

AD-779 752

BIODEGRADABILITY INVESTIGATION OF A  
NONPHENOLIC AIRCRAFT PAINT STRIPPER

Ronald H. Kroop, et al

Air Force Weapons Laboratory  
Kirtland Air Force Base, New Mexico

May 1974

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UNCLASSIFIED  
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AD 779 752

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author) Air Force Weapons Laboratory (DEE) Kirtland Air Force Base, New Mexico 87117		2a. REPORT SECURITY CLASSIFICATION UNCLASSIFIED	
		2b.	
3. REPORT TITLE BIODEGRADABILITY INVESTIGATION OF A NONPHENOLIC AIRCRAFT PAINT STRIPPER			
4. DESCRIPTIVE NOTES (Type of report and inclusive dates) March 1973 through December 1973			
5. AUTHOR(S) (First name, middle initial, last name) Ronald H. Kroop, Lt, USAF and Richard L. Jambor, Sgt, USAF			
6. REPORT DATE May 1974	7a. TOTAL NO. OF PAGES 32	7b. NO. OF REFS 2	
8a. CONTRACT OR GRANT NO.	8b. ORIGINATOR'S REPORT NUMBER(S) AFWL-TR-74-19		
8c. PROJECT NO. 683M			
c.	8d. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)		
d.			
10. DISTRIBUTION STATEMENT Approved for public release; distribution unlimited.			
11. SUPPLEMENTARY NOTES		12. SPONSORING MILITARY ACTIVITY AFWL (DEE) Kirtland AFB, NM 87117	
13. ABSTRACT (Distribution Limitation Statement A) Paint stripping of aircraft and ground equipment is conducted periodically for the prevention of intergranular corrosion of the metallic surfaces. Wastewater occurs when the viscous paint stripper is rinsed from the aircraft or ground equipment surface with a high-pressure water system. The necessity and cost of on-site treatment of phenolic aircraft paint stripping wastewater have generated an urgent need to develop a nonphenolic paint stripper that is effective for removing polyurethane and epoxy paint. A nonphenolic paint stripper (for example, Turco 5873) is effective in removing at least some polyurethane and epoxy paints. Thus, a study was made by the Air Force Weapons Laboratory (AFWL) to determine if existing biological treatment processes were effective in treating the resulting nonphenolic paint stripping wastewater. The results of laboratory-scale investigations indicate that biological treatment processes are satisfactory if (1) the methylene chloride concentration is previously reduced and, (2) the chemical oxygen demand contribution from the paint stripper does not exceed 200 mg/l.			

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Springfield, VA 22151

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14	KEY WORDS	LINK A		LINK B		LINK C	
		ROLE	WT	ROLE	WT	ROLE	WT
	Paint stripper Biodegradability Activated sludge Methylene chloride Industrial wastewater						

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AFWL-TR-74-19

BIODEGRADABILITY INVESTIGATION OF A  
NONPHENOLIC AIRCRAFT PAINT STRIPPER

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Final Report for Period March 1973 through December 1973

Approved for public release; distribution unlimited.

FOREWORD

The research was performed under Program Element 63723F, Project 683M.

Inclusive dates of research were March 1973 through December 1973. The report was submitted 1 March 1974 by the Air Force Weapons Laboratory Project Officer, Lt Ronald H. Kroop (DEE).

This technical report has been reviewed and is approved.

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SECTION I  
INTRODUCTION

1. BACKGROUND

Paint stripping (depainting) of aircraft and ground equipment is conducted periodically for the prevention of intergranular corrosion of the metallic surfaces. Paint stripping is accomplished by brushing or spraying a viscous paint stripper on the aircraft or equipment and allowing it to dwell on the surface for a period of time while the paint swells, wrinkles, and softens, thus separating it from the metallic surface. The paint stripper and paint particles are then rinsed from the aircraft (ground equipment) surface with a high-pressure water stream. This constitutes the source of wastewater.

The type of paint system (topcoat and primer) dictates the type of paint stripper required. In the past, most aircraft in the Air Force inventory have had an acrylic lacquer topcoat with a zinc chromate primer. The depainting of these systems involved the use of paint strippers containing primarily methylene chloride (dichloromethane,  $\text{CH}_2\text{Cl}_2$ ) and hexavalent chromium with additional amounts of surfactants, thickeners, and wetting agents. Applicable Mil Specs are TT-T-248 and MIL-R-25134.

In recent years, the Air Force has started using a polyurethane topcoat and epoxy primer paint system. Depainting of these paint systems originally required the use of strippers containing, in addition to the above mentioned, a significant concentration of phenols (12 to 22 percent by weight). The first applicable Mil Spec was MIL-R-81294. A new Mil Spec, Remover Activated Solvent, For Difficult to Remove Finishes, will limit the phenol concentration to 10 percent by weight.

The generation of a phenolic aircraft paint stripping wastewater (PAPSW) (20,000 to 150,000 gal/day) containing 1000 to 3000 mg/l of phenols, 1000 to 3000 mg/l of methylene chloride, and 5000 to 150,000 mg/l of chemical oxygen demand (COD) at the Air Force Logistics Command (AFLC) Air Material Areas (AMA) require on-site treatment of the wastewater. This is because the biological treatment processes presently employed at the AMA industrial wastewater treatment plants could not satisfactorily treat those concentrations and contaminant

loadings. Past research at the Air Force Weapons Laboratory (AFWL) has resulted in the determination of the best treatment process to employ for on-site treatment of PAPSW. That work, reported in AFWL-TR-72-181 (ref. 1), demonstrated that granular activated carbon adsorption with thermal regeneration was the best treatment process.

The realization that on-site treatment of PAPSW would be required has generated an urgent need to develop a nonphenolic paint stripper (NPS) that would be effective for removing polyurethane and epoxy paint systems. This requirement was presented to the Air Force Materials Laboratory (AFML) and several paint stripping manufacturers. Turco Chemical Products developed a NPS Turco 5873 that was evaluated by AFML on polyurethane paint, MIL-C-83286; polyamide epoxy primer, MIL-P-22377; and polyamine epoxy primer, no Mil Spec. The paint stripper was effective in removing the polyurethane topcoat and the polyamide epoxy primer but not the polyamine epoxy primer. These results were encouraging such that the AFML amended the new Mil Spec to include a type II, NPS for difficult-to-remove finishes. Turco substituted ammonia ( $\text{NH}_3$ ) and several alcohol compounds in place of the phenols. The COD of the concentrated paint stripper is 710,000 mg/l.

## 2. PURPOSE OF STUDY

Since a NPS that was effective in removing at least some of the polyurethane and epoxy paints had been developed, it was necessary to determine if the wastewater generated from use of this stripper could be satisfactorily treated at AMAs industrial wastewater treatment (IWT) plants. Therefore, a laboratory-scale investigation was undertaken to evaluate the biodegradability of Turco's 5873 NPS. With this determination, or lack thereof, for this and similar NPS, then a rational judgement could be made as to whether the use of phenolic paint strippers with on-site treatment is more advantageous than the use of NPS with treatment of the wastewater at the IWT plant.

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1. Kroop, Ronald H., Treatment of Phenolic Aircraft Paint Stripping Wastewater, AFWL-TR-72-181, Air Force Weapons Laboratory, Kirtland AFB, NM, January 1973.

SECTION II  
MATERIALS AND METHODS

1. GENERAL

Several tests were performed using the NPS under study in conjunction with industrial wastewater from McClellan AFB, California, to simulate a realistic total industrial wastewater situation likely to be encountered at an AMA. The industrial wastewater from McClellan AFB was collected after metal precipitation. Sampling was taken on 4 different days. Preliminary studies on the paint stripper included chrome removal, biochemical oxygen demand (BOD), and batch biological growth studies. The preliminary studies performed on the industrial wastewater included BOD and batch biological growth tests. Based on information gained from the preliminary studies, the parameters were set for continuous flow activated sludge studies.

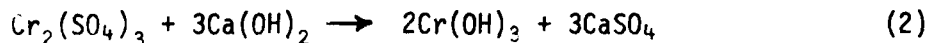
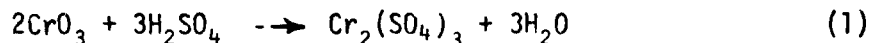
2. HEXAVALENT CHROME REMOVAL

Because of the high hexavalent chromium concentration in the paint stripper, there was concern that the chrome would interfere with and have a toxic effect on the biological systems. Therefore, chrome removal experiments were conducted in an attempt to reduce the chrome concentration without affecting the other components present.

