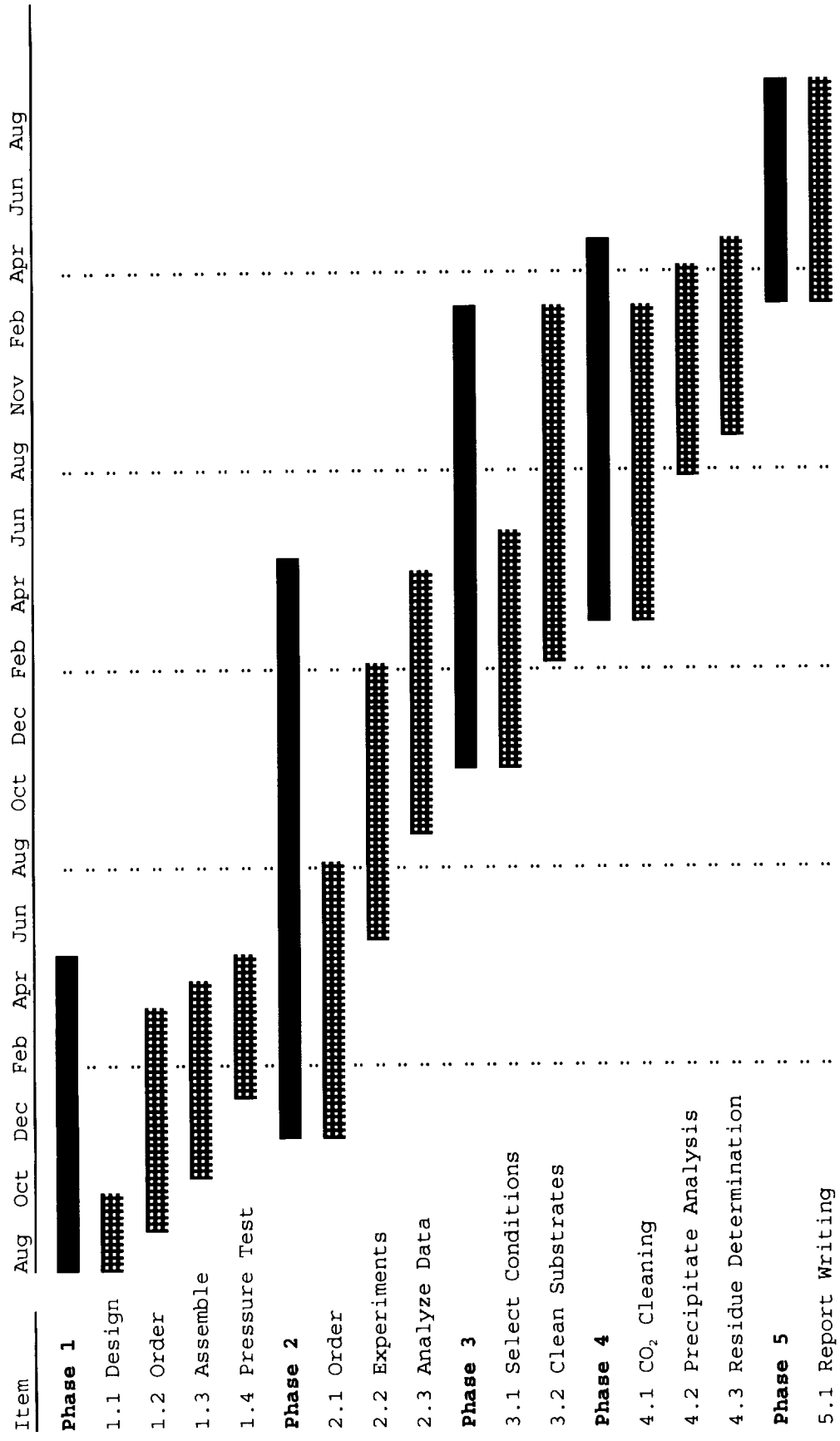
The experimental apparatus is now assembled. A picture of the system is shown below. The current arrangement of the equipment is for phase equilibria and solubility determination. The system has been pressure tested with water and found to hold pressure up to 5000 psi. Expected operating pressures for the rest of the work will be below this pressure. The system has also been leak tested with gas to eliminate all gas leaks. The system design was modified to eliminate a potential safety hazard. As the water/surfactant mixture is drawn into the system, the potential exists for the solution to be depleted and air drawn into the system. Since ethane is a flammable gas, it would present a safety hazard if air were introduced with the ethane under pressure. To eliminate this hazard, a 2 quart pressurized canister is now used as the source of the surfactant/water solution. The canister will be filled to approximately 3/4 capacity, sealed, purged of air with low-pressure ethane, and then pressurized to approximately 45 psi with ethane. Should a careless graduate student exhaust the water/surfactant solution, only ethane will be introduced to the system under pressure.



