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METHODS FOR DEMETALLATION OF WASTE OIL

by

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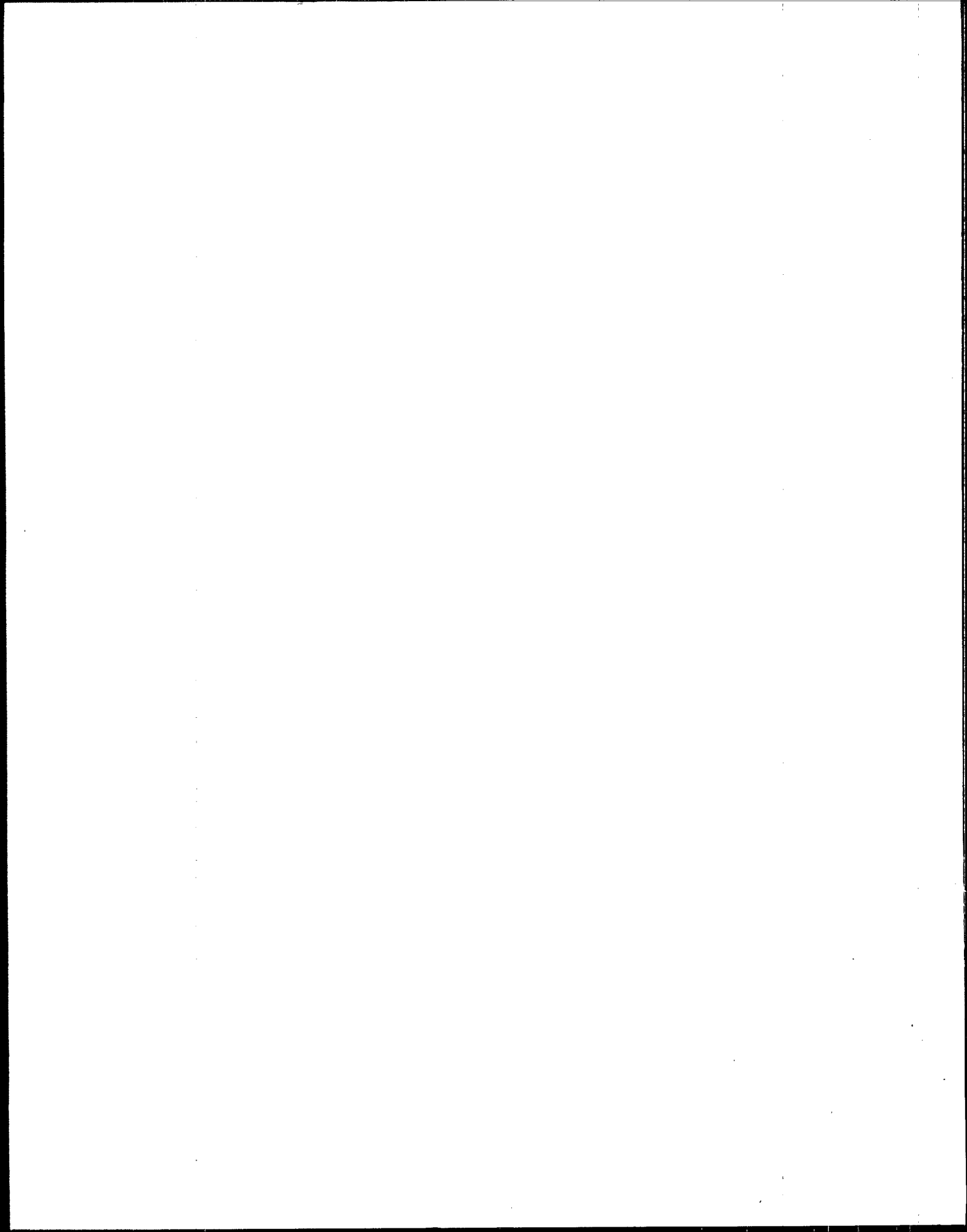
Contract No. EPA-CR814635-01

Project Officer

Edward R. Bates
Alternative Technologies Division
Risk Reduction Engineering Laboratory
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Cincinnati, Ohio 45268

This study was conducted in cooperation with
The U.S. Department of Defense.

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OFFICE OF RESEARCH AND DEVELOPMENT
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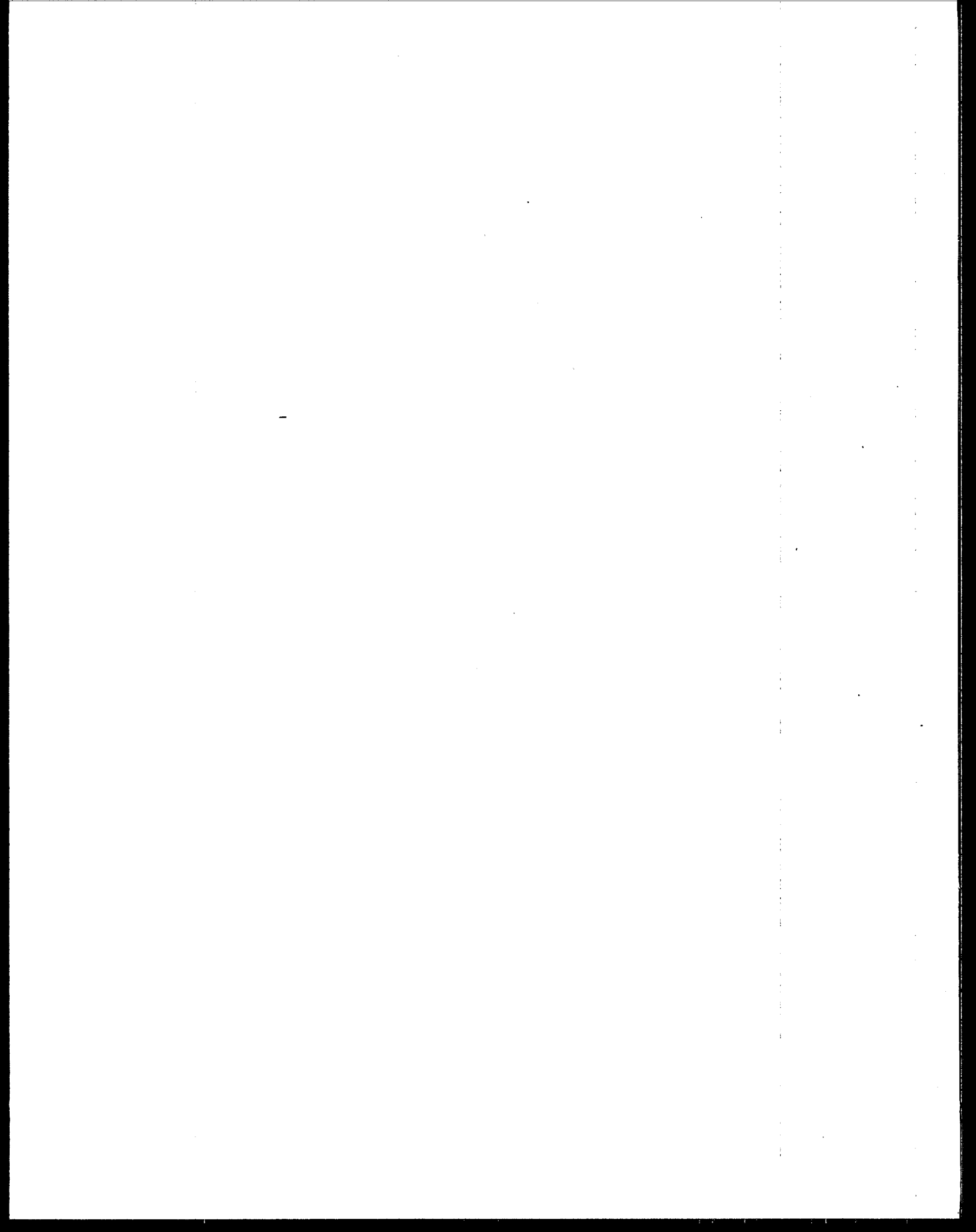
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DISCLAIMER

The information in this document has been funded wholly or in part by the United States Environmental Protection Agency under contract number EPA-CR814635-01 to Auburn University. It has been subjected to the Agency's peer and administrative review, and it has been approved for publication as an EPA document. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

FOREWORD

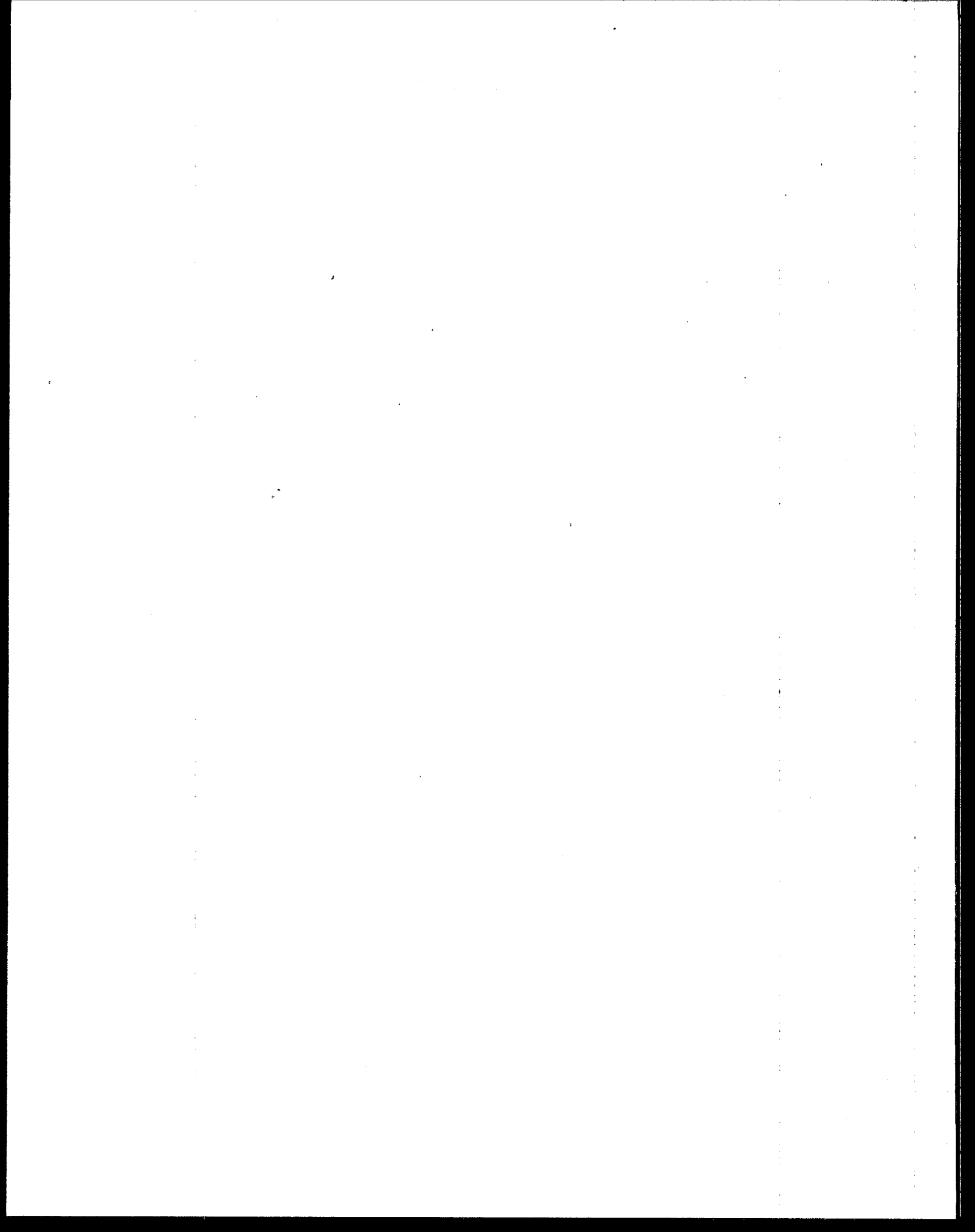
A variety of research efforts have clearly established that used oil is a valuable, renewable resource, and that proper implementation and management of viable technology can ensure its effective reutilization.

Over the past few years, researchers with the Chemical Engineering Department of Auburn University have been working to develop economically and environmentally sound technology for reprocessing used oil. The result of these efforts is a systematic demetallation procedure, whereby soluble metals are converted to insolubles and removed with other impurities. The final product is a high-grade, EPA-specification used fuel oil which can be used for heating or as a reusable base stock for lubrication and hydraulic fluids.

The product meets EPA air quality regulations and can be burned in most industrial boilers without the requirement of a special burn permit. Also, an EPA tracking system is not required for the oil beyond the demetallation procedure. In addition, liability risks are lowered for users, since the product qualifies as an ASTM No. 5 grade fuel oil with an ash content of less than .1 weight percent; thus, no mixing of the product with other fuel oils is needed to meet particulate emissions requirements.

For several years, the Chemical Engineering Department and its primary research unit, the Auburn Waste Oil Reprocessing Laboratory, have interacted with a number of industries and military installations to develop and provide useful reprocessing technology. This report offers an account of recent developments in the Department's ongoing goal of developing the finest state-of-the-art oil reutilization technology.

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ABSTRACT

Under a contract from the Department of Defense (DoD), work was initiated by the Chemical Engineering Department of Auburn University to develop technology for converting waste oils into EPA specification grade fuel oil. DoD is particularly concerned with the development and utilization of this technology because it is one of the largest generator of waste oils in the U.S.

A process objective was to dehydrate the waste oil, reduce its total ash content (< 0.1 wt%), and remove the impurities (such as sludge, carbon particles, acids, etc.) present in used oil. Particular emphasis was placed on demetallization and neutralization of waste oils by a chemical treatment. It was found from bench-scale studies that diammonium phosphate and triethanol amine were very effective in deashing, as well as in precipitating sludge and impurities from used oil. An extensive study was performed to determine the effect of various parameters on the ash and lead reduction of waste oil. Based on the bench-scale studies, the pilot plant was developed at the Auburn Waste Oil Reprocessing Laboratory (AWORL) to transform waste oil into specification grade fuel oil. The pilot plant has the capacity to treat 5 gallons/minute of used oil. So far, a total of 7,000 gallons of waste oil has been reprocessed. The ash and lead content of the processed oil was reduced to less than 0.1 wt% and 100 ppm, respectively. This process was successful in converting waste oil into specification grade fuel oil.

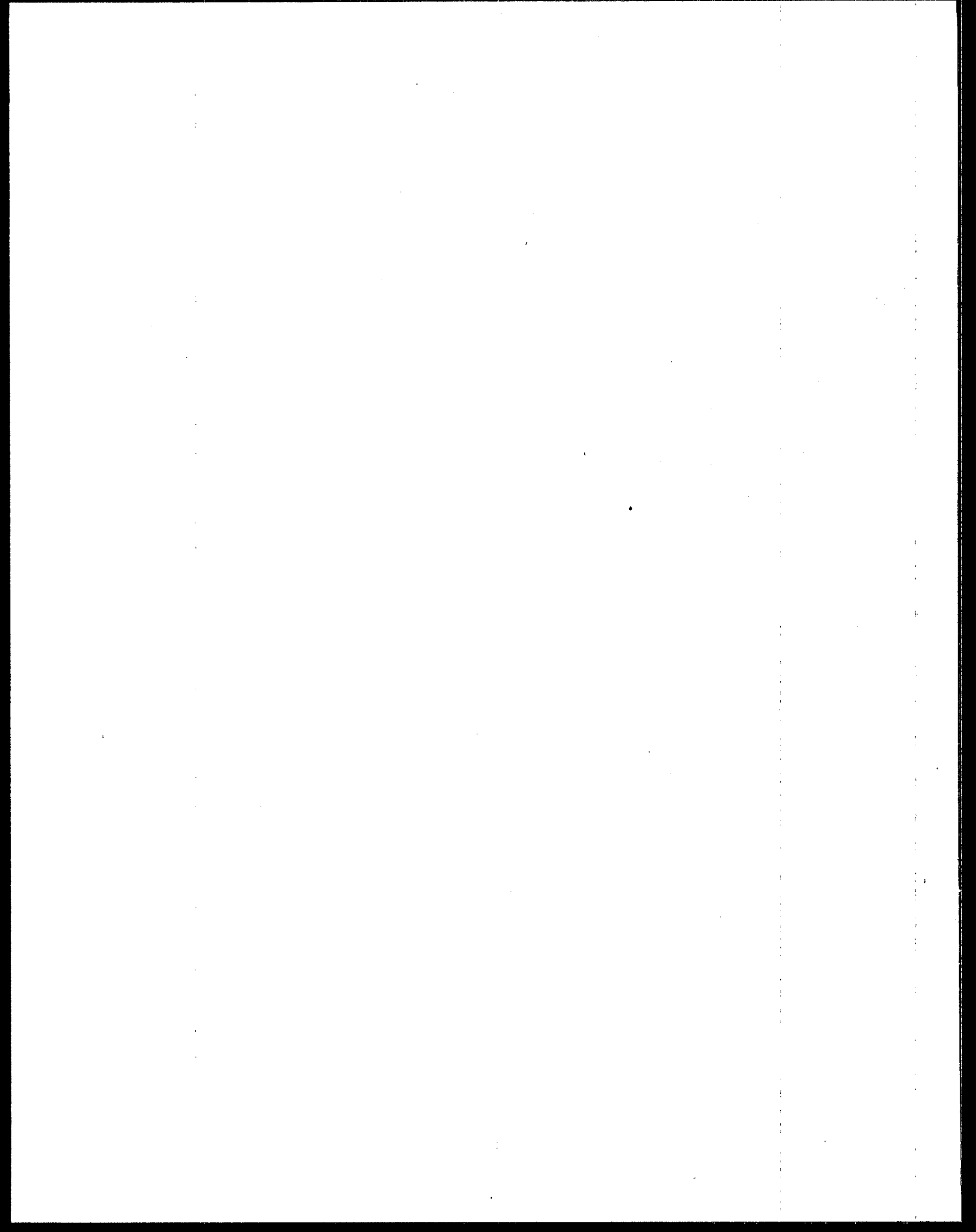


TABLE OF CONTENTS

DISCLAIMER	ii
FOREWORD.	iii
ABSTRACT	iv
TABLE OF CONTENTS.	v
LIST OF TABLES.	viii
LIST OF FIGURES	xi
 I. INTRODUCTION.	 1
II. LITERATURE REVIEW	4
Recovery Processes	4
Acid-Clay Process	5
Solvent Extraction-Distillation Process	5
Chemical Deashing-Hydrotreatment Process.	9
Classification of Used Oil	13
Resource Conservation and Recovery Act	13
Final Rule, Burning of Used Oil.	16
Proposed Rule, Recycled Used Oil Standards	16
Identification and Listing of Used Oil, Proposed Rule	16
Waste Oil Categorization	17
Standards Applicable to Generators, Processors, Marketers, Burners	17
Recent Developments in Classification of Used Oil.	19
 III. CHARACTERISTICS OF USED OIL	 24
Origin of Base Stocks	25
Lubricant Additives (27, 28, 29)	28
Antiwear and Extreme Pressure Agents	28
Corrosion and Rust Inhibitors	28
Detergent and Dispersants.	28
Antioxidants	29
Metal Deactivators and Rust Inhibitors	29
Industrial Lubricants	29
Mechanism of Oil Oxidation	31
Metals in Used Oil	31
Naturally Occurring Metals	32
Metals Incorporated in Additives	32

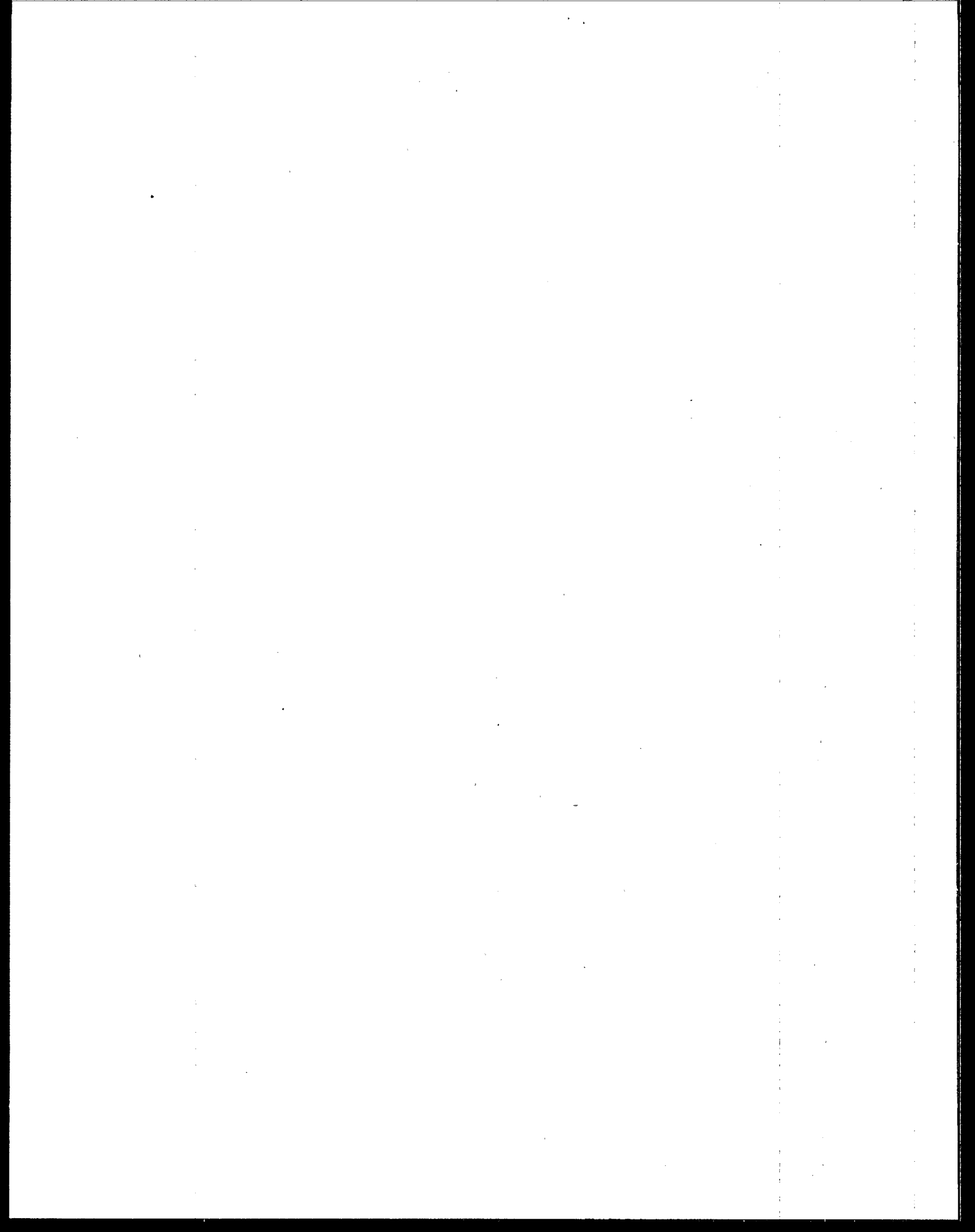


TABLE OF CONTENTS (CONTINUED)

Metals Introduced During Use.	32
Chemical and Physical Nature of Metals in Oil	32
IV. EXPERIMENTAL PROCEDURES	35
Tubing Bomb Micro-Reactor (TBMR)	35
Distillation Flask Reactor	38
Autoclave	38
Three-Neck Flask	38
Materials	44
Analysis	44
V. USE OF METALLIC BOROHYDRIDE AS A DEMETALLIZING REAGENT.	45
Results and Discussion.	46
Effect of Reaction-Temperature	48
Investigation of Gel Formation	52
Effect of Caustics	52
Effect of Water	52
Autoclave Study	56
Conclusions	58
VI. USE OF DIAMMONIUM PHOSPHATE AS A DEMETALLIZATION REAGENT	59
Mechanism of Demetallization Reaction.	59
Experimental Procedure.	60
Solids Removed by Sedimentation.	60
Results and Discussion.	60
Effect of Reaction Time	60
Effect of Reaction Temperature	62
Effect of Ash Content	62
Solids Removed by Filtration.	69
Effect of Diammonium Phosphate on Ash and Lead Reduction	69
Effect of Water on Ash and Lead Reduction	69
Effect of Temperature and Residence Time on Lead Reduction.	73
Mechanism for Lead and Metals Removal.	73
Limitations	73
Conclusions	78

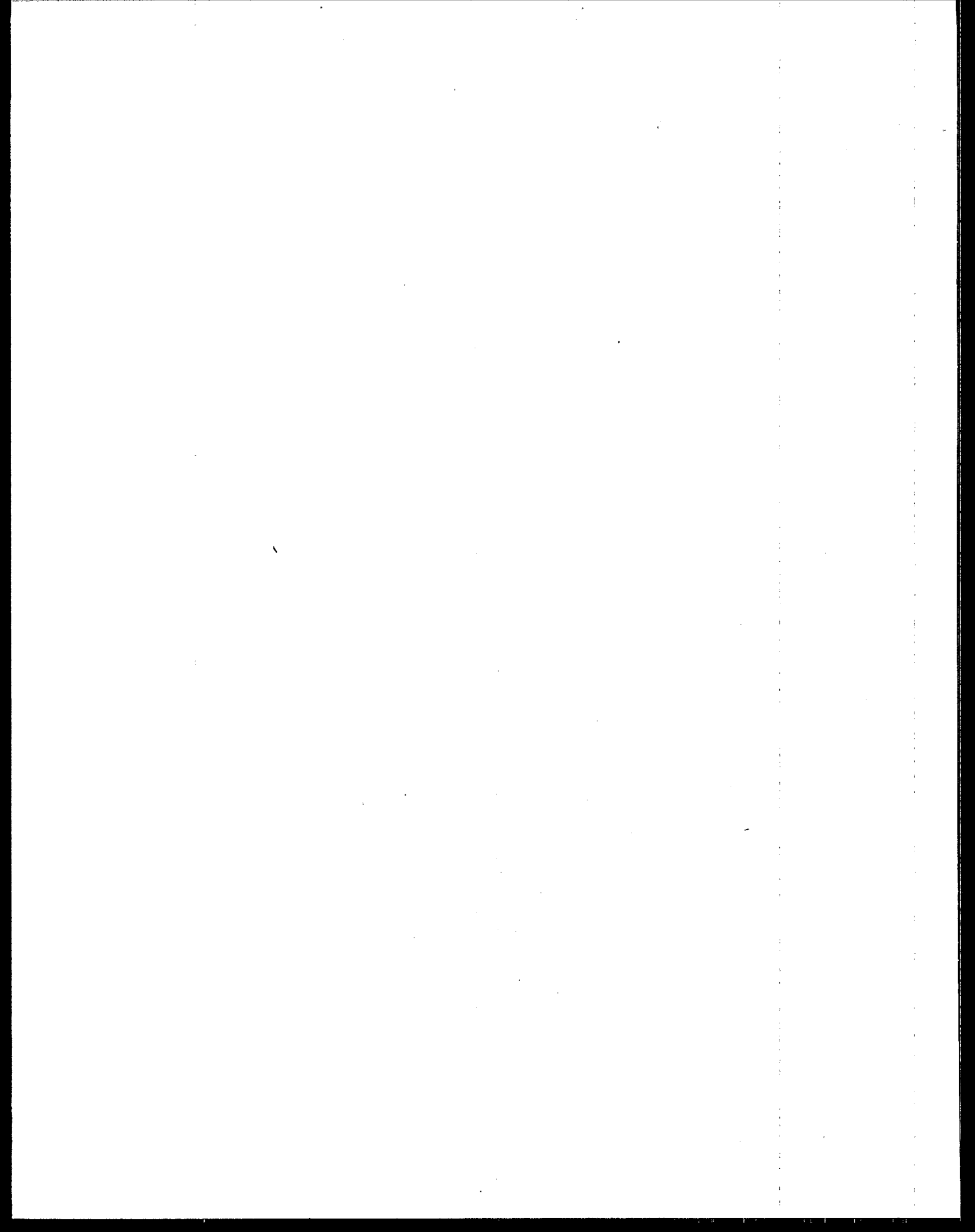
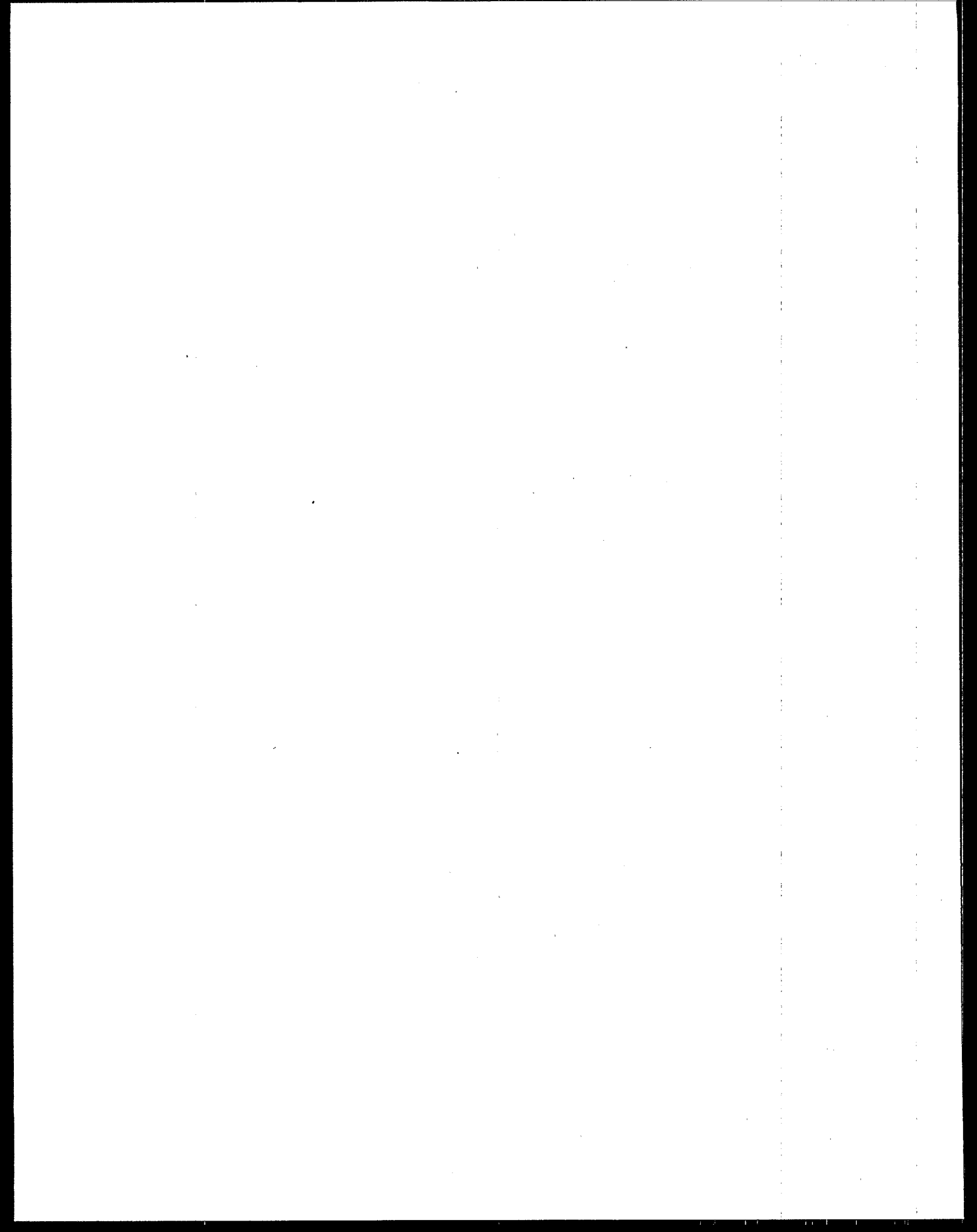