It should be noted that metals precipitation would be accomplished at an AMA industrial wastewater treatment plant prior to biological treatment.

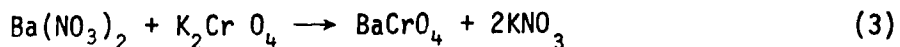
The concentrated paint stripper contained approximately 1600 mg/l as hexavalent chrome based upon the manufacturer's specifications. This was substantiated by atomic absorption analysis on the product. Prior experience indicated that each gallon of paint stripper was diluted with approximately 40 gallons of rinse water during the paint stripping operation. Therefore, for the chrome removal tests, a solution containing 40 mg/l of chrome was used.

The first chrome removal method studies consisted of acidifying the sample, adding a reducing agent, and then increasing the pH, thus causing the precipitation of the metallic hydroxide, according to



For this test 500 ml of a 40-mg/l chrome paint stripper solution were used. The pH was lowered to 2.5 by the sulfuric acid. At this point sodium bisulfite was added to different beakers of the sample in quantities that ranged from 1/2 to twice the calculated stoichiometric amount of bisulfite required. The samples were treated next with lime to raise the pH to 8.5, then quick mixed at 100 rpm for 5 minutes, and then at a slow floc mix of 20 rpm for an additional 15 minutes. The precipitates were removed from the solution by filtration through GFC filter paper and then analyzed by atomic absorption for residual chrome.

The other chrome removal method investigated was direct precipitation of chrome by the addition of barium salts. In this study, 40 mg/l of chrome paint stripper solution was used in 500-ml aliquots. Amounts of barium nitrate ranging from 1/2 to twice the stoichiometric quantity were added, based upon



Again, the precipitates were removed by filtration through GFC filter paper, and the filtrate was analyzed for residual chrome by atomic absorption.

### 3. BIOCHEMICAL OXYGEN DEMAND STUDIES

Biochemical oxygen demand tests were run on both the paint stripper and the industrial wastewater. The dilutions used for this study were determined by assuming that the BOD values expected would be of the order of 1/2 the COD values. The dilution water for each set of tests was aerated for 24 hours prior to adding nutrients and seed. Seed solutions used were acquired by removing a sample from an activated sludge reactor that had been receiving a synthetic sewage. Seeding of the dilution water was done at the ratio of 2 ml seed per liter of dilution water.

Two dilutions of paint stripper were chosen. The paint stripper was mixed at two different concentrations and half of each sample was aerated for 24 hours in an attempt to strip the major constituent, methylene chloride, from solution.

This was done to determine the toxic effects, if any, of methylene chloride on micro-organisms. BOD tests were then set up on dilutions of 5/100,000 aerated and nonaerated and 2/100,000 aerated and nonaerated samples. Samples were titrated for dissolved oxygen on a daily basis for a 15-day period in accordance with Standard Methods for the Examination of Water and Wastewater (ref. 2).

The industrial wastewater samples were seeded and run at 1/100 and 2/100 dilutions for the period of 15 days with samples being titrated daily for dissolved oxygen content.

#### 4. GROWTH STUDIES

Batch biological growth studies were conducted on both the paint stripper and the industrial wastewater. The reactors used were 4000 ml Erlenmeyer flasks that initially contained 3 liters of solution. One reactor contained diluted paint stripper solution to yield an initial COD of 2300 mg/l, another had an equivalent COD of 550 mg/l diluted paint stripper, and the third had straight industrial wastewater. Nitrogen and phosphorous were added for nutrients, using 40 mg/l  $\text{NH}_3\text{-N}$  and 20 mg/l  $\text{PO}_4\text{-P}$ . Fifteen-ml samples were drawn daily for analysis. Each sample was filtered to determine suspended solids, and the filtrate was used for COD. Daily evaporation losses in the reactor were made up by adding tap water, based upon a simultaneous evaporation study.

The flasks were first aerated to strip methylene chloride and other volatile compounds; then seeded. Aeration continued during the growth tests.

#### 5. ACTIVATED SLUDGE EXPERIMENTS

A continuous flow, completely mixed, activated sludge reactor was set up and run with the paint stripper mixed with the industrial wastewater. The reactor volume was 8 liters, and the final clarifier volume was 4 liters. Refer to figure 1 for a diagram of the system used.

A 6-hour detention time was used. The clarified effluent discharged into a reservoir which permitted collection of a 24-hour composite sample.

The reactor was initially fed with the industrial wastewater to which 40 mg/l  $\text{NH}_3\text{-N}$  and 20 mg/l  $\text{PO}_4\text{-P}$  were added. Mixed liquor suspended solids (MLSS), effluent solids (ESS), sludge volume index (SVI), and COD removal were monitored

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2. Standard Methods for the Examination of Water and Wastewater, 13th Ed., 1971.

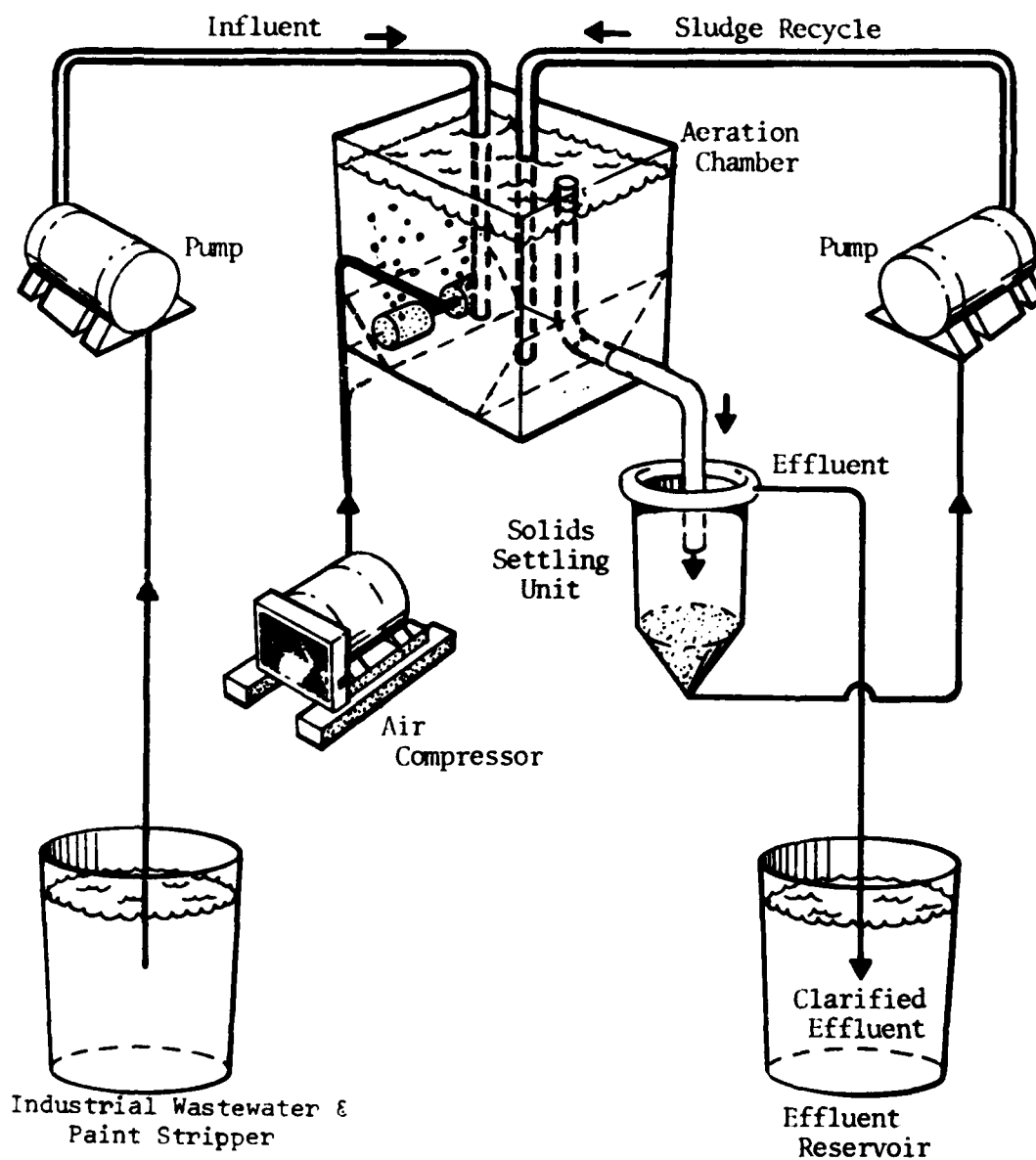


Figure 1. Activated Sludge Reactor

on a daily basis until the system appeared to have approached a steady state. At this time, previously aerated paint stripper was added to the influent wastewater to increase the influent COD by 50 mg/l. The system was allowed to approach an apparent steady state. This procedure was continued increasing the influent concentration by 100 mg/l, 175 mg/l, 250 mg/l, 350 mg/l, 450 mg/l, and 750 mg/l.