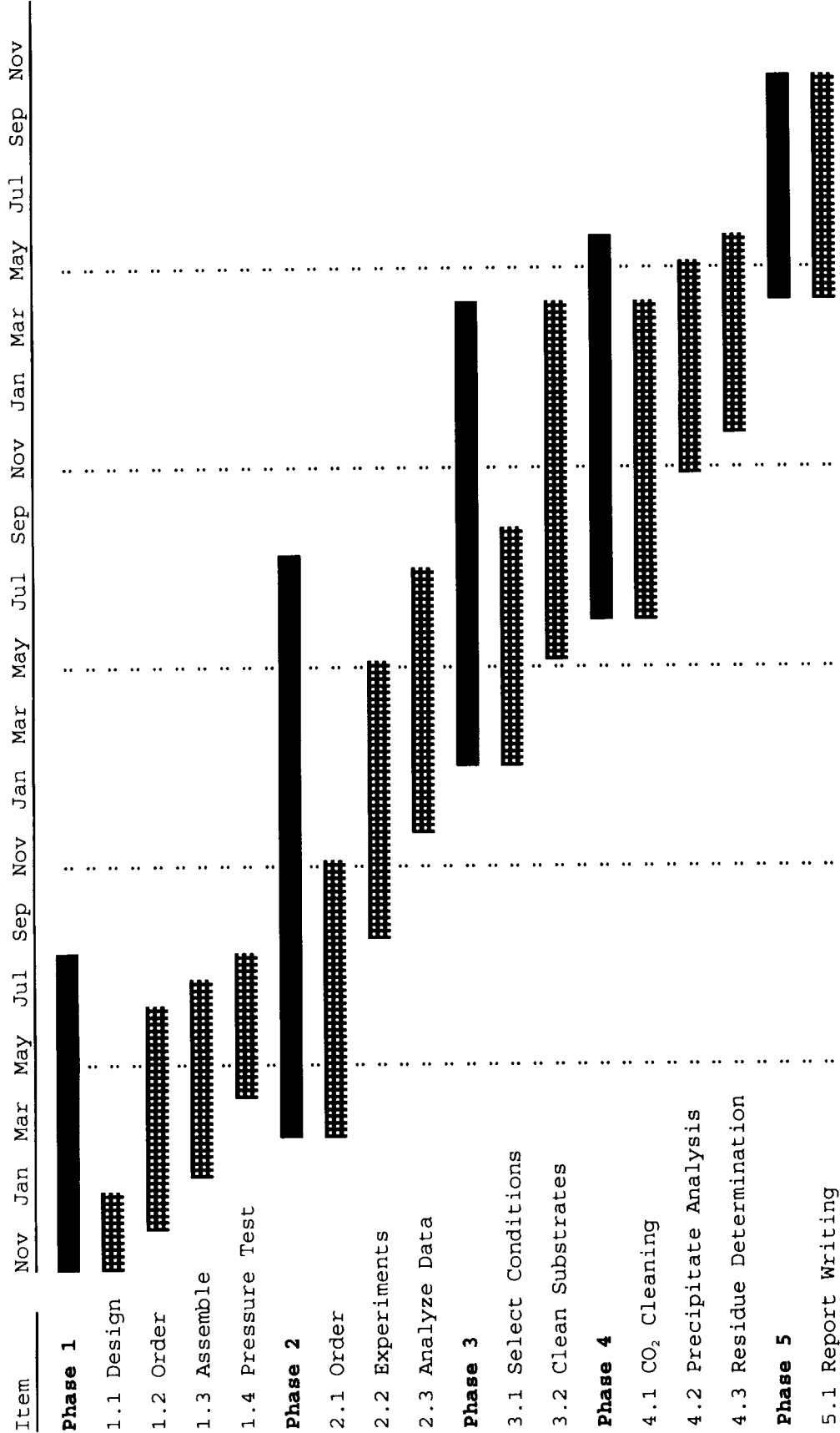
Anticipated 08/16/97 – 10/23/97

Two surfactants have been ordered: AOT and lecithin. These constitute two of the four classes of surfactants to be considered in this work. The first experiments, using AOT, water, and ethane will be started when they arrive. The first purpose of these experiments will be to validate the experimental method by determining the phase boundaries for the AOT/water/ethane system at 35 °C and 55 °C for at least three pressures between 800 and 3000 psi. Solubility studies will then be conducted with the model compounds at these temperatures and pressures. After the AOT studies are done, the next set of experiments with lecithin will begin. The remaining two types of surfactants will be ordered within the next month.

Original Proposal Timeline



Actual Timeline



Plans for the Next Year

During the coming year, all the solubility experiments will be completed. Data obtained from the experiments will be analyzed and incorporated into a paper to be presented at a national conference next fall and subsequently submitted for publication. Based on the results of the solubility studies, the best conditions for removing contaminants from surfaces using a water/surfactant/supercritical fluid mixture will be chosen. The cleaning ability of the mixtures will be tested on several coupons of metal, which have initial deposits of the sample contaminants. Some coupons of metal contaminated with the same contaminants will also be subjected to supercritical fluid cleaning with carbon dioxide.

Students Supported

Cherell Carr, a graduate student, assisted in training other students on high-pressure equipment.

Joy Forbes, a graduate student, helped assemble the equipment. She is working on phase equilibria and solubility studies for her MS thesis. It is anticipated that she will finish her work during this coming winter.

Vonzella Pritchard, a graduate student, is working on the solubility studies and cleaning of substrates for her MS thesis. It is anticipated that she will finish her work Spring or summer of 1998.

Allyn Cottemond, an undergraduate assistant, assisted in assembling the equipment, and doing library research related to the project.