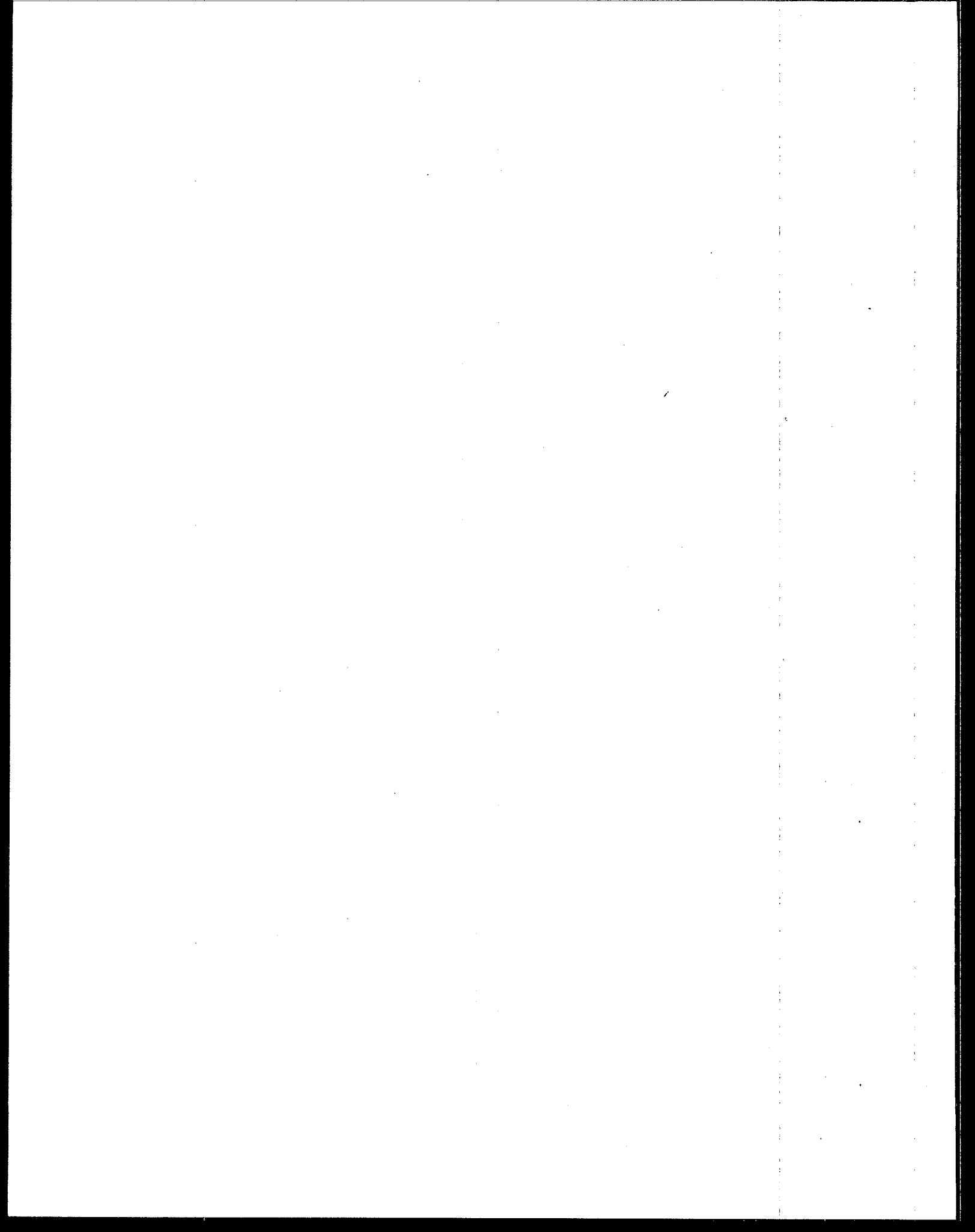
TABLE OF CONTENTS (CONTINUED)

VII.	USE OF TRIETHANOL AMINE AS A FLOCCULATING REAGENT	80
	Effect of Triethanol Amine on Ash and Lead Reduction.	81
	Effect of Temperature and Time on Ash and Lead Reduction	84
	Effect of Water on the Demetallization of Oil	84
	Mechanism of Metals Removal	89
	Solid-Liquid Separation	89
	Filtration.	89
	Centrifugation	91
	Gravity Sedimentation	92
	Conclusions	92
VIII.	PILOT PLANT	94
	Demetallization	94
	Lamella.	94
	Sludge Treatment.	98
	Results.	98
	Conclusions	101
IX.	BURN TEST.	102
X.	BIBLIOGRAPHY.	104
APPENDIX		
A.	QUALITY ASSURANCE ACTIVITIES	108
B.	QUALITY ASSURANCE/QUALITY CONTROL PLAN - RECLAIMED OIL TRIAL BURN	117
	Results and Discussion.	117
	Comparison of Measured Emission-Reclaimed Fuel Oil and No. 5 Fuel Oil	118
	Reclaimed Fuel Oil	118
	Commercial No. 5 Fuel Oil.	118
	Sampling Procedures.	118
	Quality Control	123
	Quality Assurance Objectives.	125
	Sampling Procedures.	125



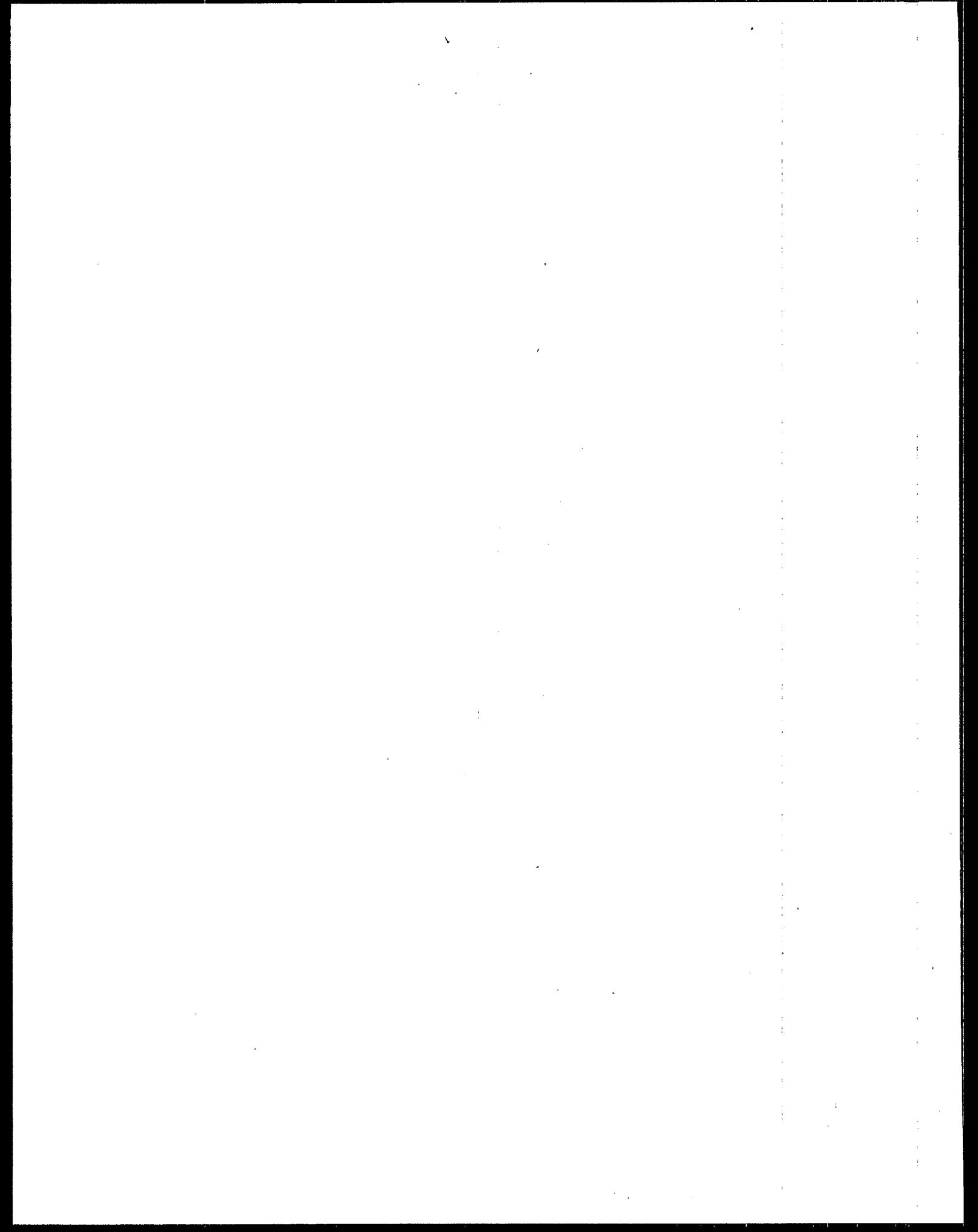
LIST OF TABLES

1.	Characteristics of Hazardous Wastes	14
2.	Contaminants in Extract	15
3.	Specification Used Oil	17
4.	Industrial Oil Sales for 1975	30
5.	Elemental Analysis of Metals in Used Motor Oil	34
6.	TBMR Reaction Condition for Venpure Product Treatment	46
7.	Effect of Metal Borohydride on Lead Reduction for Type B Oil	47
8.	Effect of Oil Type on Lead Reduction Efficiency	49
9.	Effect of Metal Borohydride on Lead Reduction for type A Oil.	50
10.	Effect of Reaction Temperature on Sludge Formation	51
11.	Influence of Caustics on Formation of Gelatinous Mass	53
12.	Effect of NaOH on Sludge Production and Lead Reduction	54
13.	Influence of Water on Lead Removal	55
14.	Results of Autoclave Runs	57
15.	Effect of Reaction Time on Lead Removal	63
16.	Effect of Reaction Temperature on Lead Reduction.	65
17.	Effect of Reaction Temperature on Lead Reduction (1 Hour)	65
18.	Effect of Ash Content on Lead Reduction.	67
19.	Effect of Filtration on Ash and Lead Reduction	67



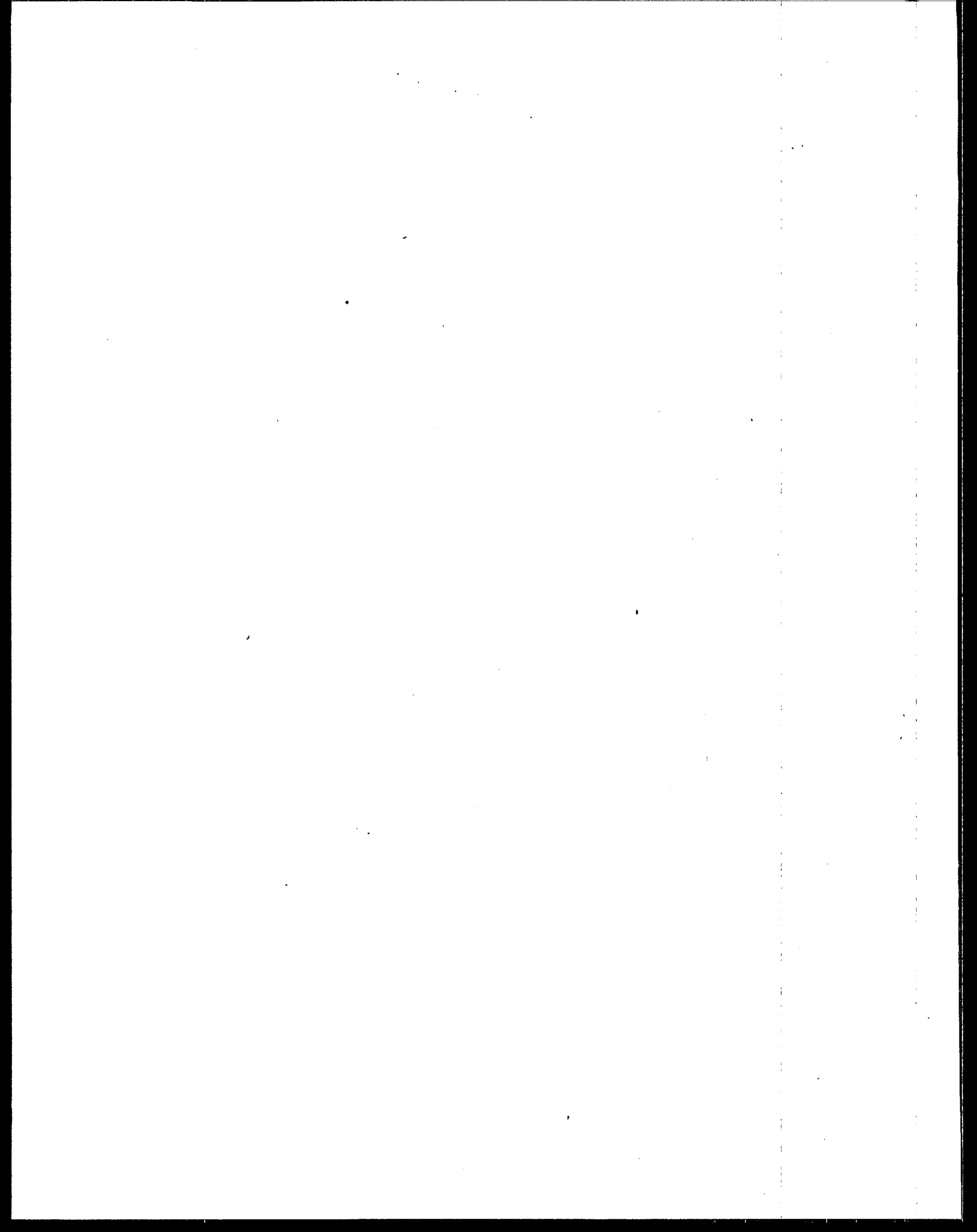
LIST OF TABLES (CONTINUED)

20.	Effect of DAP on Lead Reduction	70
21.	Effect of Water on Ash and Lead Reduction	72
22.	DAP Demetallization Study Using a One-Gallon Autoclave.	77
23.	Effect of Diluent and Filter Aid on Filtration Rate.	79
24.	Effect of TEA on Ash and Lead Reduction.	82
25.	Additive Metals Content of TEA-Treated Oil.	82
26.	Effect of DAP on Ash and Lead Reduction (0.5 wt. %).	83
27.	Effect of DAP on Ash and Lead Reduction (1.0 wt. %)	83
28.	Effect of Reaction Time on Ash and Lead Reduction	85
29.	Effect of Reaction Temperature on Ash and Lead Reduction	85
30.	Effect of Water on Oil Recovery	86
31.	Effect of Different Modes of Separation on Ash Content.	91
32.	Metal Contents of Used Oil Processed by Chemical Treatment	93
33.	Metals Content of Oil Processed at Pilot Plant	100
A-1.	Volatility Test of Organometallic Lead Compound in Muffle Furnace at 600°C for 12 Hours.	112
A-2.	Accuracy of Lead Analysis Procedure	114
A-3.	Determination of Ash and Lead Contents of Virgin Motor Oil	115
A-4.	Precision Test for Lead and Ash Analysis	116



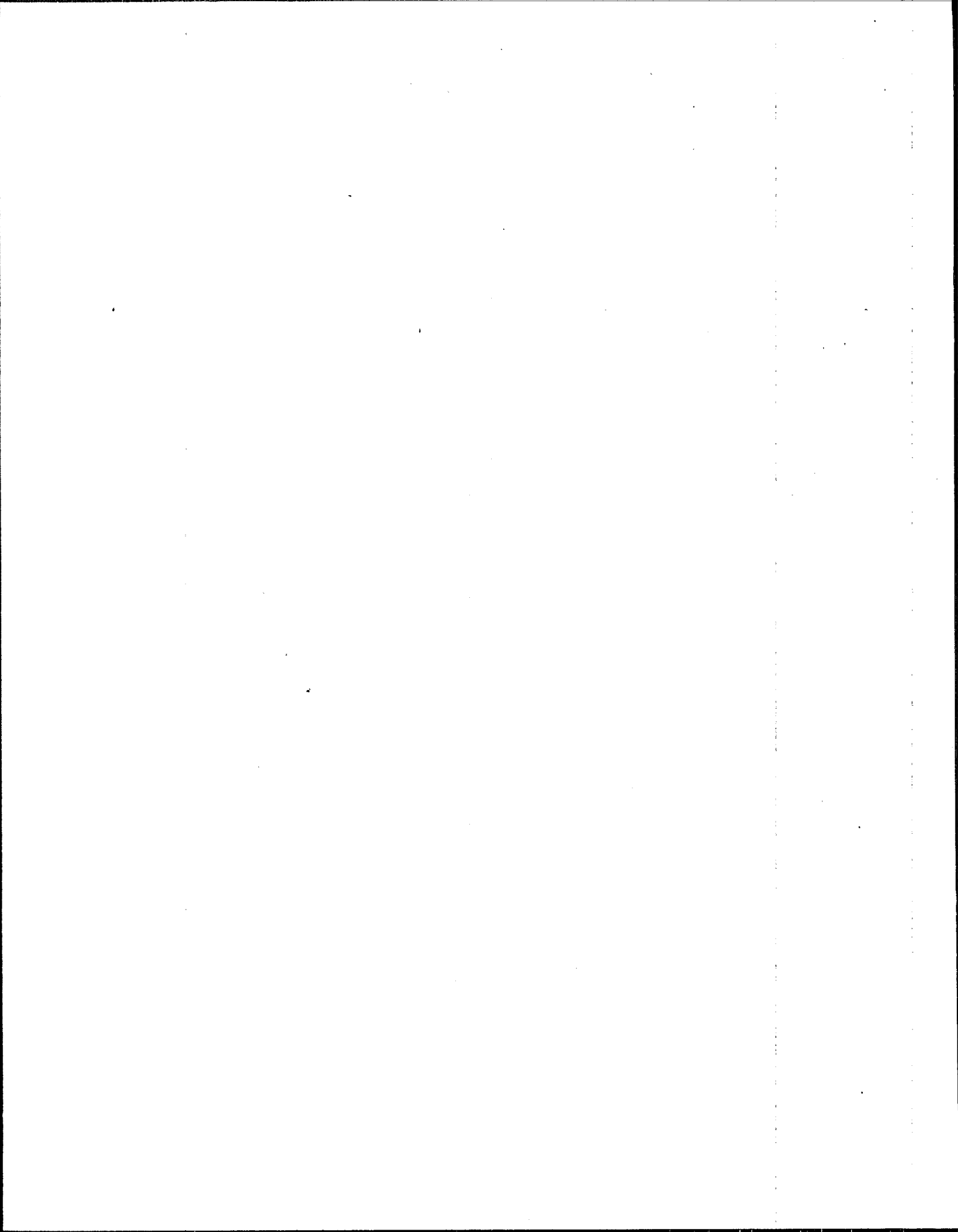
LIST OF TABLES (CONTINUED)

B-1.	Comparison of Measured Emission Rates	119
B-2.	Reclaimed Fuel Oil Emission Data	119
B-3.	Commercial No. 5 Fuel Oil Emission Data.	121
B-4.	Summary of Duplicate Analyses	126
B-5.	Summary of Spiked Sample Results	126



LIST OF FIGURES

1.	Waste Oil Generation and Disposal	2
2.	Acid-Clay Process	6
3.	KTI Vacuum Distillation and Hydrofinishing Process	7
4.	Recyclon Process.	8
5.	Demetallization Section of the Phillips Process	10
6.	Hydrotreating Section of the Phillips Process	11
7.	Waste Oil Categorization	18
8.	Compliance with Generator Regulations.	20
9.	Compliance with Processor Regulations.	21
10.	Compliance with Marketer Regulations	22
11.	Compliance with Burner Regulations	23
12.	Production of Paraffinic Base Oils.	26
13.	Production of Naphthenic Base Oils	27
14.	Drawing of Tubing Bomb Micro-Reactor	36
15.	Agitation Assembly for TBMR	37
16.	Diagram of Filtration Apparatus	39
17.	Drawing of Distillation Unit	40
18.	Cross-Sectional View of the Autoclave	41
19.	Schematic Diagram for the Autoclave Reaction System	42

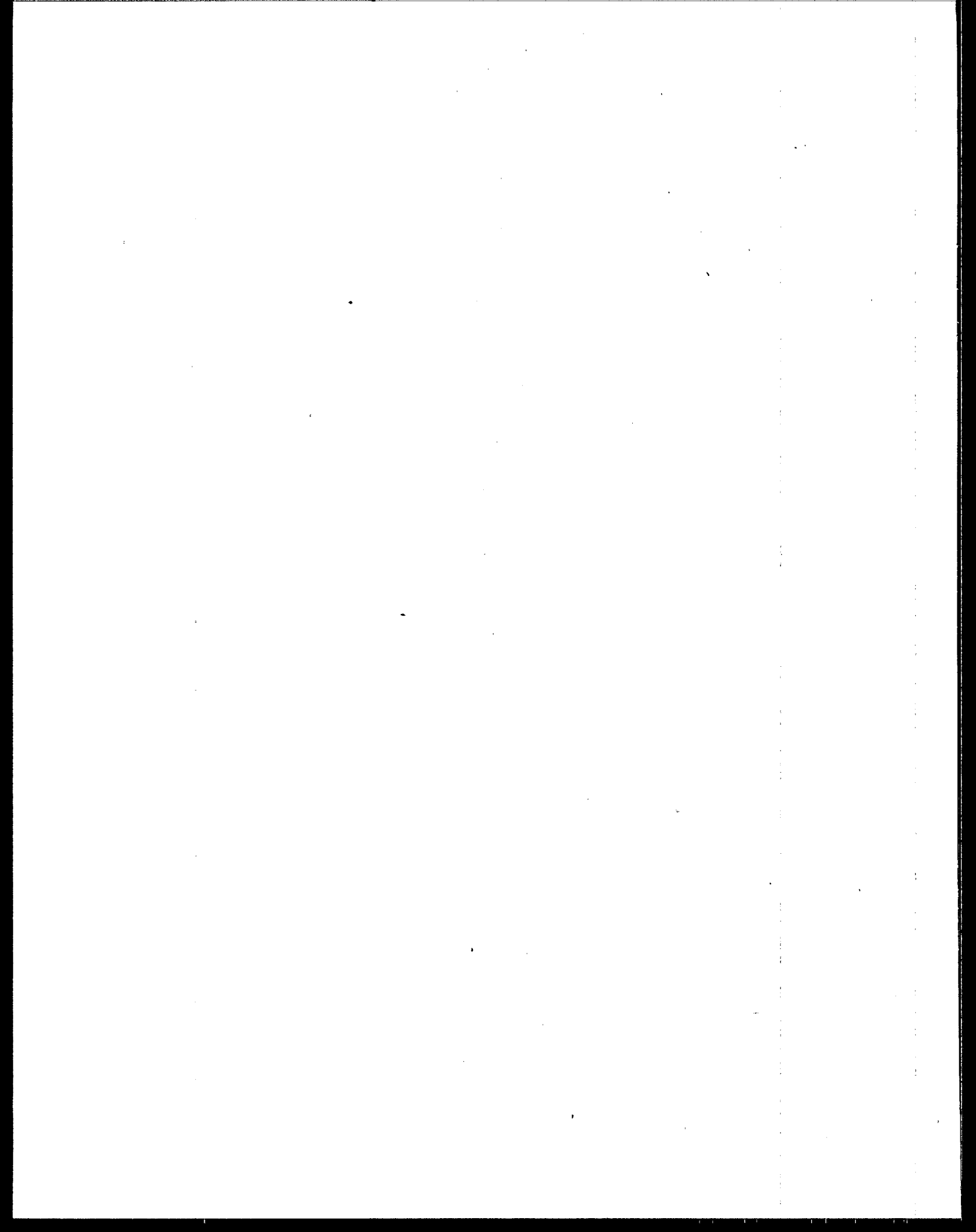


LIST OF FIGURES (CONTINUED)

20.	Three-Neck Flask Reactor	43
21.	Effect of Reaction Time on Lead Reduction.	61
22.	Effect of Reaction Temperature on Lead Reduction	64
23.	Effect of Reaction Temperature on Lead Reduction (1 Hour)	66
24.	Effect of Ash Content on Lead Reduction.	68
25.	Effect of Reaction Temperature on Lead Reduction.	74
26.	Effect of Residence Time on Lead Reduction.	75
27.	Proposed Mechanisms for Additive Metal and Lead Removal	76
28.	Effect of Settling Temperature on Oil Recovery	87
29.	Effect of Settling Time on Oil Recovery.	88
30.	Proposed Mechanisms for Metal Removal	90
31.	Flow Sheet for Waste Oil Recovery Pilot Plant.	95
32.	Flow Sheet for Demetallization Section	96
33.	Lamella Clarifier	97
34.	Solid Sludge and Wastewater Pretreatment System	99
35.	Project Organization Chart	103
A-1.	Lead Analysis Procedure	109
A-2.	Ash Analysis Procedure	110
A-3.	AA Calibration Procedure.	111

LIST OF FIGURES (CONTINUED)

B-1.	Location of Sampling Forts	119
B-2.	Location of Traverse Points.	119



SECTION I INTRODUCTION

In the United States, automotive and other industrial sources generate about 1.2 billion gallons of used oil each year. These figures, although less than 1% of the nation's petroleum consumption, are substantial and create a significant problem in the area of waste oil recovery both for conservation of resources and for the protection of the environment.

The major sources of waste oil recycling are automotive and industrial lubricating oil, which account for 46% of waste oil generation as shown in Figure 1. Only a small amount of used oil is rerefined for its original use, while the rest is reprocessed as a fuel. The rerefining industry has experienced a recent decline for both technical and economic reasons. For instance, lubricating oils have become more complex with the blending of 15 to 20 chemical additives, and rerefined lube oil markets have suffered somewhat from the controversy over whether the quality meets current-day specifications. Also, extended drain periods have concentrated additives and impurities in waste oil, making it more difficult to rerefine; collection costs have increased; and disposal of the sludge by-product has become more difficult and expensive. Further uncertainty regarding classification of used oil as hazardous or nonhazardous wastes has placed oil recyclers, transporters, service stations and other companies that handled used oil into a dilemma.

Waste oils are in some respects superior for lube manufacture compared with crude oil. They are generally rich in lubricating oil (65-80%), compared to 10-17% from most crude oils used in lube manufacture.^{1,2} Also, less than 30% of waste oil is rejected as residue, compared with 45-65% rejected in regular lube manufacture. Waste oil, although contaminated, has a high energy value, between 15,000 to 20,000 BTU/lb., and burning it as a fuel is a major outlet for used oil. Burning offers an efficient and inexpensive alternative to dumping, land spreading, road oiling or incineration. Unfortunately, used oil contains high concentrations of metallic contaminants, and combustion of the oil without removing these contaminants can cause adverse environmental effects. From the public health point of view, lead is the most significant contaminant. If all waste oil was disposed by burning, the EPA estimates that this would account for as much as 5% or even 10% of all atmospheric lead. However, amounts have substantially decreased in recent years due to the elimination of leaded gasoline. Due to the toxicity of heavy metals, the use of recycled oil as a fuel is subject to certain regulations, unless the fuel meets a specification for toxic contaminants and the flash point is exempt from regulation.