An average time period of 3 days was utilized between paint stripper increases. After the first 24 hours at 750 mg/l of increased COD, the available industrial wastewater supply had been depleted. Therefore, the test was then continued using tap water to dilute the paint stripper to the equivalent of 750 mg/l of COD. Again, using MLSS and ESS, COD removal, and SCI as indicators, the system approached steady state after 12 days of running. Finally, the paint stripper concentration was increased to 1000 mg/l COD. This concentration was maintained for another 8 days, at which time the reactor was shut down.

#### 6. ANALYTICAL PROCEDURE

During the experimentation, several analyses of the wastewater were performed. Chrome concentrations, COD, and methylene blue active substances (MBAS) were analyzed in accordance with reference 2. Sludge volume index was monitored in accordance with the same standard except that a 100-ml graduated cylinder rather than a 1000-ml Imhoff cone was used. Suspended solids in the mixed liquor and effluent were monitored by filtering 100-ml samples through GFC or 0.45-millipore filter paper. Analysis of methylene chloride was attempted to develop a useful method of monitoring the removal of this constituent. Distillation was used to separate and concentrate methylene chloride from a given volume of solution which then was run on a gas chromatograph. Inconsistent recovery during the distillation procedure proved instability for the low levels of methylene chloride that would be experienced during the experiments. Therefore, the monitoring methylene chloride was abandoned.

## SECTION III

## RESULTS

## 1. HEXAVALENT CHROME REMOVAL

Direct precipitation of hexavalent chrome, using barium nitrate ( $\text{Ba}(\text{NO}_3)_2$ ), from a 40-mg/l chrome solution of the paint stripper (1:40 dilution) proved to be ineffective, with virtually no chrome being precipitated, even with two times the stoichiometric amount of  $\text{Ba}(\text{NO}_3)_2$ . Although the COD concentration of the paint stripper solution did not change when the  $\text{Ba}(\text{NO}_3)_2$  was added, a residual barium concentration remained in the solution. The toxicity of barium to microorganisms and the ineffectiveness of this method eliminated its potential usefulness.

Precipitation of hexavalent chrome by reducing it to trivalent chrome in an acidic solution of pH 2.5 and then forming an insoluble metal hydroxide,  $\text{Cr}(\text{OH})_3$ , by raising the pH to 8.5 with calcium hydroxide,  $\text{Ca}(\text{OH})_2$ , was accomplished with moderate success. The total chrome concentration was reduced from 39.4 mg/l in the untreated solution to 10.6 mg/l after precipitation using approximately 0.12 gm of  $\text{NaHSO}_3$  to the 500-ml paint stripper solution. The decrease in COD of the paint stripper solution was less than 6 percent.

Since both the chrome precipitation procedures were not as successful as desired and since the literature indicated at least moderate tolerance of bacteria to hexavalent chrome (10 mg/l having no noticeable effects in 6 weeks of testing), it was decided to discontinue the chrome precipitation tests.

## 2. BIOCHEMICAL OXYGEN DEMAND

Figures 2 through 4 show the BOD exertion for the paint stripper and the industrial wastewater received from McClellan AFB. For the concentrated paint stripper two different dilutions were selected, and both aerated and nonaerated solutions were used. The aerated solutions were used to determine whether the methylene chloride had any effect on the BOD. From figure 2 it is seen that the BOD exertion did not follow the typical first order rate but rather was sporadic. The  $\text{BOD}_5$  for both aerated and nonaerated samples was approximately 80,000 mg/l.



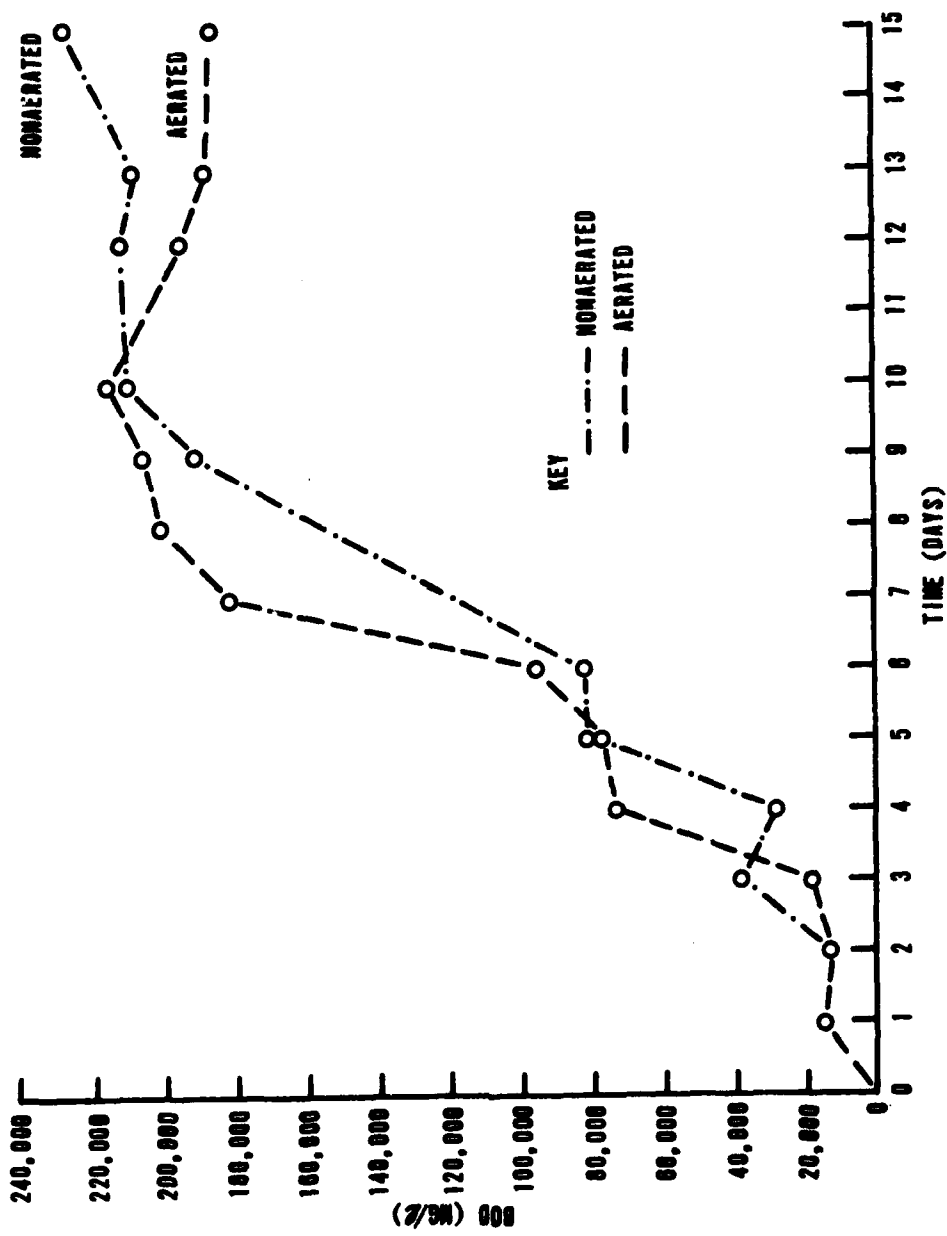


Figure 2. BOD Curves for Aerated and Nonaerated Paint Stripper at 2:100,000 Dilution