One major obstacle to the reuse of used oil in many applications is the presence of various ash-forming impurities that remain dispersed in the oil due to the very effective dispersant characteristics of the additives in a modern-day lubricant system. Materials contained in a typical sample of used oil that are considered to contribute to the ash content of the oil include sub-micron size carbon particles, metal

WASTE OIL GENERATION

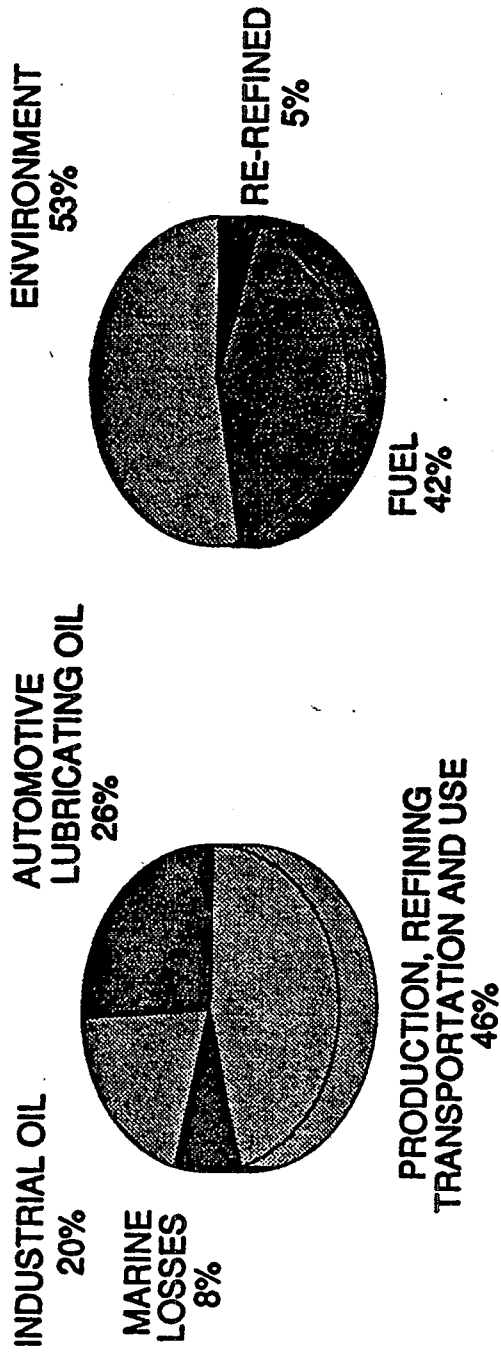


Figure 1. Waste Oil Generation and Disposal.

particles, inorganic materials such as atmospheric dust, and lead and other metal compounds originating from fuel combustion.³ In addition to lead, appreciable amounts of zinc, barium, calcium, magnesium, phosphorous and iron are generally present in used motor oil. Examination with an optical microscope reveals that the particle size of the particulates ranges between 0.1 and 1 microns with no sign of agglomeration.⁴

A number of rerefining processes have been used in the past. The major processes used for waste oil recycling are: (1) acid-clay treatment and (2) solvent extraction-distillation.

The acid-clay treatment produces a rather large amount of acidic sludge, which could pose a larger pollution problem than that caused by used oil. A relatively low process yield (50-60%) and almost intractable residue problems have resulted in a firm recommendation against its use by the rerefining industry. Solvent extraction requires a large ratio of solvent to oil, and metal contaminants still remain present after treatment due to the high dispersant characteristics of additive compounds. Solvent extraction and distillation is mainly used for rerefining due to the high cost of the treatment.

In principle, many methods could be employed for removing the contaminants, but economic considerations frequently dictate using chemical treatment as a viable alternative in producing fuel oils. Although demulsifiers, flocculating aids, contaminant oxidizer and conditioning reagents (caustics) are available commercially, chemical treatment of waste oils has not yet been demonstrated on a large scale. However, low capital and operating costs, high product yields, potentially wide application, low energy treatments and especially low residue production make chemical treatment an attractive choice for waste oil processing facilities involved in fuel oil production.

After reviewing the literature on existing processes, it seems that chemical treatment is a viable and more suitable technology for converting waste oils into EPA specification grade fuel oil (see Chapter 2). Under a contract from the Department of Defense (DoD), work was initiated by the Chemical Engineering Department at Auburn University to develop related technology for fuel oil production. DoD is particularly concerned with the development and utilization of this technology because it is one of the largest generators of waste oils (and may be the largest) in the United States.

A process objective was to dehydrate the feed waste oil, reduce its total ash content (0.1 wt%), and remove impurities (such as sludge, carbon particles, acids, etc.) present in used oil, so it can be burned as a fuel without harming the environment. Moreover, through further upgrading techniques, the treated oil can be reprocessed to produce a high-quality lubricating oil. The project was to be focused on simple, high product yielding, low capital intensive, and efficient processing methods.

To achieve these goals, the project was divided into three major tasks:

Task 1: Demetallization and removal of impurities from waste oil by chemical treatment.

Task 2: Design and development of a pilot scale plant based on the bench-scale results obtained from Task 1.

SECTION II LITERATURE REVIEW

As previously mentioned, the waste oil rerefining industry has suffered a sharp decline in activity over the past few years. There are presently fewer than 10 rerefining firms and about 250 fuel processors in the U.S. Many of the fuel processors once made lubricants from waste oil, but have since ceased because it costs more to produce lubricants than to simply clean the used oil to use as industrial fuel. Among the major problems faced by the industry are:

- (1) rising costs in collection and purchase of used oil;
- (2) the growing complexity of additives blended with lube oils, thus making removal more expensive;
- (3) existing rerefining technology resulting in hazardous wastes, the disposal of which is an expensive undertaking as well as a threat to the environment; and
- (4) uncertainty regarding classification of used oil.

The purpose of this chapter is to review the existing recovery processes and discuss the merits and limitation of commercial processes. The second part of this chapter deals with classification of used oil, which is a determining factor in the future growth of the waste oil industry.

RECOVERY PROCESSES

There are a large number of physical and chemical processes which have been developed for reclamation of industrial and automotive lubricants. Some of these processes are directed toward upgrading the oil slightly for use in the same machines, while other processes are very complicated and produce a whole range of petroleum products.

The processing of crankcase oils from diesel and gasoline engines has developed over the years from simple settling, filtration and dehydration processes into complicated petrochemical-type processes producing a multiple product line. Because of the complexity of crankcase oils, their renovation and separation generally is more complicated. There are many proprietary processes available for waste oil

recycling, but the major commercial processes generally fall into three categories: (1) acid-clay treatment, (2) solvent extraction-distillation, and (3) chemical deashing hydrotreatment.

Acid-Clay Treatment

The acid-clay process dominated the rerefining industry during the 1960s. A flow sheet for the traditional acid-clay process is shown in Figure 2.

In this procedure, waste oil is dehydrated and stripped of light fractions prior to acid treatment. Dry oil is reacted with 4-6 percent of 93% sulfuric acid in the reactor at 100°F. Although fresh acid is generally used, several rerefiners use spent alkylation acid from petroleum refineries. The acid sludge, containing oil contaminants and ash, separates from the oil and is drawn off from the reactor bottom.

The acid-treated dehydrated oil is then transferred to the steam-stripping/clay-treating operations, in which the temperature raised from 550-660°F. The stripping operation removes the remaining light fuel fractions and odorous compounds which may be present.

The clay, often a 50% mixture of activated clay and diatomaceous earth, is mixed into the oil, where it removes color bodies and colloidal carbon by adsorption. The clay dose should be approximately 0.4 lb/gallon of oil. The hot oil containing the clay is filtered through a plate and frame filter press. The filter cake, a mixture of clay, impurities, and oil, is then discarded by landfill.

Acid-clay treatment is not a mild treatment, as evidenced by product yields of only 45 to 60% (6). It also generates a very large amount of acid sludge, which can be difficult to dispose. Odors can be a problem with acid-clay rerefining. However, metals were effectively removed by the treatment. Acid-clay treatment has become obsolete in the rerefining industry due to the low yield and disposal problems of by-products acidic sludge.

Solvent Extraction-Distillation

Distillation as a tool for rerefining used crankcase oil is not an innovative approach. In Europe, Kinetics Technology International (KTI) has developed the process based on distillation and hydrofinishing.

In the KTI process, distillation removes water and gasoline. Vacuum distillation produces an overhead in the lube oil range and a heavy residue containing metals, polymerization products and asphaltenes. The process diagram is shown in Figure 3.⁵ KTI uses the refinishing process developed by Gulf Science and Technology Company to improve the color and odor of the overheads. The lube oil is mixed with a hydrogen-rich gas, heated and passed through a reactor holding a fixed catalyst bed. To obtain a product with the right specifications, the treated oil is either stripped with steam or fractionated into different lube cuts and then dried in a vacuum column.

Another commercial distillation process, the Recyclon process, uses sodium to remove oil contaminants from waste oils. The process flow diagram of the Recyclon process is shown in Figure 4.⁶ Waste oils are first distilled to remove water and light ends. Sodium particles from 5 to 15 micrometers

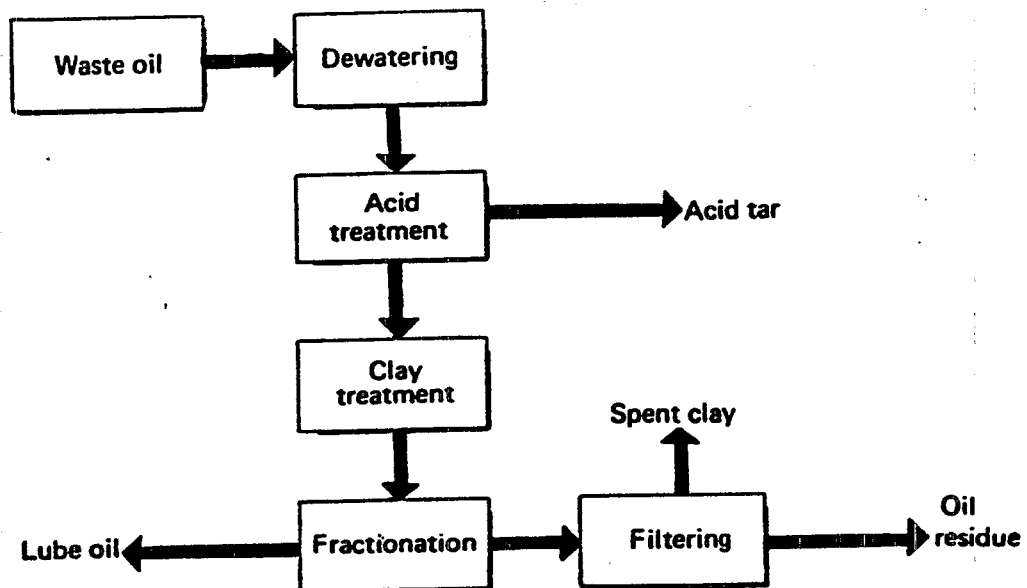


Figure 2. Acid-Clay Process.

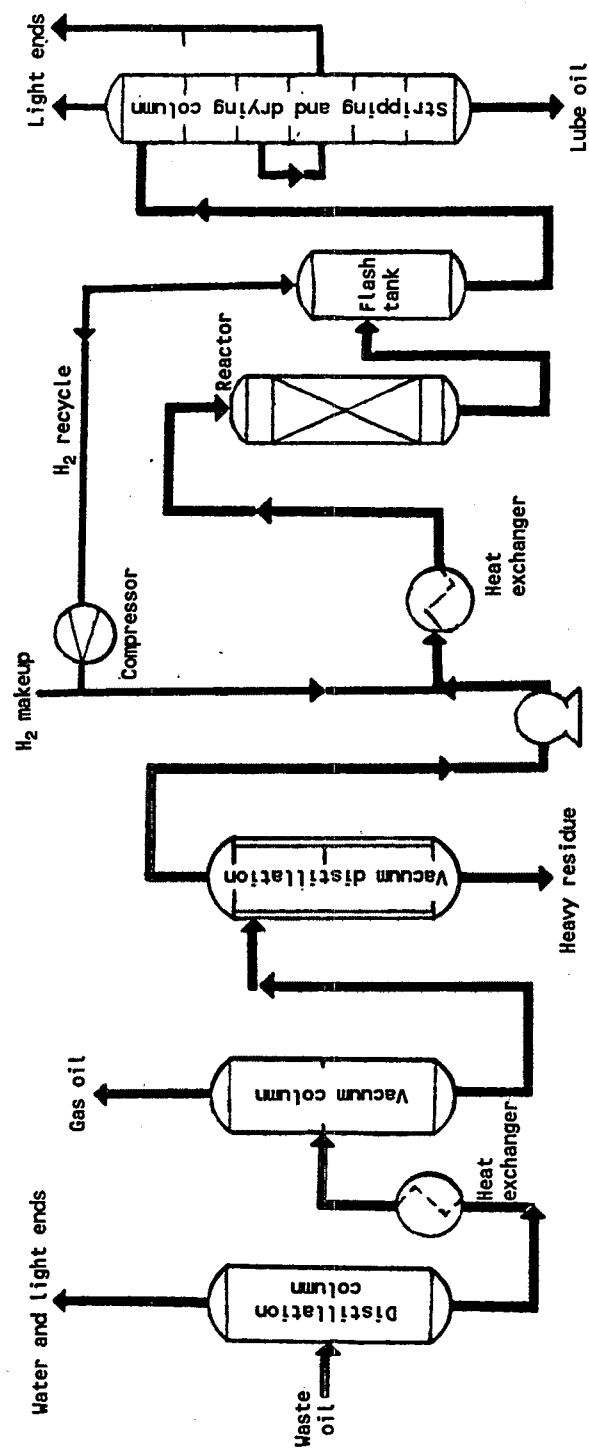


Figure 3. KTI Vacuum Distillation and Hydrotreating Process.

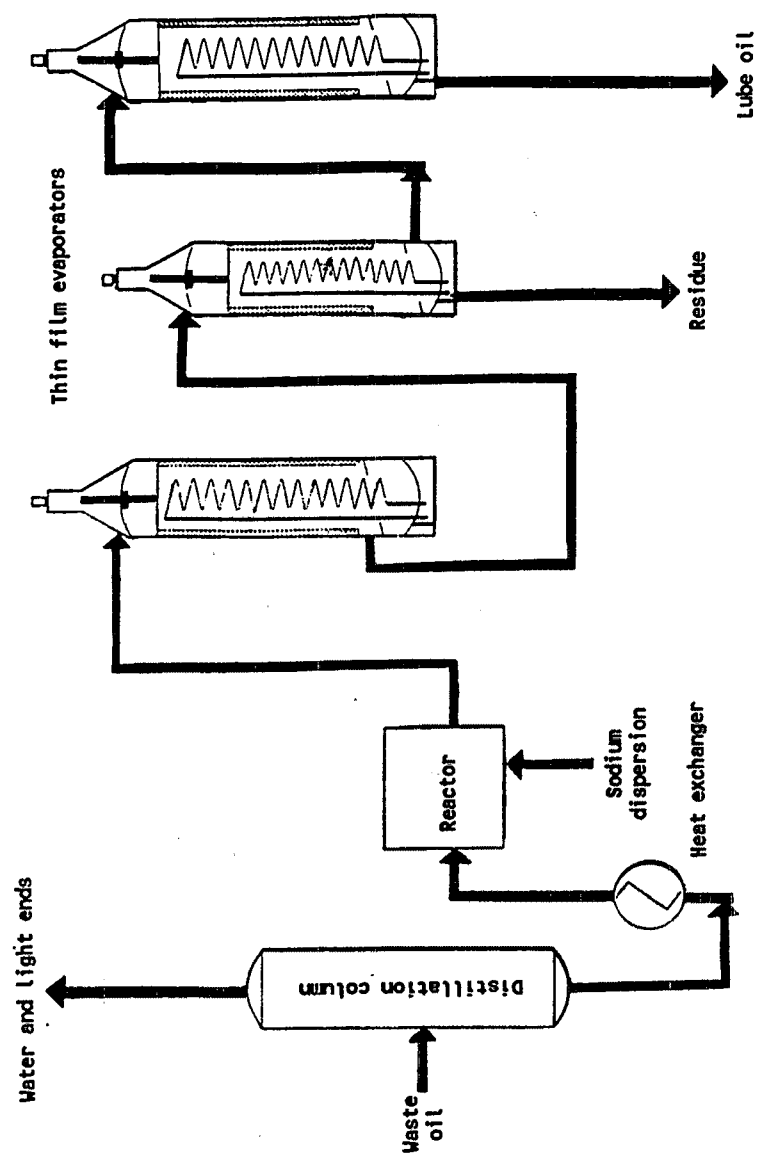


Figure 4. Recyclon Process.

in size are then dispersed into the dry oil in amounts less than 1 wt.% of oil. Typical reactions which occur in the oil are: polymerization of unsaturated olefins, conversion of halogen compounds to sodium salts, and conversion of mercaptans into materials that remain in the residue. Next, low-boiling compounds are flashed in thin-film evaporators at a pressure lower than 1 millibar. The Recyclon process yields over 70% rerefined lubricating oil, while the rest is fuel.

Although distillation of used oil appeared more effective than any other treatment in reducing contaminants, the oil in the distillation bottoms forms a gelatinous mass with considerable cracking. Without pretreatment, distillation is slow, and excessive distillate must be left to keep the residue fluid. This produces undesirable hydrocarbon compositional changes selectively removing di- and polyaromatics as well as polar materials that are required for good lubricity and oxidation stability.⁷

Coking and fouling problems encountered with direct distillation of used lubricating oils indicate the need for a pretreatment step in rerefining processes which employ distillation. A number of solvents have been used to pretreat waste oil before the distillation; examples of solvents used in rerefining processes include hydrocarbon as propane⁸; alcohol as butanol,⁹ isopropanol,¹⁰ and tetrahydrofurfuryl alcohol¹¹; and ketone as methylethyl ketone¹². A systematic, detailed study of pretreatment by solvent precipitation was reported by the Bartlesville Energy Technology Center in Oklahoma.^{13,14,15,16} Out of 64 tested solvents, the optimum system was determined to be a mixture of 2-propanol, 1-butanol, and methylethyl ketone in a ratio of 1:2:1 by volume. The pretreatment step removes coking and fouling compounds; the resulting sludge is separated from the oil/solvent mixture in enclosed vertical solid-bowl centrifuges. The solvent pretreatment, performed in conjunction with dehydration, distillation, and a finishing process, produces a high-quality lube oil. It was reported that more than 99.5% of the solvent can be recovered from the process.

Among the disadvantages of the BERC process are: (1) the pretreatment requirement is energy consuming, and (2) the lack of definitive full-scale demonstration plant data, which could be made available to potential licensees of the process.

Chemical De-Ashing-Hydrotreatment Process

The Phillips Rerefined Oil Process (trademarked PROP) is a recent, innovative development.^{17,18,19} This process uses a new method of waste oil demetallization in which oil is reacted with a slurry of diammonium phosphate. Since the reaction conditions are base in pH, metal reaction vessels may be used, and the metals in the oil react to form insoluble metal phosphates rather than the acidic sludges that form in some other rerefining processes.

Another innovation offered by the Phillips process is the low volume of hazardous by-products produced. By-products of the process include kerosene, spent clay and charcoal, a filter cake, spent caustic, spent catalyst and off gases. The metals contained in the filter cake, clay, and charcoal after use are bound in an inert form. PROP also offers up to an 80% recovery, as usable rerefined oil, of the oil actually present in the waste oil feedstock.

The PROP plant consists of two sections: (i) the demetallization section and (ii) the hydrotreating section. Figures 5 and 6 show a schematic of the PROP plant. The demetallization section of the PROP

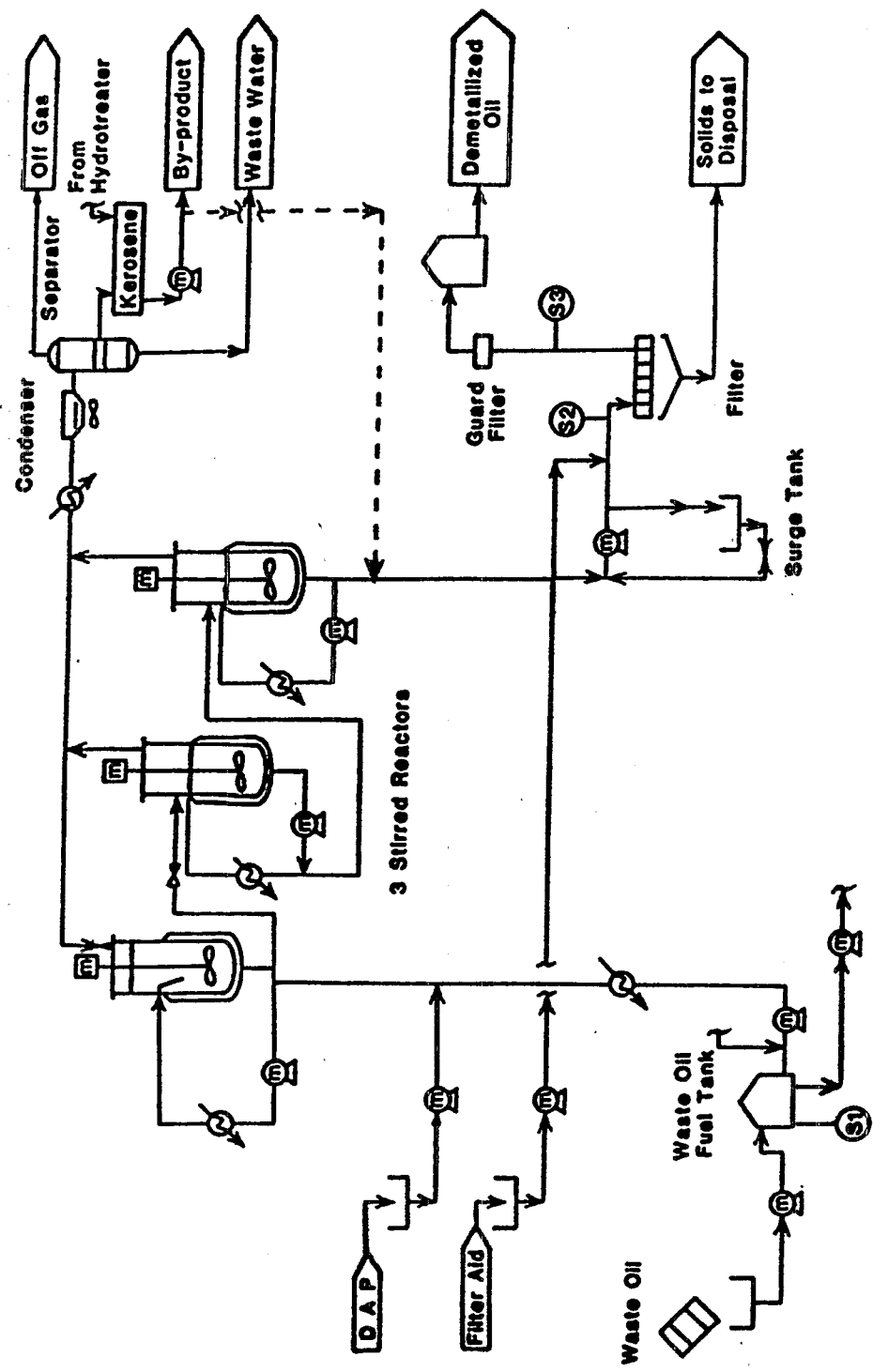


Figure 5. Demetallization Section of the Phillips Process.

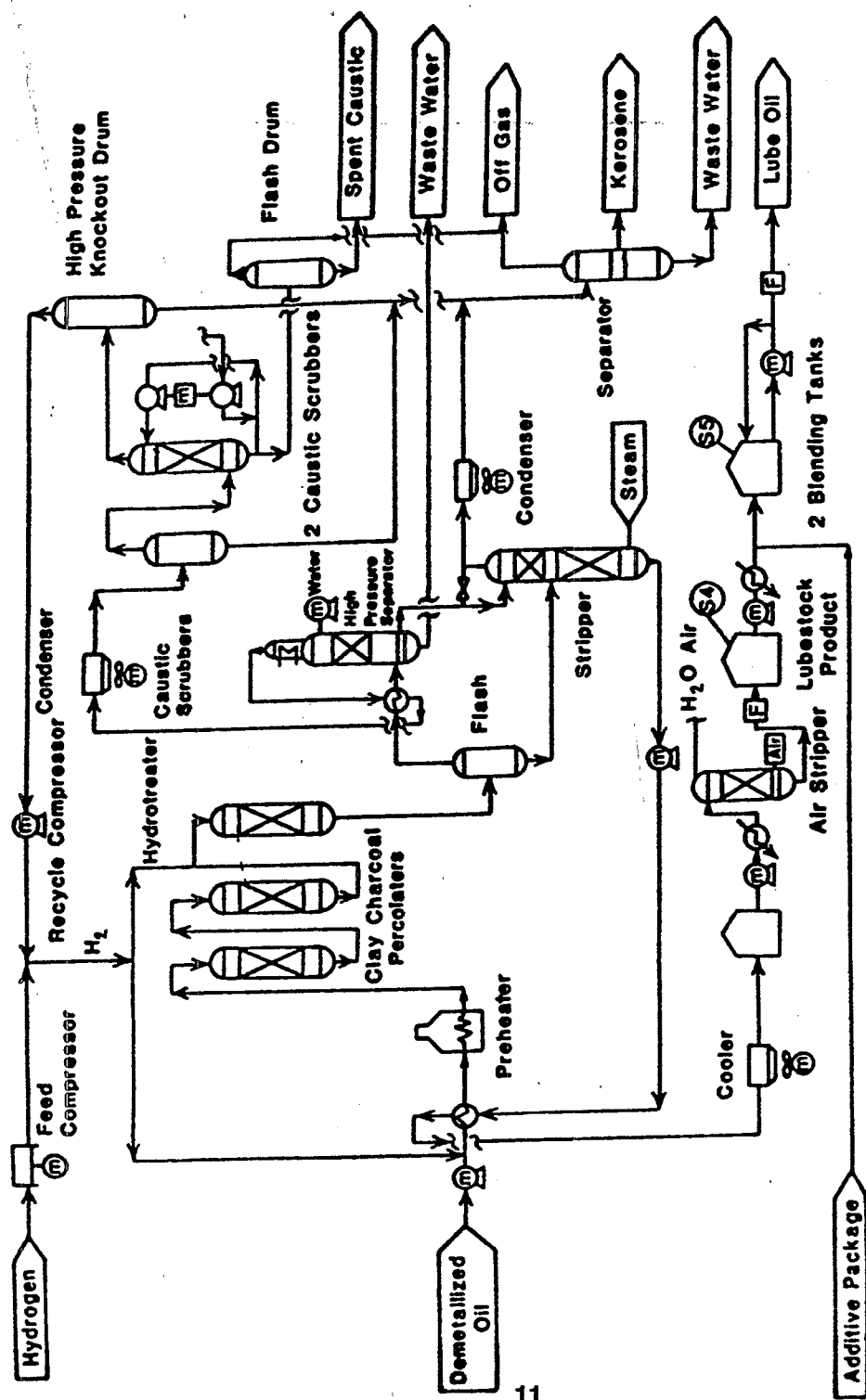


Figure 6. Hydrotreating Section of the Phillips Process.

plant consists of three stirred tank reactors in a series and a filtration step. Each reactor has a slightly different function and operates at a different temperature. Reactor No. 1 operates at 210°F; the waste oil feedstock and the diammonium phosphate are mixed and the reaction begins here. In reactor No. 2, which operates at 225°F, demetallization continues while the higher temperature distills most of the water and some of the lighter hydrocarbons found in the oil. The third reactor operates at 310°F; at this elevated temperature, ammonium salts of organic acids formed in the diammonium reaction begin to break down into ammonium and organic acids. Also, the remaining water and light ends are removed in this reactor. After the oil passes through the third unit, it is filtered through diatomaceous earth. The filtration step removes the metal phosphates formed in the reaction as well as any remaining large particulates.

The demetallized oil is then percolated through a series of two clay beds and one charcoal bed. The remaining ammonium salts of sulfuric and phosphoric acids formed in the demetallization step are broken down in the beds. Ashless detergents (containing no metals) are also broken down in the clay and charcoal beds. Tetra-ethyllead, present in the oil due to contamination with gasoline, is broken down and removed by the beds. This not only serves as a final step in the demetallization process but also protects the hydrotreating catalyst from being poisoned by heavy metal contaminants.

Hydrotreatment of the demetallized oil is the next step. The hydrotreatment occurs at 670°F and 615 psig pressure. Reaction of the oil with hydrogen removes the remaining (nonmetal) portion of the oil additives. Compounds containing Cl, S, O, and N are converted to analogous hydrocarbons and HCl, H₂S, H₂O, and NH₃, respectively. A series of strippers and scrubbers remove these product gases from the hydrogen stream, which is then recycled.

After hydrotreatment and removal of unwanted reaction products, the oil is blended with fresh additives to create a 30-weight motor oil. This oil meets or exceeds all applicable API and SAE standards.

Among the major disadvantages of the PROP process:

- (1) filtration is very slow and cumbersome to operate;
- (2) the process is energy intensive; and
- (3) large amounts of solid waste are generated.

In summary, current commercial waste oil reclaiming processes utilize many of the following basic steps:

- (1) Removal of water and solid particles by settling.
- (2) Solvent pretreatment to remove gums, grease, sludge, asphaltenes, etc.
- (3) Alkaline treatment to neutralize acid.
- (4) Clay contacting to bleach the oil and adsorb impurities.
- (5) Stripping to drive off moisture and volatile oils.
- (6) Filtering to remove clay and other solids.
- (7) Hydrotreatment to improve the oxidation stability of lubricating oil.
- (8) Blending to specification.

In view of today's environmental concerns, it appears that an economically viable rerefining process is needed which is able to:

- (1) Eliminate or minimize potential by-product pollutants (spent acid, spent caustic, spent clay, SO₂, etc.).
- (2) Produce acceptable products.
- (3) Remain flexible enough to adapt to changing additives and/or environmental considerations.

CLASSIFICATION OF USED OIL

The legislative curb on industrial practices for disposal of hazardous waste has become more stringent in recent years. To understand the existing regulatory compliances, one must comprehend a host of related statutes and environmental policies and programs of the U.S. Congress, as well as state and local governments. A basic understanding of major federal statutes and various state and local regulations is regarded as essential in today's litigious society. Notwithstanding the need for a knowledge of various regulations, the most heated topic of environmental policies and programs centers around hazardous materials.

Congress delivered a strong environmental message in 1976 when it passed the Resource Conservation and Recovery Act (RCRA). The mandates formulated under RCRA affect all manufacturing and business operations that dispose of waste materials on land. Before discussing the regulatory aspects of used oil management, a brief overview of the RCRA is warranted.

Resource Conservation and Recovery Act

Since its enactment in 1976, RCRA has been amended several times. Subtitle C of this act, which deals with hazardous waste, remains the centerpiece of RCRA. EPA regulations define a solid waste as hazardous waste if it exhibits any of the characteristics listed in Table 1.²⁰ Under EPA regulations, certain types of solid wastes (for example, household waste) are not to be considered hazardous wastes.

Besides the four characteristics of hazardous waste given in Table 1, the EPA has also established three hazardous waste lists: hazardous wastes from nonspecific sources (such as spent nonhalogenated solvents), hazardous wastes from specific sources (for example, bottom sediment sludge from the treatment of wastewater from wood preserving), and discarded commercial chemical products and all off-specification species, containers, and spill residues.

The EPA has provided certain regulatory exemptions based on very specific criteria. For example, hazardous waste generated in a product or raw material storage tank or transport vehicle or in manufacturing processes, as well as samples for monitoring and testing purposes, are exempt from regulations. Used oil being recycled also would not be listed as a hazardous waste under RCRA.

TABLE 1. CHARACTERISTICS OF HAZARDOUS WASTES

Ignitability

Any liquid with a flash point of less than 140°F.

Any nonliquid capable of causing fire through friction, absorption of moisture, or spontaneous chemical changes that, when ignited, burns so vigorously and persistently that it creates a hazard.

Any ignitable compressed gas or oxidizer (see DoT transportation regulation 49 CFR 173.30 or 173.151).

Corrosivity

Any aqueous liquid with a pH less than or equal to 2.0 or greater than or equal to 12.5.

Any liquid that corrodes steel at a rate $> 1/4$ in./yr.

Reactivity

Any waste that is normally unstable and readily undergoes violent changes with detonations.

Any waste that reacts violently with water.

Any waste that forms potentially explosive mixtures with water.

Any waste that, when mixed with water, generates toxic gases, vapors, or fumes in a quantity sufficient to present a danger to human health or the environment.

Any waste capable of detonating or undergoing an explosive reaction if it is subjected to a strong initiating sources or heated under confinement.

Any material readily capable of detonation or explosive decomposition or reaction at standard temperature and pressure.

Toxicity

Any waste material whose extract contains any of the contaminants at concentrations equal to or greater than the values given in Table 2. (The extract consists of the liquid component of a solid waste and deionized water at pH 5.0 that has been continuously brought into contact with the solid phase of the waste for a 24-hour period.)

TABLE 2. CONTAMINANTS IN EXTRACT

Contaminant	Max. Concentration (mg/L)
Arsenic	4.0
Barium	100.0
Cadmium	1.0
Chromium	5.0
Lead	5.0
Mercury	0.2
Selenium	1.0
Silver	5.0
Endrin	0.02
Lindan	0.4
Methoxychlor	10.0
Toxaphene (C ₁₀ H ₁₀ Cl ₈ , Technical Chlorinated Camphene, 67-69% Chlorine)	0.5
2,4-D (2,4-Dichlorophenoxyacetic Acid)	10.0
Silvex (2,4-5-Trichlorophenoxypropionic Acid)	1.0

The act specifies that a hazardous waste management program is to be based on the "cradle to grave" concept, so that all hazardous wastes can be traced and fully accounted for. All treatment, storage, and disposal (TSD) facilities are required to satisfy certain minimum recordkeeping requirements. In addition to using a manifest for transporting hazardous waste, the facilities must keep records of vital information about the waste, such as the results of waste analysis, trial tests and inspections, a description and the quantity of each hazardous waste received, and methods and dates of treatment, storage, and disposal.

Under RCRA, the states are authorized to develop and carry out their own hazardous waste programs in lieu of the EPA-administered federal program. Several states have already done so.

Final Rule, Burning of Used Oil

The EPA published its final rule related to a hazardous waste management system (burning of waste fuel and used oil in boilers and industrial furnaces) in the Federal Register on November 29, 1985. These regulations were described in 40 CFR, Parts 261, 264, 265, 266, and 271. On January 11, 1985, the EPA proposed under subtitle C of the RCRA to begin regulation of hazardous waste and off-specification used oil burned for energy recovery in boilers and industrial furnaces. The proposal included administration controls for marketers and burriers of hazardous waste and used oil fuels. The final rule prohibits the marketing and burning in nonindustrial boilers of both hazardous waste fuel and used oil that does not meet specification levels for certain hazardous contaminants and flash point. It also provides administrative controls to record marketing and burning activities; these include notifying the EPA of waste-as-fuel activities and using a manifest, or an invoice system, for shipments and recordkeeping. Also, hazardous waste fuels are subject to storage requirements.

Proposed Rule, Recycled Used Oil Standards

This proposal meets the RCRA requirement for the EPA to provide standards for used oil that is recycled. The standards are proposed for generators and transporters of recycled oil and owners and operators of used oil recycling facilities. This proposal includes tracking requirements when used oil is shipped off-site for recycling. Recycled oil used as fuel would be subject to certain regulations, except that fuel meeting a specification for toxic contaminants and flash point would be exempt from regulation. Uses of recycled oil that constitute disposal would be prohibited completely. The proposal defined used fuel specifications (applying only to used oil that is not mixed with hazardous waste), which are listed in Table 3.

Identification and Listing of Used Oil, Proposed Rule

In this regulation, the EPA announced its determination that used oil being recycled should not be listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA). The EPA intends, however, to issue recycled oil management standards and is conducting studies to determine whether standards are appropriate under Section 3014 of RCRA. The EPA is also conducting certain studies to determine whether used oil being disposed (i.e., not being recycled) should be listed as a RCRA hazardous waste, or whether it should be regulated instead under different statutes.

TABLE 3. SPECIFICATION USED OIL

Constitute/Property	Allowable Level
Arsenic	5 ppm maximum
Cadmium	2 ppm maximum
Chromium	10 ppm maximum
Lead	100 ppm maximum
Flash Point	100°F minimum
Total Halogens	4000 ppm maximum*

* Used oil containing more than 1000 ppm total halogens must be shown not to have been mixed with hazardous waste. This is referred to as the 'rebuttable presumption.'

WASTE OIL CATEGORIZATION

Figure 7 offers a categorization of waste oils. Waste oil containing more than 1,000 ppm of halogens should not be mixed with hazardous waste, otherwise used oil is classified as a hazardous waste. If the energy content of hazardous waste is more than 5,000 BTU/lb., then the waste can be burned as a hazardous waste fuel. Waste oils meeting metals and halogens specifications are classified as specification used oil fuel.

Standards Applicable to Generators, Processors, Marketers, Burners

A detailed listing of the requirements for these various waste oil handlers is given in 40 CFR. Part 262 deals with generators, while parts 264 and 265 deal with processors, marketers, and burners (i.e. TSD

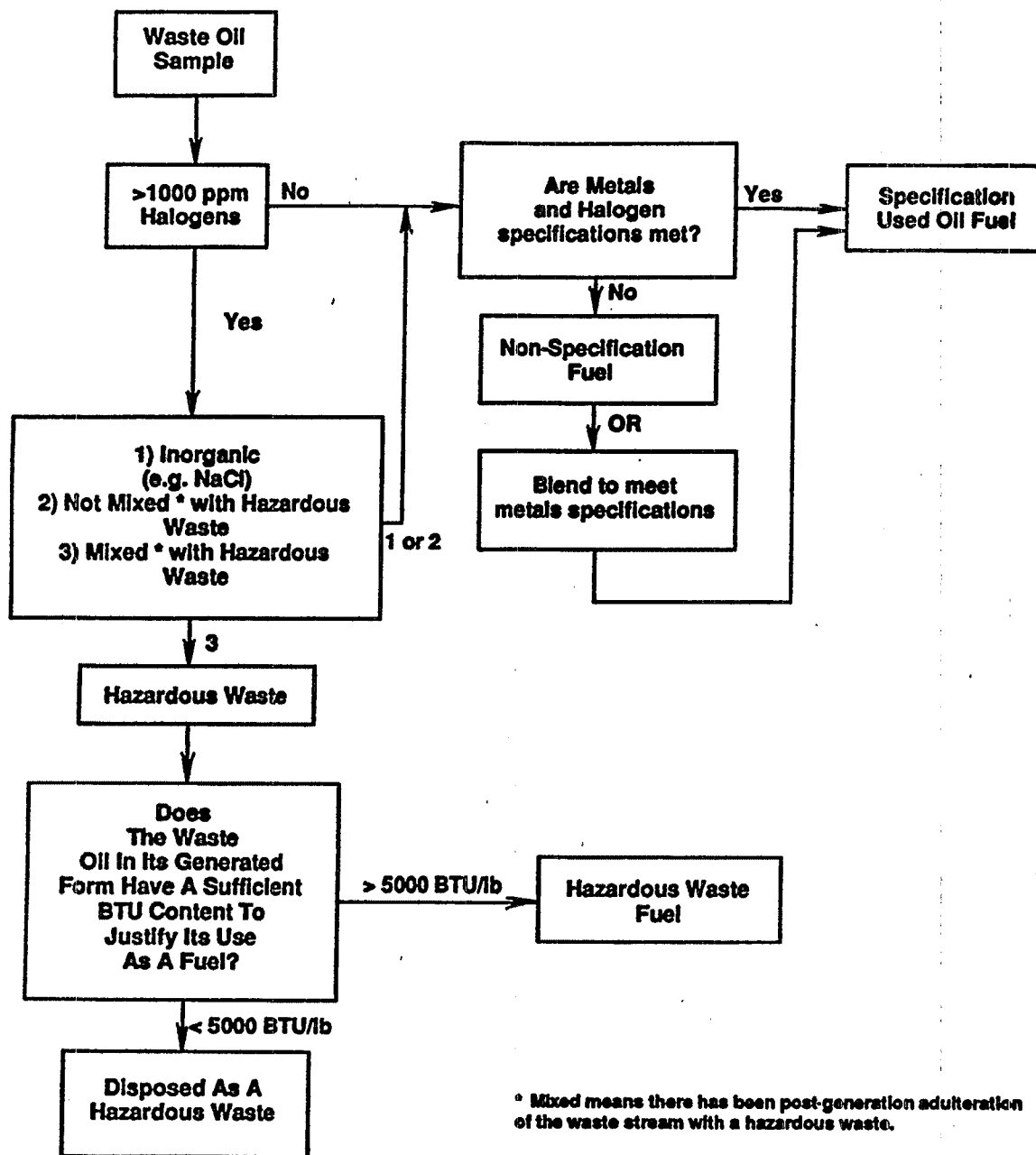


Figure 7. Waste Oil Categorization Decision Tree.

facilities). Figures 8, 9, 10, and 11 schematically depict the various steps to compliance with the regulations for the different waste oil handlers in a systematic form.

Recent Development in Classification of Used Oil

The possibility of hazardous waste classification of oil has loomed larger ever since a recent U.S. Court of Appeals decision. The District of Columbia court overruled a 1986 EPA determination not to classify used oil as a hazardous waste because that stigma would hurt recycling efforts. The court ordered the EPA to decide whether recycled oils meet technical criteria for listing as hazardous wastes and then to treat them accordingly. The agency is now studying how to list oils on the basis of technical requirements.

As a result of a lawsuit, Rep. Ike Skelton and 44 other U.S. House members introduced legislation that would direct EPA to set standards for waste oil recycling and require the agency to not list used oil as a hazardous waste.²¹ Federal agencies would be directed to give preference to lubricants and fuels made from waste oil. The second used-oil bill before Congress is the Consumer Product Recovery Act, also known as the Torres bill. The bill sets management standards for the handling of waste oil by transporters and recyclers. It also seeks to encourage reuse of waste oil through recycling credits. Producers of oil products would be required to ensure that a percentage of their products are recycled. Oil producers could meet that standard by rerefining oil into lubricants or purchasing credits from fuel processors or rerefiners.

Affected by any regulation would be more than 1.2 billion gallons of waste oils generated annually. A concern expressed by many is that hazardous waste classification will discourage service stations and other garages from accepting oil from do-it-yourself (DIY) operators, considered by oil change firms to be a major source of waste crankcase oil in the U.S. The result would be improper disposal of more oil, rather than less. If oil is listed as a hazardous waste, liability insurance would undoubtedly increase, and service station operators would be discouraged from accepting oil from the general public.²² The National Oil Recyclers Association (NORA) opposes a hazardous waste classification. Its position is that categorizing oil as a hazardous waste will hurt the waste oil business and cause many customers to avoid utilizing it.

However, members of the Hazardous Waste Treatment Consul and the Association of Petroleum Rerefiners believe that waste oil should be regulated as a hazardous waste to ensure its proper treatment. They feel that a regulated system discourages illegal mixing or environmentally unsound practices.

With the recycled oil industry divided over the merits of classifying used oil as hazardous, politics may be the deciding factor. If the Skelton bill were passed, handling standards would be raised, but the critical label of "hazardous" would not be applied. If the bill were not passed, the EPA would then judge used oil to be hazardous.²³

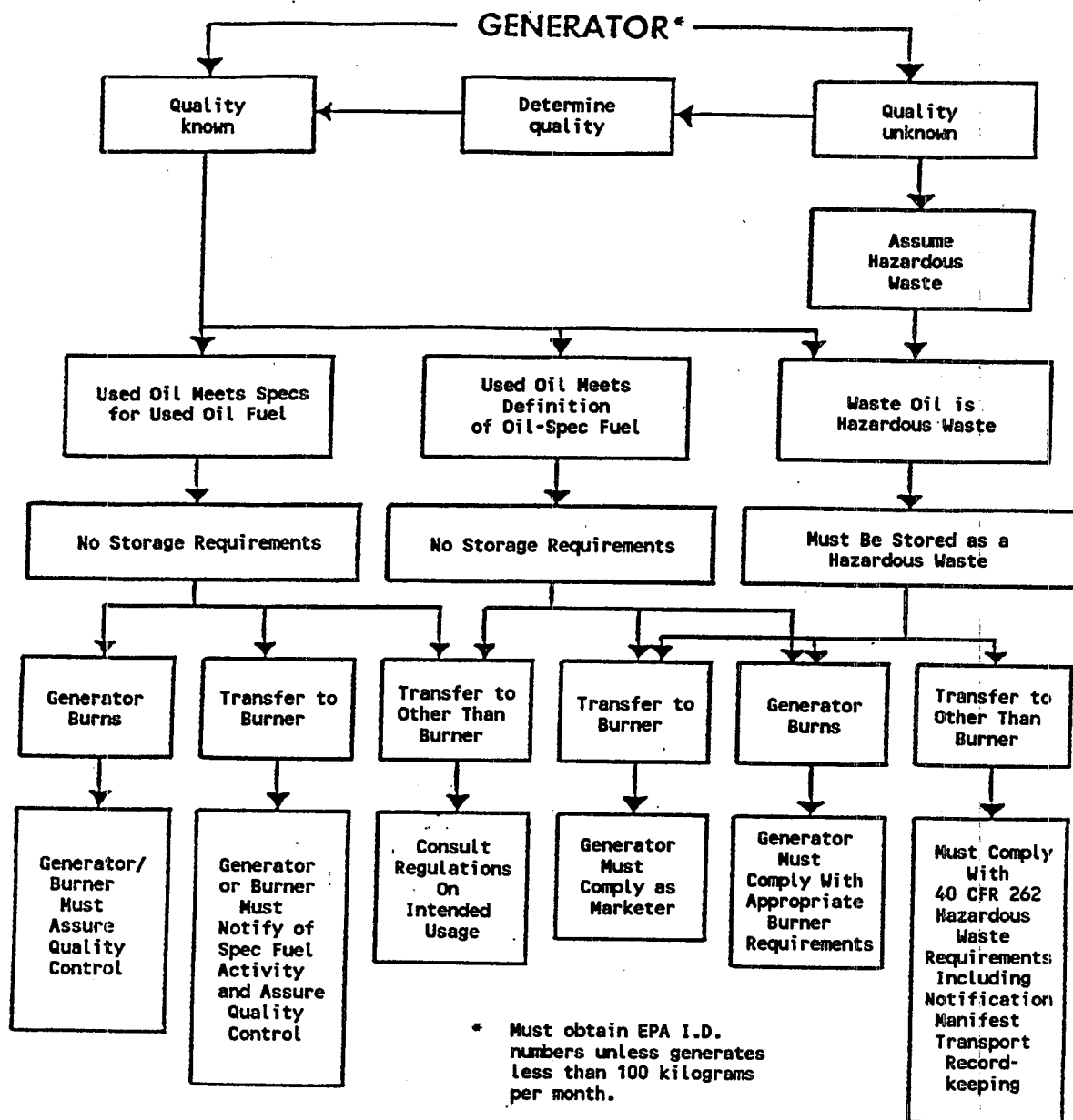


Figure 8. Compliance With Generator Regulations.

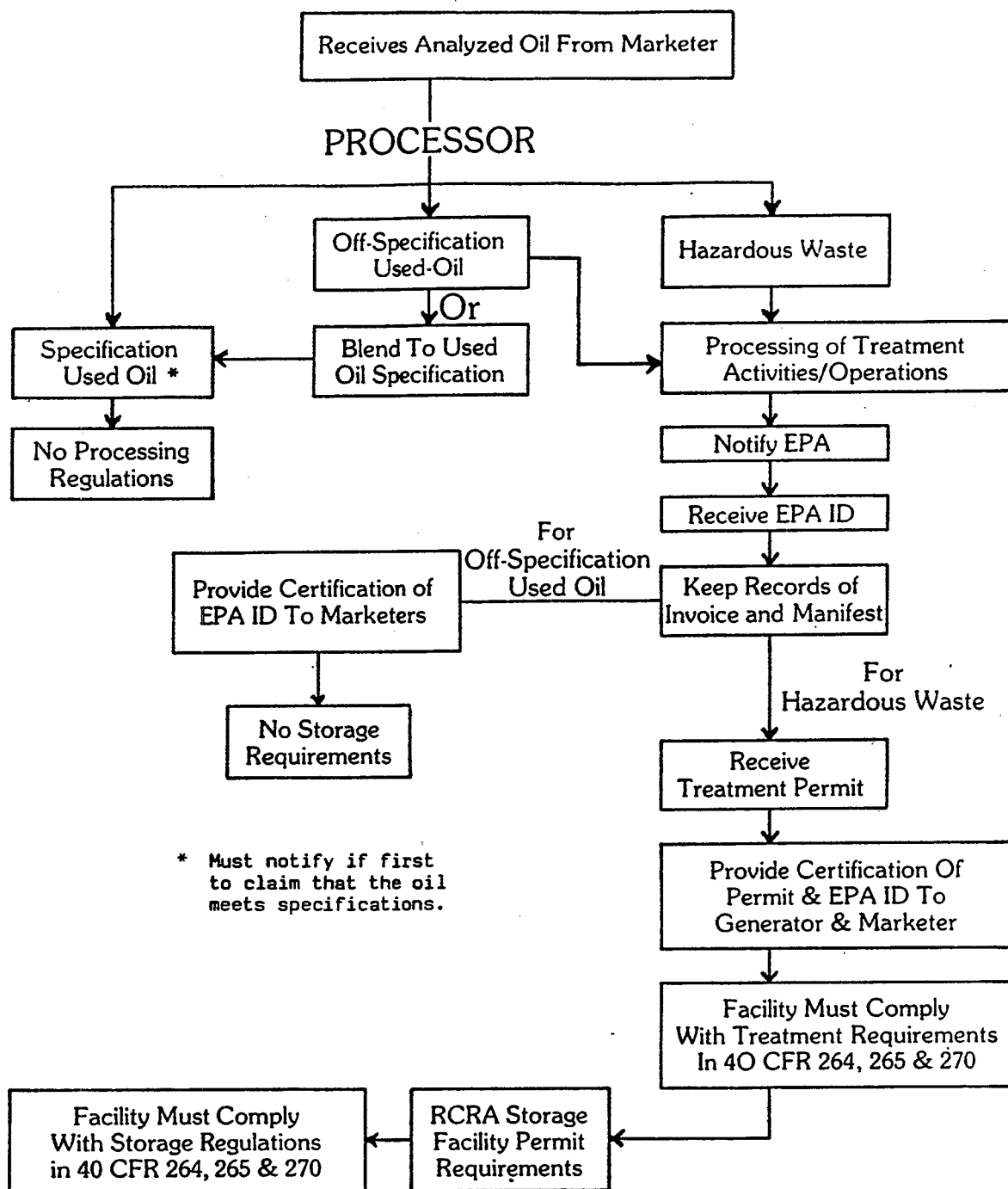


Figure 9. Compliance With Processor Regulations.

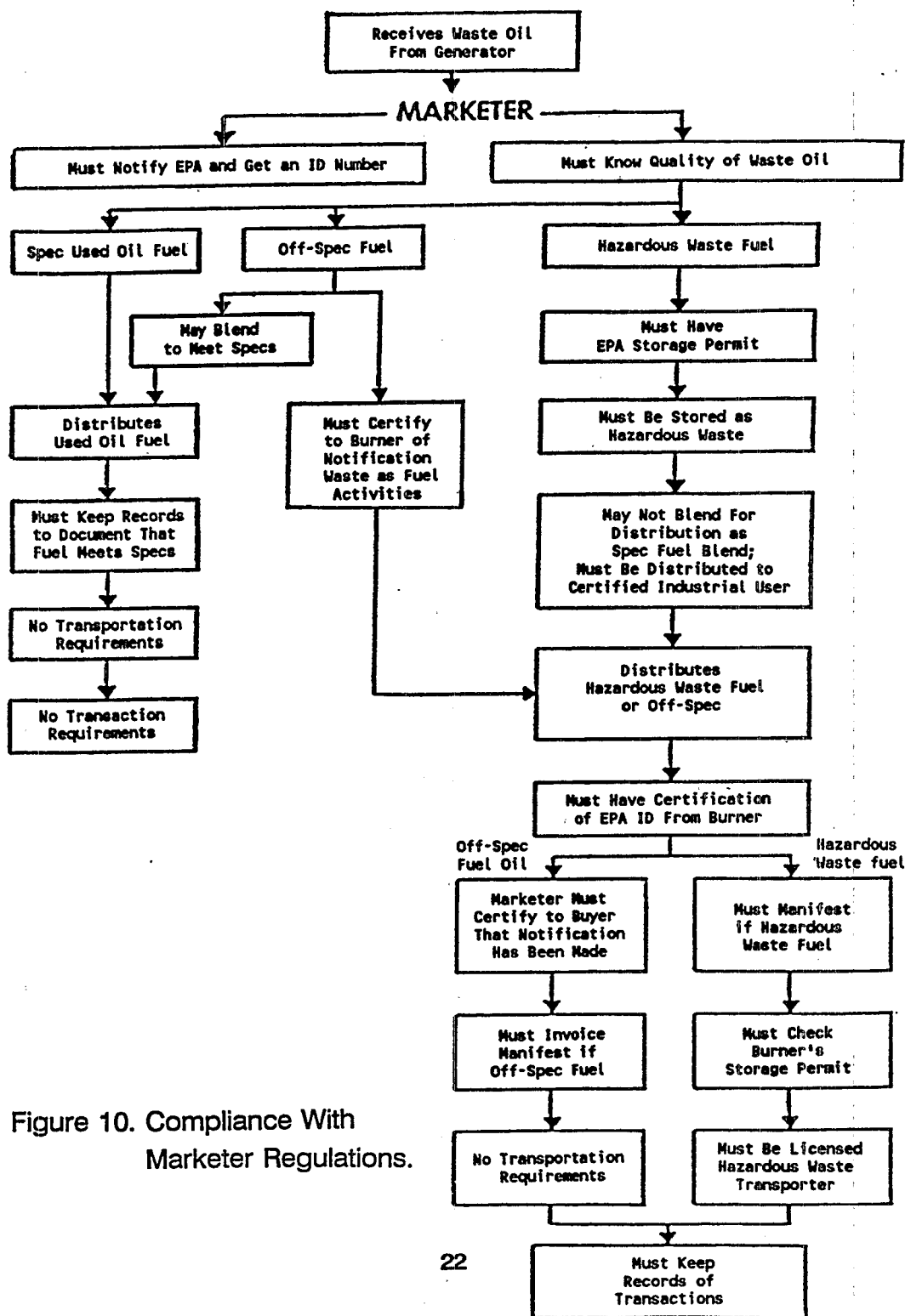


Figure 10. Compliance With Marketer Regulations.

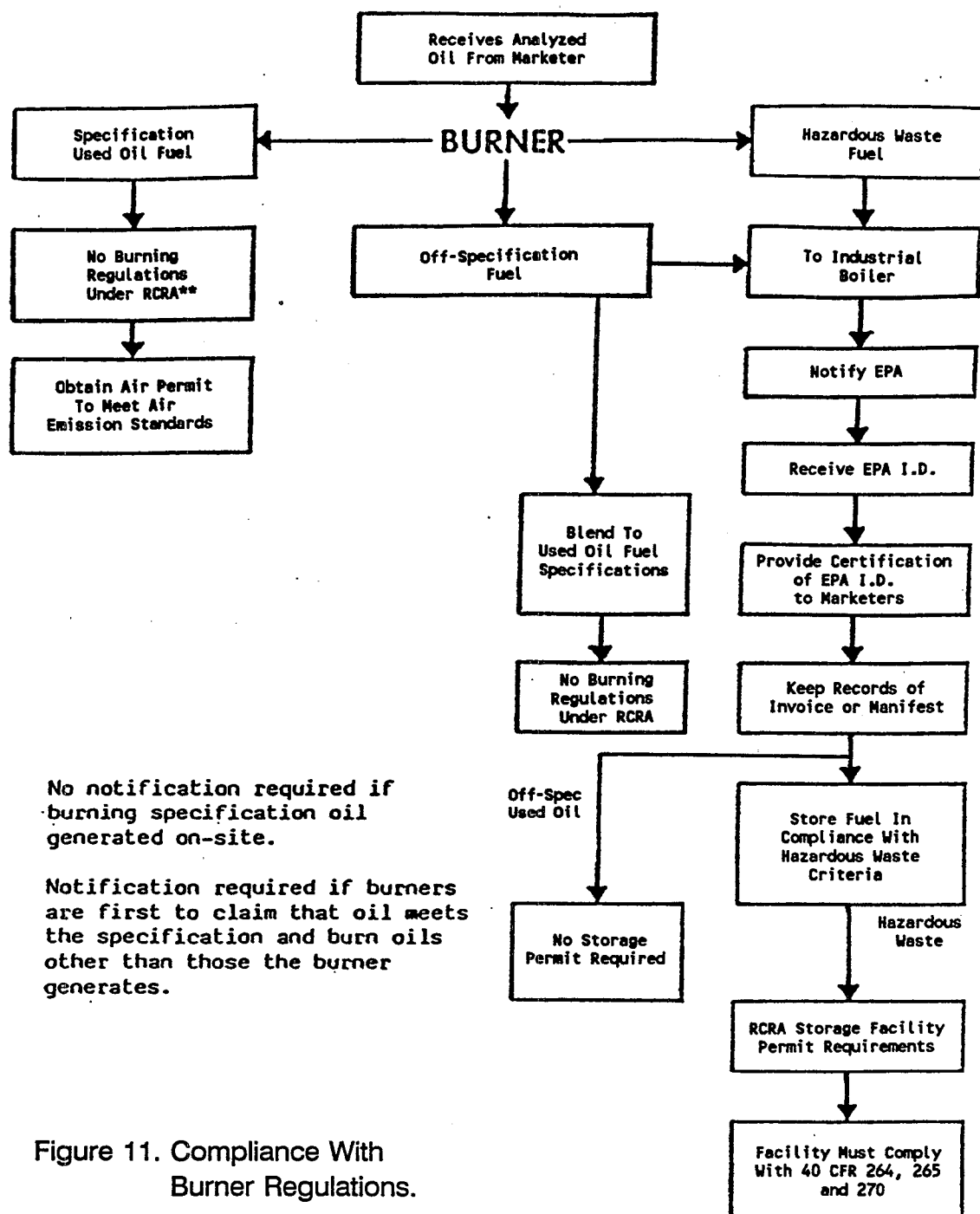


Figure 11. Compliance With Burner Regulations.

SECTION III CHARACTERISTICS OF USED OIL

The characterization of lubricating oils plays an important role in establishing the quality, consistency and additive response of a given oil. Lubricating oil fractions contain the largest and most complex hydrocarbon molecules found in petroleum crudes. These hydrocarbons may contain from 20 to 70 or more carbon atoms per molecule, with corresponding molecular weights of 250 up to 1,000 or more. An idea of their complex structure can be gained from the fact that literally millions of different molecular arrangements of carbon and hydrogen atoms are possible in hydrocarbon molecules of this size.