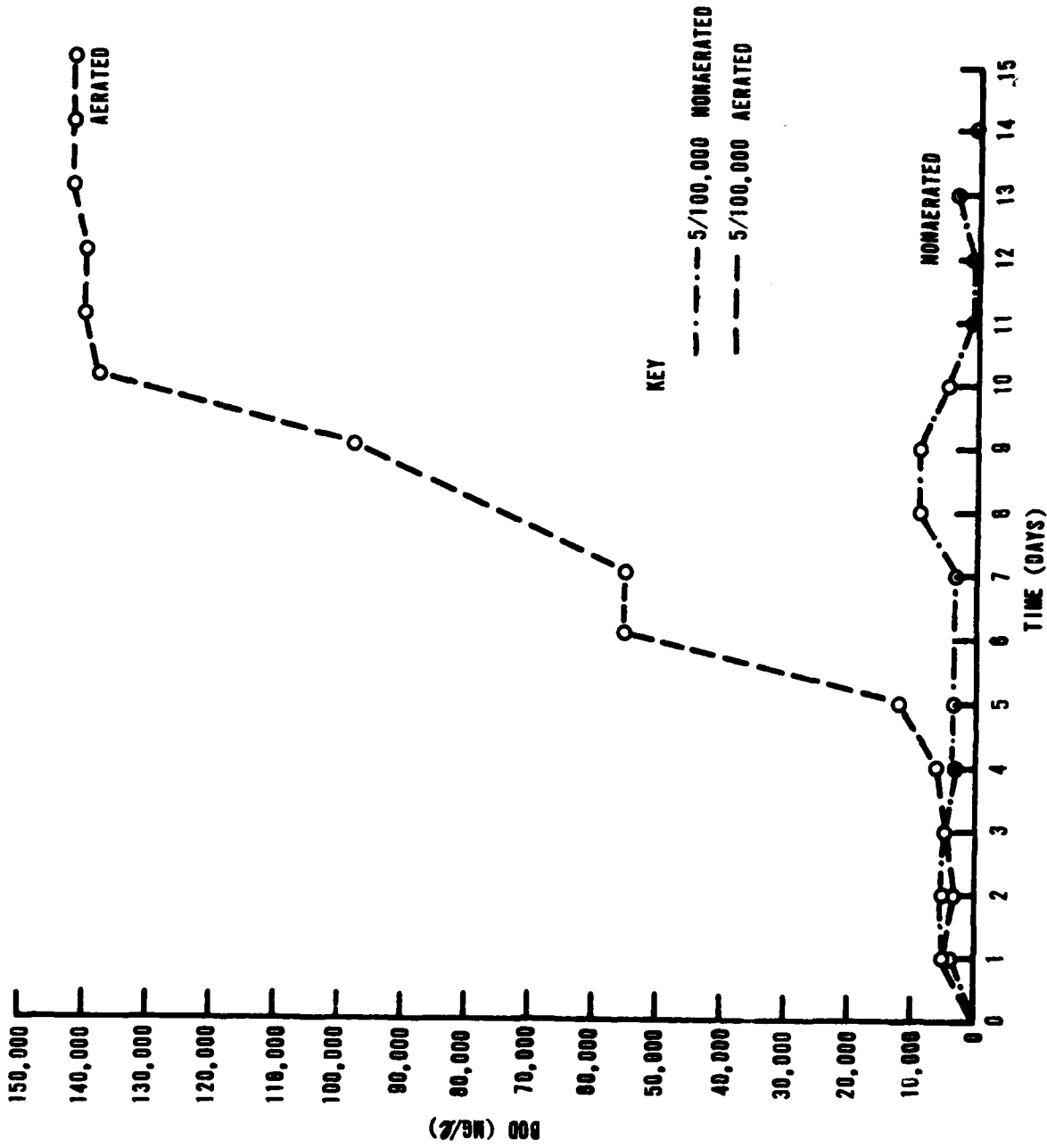


Figure 3. BOD Curves for Aerated and Nonaerated Paint Stripper at 5:100,000 Dilution

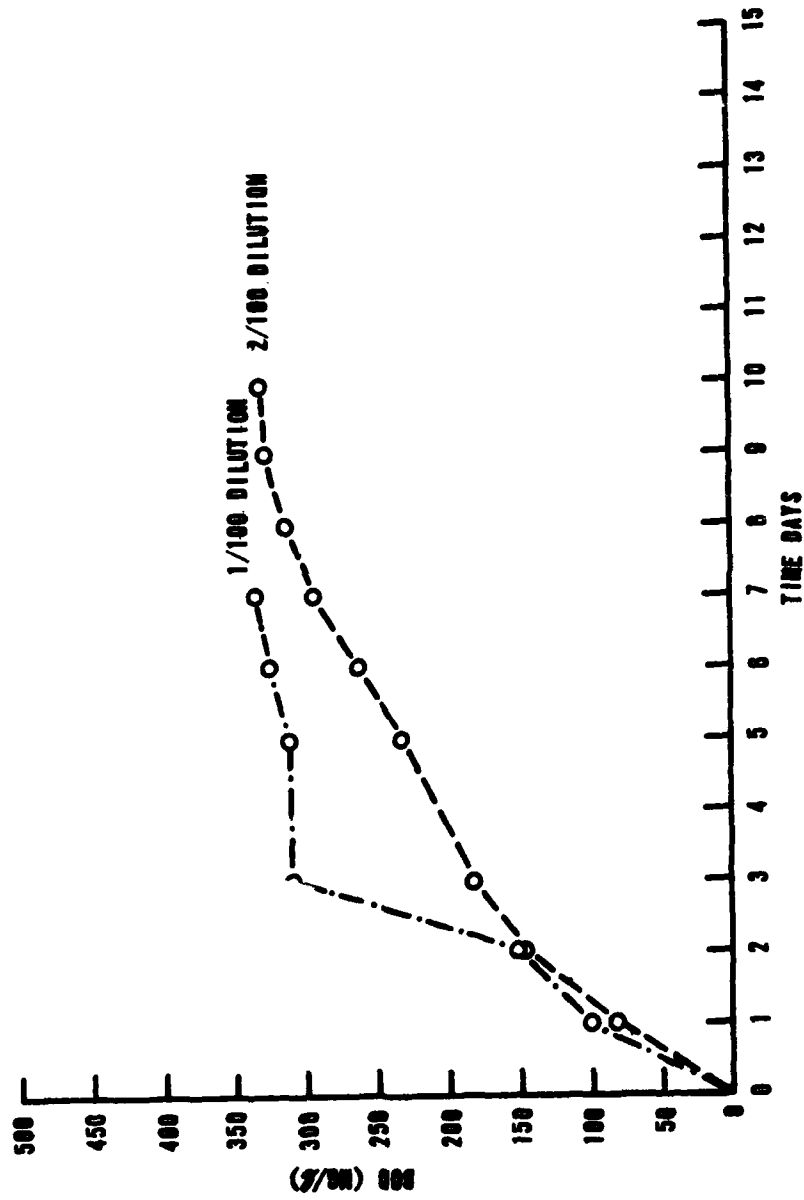


Figure 4. BOD Curves for McClellan AFB Industrial Wastewater

The ultimate BOD could not be determined but appeared to be in excess of 200,000 mg/l. At the 2:100,000 dilution, preaeration of the paint stripper did not appear to have a significant effect on the BOD exertion. This is contrasted with figure 3 where at a dilution of 5:100,000 the BOD exertion of the nonaerated samples was minimal relative to the aerated samples. This indicates that the higher concentrations of methylene chloride were having an inhibitory effect on the micro-organisms.

Theoretically, the BOD should have been the same at any time, regardless of which dilution was used. Comparing figures 2 and 3, it is seen that the 5:100,000 actually yielded a lower BOD. Since both dilutions are very high, this discrepancy is not unlikely for the BOD test. The absolute numbers are not as important as the rate of oxygen uptake. For both dilutions there is a lag for the first 3 to 4 days followed by rapid uptake for the next few days. This is indicative of the micro-organisms undergoing an acclimation period.

The BOD exertion of the industrial wastewater is shown in figure 4. The 2:100 dilution yielded a smooth curve with a  $BOD_5$  of 230 mg/l and an ultimate BOD in excess 325 mg/l. The 1:100 dilution did not yield a smooth oxygen uptake curve.

### 3. GROWTH TESTS

The results of the batch growth tests on just the paint stripper alone at two different dilutions are given in figures 5 and 6. These tests were conducted while aerating the paint stripper solutions and addition of 1 ml of settled secondary effluent from an activated sludge reactor. Surprisingly, there was no significant lag period in the COD reduction or biological solids concentration. At the 1:130 dilution, 50 percent of the initial COD had been removed at the time maximum biological solids concentration was achieved, whereas at the 1:32 dilution only 37 percent of the COD had been removed. It is significant to note that for both dilutions the biological solids concentration started to decrease with approximately 50 percent of the COD remaining. This tends to indicate that some of the components in the paint stripper were not easily biodegradable. Unfortunately, not enough data were obtained to determine the validity of this observation.

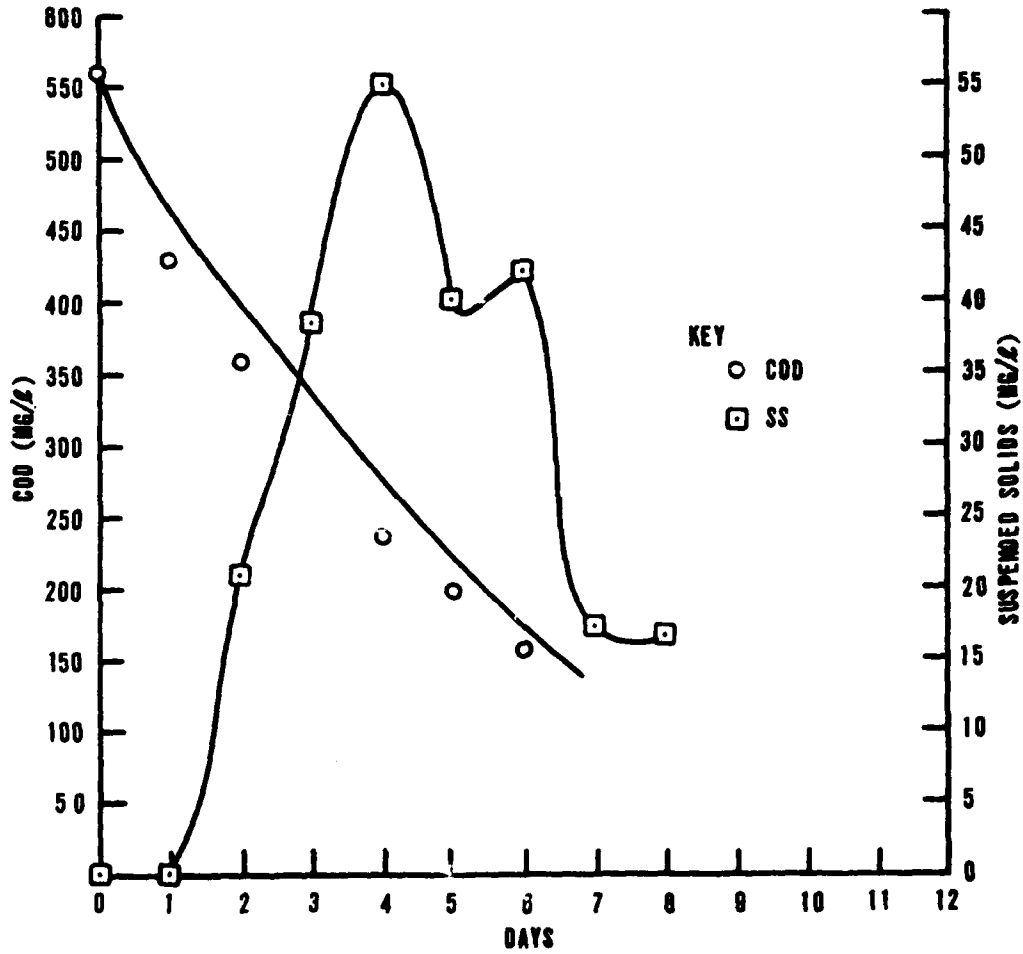


Figure 5. Growth Data for 1:130 Dilution of Paint Stripper

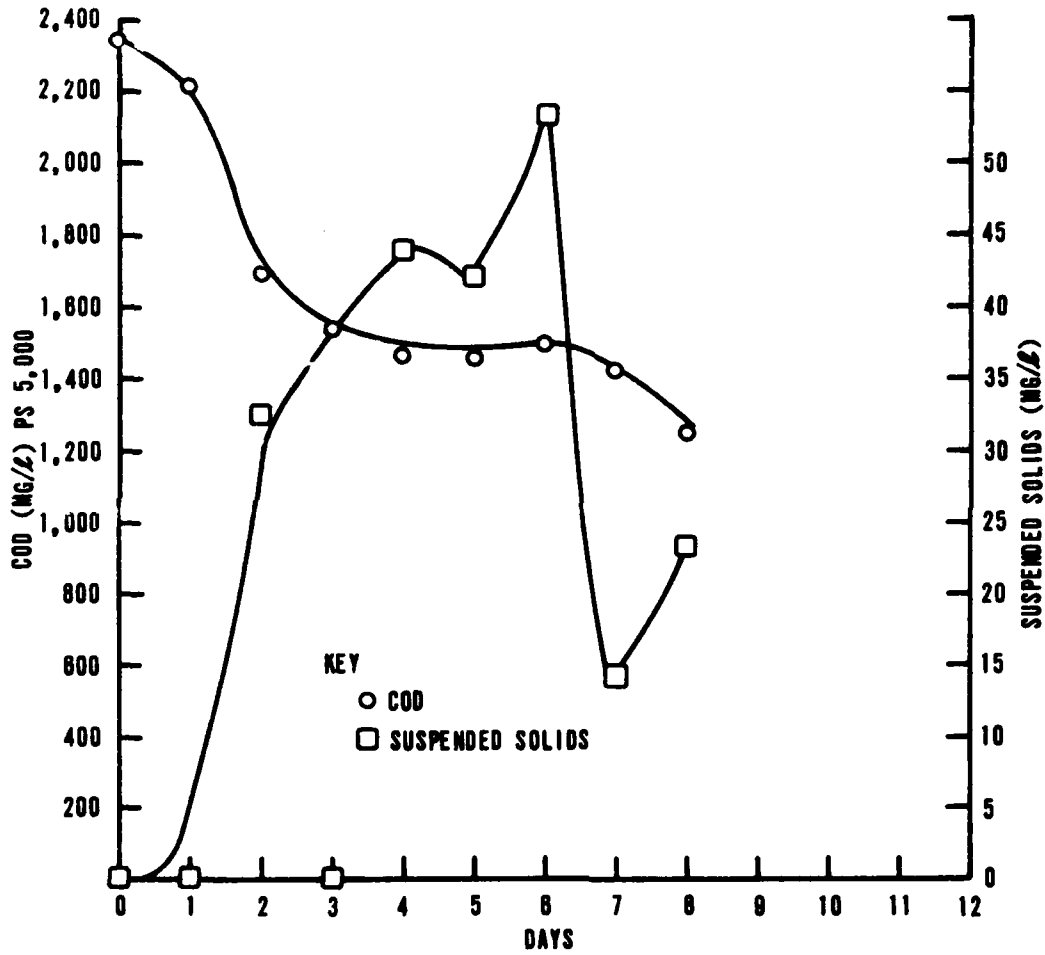


Figure 6. Growth Data for 1:32 Dilution of Paint Stripper

The batch-growth test results for the industrial wastewater are shown in figure 7. It is seen that the COD concentration was reduced from 850 mg/l to approximately 150 mg/l. One hundred and fifty mg/l of residual COD was higher than expected from bacterial metabolic by-products, thus indicating that something in the wastewater was not biodegradable. This is somewhat substantiated by the low  $BOD_5$ :COD ratio of 1:3. Of more significance, the largest biological solids growth occurred approximately 2 days after most of the COD had been removed. This can be explained only by assuming that some of the organic components in the wastewater were volatile and "stripped" from the reactor during aeration.

#### 4. ACTIVATED SLUDGE EXPERIMENTS

With the data obtained from the BOD and growth tests indicating that the paint stripper was at least partially biodegradable, activated sludge experiments were begun. The experiments, as described in detail in section II, consisted basically of acclimating micro-organisms to the McClellan AFB industrial wastewater for 14 days, at which time the previously aerated paint stripper was added in increments based on its COD concentration. The COD concentration of the concentrated paint stripper was 710,000 mg/l. Therefore, for every 10 mg/l COD increment from the paint stripper added to the influent industrial wastewater, this would represent a dilution of 1 gallon of paint stripper per 71,000 gallons of wastewater.