Many investigators have studied the composition of crudes used as feedstock for lubricating oils, and Georgi has articulately theorized on the general types of hydrocarbon. They are constituted as follows:

(1) Straight Chain Paraffins - These are saturated compounds and are essentially high melting point paraffin waxes which must be removed from paraffinic lubricating oil fractions by dewaxing.

(2) Branched Chain Paraffins - There are two types:

(a) Long parent chains with short side chains - These are probably similar to straight chain paraffins and have high melting or pour points.

(b) Parent chains with long side chains - These possess high viscosity indices, low volatility, optimum stability and adequately low pour points. These are desired constituents in lubricating oil.

(3) Naphthenes - There are also two types of these:

(a) Naphthenes having only a few rings per molecule and an abundance of paraffin chains of considerable length; these have properties similar to 2(b) above and are desirable fractions of lubricating oils.

(b) Naphthenes having a larger number of rings per molecule and/or paraffin side chains of shorter length; these have lower viscosity indices. The desirability of this fraction decreases as the number of carbon atoms in the ring form increases in relation to those in attached paraffin chains.

(4) Aromatics - The unsaturated ring structure of the alkyl-aromatics tends to be readily susceptible to oxidation. Aromatics also tend to have low viscosity indices. Asphalts and resins are

highly condensed aromatics containing numerous fused rings. Aromatics are undesirable in lubricating oils, and refining methods are usually directed toward their removal.

(5) Mixed Aromatic-Naphthene-Paraffin:

(a) Types having only a few aromatic rings combined with a number of naphthene rings and paraffin chains; these are similar, in their general properties, to the straight naphthenes as per 3(a) and (b) above.

(b) Types having more than 2 or 3 aromatic rings and correspondingly fewer naphthenes rings and paraffin chains. These are similar to straight aromatics as per (4) above.²⁴

In addition to the major constituents discussed above, petroleum oils may contain small proportions of olefins as well as nitrogen, oxygen and sulfur compounds.

ORIGIN OF BASE STOCKS

Natural lubricating oils are separated from crude oils to form a group of lubricating oil base stocks. By blending different additives with these base stocks, finished lubricating oils are formed. The preparation of these base stocks from crude oil is a complex and expensive procedure, and also depends on the nature of the crude oil.

The first step in the production of lube oil base stocks is the vacuum distillation of crude oil. The heavy oil resulting from vacuum distillation bottoms can be treated to remove asphaltic materials by two major commercial processes, propane deasphalting and Duo Sol.^{25,26} Most modern plants use the former. Base stocks which have been propane deasphalted are commonly referred to as bright stocks. Figure 12 shows the different processing steps for lube oil base stock formation for paraffinic base oils. Both solvent extraction and dewaxing are necessary when processing paraffinic oil only. The primary purpose of these steps is to improve the viscosity-temperature characteristics, as well as the oxidative and thermal stability of the base stocks. A finishing step is frequently required to remove trace contaminants and to improve color and the oxidative and thermal stability of base stocks. Most refineries use hydrotreatment as a finishing step on a continuous basis.

Naphthenic base oils are derived from special naphthenic crudes and require less processing than paraffinic oils. Figure 13 shows a typical process scheme used to produce naphthenic base oils. The principal advantages of naphthenic base oils are their low production costs and their naturally occurring low pour points, while their disadvantages include poor oxidative stability and rapid increases in viscosities at low temperature.

Naphthenic oils usually can be identified by their low API gravity and their low viscosity index. Naphthenic base oil can be used to make motor oil, but the majority is used in formulating rubber process oils, refrigeration oils, shock absorber fluids, etc. The production of paraffinic stocks is expected to increase, while the production of naphthenic oils is declining. By understanding what oils use naphthenic and paraffinic base oil, a refiner can control his feedstock to ensure a high quality finished product.

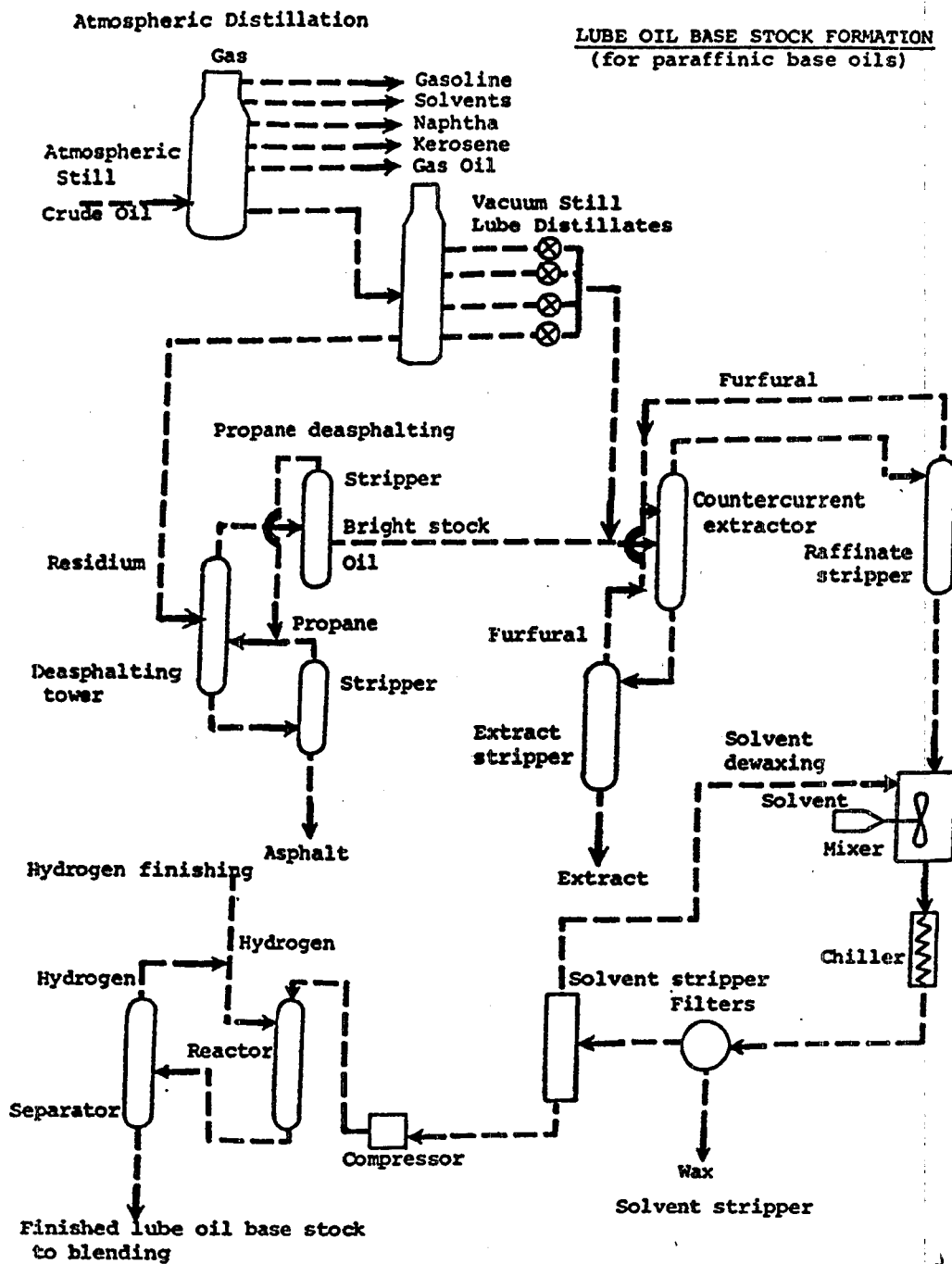


Figure 12. Production of Paraffinic Base Oils.

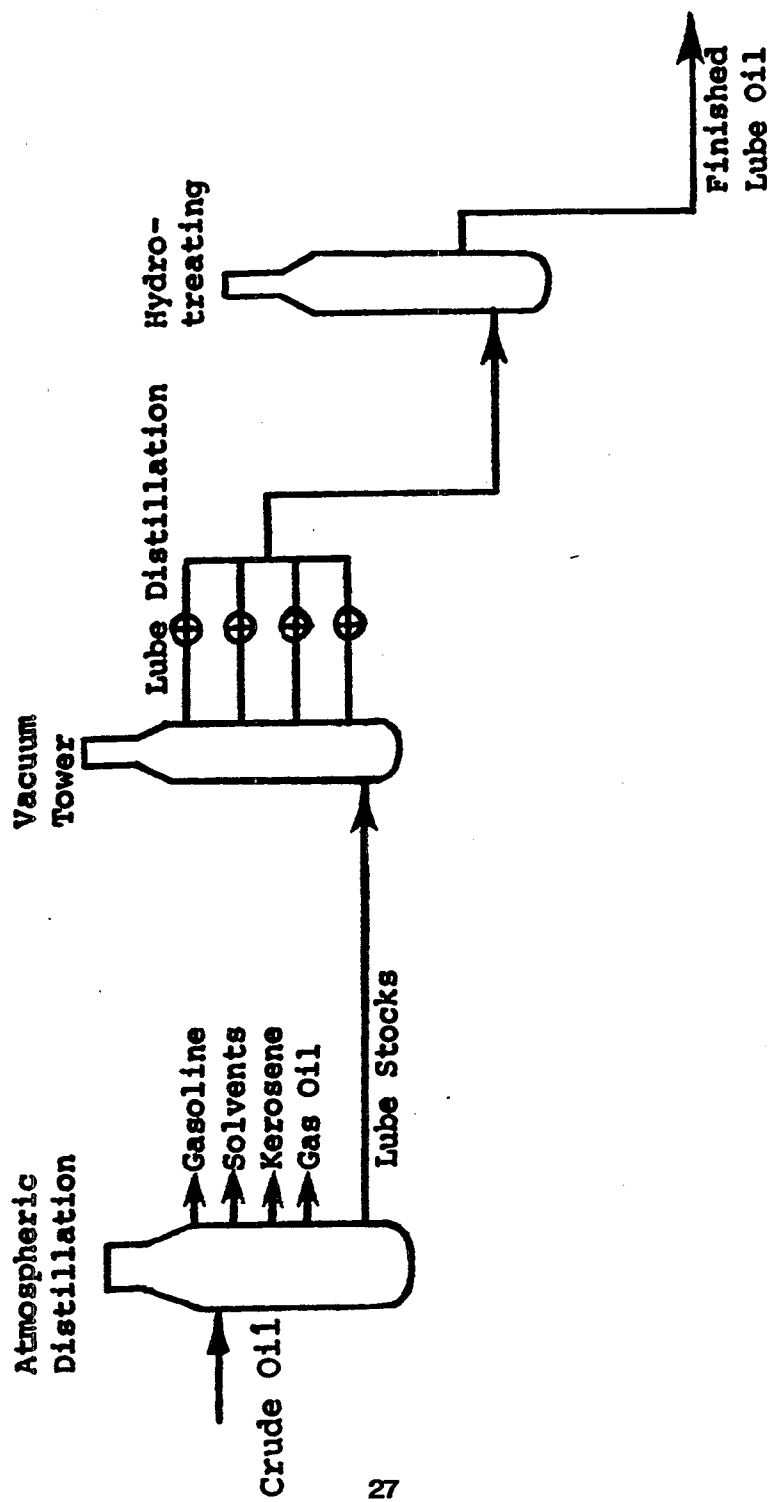


Figure 13. Production of Naphthenic Base Oils.

Lubricant Additives (27,28,29)

Additives are used for three main reasons: (1) to protect the surface being lubricated; (2) to improve the performance of the lubricant; and (3) to preserve the lubricant.

An understanding of additives will help the rerefiner to improve processing and make better reformulated lubricants. The characteristics and purpose of different additives used in automotive engine lubricants are described below.

Antiwear and Extreme Pressure Agents

Purpose: To reduce friction and prevent wear and metal-to-metal contact.

Action: A chemical reaction takes place with the additive on the metal surface, which forms a film and separates the two metal surfaces.

Typical Composition: Zinc dithiophosphates, phosphates, and organic sulfur.

Zinc dithiophosphates (ZDP) additives provide both antiwear and antirust protection and are used in a wide range of products, including engine oils, hydraulic oils, gear lubricants and many others. ZDP are intended to form films of zinc sulfide on moving parts, and so it is reasonable to expect that zinc sulfide will occur in the oil. It also provides special problems for the rerefiner. When heated above their decomposition point (approximately 300°F), toxic sulfur compounds are emitted.

Corrosion and Rust Inhibitors

Purpose: To prevent corrosion of metal parts.

Action: Chemical adsorption of polar functional groups. Acids are also neutralized.

Typical Composition: Zinc dithiophosphates, basic sulfonates, metal phenolates, fatty acids and amines.

Detergent and Dispersants

Purpose: To disperse insoluble contaminants and control deposits at high temperatures.

Action: Sludge and varnish precursors are neutralized and kept in suspension.

Typical composition: Barium, calcium and magnesium phenolates, organic phosphates, and sulfates are used as detergents, while polymeric alkylthiophosphates are considered dispersants.

The detergent/dispersant package and the dirt, water, wear metals and lead salts that are suspended in waste oil present the greatest problem for rerefiners.

Antioxidants

Purpose: To inhibit oxidation of oil and additives.

Action: Free radical termination and peroxide decomposition.

Typical Composition: Zinc dithiophosphates, aromatic amines, hindered and sulfurized phenols.

Metal Deactivators and Rust Inhibitors

Purpose: To reduce oxidation of lubricants and rust and corrosion of metal parts.

Action: Deactivate the catalytic effect of such metals as copper, lead and iron by forming a film on the particle or surface.

Typical Composition: Weak organic acids, organic complexes of amines, sulfides and phosphites.

The additives for the viscosity index improver and pour point depressants do not contain metals and should not create any problems for the rerefiners, as they can be left in the rerefined oil. The most commonly used antifoam additives by far are the silicon compounds. These silicon polymers are very stable and, even if they are not removed from the oil, they improve the antifoam properties of a rerefined oil.

Industrial Lubricants

Industrial lubricants include a wide range of special products for specific purposes. Common uses include: turbine oils, compressor oils, industrial gear lubes, transformer oils, and metalworking fluids. Table 4 shows the breakdown of industrial oil sales for 1975. Many of the additives discussed previously are used in industrial oils along with a special purpose additive, or in lesser amounts to formulate a special lubricant.

The oils used most frequently in industry are hydraulic oils, followed by metal working oils, quenching oils, gear oils and greases, and such specialty oils as compressor, air conditioner, and transformer oils.

Most of the hydraulic oil used is the petroleum-based type, although synthetic nonflammable ester, water-glycol, and water-in-oil emulsion products are used in special operations. Metalworking fluids range from low viscosity oils to high viscosity oils with fatty oils, sulfur, chlorine, and phosphorus additives, among others. Emulsifiable petroleum oils, often with extreme pressure and antiweld additives, are widely used.

Used industrial oils also often contain lower flash point solvents such as kerosene, Stoddard solvents (naptha) and chlorinated solvents such as trichloroethylene. Industrial oils seem to present fewer problems in fuel use than used automotive oils. For example, they have a lower ash content. However,

TABLE 4. INDUSTRIAL OIL SALES FOR 1975

	(Million Gallons)
Hydraulic oils	314
Metalworking oils	145
Railroad engine oils	58
Aviation and other oils	145
Gas engine oils	58
Process oils	340
Electrical oils	62
Refrigeration oils	11

| Total | 1133 |

there are other constituents which may also be undesirable from an operational standpoint, such as sulfur, chlorine, and fatty oils.

Mechanism of Oil Oxidation

All hydrocarbon oils will react with oxygen upon exposure to air at sufficiently elevated temperatures for sufficiently long periods of time. The internal combustion engine is an ideal oxidizing machine, since the motor oil is violently agitated in the presence of air, frequently at quite elevated temperatures, and for lengthy periods of time between the customary crankcase drain intervals. Over the range of temperatures developed in engines, the rate of oil oxidation approximately doubles for each 20°F rise of temperature. In addition, metals act as powerful oxidation catalysts or accelerators, with iron, copper and lead being particularly active. The rate of motor oil oxidation may be increased accordingly, as much as 100-fold at any given temperature, due to exposure to engine metal surfaces, metal particles resulting from normal engine wear, and contamination with combustion chamber blow-by solids and airborne dust.

Although all lubricating oil hydrocarbons are susceptible to oxidation under adverse conditions, little is known about the oxidation products. It is probable that the first oxidation products formed are organic peroxides, which act as catalysts for further oxidation of lubricating oil components. Peroxides are also vigorously corrosive to engine bearings.^{30,31,32}

Paraffinic hydrocarbons apparently combine with oxygen at the carbon atoms near the end of the chains, and the mechanism of the oxidation has been suggested as:

- (1) paraffinic hydrocarbons—> primary alcohols—> aldehydes—> acids.
- (2) paraffinic hydrocarbons—> secondary alcohols—> ketones—> ketonic acids.^{33,34}

Thus, oxidation of paraffinic hydrocarbons tends to yield primarily acids, corrosive products, and secondary viscous compounds of complex composition. The acids formed during the service life of lubricating oil oxidize the lead, copper and cadmium bearings. These metal oxides are soluble in the acids formed by oxidation of lubricating oil.

Naphthenic hydrocarbons oxidize and yield oxy-products in a manner similar to paraffins, and oxidation end products are largely of the oil-soluble type. The aromatic hydrocarbon constituents of lubricating oils tend to be the most readily oxidized, possibly because of the sensitivity of the hydrocarbon atoms attached to carbon atoms in side chains adjacent to the aromatic nuclei. The end products are very complex condensation and polymerization products and tend to be insoluble in the oil; these products constitute the sludges, resins and varnishes. In particular, detergent/ dispersant additives are used to disperse oxidative products and other contaminants, and to keep them in suspension. These impurities clog the filter media and slow down the filtration rate considerably if filtration is a part of the waste oil recycling process.

Metals in Used Oil

Metals in used oil generally are categorized according to their sources: (1) naturally occurring metals; (2) metals incorporated in additives; and (3) metals introduced during use.

Naturally Occurring Metals

Crude petroleum contains metals in low concentrations, principally zinc, iron, nickel, and vanadium.³⁵ Since these metals can interfere with catalytic refining processes, they are removed during the refining operations. Consequently, these metals are present at negligible levels in lubricating oil base stock.

Metals Incorporated in Additives

The purposes and actions of different additives in lubricating oil have been discussed previously in this chapter. Metals such as K, Na, Ca, Ba, Mg, Zn, P, and Si are due to additive compounds.

The additives are surface active compounds and are, in their most common form, constituted of a hydrocarbon portion and a polar or ionic portion. The hydrocarbon portion, which may be linear or branched, interacts very weakly with the water molecules. However, the polar or ionic portion of the molecule, usually termed the head-group, interacts strongly with the water via dipole-dipole or ion-dipole interactions and is solvated. Consequently, the head-group (metals) is said to be hydrophilic.

Metals Introduced During Use

Metals are introduced in the oils due to wear and tear, and due to corrosion of machine parts during the service life of lubricating oils. As previously discussed, oxidation products of lubricating oils are highly corrosive, and these oxidation products oxidize the lead, copper and aluminum bearings when they come in contact with lubricating oil. As a result of oxidation these metal oxides are soluble in the acids formed. Both metallic iron and iron oxides are formed as wear debris from ferrous metals, so it is likely that at least some of the iron in waste oil is present as:



Chemical and Physical Nature of Metals in Oil

Information about the nature of metal-containing species in waste oil is inferential, primitive, and fragmentary. Knowledge of the chemical and physical forms in which metals occur in oil is important in at least two ways. First, the cost and effectiveness of recycling processes in removing metals from used oils depends to some extent on the specific form of the metals in the oil. Second, the precise form of metals in used oil will be significant from the viewpoint of impact on the environment.

Because very little is known about the chemical nature of metal-containing species in used oil, it is necessary to draw inferences from the fragmentary data that do exist. Data presented by Belton R. Williams³⁶ from his rerefining operations have proven useful. In these operations, water is separated from oil prior to filtration and distillation. This aqueous phase contains large amounts of Na, Zn, Ba, Ca, Fe, P, Mg, B, and Pb. These data suggest that the metals mentioned occur to a significant extent in water-soluble forms.

In another study dealing with the toxicity of waste oil to marine life, the oil was extracted with water (9:1 ratio for 18 hours). Large amounts of lead and zinc were found in the water phase. Filtration studies indicated that more than 90% of the lead, cadmium, and zinc in the water passed through a filter with a pore size of 0.05 micrometers or less in diameter.³⁷

Vacuum distillation of dehydrated crankcase drainings results in a product with a low metal content. The data indicate that some lead and phosphorus is present as volatile species and that other metals occur in forms with little or no volatility. The lead in the distillate could either be entrained or present as tetra-ethyl lead. The latter possibility appears unlikely, since tetraethyl lead is decomposed by heating with aqueous acids, organic acids, and phenols.³⁸

The use of physical techniques such as settling, centrifugation and ultrafiltration to reduce metal levels have been studied, and results indicate that significant quantities of metals, specifically about 50% of the lead, occur in particulates.^{39,40}

Fractionation and infrared analysis of an SAE 30 additive-containing lubricating oil indicated that, after use in an automobile over 3500 Km, calcium dialkylnaphthalene sulfonates were converted in part to inorganic calcium compounds and organic products. The filtration and centrifugation studies indicate that many metals, notably lead, zinc, calcium, barium, magnesium, and iron are present in used oil mainly as small-sized particles. Another obvious form in which metals may occur is as original additives. Zinc dialkylthiophosphates are intended to form films of zinc sulfide on moving parts, so it is reasonable to expect that zinc sulfide will occur in the oil. Alkali earth metal sulfonates may hydrolyze slowly to produce hydroxides of calcium, magnesium, and barium.⁴¹

Table 5 shows the metal concentrations in used motor oil. This motor oil was collected from the service stations in the vicinity of Auburn, Alabama. The most interesting result was the lead content of used motor oil; lead content of used motor oil is declining in general, and was found to be between 100 to 200 ppm, compared with more than 1,000 ppm in the early part of the 1980s.

In conclusion, information on the chemical nature of metallic species in used oil is very scant. A definite need exists for research to obtain more succinct characterization of the physical and chemical forms in which metals occur in used oil.

TABLE 5. ELEMENTAL ANALYSIS OF METALS IN USED MOTOR OIL.

Metal (ppm)	Concentration	Metal (ppm)	Concentration
K	120	Fe	225
Ca	1570	Pb	150
Mg	900	Al	25
Ba	150	Co	0.5
Zn	1800	Mo	11
P	1375	Cr	3
Mn	9	Si	35
Cu	350	B	5

SECTION IV EXPERIMENTAL PROCEDURES

Waste oil, although contaminated, has a high energy value, and burning it as a fuel is a major outlet for used oil. Unfortunately, used oil contains high concentrations of metallic contaminants, carbon particles, and other oxidation products. Burning the oil without removing the contaminants can cause adverse environmental effects.

The major objective of the bench-scale studies was to develop a process to convert off-specification used oil to specification grade fuel oil; hence, most experimental work was directed toward reducing the ash and lead content of the used oil. The experimental work was divided into two parts: (1) demetallization of waste oil by chemical reagents (metal borohydrides and diammonium phosphate), and (2) removal of oxidation products, coking and fouling precursors, and acids neutralization by alkaline amines.

A detailed parametric study for demetallization reaction was done in a tubing bomb micro-reactor and a distillation flask. Experiments were also extended to a larger batch reactor, i.e. a 3785 ml autoclave, to simulate actual operating conditions as much as possible, while most of the experiments in the second part of the project were carried out in a 1000 ml three-neck flask. The experimental setups are discussed in detail below.

TUBING BOMB MICRO-REACTOR (TBMR)

It is constructed from 316 stainless steel tubing, with 3/4-inch (1.905 cm) O.D., 0.065 inch (0.165 cm) wall thickness and a length of 9 inches (22.86 cm), as shown in Figure 14. One end of the reactor was sealed with a Swagelok cap. Gas (if used) was introduced through a connection unit consisting of a Nupro fine metering valve, 1/4 inch (0.635 cm) O.D. 316 stainless steel tubing having a length of 2.75 inches (6.985 cm), and Swagelok reducing unions.

In a typical run, the TBMR was charged with 20 gms of waste oil and a specified amount of reagents. The reactor was then sealed and checked for leakage. After charging, the TBMR was attached to the vertical shaft on the agitation assembly and agitated at ambient temperature, for 3 minutes at 860 rpm. The TBMR was immersed in the preheated fluidized sand bath (Techne Inc., SBL-20) as shown in Figure 15. A Techne TC4D temperature controller was used to maintain the temperature to within 2°C. The heating time was about 1 minute. At the end of the chosen reaction time, the TBMR was removed from the sand bath, immediately quenched in tap water, and checked for any leaks. The liquid product

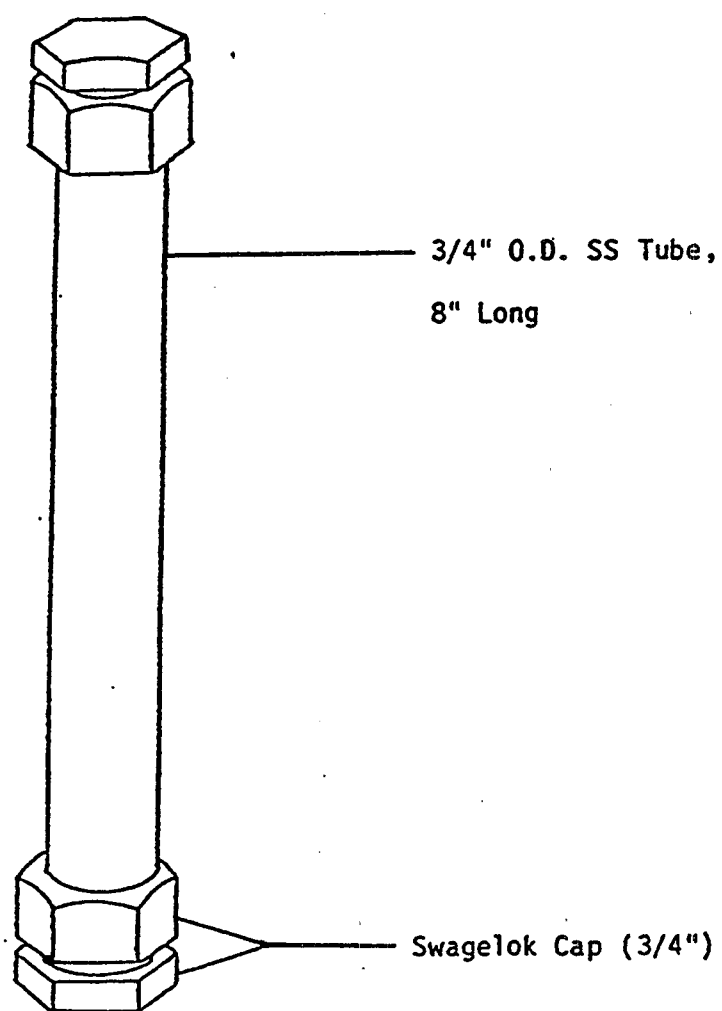


Figure 14. Drawing of Tubing Bomb Microreactor.

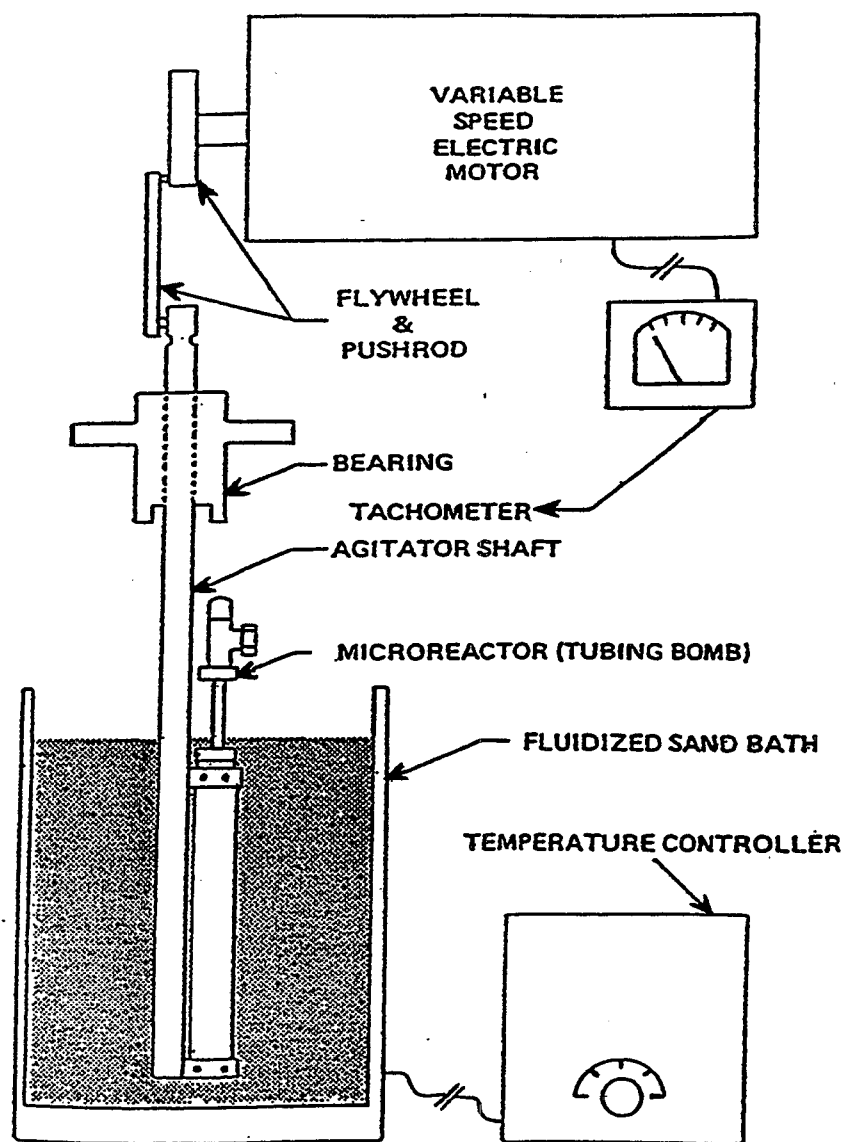


Figure 15. Agitation Assembly for TBMR.

was then collected and filtered via a vacuum filtration unit as shown in Figure 16. The filtrate (or so-called product oil) was collected for ash and lead analysis.