The data obtained during the activated sludge experiments are shown in figures 8 through 10. The figures show the data points from each day's samples, and the data points are connected to reveal any trends or responses due to the increasing addition of the paint stripper.

From figure 8, it is seen that up to day 14, the effluent COD (total and filtrate) continued to decrease but remained above 100 mg/l. Since the influent COD of the industrial wastewater was approximately 600 mg/l, this yields a treatment efficiency of 84 percent. Upon addition of the paint stripper on day 14, which increased the influent COD by 50 mg/l, it is seen that the effluent COD did increase but then started to decrease on day 19. This increase followed by the decrease in effluent COD can be expected and is simply the time required for acclimation of the micro-organisms. It should be observed that at 175 mg/l incremental COD from the paint stripper, the effluent COD was approximately the

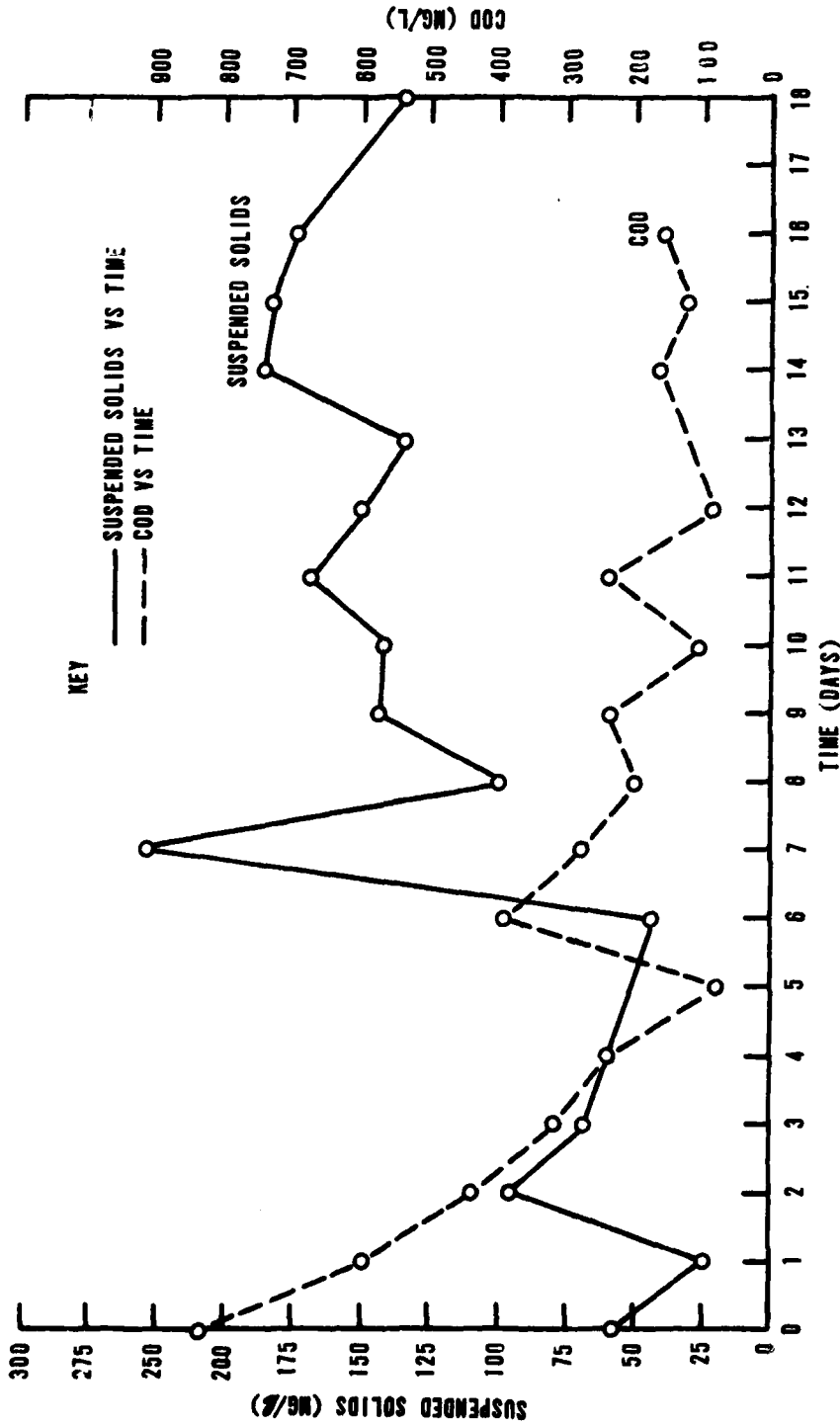


Figure 7. Growth Data for McClellan Industrial Wastewater



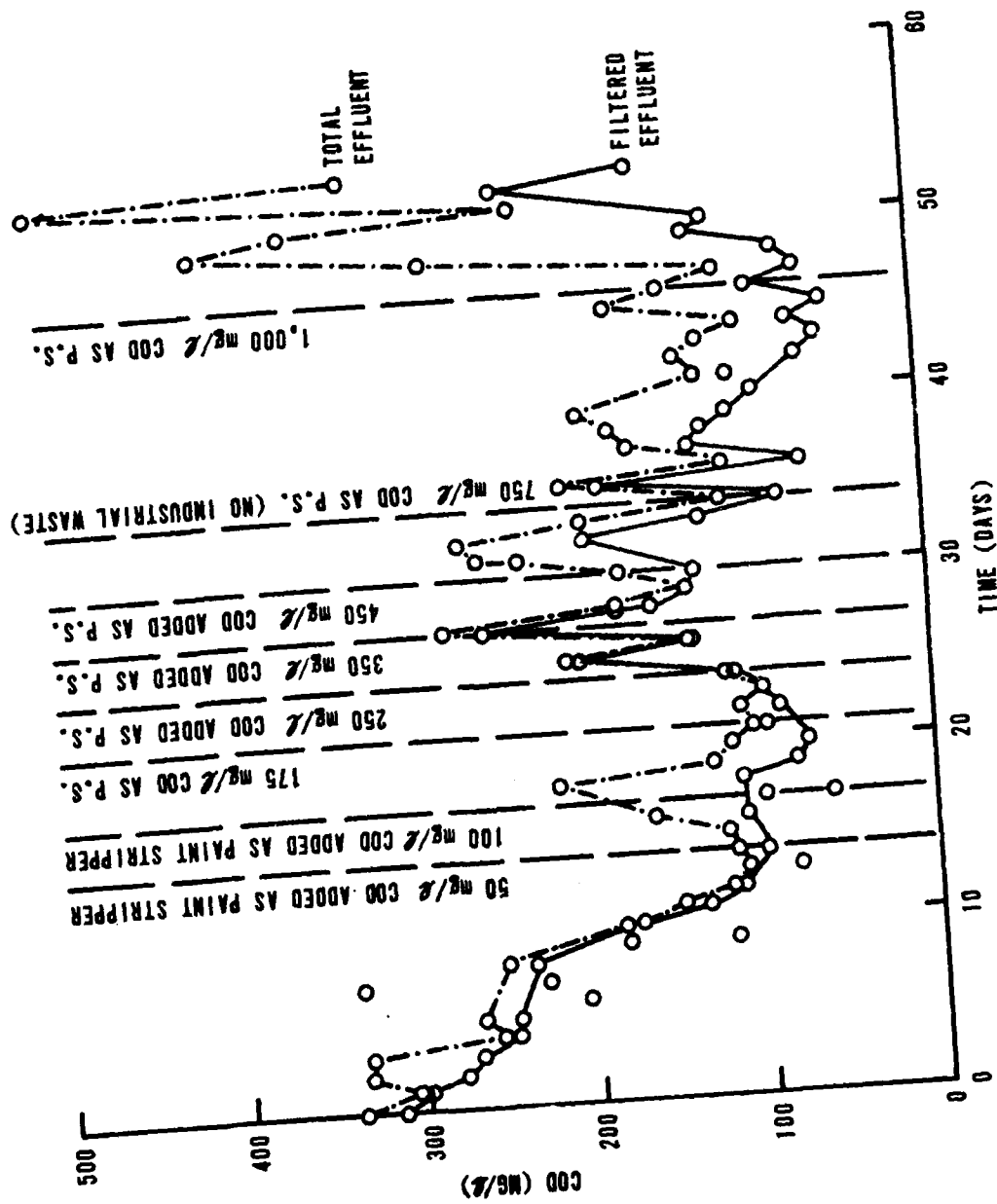


Figure 8. Effluent COD Concentration from the Activated Sludge Reactor

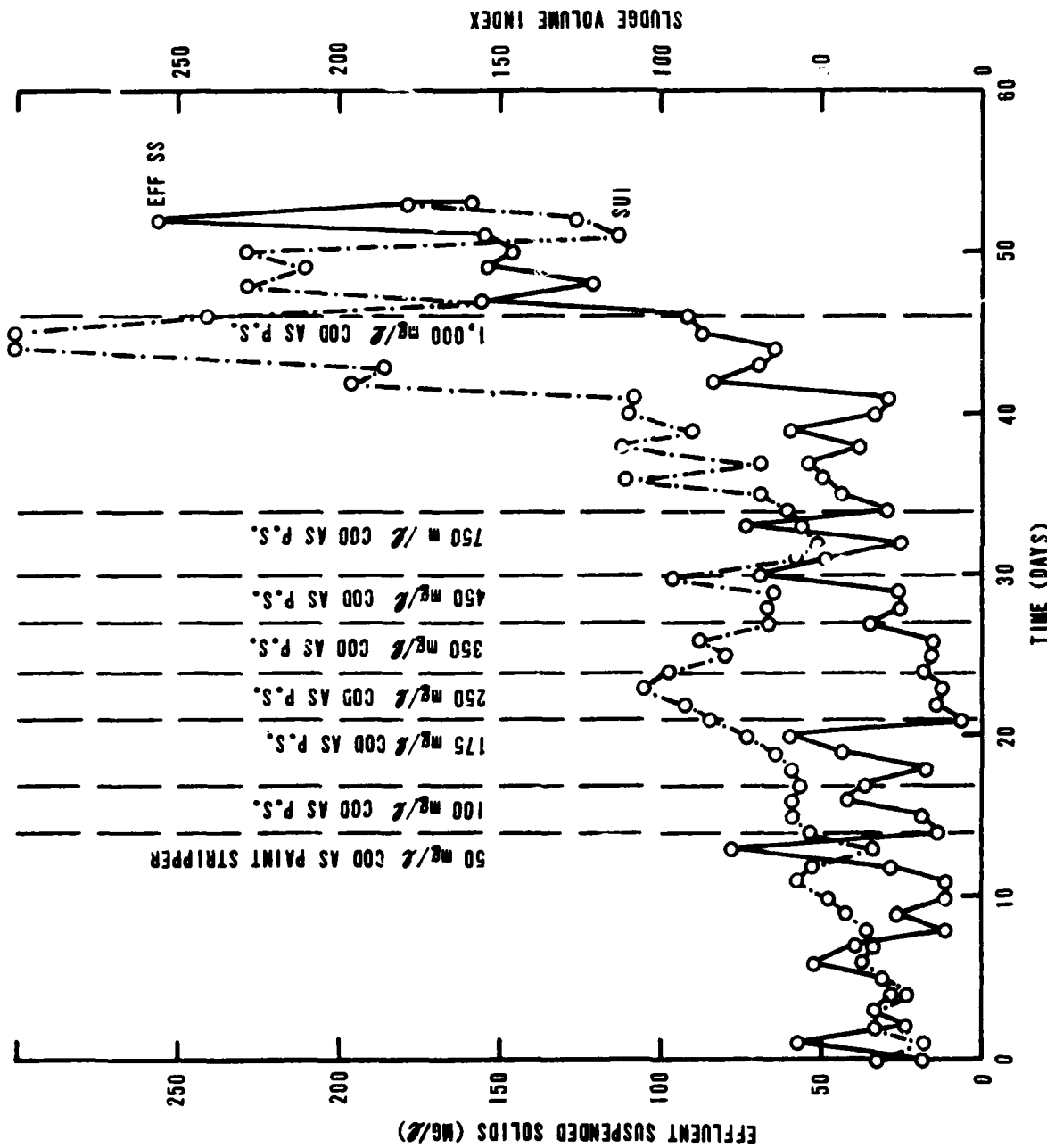


Figure 9. Effluent Suspended Solid Concentration and Sludge Volume Index from Activated Sludge Reactor

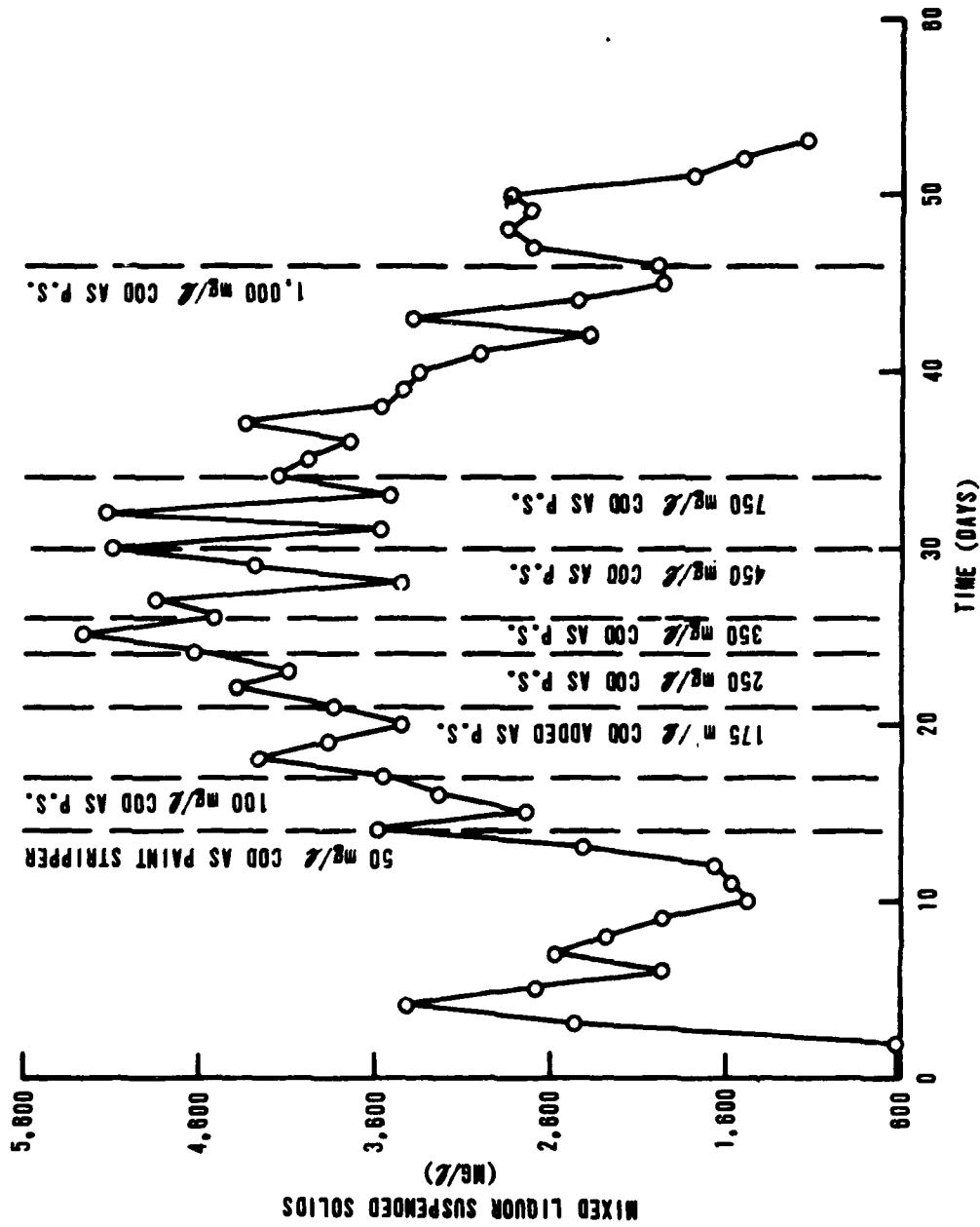


Figure 10. Mixed Liquor Suspended Solid Concentration from Activated Sludge Reactor

same as when the activated sludge reactor was receiving only the industrial wastewater. Addition of 250 mg/l incremental COD from the paint stripper did cause the effluent COD to increase. This increase stabilized even though the influent COD continued to increase due to additional paint stripper.

On day 34, the industrial wastewater was depleted, and operation of the reactor was continued using only the paint stripper as wastewater. This resulted in a decrease in effluent COD mostly as a result of the decrease in influent COD from approximately 1300 mg/l to 750 mg/l. Refer to figure 11 and subsequent discussion of that figure. On day 45 the influent COD was increased to 1000 mg/l by utilizing more paint stripper. This resulted in an immediate significant increase in effluent COD and caused conclusion of the experiment. It should be noted that, for most of the samples, the difference between total effluent COD and filtrate effluent COD was of small magnitude. This indicates good settling in the clarifier.

The effluent suspended solids concentration and the sludge volume index (SVI) results are shown in figure 9. Sludge Volume Indexes of less than 100 are considered to be representative of good settling activated sludge micro-organisms. It is seen that up through day 34 the SVI was well under 100. After day 34, which coincided with utilization of only the paint stripper for the influent wastewater, the SVI significantly increased. The effluent suspended solids concentration followed the same trend, although it was not until day 40 that a significant increase occurred. This could be attributed to an oversized final clarifier.

The mixed liquor suspended solids (MLSS) concentration in the activated sludge reactor is shown in figure 10. Up to day 14 the MLSS is seen to fluctuate significantly, varying from a low of 1500 mg/l to 3400 mg/l. Starting with the addition of the paint stripper on day 14, the MLSS started to increase even with sludge wasting. As soon as the industrial wastewater was depleted the MLSS started to decrease and dropped from 4300 mg/l to 1100 mg/l in 16 days. This can be partially attributed to the decrease in influent COD, but based on the drastic decrease in MLSS on days 50 through 53 and the concurrent increase in SVI and effluent suspended solids, the primary reason is believed to be due to toxic effects of the paint stripper on the micro-organisms.

The performance of the activated sludge reactor relative to the influent paint stripper, expressed as COD, is summarized in figure 11. The effluent COD, total and filtrate, and the percent COD removal is plotted against the incremental

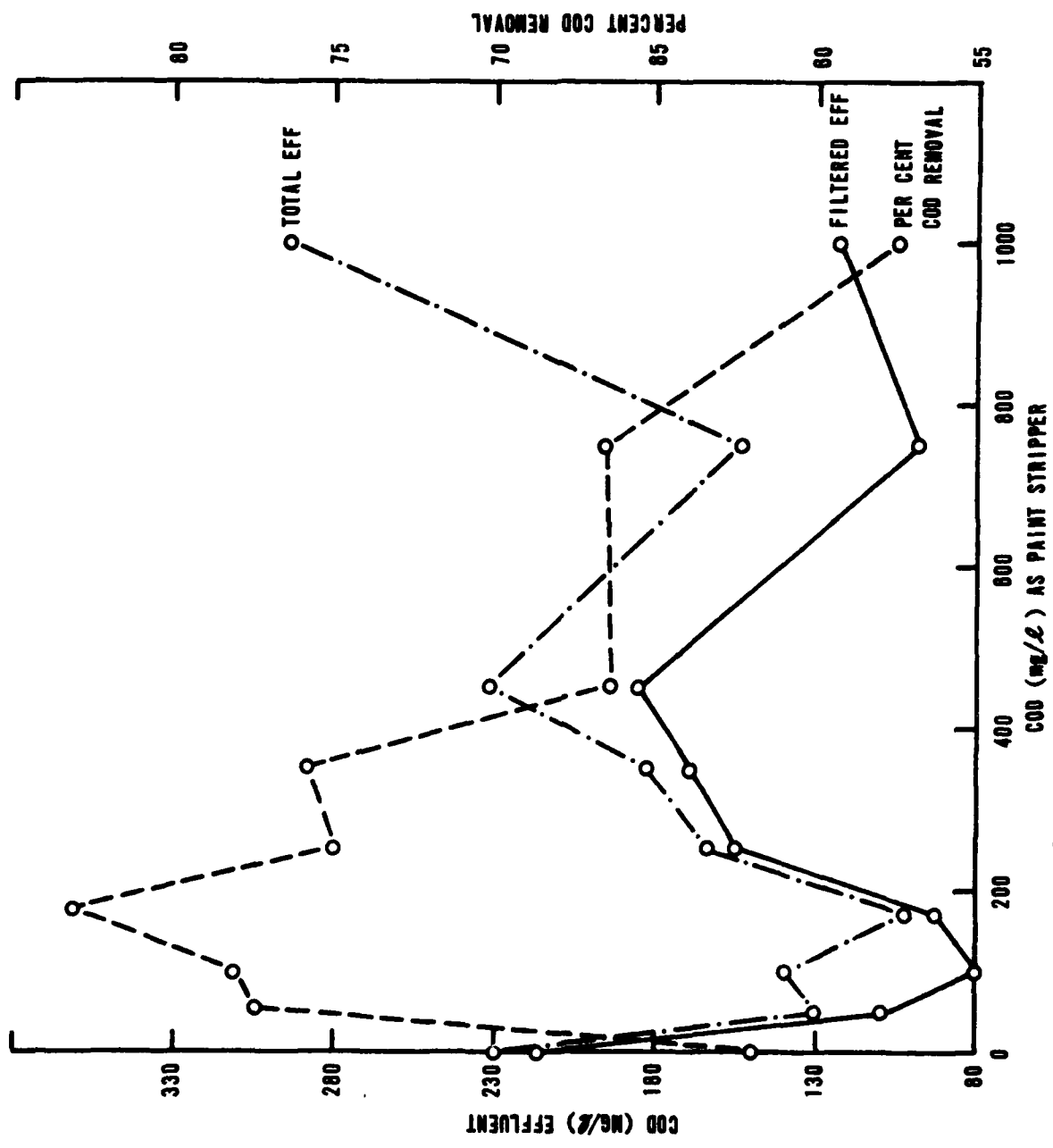


Figure 11. Effluent COD Concentration and Percent COD Removal versus COD Concentration of Paint Stripper in Influent

COD added to the influent from the paint stripper. The data points are the averages of the values obtained for each paint stripper COD concentration. The percent COD removal is based on total effluent COD. It is seen that the effluent COD, total, and filtrate began to increase when the COD added from the paint stripper was increased from 100 mg/l to 175 mg/l. The effluent COD does decrease between 450 and 750 mg/l, but this is only because of the depletion of the industrial wastewater, which resulted in lowering the influent COD from 1300 mg/l to 750 mg/l.

With respect to percent COD removal, it must be remembered that the influent COD was increasing with increasing addition of the paint stripper. Thus, the percent COD removal could actually increase or stay the same even though the effluent COD increased. This is seen to be the case when the incremental COD of the paint stripper in the influent was increased from 100 mg/l to 175 mg/l. However, beyond that point the percent COD removal sharply decreased from a high of 82 percent to 57 percent.

SECTION IV  
CONCLUSIONS AND RECOMMENDATIONS

The tests conducted on the biodegradability of Turco 5873 nonphenolic paint stripper permit the following conclusions to be made.

a. Methylene chloride present in the paint stripper has an inhibitory effect on bacterial metabolism even at very low concentrations.

b. Aeration or alternate methods of stripping the methylene chloride and other volatile compounds result in the paint stripper being at least partially amenable to microbiological degradation.

c. The limiting concentration of paint stripper, expressed as COD, that should be present in the industrial wastewater influent to a biological treatment process at the AMA industrial wastewater treatment plants should be 175 to 200 mg/l. Based on a COD of the concentrated paint stripper of 710,000 mg/l, this means that for each gallon of paint stripper used per day, the flow of industrial wastewater should be 710,000/175 which is equivalent to approximately 4000 gallons. Thus, if 300 gallons of Turco 5873 are used in one day to depaint an aircraft, the industrial wastewater flow for that day should be 1.2 million gallons. This is assuming perfect equalization of the paint stripper concentration with the industrial wastewater. A further assumption is that the paint stripper is being discharged continuously into the industrial sewer for treatment and not used only 1 or 2 days per week.