DISTILLATION FLASK REACTOR

A 300 ml distillation flask was connected with a condenser via a distilling head. The entire assembly is shown in Figure 17. In a typical run, the flask was charged with 60 gms of waste oil and demetallizing reagents. The oil was agitated and heated by a magnetic stirrer and a heating mantle, respectively. Heating was controlled by a power transformer. Water and light ends evaporated during the reaction were condensed and collected in a flask. After the reaction, the oil was filtered immediately by a vacuum filtration system (Figure 16). The filtrate was collected for lead and ash analysis.

AUTOClave

The reactor used was a 1-gallon autoclave built by Autoclave Engineers Inc. A cross-sectional view of the reactor and a schematic diagram of the reaction system are provided in Figures 18 and 19, respectively. The autoclave is equipped with a turbine agitator, a cooling coil, and a thermowell made of 316 stainless steel. It also features ports for a gas outlet and inlet, a pressure gauge tap, and a rupture disc safety device. All feed and exhaust lines are 1/4-inch O.D. 316 stainless steel tubing. The autoclave was heated by an Autoclave Engineers 3.5 KW electric furnace, and reaction temperature was controlled by a proportional-integral controller (model 523C Barber Coleman). The controller has a dual input from the specimen thermocouple in the reactor and the furnace. Both thermocouples were type-k (i.e. chromel-alumel). The reaction temperature was recorded on a Fisher Recordall series 5000 and displayed simultaneously on an Omega model 199 digital thermometer. Agitation was provided by a magne-drive stirrer with a 3/4 HP Impak V.S. drive system from the Reliance Electric Company.

THREE-NECK FLASK

Reactions were carried out in a 1,000 ml three-neck flask as shown in Figure 20. In a typical run, the reactor was charged with 400 gm of waste oil and desired amounts of chemicals. The reaction mixture was heated and agitated by a heating mantle and a motor-driven agitator. Reaction was maintained at the desired temperature by a power transformer. After the reaction, oil was decanted into a 500 ml graduated cylinder and allowed to settle in a constant temperature oven. The clarified oil above the sludge was analyzed for ash and lead content.

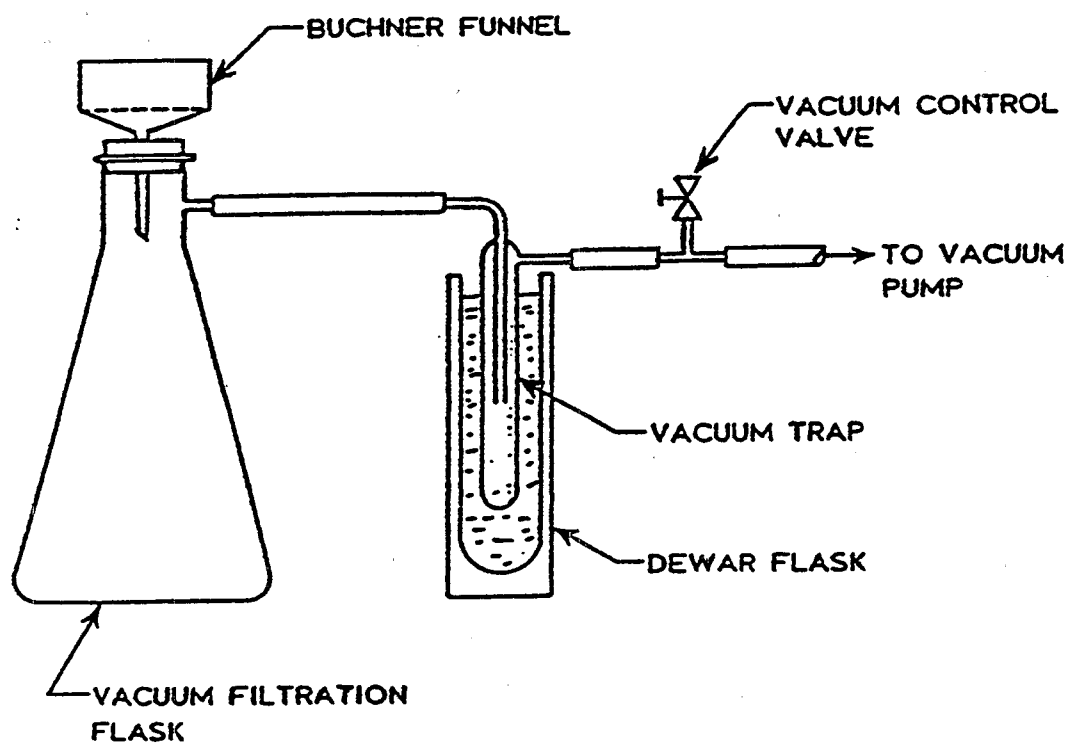


Figure 16. Diagram of Filtration Apparatus.

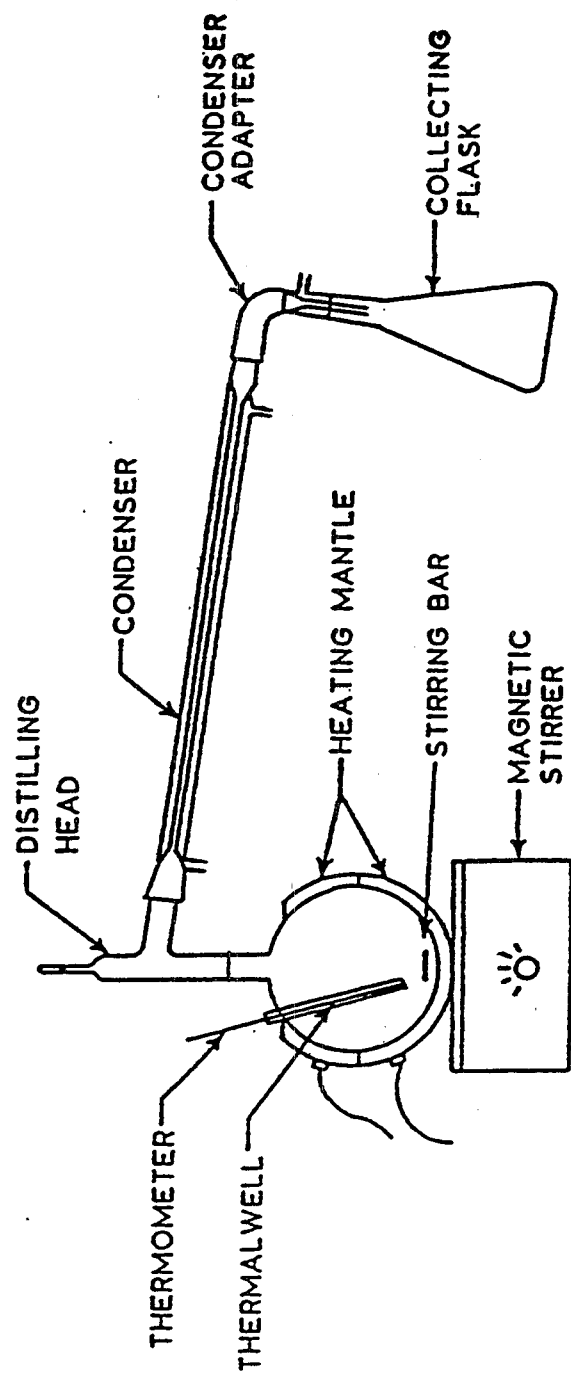


Figure 17. Drawing of Distillation Unit.

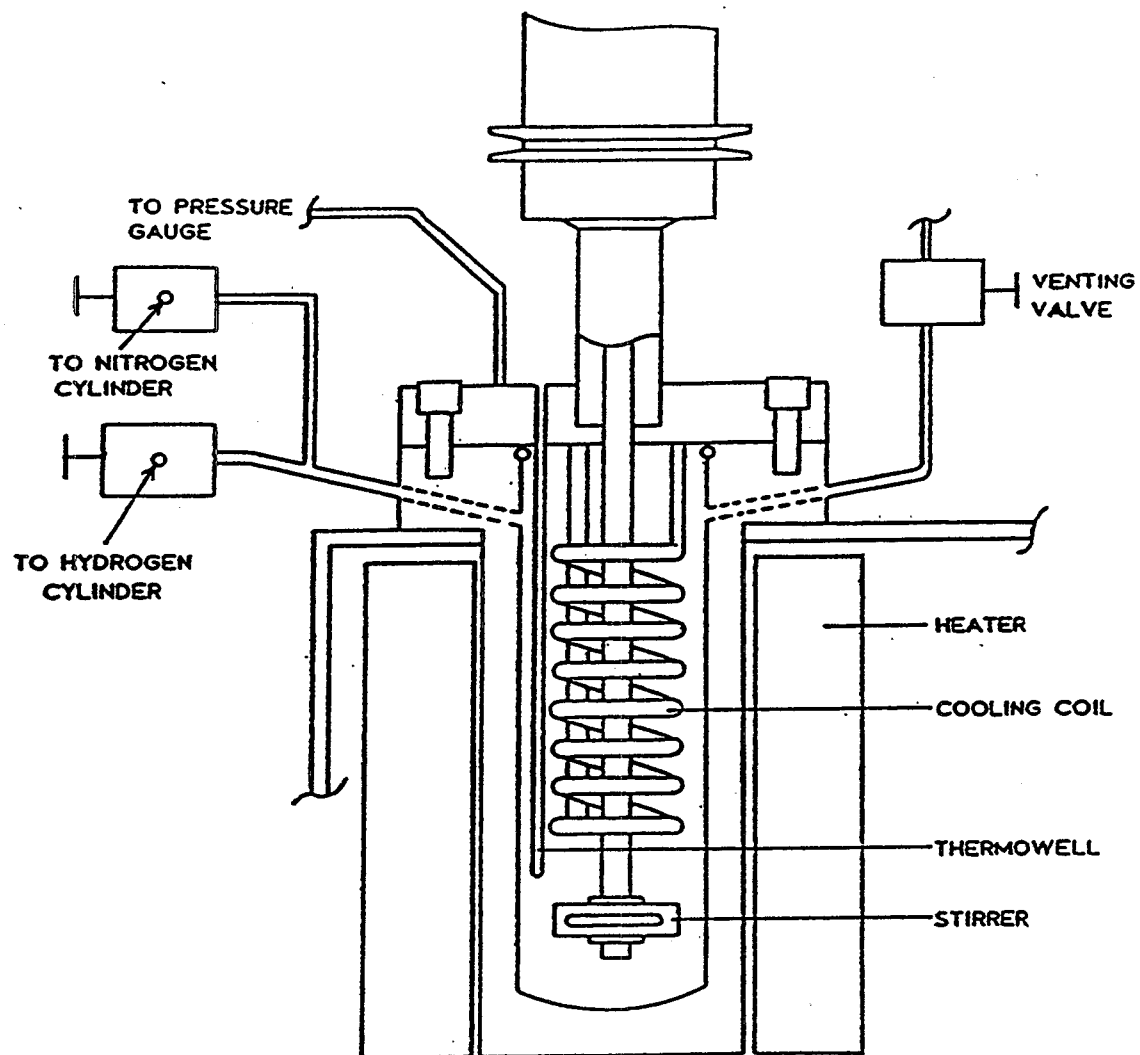


Figure 18. Cross-Sectional View of Autoclave.

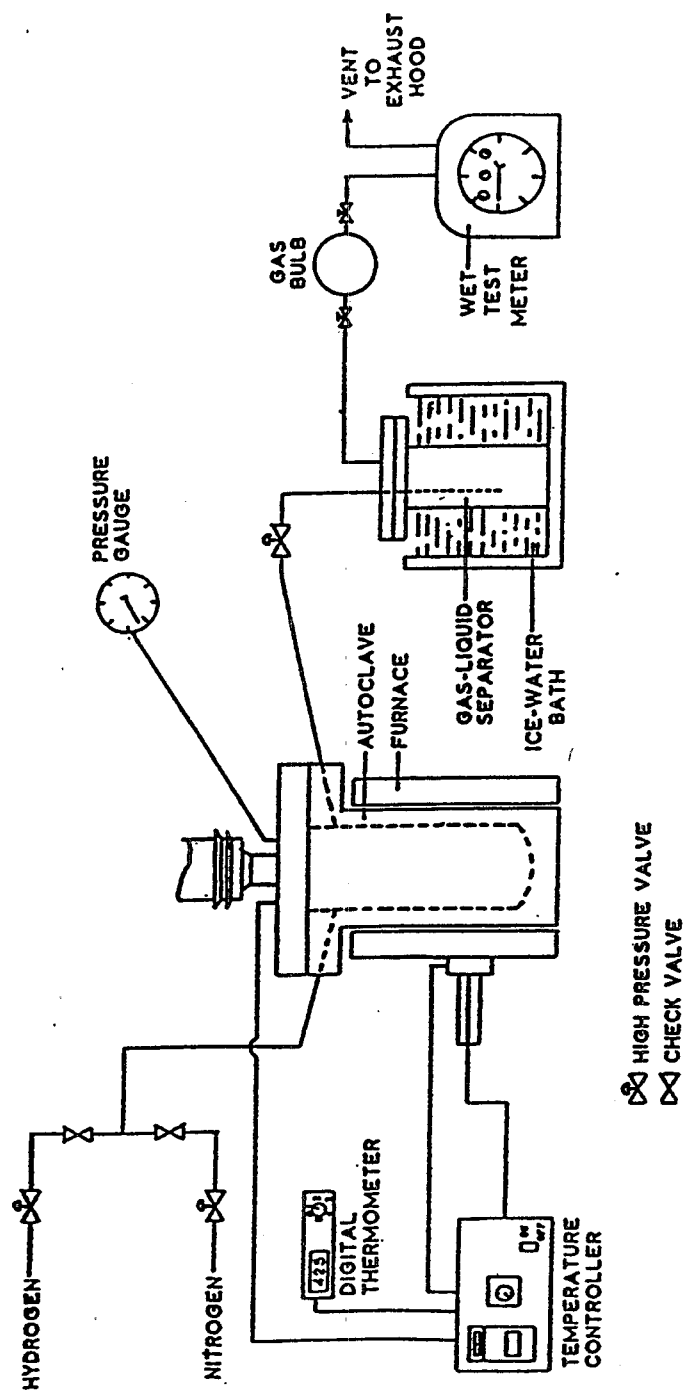


Figure 19. Schematic Diagram of Autoclave Reaction System.

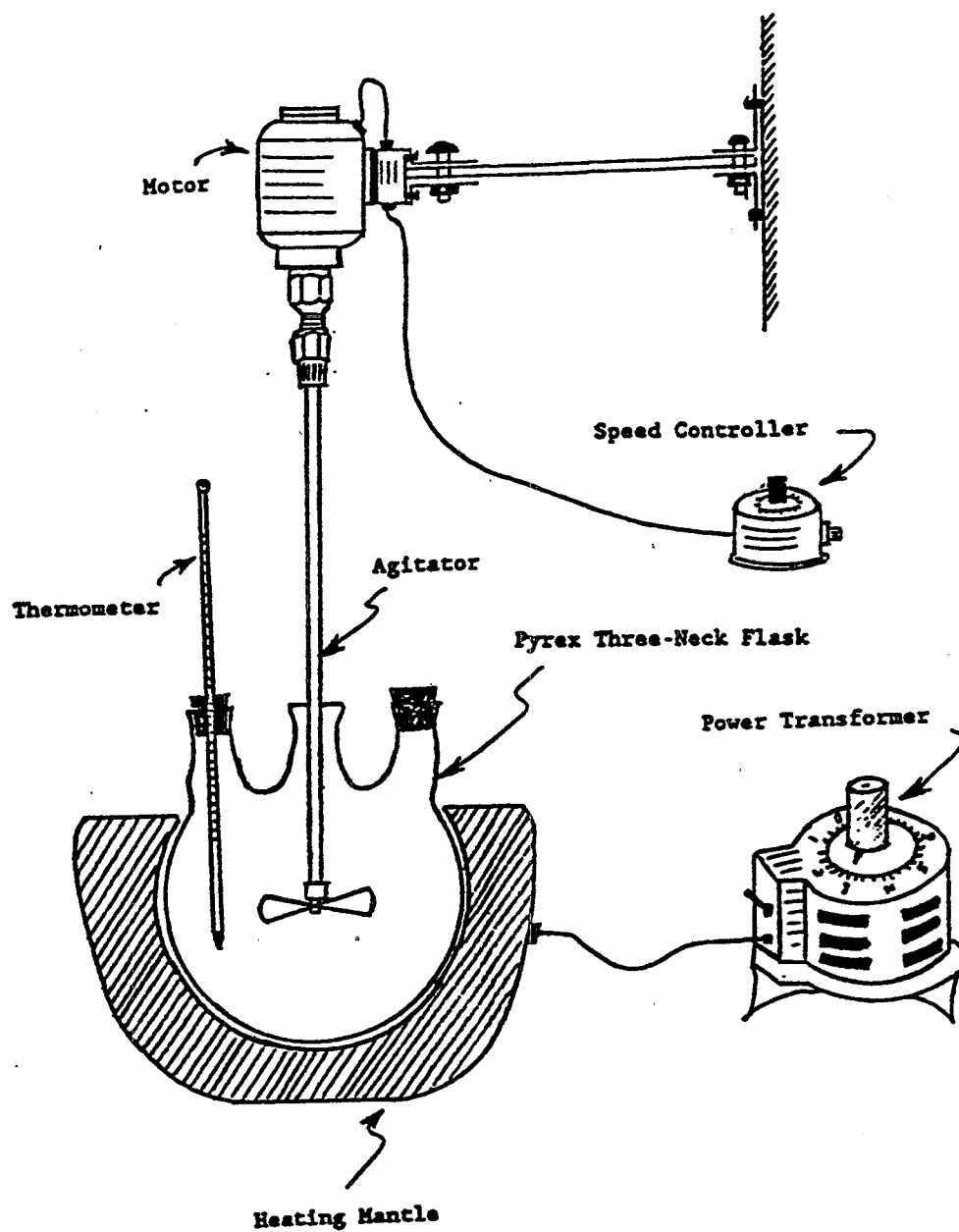


Figure 20. Three-Neck Flask Reactor.

MATERIALS

Used oil was collected from the Auburn Waste Oil Reprocessing Laboratory and from various service stations in the Auburn area.

ANALYSIS

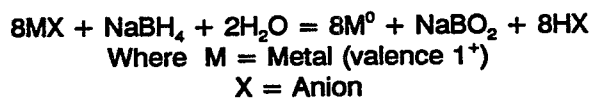
Experimental results were verified in accordance with an EPA approved quality assurance project plan. The properties of the demetallized used oil were evaluated to assess its potential as an EPA specification-grade fuel oil by using the following test methods: water content, ASTM D4006-81 (water in crude oil by distillation); ash content, a modification of ASTM D482-80 (ash from petroleum products); lead content by standard atomic absorption analysis, and other metals content by ICAP (Inductively Coupled Argon Plasma) spectroscopy.

SECTION V

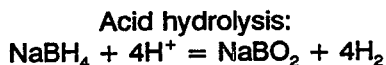
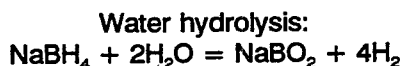
USE OF METALLIC BOROHYDRIDE AS A DEMETALLIZING REAGENT

Process stream purification (PSP) with sodium borohydride (SBH) is extensively used within the chemical processing industry to improve product quality and to lower operating costs (42). SBH can effectively control color, odor and product stability problems, most recently in natural fats and oils. There are three major impurities which can cause quality problems in organic chemicals: carbonyls, peroxides and metal compounds. Although these impurities or contaminants are normally present only at the parts-per-million level, they are costly and difficult to remove by traditional purification methods such as distillation, hydrogenation, absorption or oxidation. Since these compounds are present in used oils, SBH may offer the refineries an effective, low-cost, highly efficient alternative. It is a versatile reducing agent and ligand for inorganic reactions. Reduction of toxic or valuable heavy metals in process waste streams is an important industrial application for sodium borohydride; the substance can reduce metal compounds to a lower valence state or to the metal's elemental form.

Metallic borohydrides (e.g. sodium borohydride) are strong reducing agents. The following reaction is typical of the metal reduction that occurs with sodium borohydride (43).

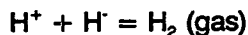


In this chemical reaction, stoichiometrically, SBH has eight reducing equivalents per molecule. Based on some bench-scale experimental results, Morton Thiokol Inc. reported that stabilized water solution (an aqueous solution of 12 wt.% SBH and 40 wt.% sodium hydroxide) was an effective agent for removing lead from used crankcase oil. It should be noted that SBH degrades at low pH in the presence of water or acid, via hydrolysis, to form salt and to liberate hydrogen. The representative chemical reactions are



Hydrogen provides a source of hydride ion H^- for NaBH_4 . This hydride ion acts as a nucleophile, so most of the reduction reactions occur by nucleophilic addition reaction mechanism. NaBH_4 reacts

when it comes in contact with a proton source (such as water or an acid); hydride ion unites with a proton to form hydrogen gas



A parametric study was done to investigate the lead reduction efficiency of two Morton Thiokol products: Venpure powders (NaBH_4 and KBH_4) and stabilized water solution (SWS). The study was done in a tubing bomb microreactor (TBMR) at the reaction conditions listed in Table 6. A concentrated NaOH aqueous solution (50 wt.%) was usually added to maintain a high pH and thus a low hydrolysis activity of the metal borohydrides.

In a typical run, the TBMR was charged with 20 gms of waste oil, the specified amounts of 50 wt.% NaOH aqueous solution, and Venpure product. At the end of the chosen reaction time, liquid product was collected and vacuum filtered. The filtrate (product oil) was collected for ash and lead analysis.

RESULTS AND DISCUSSION

The lead content of the type B oil was markedly reduced from 480 to 70 ppm (Run 1), as shown in Table 7, with 0.65 wt.% SWS and 1.2 wt.% NaOH solutions. This is well within the allowable maximum lead content of 100 ppm for specification grade used oil. However, high sludge production (16 wt.%) resulted from this run.

To evaluate the effect of SWS and NaOH solution on the demetallization of waste oil, the charge of SWS and NaOH was reduced (2/3 of Run 1) to 0.43 and 0.8 wt.% in Run 2. The result was that the lead content of the oil decreased by only about 50%, to 240 ppm. Ash content of the product oil was 0.58 wt.%, while sludge production was about the same as that for Run 1.

It was thought that the large amount of sludge production was due to saponification of fatty acids or due to a polymerization reaction promoted by NaOH in the oil. In order to reduce the sludge production, only 0.05 wt.% NaBH_4 powder was used in Run 3. The amount of lead reduction was only 10.4%; however, less sludge was produced (2 wt.%) compared to previous runs. It can be concluded

TABLE 6. TBMR REACTION CONDITION FOR VENPURE PRODUCT TREATMENT

Reaction Volume	45 ml
Reaction Temperature	110°C
Reaction Time	2 hrs.
Agitation Rate	860 cpm

**TABLE 7. EFFECT OF METAL BOROHYDRIDE ON LEAD REDUCTION
FOR TYPE B OIL**

Run No.	1	2	3	4	5	6
Oil charge, gms	20	20	20	20	20	20
50% NaOH added to the oil, wt. %	1.2	0.8	0	0.8	0	0.8
SWS solution, wt. %	0.65	0.43	0	0	0	0
NaBH ₄ powder, wt. %	0	0	0.05	0.05	0.05	0.05
Phase Transfer catalyst, wt. %	0	0	0	0	0.1	0.1

After reaction:

Sludge Production, wt. %	16	15	2	--	6	7
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Product Oil Analysis:

Ash content, wt. %	0.36	0.58	-	0.77	0.40	0.53
Lead content, PPM	70	240	430	300	400	289
Lead reduction, %	85.4	50	10.4	37.5	16.7	39.8

As received lead content of type B oil = 480 PPM and
ash content = 0.52%

from the results that lead reduction depends on NaOH rather than NaBH_4 . Since most of the lead is present in a particulate form, it may be removed due to an entrainment of these particulates in the sludge. It seems that lead removal from the oil is a physical phenomenon rather than due to chemical reaction with NaBH_4 .

In order to enhance the demetallization activity, 0.8 wt.% NaOH (50 wt.% solution) was added in Run 4, while other reaction conditions were kept the same as in Run 3. The lead removal efficiency did increase from 10.4% for Run 3 to 37.5% for Run 4. Hence, addition of NaOH did reduce the lead content of used oil.

To improve the solubility of NaBH_4 in oil phase, 0.10 wt.% of phase transfer catalyst (tri-n-butyl-methyl ammonium chloride) was added to the oil (Run 5). Comparing the results with those of Run 3, the addition of the phase transfer catalyst did result in an increase in lead removal efficiency from 10.4 to 16.7%, while addition of 0.8 wt.% NaOH in Run 6 increased the lead reduction efficiency to 39.8%. To determine the reproducibility of the demetallization experiments, some of the runs were duplicated, and the results obtained were essentially the same.

Waste oil is usually collected from various sources, and it is possible that lead removal efficiency using a demetallizing reagent might respond differently to various types of waste oil. Thus, a different oil (Type A) was used for the demetallization studies. The lead content of Type A was higher than for Type B oil, so the amount of metal borohydride and NaOH required for demetallizing Type A should be more than required for Type B.

In Run 8, reaction conditions similar to Run 1 were used to study the effectiveness of an equal amount of caustic and SWS solution in demetallizing the two types of oil. Table 8 shows that with the same charge of caustic and borohydride, the lead content of Type B oil was reduced by 85%, whereas only 24% reduction was achieved for Type A.

Because of the 24% lead reduction obtained in Run 8, the charge of SWS solution was doubled in Run 9 to observe its effectiveness while the reaction conditions of Run 8 were maintained (Table 9). The lead content of type A oil was reduced by only 58%. However, the high concentration of sodium borohydride reduces the economic viability of using SWS solution in demetallizing waste oils.

In Run 10, the charge of NaBH_4 and NaOH was the same as in Run 9, but they were added separately. The lead reduction efficiency was more or less the same for both runs, which shows that lead reduction is more dependent on NaOH than on NaBH_4 . The addition of phase transfer catalyst increased the lead reduction efficiency, but the lead content of the product oil was higher than 100 ppm (Run 11). When potassium borohydride (KBH_4) was used in Run 12, the lead content was 270 ppm; hence, the lead content of Type A oil was not successfully reduced to an acceptable limit.

Effect of Reaction Temperature

In all the previous runs, the reaction temperature was 110°C. When the reaction temperature was increased to 150°C, the entire product oil became a gelatinous mass (Table 10). Hence, increase in reaction temperature had an adverse effect on the recovery of oil and demetallization reactions.

TABLE 8. EFFECT OF OIL TYPE ON LEAD REDUCTION EFFICIENCY

Run No.	Type of Oil	Lead content PPM	% Ash content	% lead reduction
1	B	70	0.36	85.4
8	A	500	0.55	24.2

Oil charge = 20 gms

50% NaOH charge = 1.2 wt.% of the oil

SWS solution charge = 0.65 wt.% of the oil

Lead content of the type A oil = 660 ppm

Lead content of the type B oil = 480 ppm

**TABLE 9. EFFECT OF METAL BOROHYDRIDE ON LEAD REDUCTION
FOR TYPE A OIL**

Run No.	8	9	10	11	12
Oil charge	20	20	20	20	20
50% NaOH, wt. %	1.2	1.2	1.8	1.8	1.8
SWS solution, wt. %	0.65	1.3	0	0	0
KBH ₄ powder, wt. %	0	0	0	0	0.15
NaBH ₄ powder, wt. %	0	0	0.15	0.15	0
Phase transfer catalyst, wt. %	0	0	0	0.10	0.35
<u>Product oil analysis:</u>					
Ash content, wt. %	--	0.62	0.56	0.50	0.68
Lead content, PPM	500	280	300	180	270
Lead reduction, %	24.2	57.6	54.5	72.7	59.1

Lead content of the type A oil = 660 ppm and ash content = 0.59%

TABLE 10. EFFECT OF REACTION TEMPERATURE ON SLUDGE FORMATION

Run No.	1	13	14
Oil Type	B	B	B
Reaction Temp., °C	110	150	150
NaOH wt. %	1.2	1.2	1.2
SWS wt. %	0.65	0.65	0.65
<u>After Reaction:</u>			
Sludge Production, wt. % (gelatinous mass)	15.5	100%	100%
<u>Product Oil Analysis:</u>			
Lead Content, ppm	70	--	--
Lead Reduction, %	85.4	--	--

Investigation of Gel Formation

Several experiments were conducted in which a cottonseed oil and a non-detergent virgin motor oil was reacted with either SWS solution or NaBH_4 powder to confirm that saponification does occur when fatty acids are present.

A cottonseed oil was blended with 1.2 wt.% NaOH (50% solution) and then reacted with 0.65 wt.% SWS in a TBMR (Run 15). The reaction was conducted under the same reaction conditions as given in Table 6. The oil was collected in a test tube after the reaction to measure a volume of the sludge. The sludge produced was about 35 volume % (Table 11), and was probably due to the salt resulting from the saponification of fatty acids present in the cottonseed oil. The cottonseed oil was reacted with 0.05 wt.% NaBH_4 powder in the absence of NaOH (Run 16). In this case, no sludge was formed, confirming that the sludge was due to the reaction of fatty acids with NaOH . The amount of NaBH_4 was doubled; however, there still was no sludge formed (Run 17). The effect of NaOH on nondetergent motor oil was observed by reacting a SAE-30 nondetergent motor oil with SWS (Run 18). After the reaction, two layers of liquid were formed. The top layer was reddish brown, while the bottom layer was bluish green in color. A trace amount of suspended solids was also observed.

In summary, the gelatinous mass formed while treating used oil with SWS was probably due to the saponification of fatty acids or the polymerization reaction promoted by caustics at higher temperature.

Effect of Caustics

It was thought that sludge production was due to the reaction products of NaOH and used oil. In order to investigate the effect of NaOH on sludge production and lead reduction, several reactions were performed in which different amounts of NaOH were reacted with the oil without SWS or Venpure products. The reaction conditions were the same as those listed in Table 6.

Results from Table 12 clearly show that sludge generation depends on the amount of NaOH reacted with the oil. A higher amount of NaOH produced a large volume of sludge. One noteworthy aspect of these results was that the lead content of oil depends on the amount of sludge generation. Lead reduction is increased when a large amount of sludge is produced due to the entrainment of lead particulates in the reaction products.

Effect of Water

As discussed earlier, the reducing ability of metallic borohydrides can be hampered substantially by hydrolysis in the presence of water. Since waste oils normally contain 1-10% of water, the poor performance of metallic borohydrides in terms of ash and lead reduction can be due to hydrolysis of metallic borohydrides. To investigate the effect of water on demetallization of waste oil, a sufficient amount of Type A oil (containing 5 vol.% water) was blended with 0.25 wt.% NaOH (50 wt.% solution). Water, along with light ends, were then distilled by atmospheric distillation.

In Run 22, dry oil was reacted with 0.9 wt.% of SWS solution in a TBMR under reaction conditions given in Table 6. As shown in Table 13, the lead content of the oil was successfully reduced from 700

TABLE 11. INFLUENCE OF CAUSTICS ON FORMULATION OF GELATINOUS MASS

Run No.	15	16	17	18
Oil Type	Cottonseed (CS)	CS	CS	Motor Oil ^a
NaOH, wt.%	1.2	0	0	1.2
SWS, wt.%	0.65	0	0	0.65
NaBH ₄	0	0.05	0.10	0
<u>After Reaction:</u>				
Sludge Production, Vol.%	35	0	0	trace ^b

^aGRC, G-100 nondetergent motor oil, SAE-30, made from Gurley Refining Company, Memphis, Tenn. 38101.

^bTwo phase were formed with the top layer in reddish brown and bottom layer in dark bluish green with trace amount of suspended particles.

TABLE 12. EFFECT OF NaOH ON SLUDGE PRODUCTION AND LEAD REDUCTION

Run No.	19	20	21
Oil Type	B	B	B
Oil Charge, gm	20	20	20
NaOH, wt. %	1.75	1.25	0.75
<u>Before Reaction:</u>			
Lead Content, ppm	480	480	480
Ash Content, wt. %	0.52	0.52	0.52
<u>After Reaction:</u>			
Sludge Production, wt. %	15	12	5
<u>Product Oil Analysis:</u>			
Ash Content, wt. %	0.5	0.55	0.59
Lead Content, ppm	80	225	330

TABLE 13. INFLUENCE OF WATER ON LEAD REMOVAL

Run No.	9	22	23	24	25
Oil Type	A	C	C	C	C
Oil charge	20	20	20	20	20
50% NaOH, wt.%	1.2	--	--	--	--
SWS solution, wt.%	1.3	0.9	0.4	0.9	0.25
Phase transfer catalyst, wt.%	0	0	0	0.10	0.10
<u>Product Oil^a Analysis:</u>					
Ash content, wt.%	0.62	0.53	0.68	0.63	0.77
Lead content, PPM	280	100	180	120	300
Lead reduction, %	57.6	85.7	74.3	82.9	57.1

^aSludge production in all the runs was high (about 15-20 wt.%).

to 100 ppm; i.e. about 86% lead reduction was obtained. This suggests that a much better demetallizing performance can be obtained with a dry oil than with a wet oil (Type A).

To further minimize the use of SWS solution, the charge of SWS solution was reduced to 0.4 wt.% in Run 23. As a result, about 74% lead reduction was obtained. In Runs 24 and 25, 0.1 wt.% of a phase transfer catalyst (tri-n-butyl-methyl ammonium chloride) was added to see if the demetallizing performance could be improved. Compared to Run 22 (without catalyst), the addition of a catalyst did not improve the results.

On the whole, the presence of water in the oil has an adverse effect on the demetallization of used oils. This can be avoided by distilling the water before the reaction.

Autoclave Study

It should be noted that the results presented so far were obtained in a 45 ml tubing bomb microreactor (TBMR). Knowing that these bench-scale demetallization results were to be incorporated in the scale-up and design of the Auburn Waste Oil Reprocessing Laboratory, it was clear that experiments would have to be extended to a larger batch reactor, i.e. a 3785 ml autoclave, to simulate the operating conditions as much as possible.

As mentioned above, water can decrease the demetallization activity of metallic borohydrides. Therefore, Type A oil (containing 5 vol.% water) was blended with 0.25 wt.% NaOH (50 wt.% solution) and then distilled to a specified temperature under atmospheric pressure. The residual oil, assumed to be moisture free, was treated with metallic borohydrides in the 1-gallon autoclave. The results are given in Table 14 and are discussed below.

In Run AS1, 890 gms. of dry oil was reacted with 0.9 wt.% of SWS. For this run, only 37% lead reduction was obtained, compared to 96% for Run AS2. The poor demetallizing performance was probably due to the low distillation cutoff temperature (129°C) for Run AS1, which resulted in a certain amount of water being left behind in the residual oil.

Thus, in Run AS2, the distillation cutoff temperature was further raised to 175°C. The oil and SWS charges to the autoclave were about the same as in Run AS1. Under the same reaction conditions, the lead content of the oil was markedly reduced from 700 ppm to 25 ppm. Although a promising result was obtained in Run AS2, the amount of SWS used was considerable and uneconomical. The Run AS2 was duplicated by Run AS3, except that the SWS charge was halved. As a result, only a 40% lead reduction was obtained; this suggested that more SWS was required, if a better demetallizing performance was to be achieved.

To compare the demetallizing effectiveness of SWS solution and NaBH_4 powder, Run AS4 was performed with the same amount of NaBH_4 used in Run AS1. Coincidentally, the same level of lead reduction was obtained. However, with NaBH_4 powder (Run AS4), the product oil had a lower ash content and a low sludge production compared with the Run AS1.

TABLE 14. RESULTS OF AUTOCLAVE RUNS

Run No.	AS1	AS2	AS3	AS4	AS5	AS6
<u>Atmospheric Distillation</u> conditions for Type A Oil						
Oil charge, gms	890	1000	1000	600	600	600
NaOH wt.% (50% solution) 1.2	0.8	0	0.8	0	0.8	
Distillation cut point, °C	129	175	175	175	150	150
<u>Reaction Mixture:</u>						
Residue ^a from distillation, gms	890	900	900	545	545	545
SWS, wt.%	0.9	0.91	0.46	0	0	0
NaBH ₄ powder, wt.%	0	0	0	0.1	0	0.15
KBH ₄ powder, wt.%	0	0	0	0	0.1	0
Phase Transfer catalyst, wt.%	0	0	0	0.2	0.2	0.2
<u>Product Oil^b Analysis:</u>						
Ash content, wt.%	0.74	0.50	0.51	0.57	0.56	0.53
Lead content, PPM	440	25	420	440	345	200
Lead reduction, %	37.1	96.5	40.0	37.1	50.7	71.4

^aLead content = 700 ppm, Ash content = 0.59%

^bSludge production in all the runs was high (about 15-20 wt.%)

To study the demetallizing ability of KBH_4 powder, Run AS5 was made with KBH_4 instead of NaBH_4 . As shown in Table 14, the lead reduction efficiency increased from 37% to 51%, but the ash content of the oil was not changed significantly. Since KBH_4 is more expensive than NaBH_4 , the final Run (AS6) was made with higher amount of NaBH_4 (0.15 wt.%). It was found that lead reduction efficiency increased from 37% to 71%, but the ash content of the product oil did not change appreciably. Although the amount of NaBH_4 used can be further increased to improve lead reduction performance, it is uneconomical to do so when the operating costs for reprocessing waste oil are considered. Therefore, another demetallizing method was explored in an effort to seek the most economical process.

CONCLUSIONS

(1) Examination of the ash content of product oil reveals that ash content was not reduced by metal borohydride treatment.

(2) Lead content was selectively reduced in some cases. It seems that lead reduction depends on NaOH rather than NaBH_4 .

(3) A major disadvantage of metal borohydride as a demetallizing reagent is the high pH required to prevent hydrolysis.

(4) A large amount of sludge is generated due to the reaction of NaOH with fatty acids and oxidation products.

(5) Reaction is difficult to control because NaOH promotes polymerization reaction at high temperature.

SECTION VI

USE OF DIAMMONIUM PHOSPHATE AS A DEMETALLIZATION REAGENT

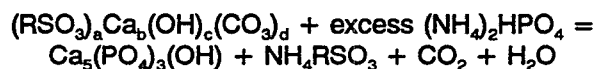
Many researchers have proposed a system by which used hydrocarbon lubricating oil is contacted with an aqueous solution containing one or more anions, such as phosphate, sulfate, chromate, etc., which form water-insoluble salts with metals to be removed from used oil.^{44,45} In these processes, the cation of the aqueous solution is exchanged with the metals of the metals-containing components of used hydrocarbon lubricating oils. In order to avoid the entry of another metal into the treated oil, which would increase its ash content, the cation of the aqueous solution is preferably ashless, and as such can be hydrogen, ammonium, hydrazine, hydroxylamine, etc. The quantity and the concentration of the aqueous solution is of little importance as long as anions are still present in the aqueous phase after treatment.

The anions in the aqueous solution form salts with the metals in the oil, the equilibrium of this reaction being dependent on the solubility of the metal salts in the aqueous solution.⁴⁵ These metal salts can be separated from the lubricating oil by distilling water from it during the reaction and then filtering the oil after treatment.

Once the initial assessment of the different salts that can be used for the demetallization of used oil is made, it was decided that ammonium salts, preferably diammonium phosphate, would be a better reagent for removing the metals from waste lubricating oils.

MECHANISM OF DEMETALLIZATION REACTION

Lead and other metal contaminants are present in waste oil in organometallic form. The DAP $((\text{NH}_4)_2\text{HPO}_4)$ react with organometallic compounds to form insoluble and easily separable products. A reaction of this type has been discussed by Miller⁴⁶:



Based on the above reaction, the calcium overbased sulfonate detergent reacts with DAP to form a metallic hydroxyl apatite $(\text{Ca}_5(\text{PO}_4)_3\text{OH})$, which is insoluble in aqueous and oil phase. The reaction products remain at the interface, so the removal of water during the reaction facilitates the separation of metal phosphates from the oil. This reaction mechanism is general for Ca, Ba, Mg, and Zn additive

compounds. In general, group II metal compounds are highly reactive with DAP, and the reaction goes to completion even at low temperature.

Experimental Procedure

A detailed parametric study was undertaken to map out the process variables so as to identify the most efficient demetallization conditions for diammonium phosphate. Different ammonium salts were used to evaluate the effectiveness of the process in terms of ash and lead reduction. An evaluation of solid-liquid separation techniques was also conducted to design an efficient solids removal operation for future pilot plant studies. Different types of reactors were used in this investigation so that dominant mechanisms over different operational ranges could be identified.

In the bench-scale experiments, three types of reactors were used: (1) a tubing bomb microreactor (TBMR); (2) a 500 ml distillation flask; and (3) a 3,785 ml autoclave reactor. The TBMR was operated under closed conditions, whereas distillation was carried out under open conditions; i.e. the flask was open to the atmosphere for distilling water and trace amounts of light components. The quality of product oil, in terms of ash and lead content, depends on the solid-liquid separation techniques. Therefore, bench-scale studies were divided into two parts: (i) solids separated by sedimentation and (ii) solids removed by filtration.

Solids Removed by Sedimentation

In a typical experiment, TBMR was charged with 20 gms. of oil and 1.6 gms. of diammonium phosphate (30 wt.% aqueous solution). An excess of DAP was used, so the reaction between metals and DAP was not limited by anions (i.e. phosphates). At the end of the reaction time, TBMR was quenched in water and reaction products were collected in a graduated glass tube. The oil-water emulsion was allowed to settle for a day at 60°C to facilitate the separation of reaction products and water from the oil. The clarified oil was analyzed for ash and lead content.

RESULTS AND DISCUSSION

Demetallization studies were conducted by varying parameters such as reaction time, temperature, and agitation rate for different types of oils. A discussion of the results follows.

Effect of Reaction Time

Several experiments were carried out to observe the effect of reaction time on lead reduction at various reaction temperatures. The variation in lead content of the DAP treated oil (150°C) was observed as shown in Figure 21. From an initial value of about 210 ppm, the lead content of the product oil decreased with increasing reaction time to a final value of 16.5 ppm. From this figure, it can be deduced that agitation has a significant effect on the lead content of the oil. For example, for a 45-minute reaction time, when the agitation rate was decreased from 800 to 400 cpm, the lead content of the treated oil was

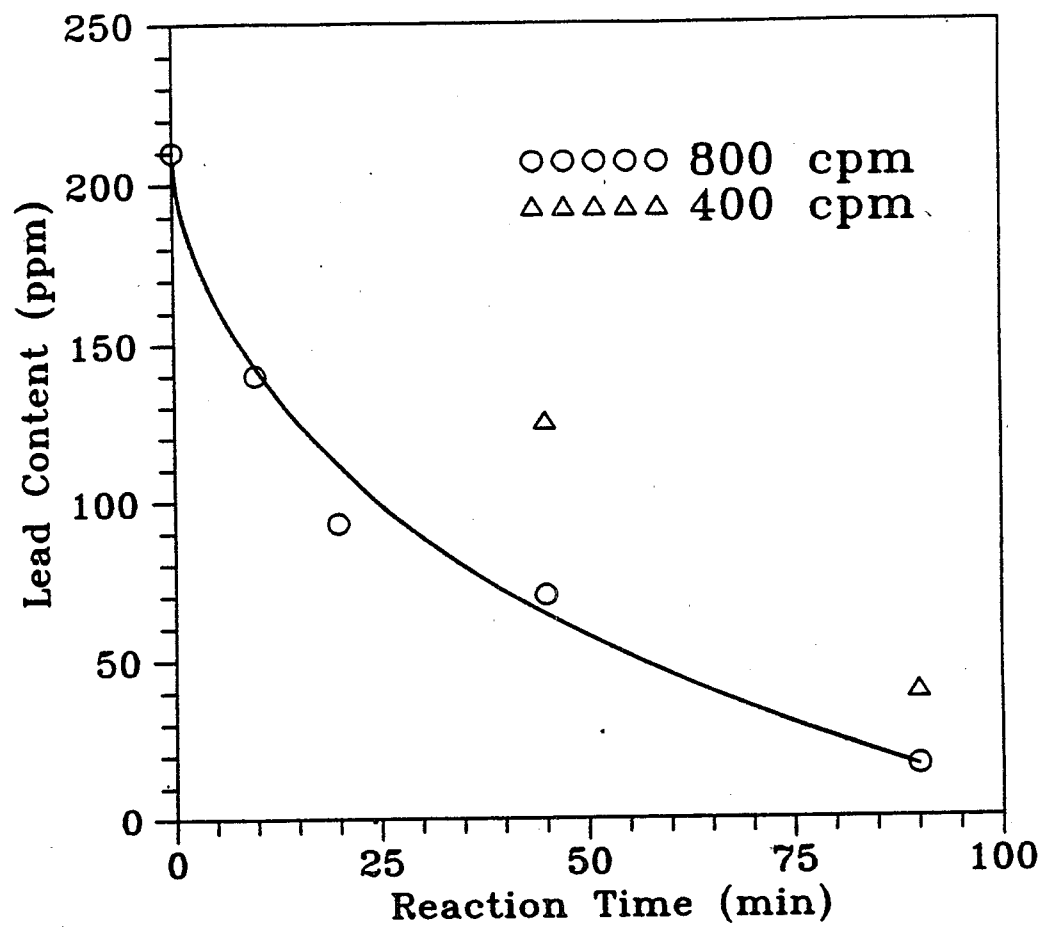


Figure 21. Effect of Reaction Time on Lead Reduction.
(DAP: 8 wt.%; reaction temp.: 150°C)

greater. An increase in agitation is thought to increase the interfacial contact area for the reaction between metals and aqueous reactant.

To investigate the effect of reaction time on other types of oil, several experiments were performed where Type B oil and DAP were reacted at temperature of 200°C and 250°C. Table 15 shows that the lead content of oil decreases with an increase in reaction time. Consequently, it can be inferred that greater reaction time favors the lead reduction from used oil.

Effect of Reaction Temperature

Demetallization experiments have been carried out at different reaction temperatures to determine the effect on lead content of used oil. As seen from Figure 22 (Table 16), an increase in reaction temperature from 150°C to 400°C greatly increased the lead reduction from 63% to 96%. The lead content of Type B oil is also reduced significantly with an increase in the reaction temperature (Figure 23, Table 17). The overall lead content of used oil depends on the reaction temperature and is reduced substantially at high temperature.

Effect of Ash Content

Although lead reduction is strongly dependent on reaction temperature and time, other factors such as the ash content of used oil (i.e. total metal contaminants) may also affect lead reduction.

In order to determine the effect of ash content on lead removal, experiments have been carried out with different oil samples, each having a different ash content. The ash content of each oil was determined in accordance with a modified ASTM procedure (see Appendix B). As shown in Table 18 (Figure 24), lead content is reduced with an increase in reaction time for oil sample 1. However, for oil Sample 2, an increase in reaction time from 45 to 90 minutes showed no significant effect on lead removal.

It may be noted that although the difference in lead content of both samples is only 40 ppm, the total amount of metal competing for DAP is not necessarily the same, as evidenced by their different ash contents.

The major problem with TBMR is immediate vaporization of water during the reaction, which allows very little time for the reaction between metals and anions (i.e. phosphates) at the interface of the oil and aqueous phase. In spite of this drawback, TBMR studies were useful in providing vital information about the demetallization reactions. To prevent the immediate vaporization of water, another type of reactor, i.e. a distillation flask, was used to study the demetallization mechanism. In this reactor, waste oil and aqueous solution of DAP were mixed and heated from a room temperature to a specified temperature. The heat-up time was about 70 minutes, and the reaction was allowed to continue for an additional time. During the reaction, water and trace amounts of light components were distilled off.

Two experiments were initially performed in which waste oil was reacted with aqueous solution of DAP at 150°C. After the reaction, one batch of oil was allowed to settle at 70°C for a day while the

TABLE 15. EFFECT OF REACTION TIME ON LEAD REMOVAL

Reaction Time Min..	Lead Content PPM	% Lead Reduction
<u>Reaction Temp. 250°C</u>		
15	190	60.4
30	66	86.2
60	31	93.5
<u>Reaction Temp. 200°C</u>		
15	300	37.5
30	263	45.2
60	217	54.8

DAP: 8 wt.%, Lead content: 480 ppm

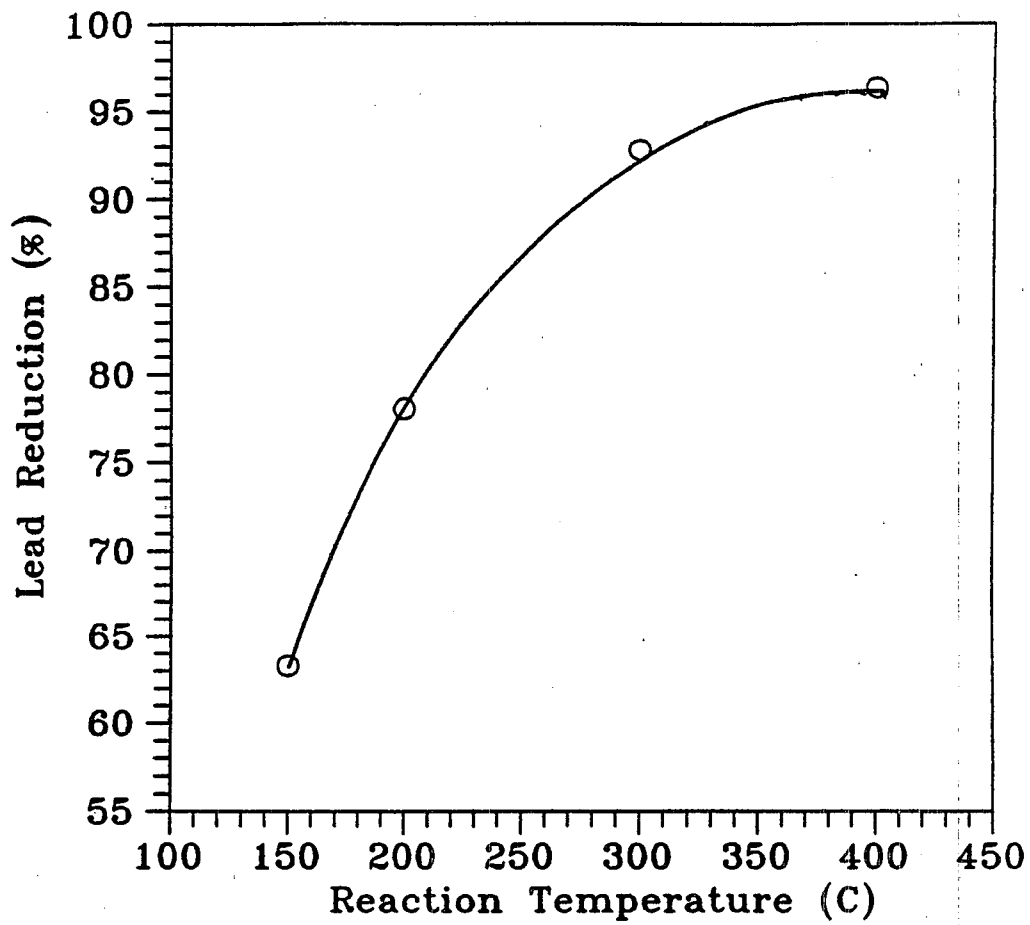


Figure 22. Effect of Reaction Temperature on Lead Reduction.
(Time: 45 min.; 8 wt.%; Lead Content: 210 ppm)

TABLE 16. EFFECT OF REACTION TEMPERATURE ON LEAD REDUCTION

Reaction Temp. °C	Lead content PPM	% Lead Reduction
150	77	63.3
200	46	78
300	15	92.8
400	7.5	96.4

Time: 45 minutes; DAP: 8 wt.%
Lead content of used oil was 210 ppm.

TABLE 17. EFFECT OF REACTION TEMPERATURE ON LEAD REDUCTION

Reaction Temp. °C	Lead content PPM	% Lead Reduction
150	325	32
200	235	51
250	30	93.7

Time: 1 hr.; DAP: 8 wt.%
Ash and Lead content of used oil was 0.52 wt.% and 480 ppm.

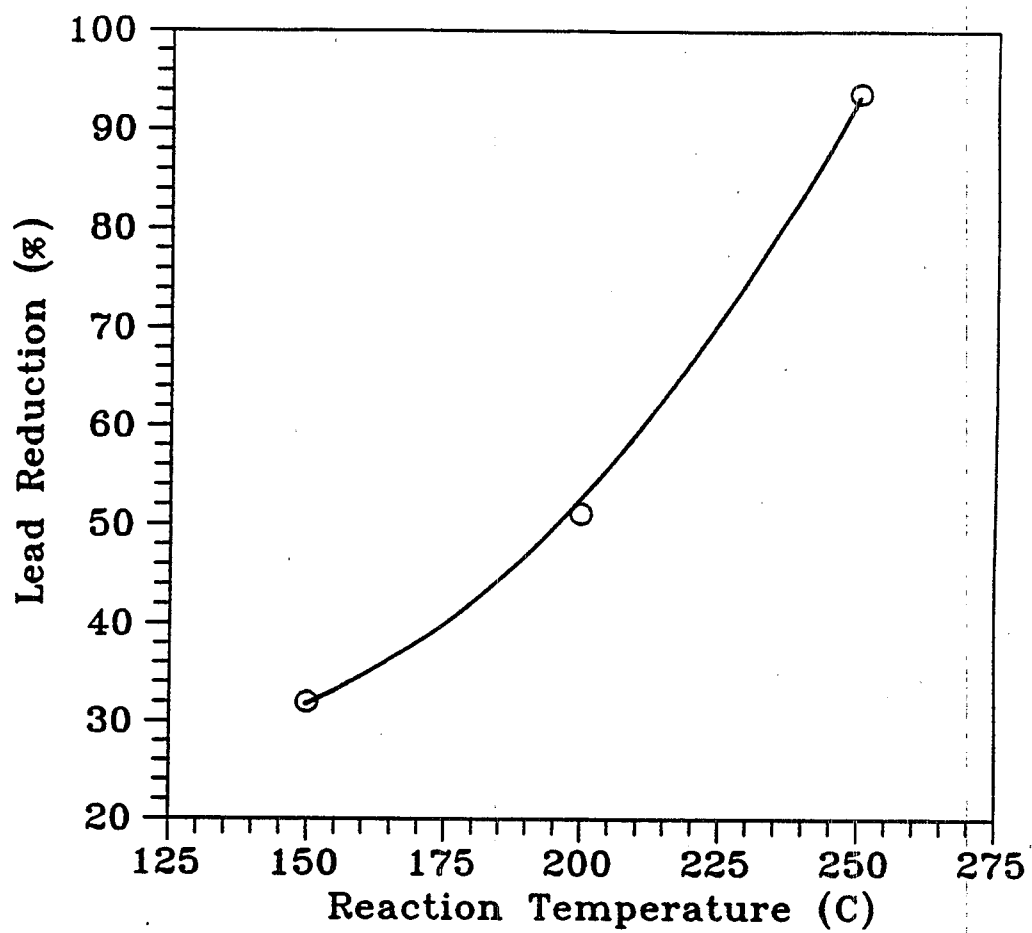


Figure 23. Effect of Reaction Temperature on Lead Reduction.
(Time: 1 hr.; 8 wt.%; Lead Content: 480 ppm)

TABLE 18. EFFECT OF ASH CONTENT ON LEAD REDUCTION

Reaction Time Min.	Lead content, PPM	
	Oil sample 1	Oil sample 2
0	210	251
45	70	100
90	16.5	95

Temperature: 150°C, DAP: 8 wt.%

Ash content (wt.%): Oil sample 1 = 0.4755

Oil sample 2 = 0.8325

TABLE 19. EFFECT OF FILTRATION ON ASH AND LEAD REDUCTION

Mode of Separation	Ash Content wt. %	Lead Content ppm	Lead Reduction %
Filtration	0.02	24	96
Sedimentation	0.4	350	47

Temperature: 150°C, Time: 1 hr., DAP: 8 wt. %

Ash and Lead content of used oil was 0.6 wt. %, 660 ppm.

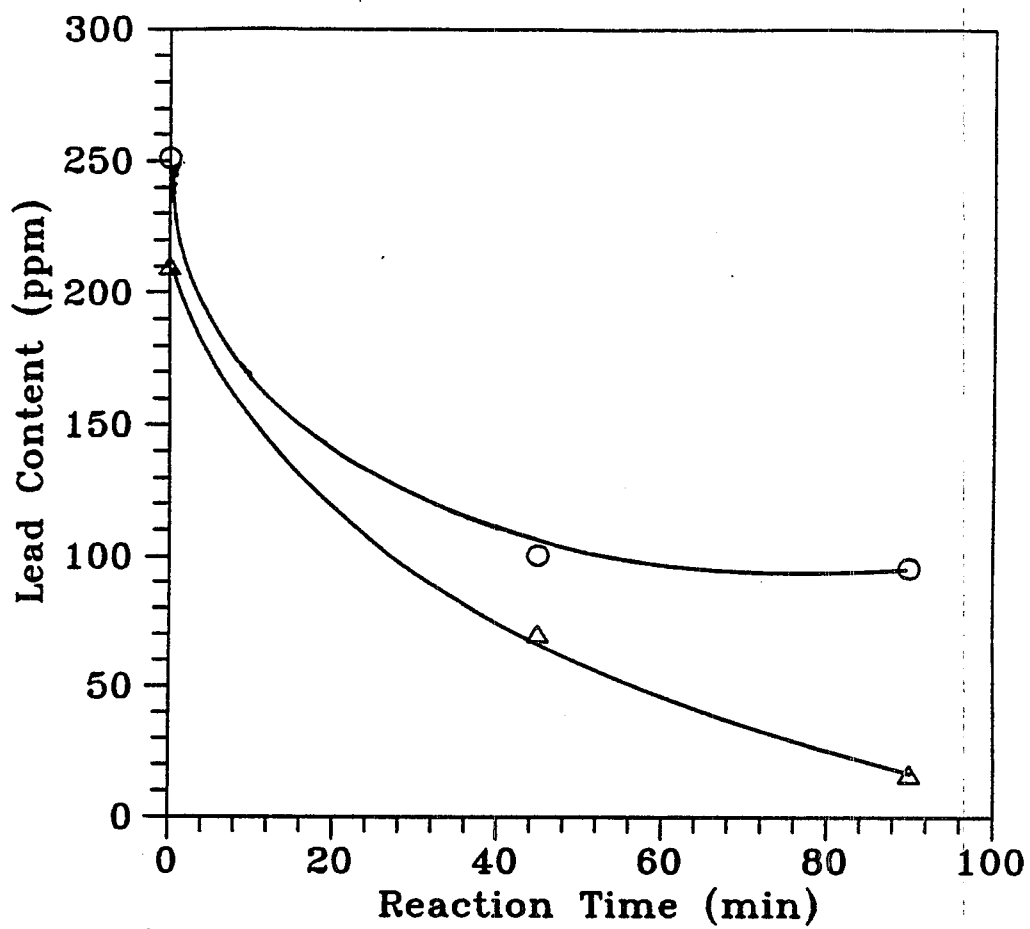


Figure 24. Effect of Ash Content on Lead Reduction.
(Temperature: 150°C; DAP: 8 wt.%)

other batch was immediately filtered. As shown in Table 19, the ash and lead content of the settled oil was much higher than the filtered oil. The high-quality product oil is produced by filtration. This may be due to the high viscosity of used oil, which prevents the separation of fine particulates by sedimentation. Hence, filtration performs better than sedimentation in the separation of reaction products (metal phosphates) from the oil.

SOLIDS REMOVED BY FILTRATION

The Environmental Protection Agency (EPA) has set the allowable maximum lead content in fuel oil to be less than 100 ppm. The purpose of the demetallization study is to find the optimum operating conditions for lead removal which will later be used to design a demetallization unit for the Auburn University Waste Oil Reprocessing Lab (AWORL). Therefore, several parameters were studied to maximize the lead reduction and, at the same time, to find the optimum reaction conditions, which will be economical on a larger scale.

It is believed that more than 50% of lead is present in a particulate form, so some part of the lead can be removed just by filtering the used oil. To determine the possibility of lead reduction by filtration, several batches of used oil were preheated (150°C) prior to filtration. After filtration the oil was analyzed and it was found that the ash and lead content of the filtered oil was not significantly changed (less than 5%) in any of the batches. This may be so because the lead particulates present in waste oil are very fine and pass out with the filtrate.³⁷

In all the previous experiments, an excess of DAP (8 wt.%) was used to demetallize the waste oils. The problems with using large amounts of DAP are: (i) generation of solid waste, which results in a disposal problem; (ii) handling of solids in the plants; (iii) clogging of the filter media; and (iv) the high cost of the reagent.

Effect of Diammonium Phosphate on Ash and Lead Reduction

Several experiments were performed in which waste oil was treated with different amounts of DAP. Table 20 shows that, although a higher amount of DAP favors the demetallization reaction, high ash and lead reduction is still obtained with a lower concentration of DAP (2 wt.%). Since the goal of this project is to reduce the ash and lead content of used oil to below 0.1 wt.% and 100 ppm respectively, it seems that there is no need to produce very high quality oil, which would otherwise increase the cost of the treatment. It should be noted that the amount of DAP required for the demetallization of used oils depends on the initial ash content of the oils. It was found that 2 wt.% DAP was sufficient to reduce the ash content to below 0.1 wt.% for used oil, with an initial ash content between 0.5 to 1.0 wt.%.

Effect of Water on Ash and Lead Reduction

The reaction between DAP and metals occurs at the interface of the oil and aqueous phase. The reaction products remain at the interfacial region unless water is removed during the reaction. It suggests that water removal during the reaction favors the agglomeration of metallic hydroxyl apatites, which would

TABLE 20. EFFECT OF DAP ON LEAD REDUCTION

% of DAP w.r.t oil content	% ash ppm	Lead Content	% lead reduction
8	0.02	24	96
5	0.03	24	96
2	0.08	60	91
1	0.25	230	65
0.5	0.40	462	30
0	0.58	650	<2

Reaction Temperature: 150°C; Residence Time: 1 hr.
Ash and Lead content of used oil was 0.6 wt.%, 660 ppm.

later facilitate the solid-liquid separation. Hence, when reaction temperature was less than 100°C (Table 21), the ash and lead content of filtered oil was not reduced significantly compared with the oil treated at a higher temperature (more than 100°C). This may be due to the presence of water, which prevents the agglomeration of metallic hydroxyl apatites.

It was very clear that water is required initially for the reaction to occur between metals and anions (phosphates) at the interfacial region of the oil and aqueous phase. However, the removal of water during the latter part of the reaction facilitates the agglomeration of metallic hydroxyl apatites, which can be separated by filtering the oil.

The additives in the oil are group II metal compounds. These compounds are more ionic and reactive compared with lead compounds. Essentially the reaction between additive metals and DAP goes to completion and is least dependent on the temperature and time.

Lead is present in a different form in the used oils. If lead is due to the contamination of blow-by products from a combustion engine, then it may be present in a halides form. Organic bromine compounds are added to gasoline to scavenge lead as lead bromide, and it has been suggested that some lead dibromide may be present in used oil. However, X-ray emission spectroscopic analysis of several samples of crankcase oil disclosed a lead/bromine ratio of 0.62-0.68:1.⁴⁷ If all the lead were present as a dibromide, a 2:1 ratio would obtain. However, chlorides or mixed salts may be present. It has been also asserted that significant quantities of metals, and particularly about 50% of the lead, occur in particulates form.

Lead may also be present in an oxide form due to oxidation of lead-copper bearings by organic acids and peroxides during the service life of lubricating oils. These lead compounds (halides, oxides) are very stable, and it is unlikely that they react with DAP; however, they strongly interact with water via dipole-dipole or ion-dipole interactions.

At a workshop on recycled oil, Belton R. Williams presented data from his rerefining operations which are useful in partially characterizing some of the metallic species.³⁶ Water (which arises as a product of fuel combustion, condensation, and seepage into storage tanks) is separated from the oil prior to filtration and distillation. This aqueous phase contains a large amount of sodium, zinc, iron, phosphorus, magnesium, boron, and lead. These data suggest that the metals mentioned occur to a significant extent in water-soluble forms.

Lead compounds present in the oil are too stable to react with DAP; hence, their removal is not dependent on the chemical reaction. But due to ionic attraction or ion-dipole attraction, lead compounds are attracted toward the aqueous phase. So, when water is removed during the reaction, lead compounds are entrained in the agglomeration of metal hydroxyl phosphates and are removed along with other reaction products by filtration. Since lead is not directly removed by chemical reaction with DAP, its removal is not independent of the temperature or the residence time.

TABLE 21. EFFECT OF WATER ON ASH AND LEAD REDUCTION

Temp. °C	Ash Content wt. %	Ash Reduction % ppm	Lead Content %	Lead Reduction %
70	0.4	33	607	8
80	0.42	30	600	9
90	0.36	40	550	17
120	0.15	75	150	77

Temperature: 150°C; Time: 1 hr.; DAP: 2 wt. %
Ash and Lead content of used oil was 0.6 wt. %, 660 ppm.

Effect of Temperature and Residence Time on Lead Reduction

Figure 25 suggests that lead reduction is a strong function of temperature. Only 9% of lead reduction was obtained at 80°C compared with 97% at 200°C. Even a moderate increase in reaction temperature (120°C) reduced the lead content very significantly. This may be due to the removal of water, which facilitates the agglomeration of metal hydroxyl phosphates and lead compounds.

As seen in Figure 26, increasing the residence time has a substantial effect on the removal of lead from used oil. When residence time was 60 minutes, more than 90% of lead reduction was obtained, compared with 60% without any residence time at the final temperature. Hence, high reaction temperature and time favor lead removal from the used oil.

A DAP demetallization study was done in an autoclave to verify the results obtained so far. Table 22 shows that the final ash and lead content of the product oil agrees with the previous results.

MECHANISM FOR LEAD AND METALS REMOVAL

The additive metal compounds are present in waste oil in organometallic form. The additives are surface active agents and, in the most common form are constituted of a hydrocarbon portion and a polar or ionic portion. The hydrocarbon portion, which can be linear or branched, interacts only very weakly with the water molecules in an aqueous environment. However, the polar or ionic portion of the molecule, usually termed the head group, i.e. metals, interacts strongly with the water by dipole-dipole or ion-dipole interactions, and is solvated.

The organometallic additives in waste oil react with DAP in the interfacial region (Figure 27) to form metallic hydroxyl apatite. The additives are groups I and II metal compounds and generally are highly reactive and more ionic in nature. These metals react with DAP, and the reaction goes to completion even at low temperature.

Lead is present in a form that is physically different from additive compounds in the used oil. The lead compounds present in used oil are too stable to react with DAP, but are attracted toward the aqueous phase due to ionic-ionic or ionic-dipole attraction. The ionic attraction is enhanced when water is removed during the reaction. The lead particles are entrained with the agglomerates of metallic hydroxyl phosphates and are separated by filtration.

LIMITATIONS

The oil obtained by treating waste oil with DAP has a very low ash and lead content. However, the major problem associated with this process is the separation of solids (reaction products) from the oil. With filtration, good solids-removing efficiency is obtained compared with sedimentation; however, filtration is an extremely slow and cumbersome method to operate. In general, used motor oil is highly

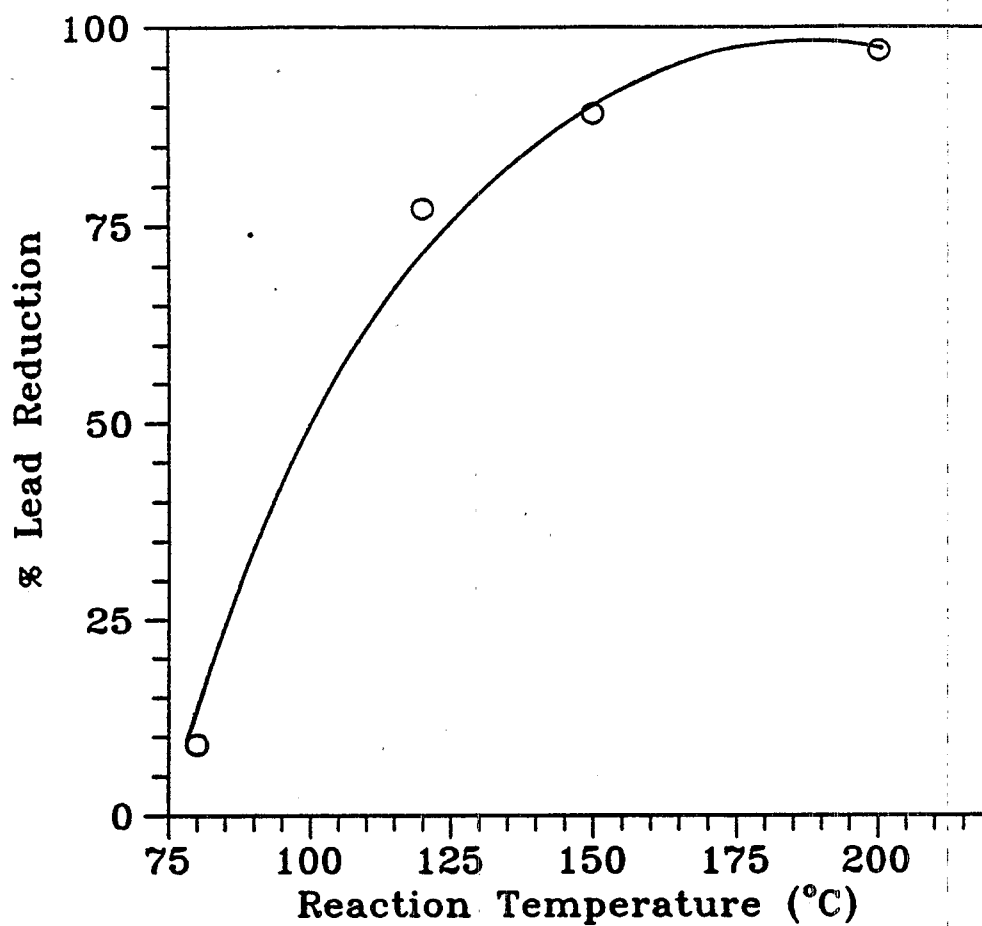


Figure 25. Effect of Reaction Temperature on Lead Reduction.
(DAP: 2 wt.%; Residence Time: 1 hr.; L.C.: 660 ppm)

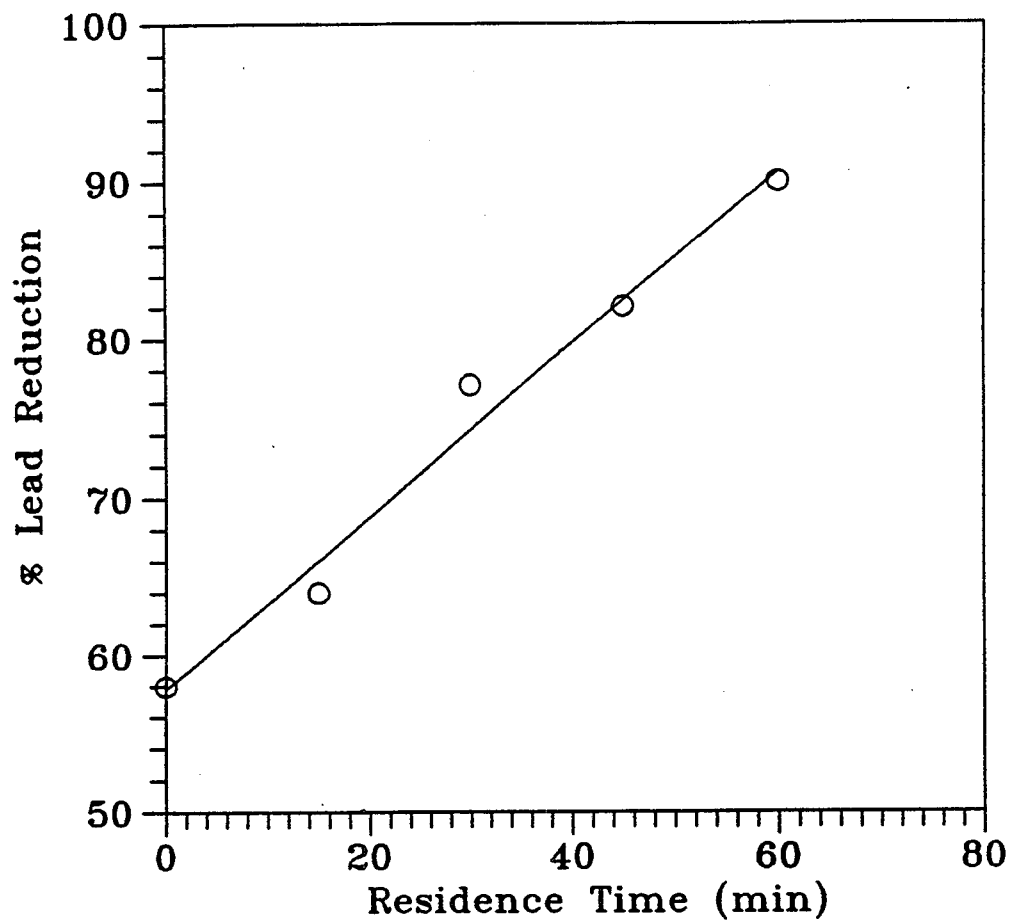


Figure 26. Effect of Residence Time on Lead Reduction.
(DAP: 2 wt.%; Reaction Temp.: 150°C)

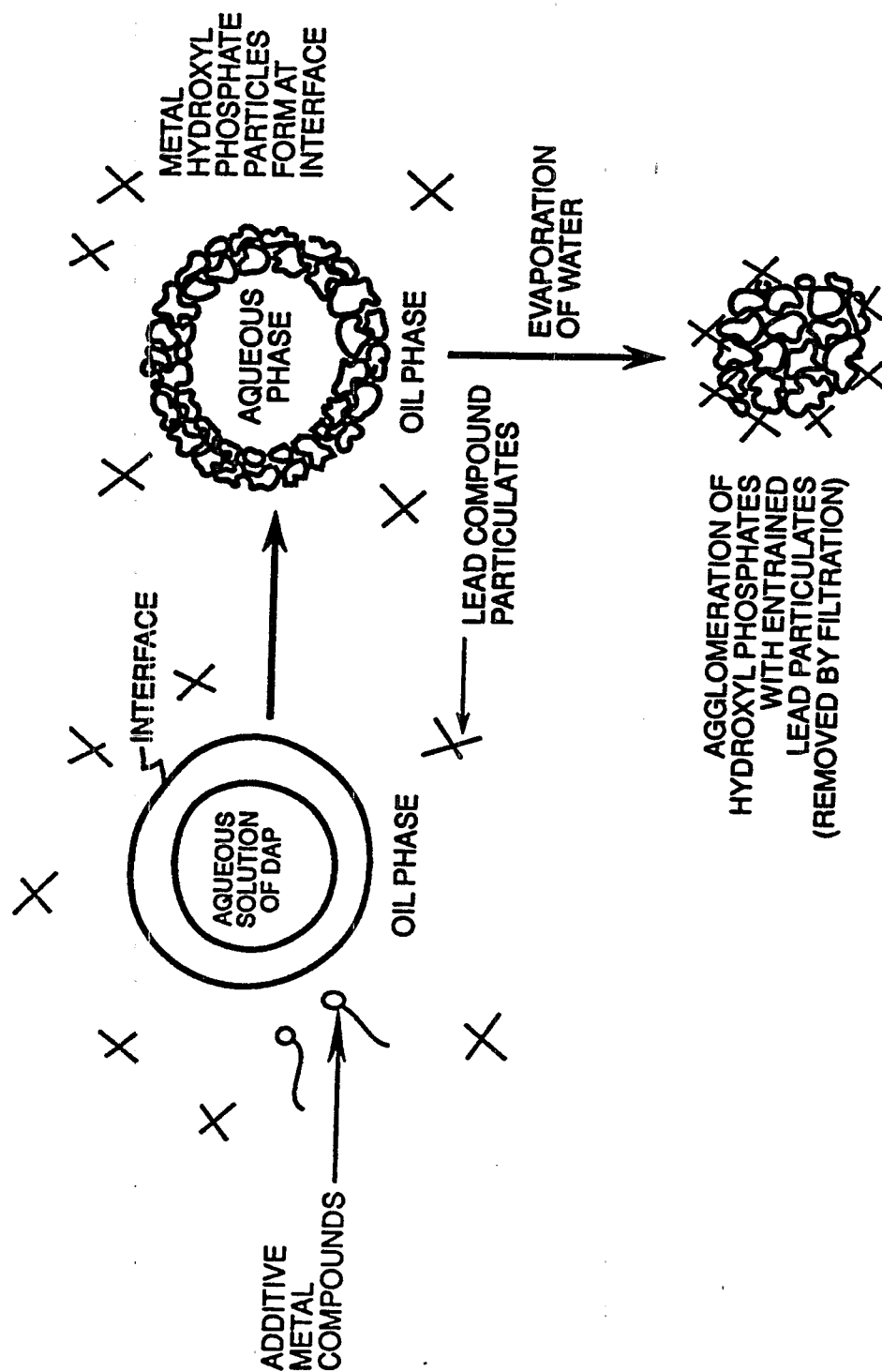


Figure 27. Proposed Mechanisms For Additive Metal and Lead Removal.

TABLE 22. DAP DEMETALLATION STUDY USING A ONE-GALLON AUTOCLAVE

Run no.	% of DAP	Lead content ppm	Ash content wt. %
A1*	4.0	380	0.51
A2	4.0	0.0	0.02
A3	1.5	0.0	0.016
A4	1.5	20	0.016
A5	1.5	2.0	0.04
A6	1.5	2.0	0.06

Reaction Temperature: 160°C; Residence Time: 1 hr.
Ash and lead content of used oil was 0.6 wt.%, 660 ppm.

Note:

*Dry oil: Lead content = 700 ppm

Runs A1 and A5: The autoclave was completely sealed.

Runs A2 to A4 and A6: One port of the autoclave was intentionally opened to allow the water vapor to escape in an effort to simulate the distillation process.

viscous and contains insoluble suspended sludge, resinous compounds, asphaltenes, carbon particles, varnishes, and other impurities. These compounds, along with reaction products, blind the filter media during the filtration cycles. Rerefiners, which employ filtration as a part of their process, have also encountered similar problems in the past.

The filtration rate can be improved either by increasing the temperature of the oil or by adding diluent to the oil. In order to evaluate the use of diluent (No. 2 fuel oil) to improve filtration rates, another DAP demetallization experiment was carried out in a 1000 ml distillation flask. After the reaction, treated oil was divided into four fractions; a specified amount of filter aid or No. 2 fuel oil or both were thoroughly blended in three of the four fractions. Viscosity of each fraction was measured using a Cannon-Manning viscometer. As seen from Table 23, the filtration rate approximately doubled after dilution. The rate was further increased with the addition of filter aid; however, filter aid increases solid waste generation. The filtration rate, like the lead removal, is directly related to the processing temperature. The filtration rate increases uniformly with temperature and increases greatly when the oil is held at the final temperature. In a process which includes a filter, the filtration rate is likely to be the limiting factor.

In summary, problems encountered with filtration are: (i) poor filtration rate; (ii) frequent changing of filter media (due to blinding); (iii) high temperature requirement; (iv) addition of the filter aid increases solid waste generation; and (v) cumbersome operation.

CONCLUSIONS

(1) The organometallic additives in waste oil react with DAP in the interfacial region to form metal phosphates.

(2) Lead is present in a different form compared with additive metals and is not directly removed by chemical reaction with DAP.

(3) Lead reduction is dependent on the reaction temperature and residence time, and is greater at higher temperature and time.

(4) Water is required in the early stages of the demetallization reaction, while in the latter stages, removal of water facilitates the agglomeration of metal hydroxyl phosphates and lead compounds.

(5) Pressure can be avoided in the reactor by venting out the water vapor and light components during the reaction.

(6) Filtration produces high-quality reclaimed oil, in terms of ash and lead content, compared with sedimentation.

(7) Filtration is cumbersome to operate and increases the cost of the process due to high temperature requirements.

(8) More than 90% of lead is removed by treating waste oil with DAP at 150°C for an hour.

TABLE 23. EFFECT OF DILUENT AND FILTER AID ON FILTRATION RATE

	Viscosity (cp)	Filtration Rate (ml/min)	Filtrate Vis. (cp)
Oil	89.9	11.5	87.7
Oil + 1 wt.% Filter Aid	95.5	12.0	87.3
Oil + 20 wt.% No. 2 Fuel Oil	32.8	25.0	37.3
Oil + 20 wt.% No. 2 Fuel Oil + 1 wt.% Filter Aid	38.4	34.0	37.6

Viscosity was measured at 25°C.

SECTION VII

USE OF TRIETHANOL AMINE AS A FLOCCULATING REAGENT

The quality of DAP treated oil depends on the solid-liquid separation. Filtration produces high quality oil in terms of ash and lead content. Although DAP reduces ash and lead content significantly, it does not remove the oxidation products present in used lubricating oils.

Oxidation products in used oils include peroxide, carbonyl compounds, organic acids, etc. These compounds are highly corrosive and difficult to remove by traditional purification methods such as distillation, hydrogenation, or absorption. These oxidation products can be removed by treating the used oil with a strong reducing agent. A better approach would be to use the reagent, which is similar in nature to an antioxidation additive in motor oils. Typically, zinc dithiophosphate is used as an antiwear and antioxidant additive; however, recently amines and phenolic compounds have been widely used as antioxidants.

The outstanding chemical properties of amines are due to the unshared pair of electrons on the nitrogen atoms. This makes amines both bases and nucleophiles.⁴⁸ The ability of amines, especially alkanolamines (e.g. triethanol amine), to neutralize organic acids is beneficial not only in removing the oxidation products but also in neutralizing sulfonated compounds (dispersant additives). The resulting oil is free of organic acids, peroxides, insoluble sludge, varnishes, and other impurities.

Alkanolamines are bifunctional molecules, having both amino and alcohol functional groups. As a result, they undergo a wide variety of useful reactions common to amines and alcohols. The amino group may be either primary, secondary or tertiary, and may display typical reactivity of a primary, secondary or tertiary amine. Since an alkanolamine combines both the amine and alcohol groups in one molecule, it is capable of many reactions which an amine or an alcohol is not. In general, the hydroxyl group is regarded as able to reduce vapor pressure and increase water solubility, while the amino group provides the alkalinity in the water solution required to neutralize acids.⁴⁹

In the past, amine compounds were tried as a flocculating agent to precipitate the sludge and impurities from used oil.^{50,51,52} From an initial experimental work, we found that triethanol amine (TEA) was a better flocculating agent in precipitating the impurities from used oil. While other alkanolamines such as monoethanol amine, diethanol amine, isopropanol amine could be used, the separation of impurities were not as good as with TEA.

A detailed parametric study was undertaken to map out the process variables in order to identify the most efficient reaction conditions. Experiments were performed to investigate the effect of different parameters on demetallization of used oil.

Effect of Triethanol Amine on Ash and Lead Reduction

Used motor oil was reacted with TEA and allowed to settle for a day. As shown in Table 24, the ash content of clarified oil was not reduced significantly compared to the lead content. The analysis of oil samples for different metal contents presented in Table 25 shows that the concentration of additive metals more or less remained the same.

It was thought that additives in the motor oil were so finely dispersed that they do not precipitate with the sludge and impurities, while particulates lead were entrained in the reaction products and removed along with sludge.

In recent years, lead contaminants in used oil have been due to corrosion of lead-copper bearings rather than blow-by products of combustion (i.e. not due to tetraethyl lead). The acids formed during the service life of lubricating oils oxidize the metal bearings and other machine parts. These metal oxides are soluble in the acids; hence, neutralizing the acids facilitates the separation of metal oxides from the used oil.

Since additive metals still remained present in the TEA treated oil, it was thought that the addition of DAP would facilitate their removal along with the neutralization products. Table 26 shows the ash and lead reduction with respect to DAP. Significant points emerging from the data of Table 26 are:

(i) without DAP, only a 24% ash reduction is obtained, because additive metals like Ca, Ba, Mg, and Zn still remain dispersed in the oil. The low ash reduction is due to the precipitation of particulate metals and metal oxides with sludge; and

(ii) ash reduction seems to increase with an increasing amount of DAP, up to 1 wt%. A further increase in the amount of DAP has very little effect on ash and lead reduction. This may be due to the limitations of solid-liquid separation achieved by sedimentation.

In all these experiments, a different concentration of DAP solution (20 wt% aqueous solution) was mixed with TEA (0.5 wt%) prior to the reaction. The addition of TEA separately also has the same effect.

The amount of TEA required to flocculate the impurities and heavy metals (lead) depends on the used oil. The highly oxidized oil (used motor oil) requires a higher amount of TEA to neutralize the acids. Table 27 shows the effect of TEA on ash and lead reduction, while keeping the concentration of DAP constant.

Without TEA, the separation of reaction products (metal phosphates) and impurities was so poor that hardly any oil was recovered. Normally, 0.5 wt% TEA is sufficient enough to flocculate the impurities from used motor oil. The higher amount of TEA favors the ash and lead reduction but decreases the recovery of oil.

TABLE 24. EFFECT OF TEA ON ASH AND LEAD REDUCTION

TEA wt%	Ash Content wt%		Reduction %	Lead Content ppm		Reduction %
	Before	After		Before	After	
0.2	0.88	0.80	9	130	114	12
0.5	0.86	0.65	24	135	55	59
1.0	0.88	0.67	24	136	45	67
1.5	0.90	0.66	27	135	45	67
2.0	0.89	0.67	25	134	43	68

Reaction Temp: 80°C; Reaction Time: 1 hr.
Settling Temp: 75°C; Settling Time: 24 hrs.

TABLE 25. ADDITIVE METALS CONTENT OF TEA TREATED OIL

Metals	Used oil ppm	Treated Oil ppm
K	120	108
Ca	1630	1525
Mg	950	825
Ba	175	147
Zn	1900	1734
P	1395	1251

Reaction Temp: 80°C; Reaction Time: 24 hrs.
Settling Temp: 75°C; Settling Time: 24 hrs.

TABLE 26. EFFECT OF DAP ON ASH AND LEAD REDUCTION

DAP wt%	Ash Content wt%		Reduction %	Lead Content ppm		Reduction %
	Before	After		Before	After	
0.0	0.86	0.65	24	114	50	56
0.5	0.89	0.47	47	91	25	7
1.0	0.89	0.11	88	109	6	94
1.5	0.80	0.10	88	89	4	96
2.0	0.82	0.11	87	69	2	97

TEA: 0.5 wt%, Reaction Temp: 80°C, Reaction Time: 1 Hr.
Settling Temp: 75°C, Settling Time: 24 Hrs.

TABLE 27. EFFECT OF DAP ON ASH AND LEAD REDUCTION

TEA wt%	Ash Content wt%		Red. %	Lead Content ppm		Red. %	Recovery (vol%)
	Before	After		Before	After		
0.0	0.87	--	--	112	--	--	--
0.5	0.89	0.11	88	110	7	94	89
1.0	0.88	0.10	89	118	4	97	85
1.5	0.88	0.07	92	122	2	98	70
2.0	0.89	0.07	92	123	2	98	70

DAP: 1.0 wt%; Reaction Temp: 80°C; Reaction Time: 60 min.
Settling Temp: 75°C; Settling Time: 24 hrs.

-- The run without TEA resulted in poor separation of impurities.

Effect of Temperature and Time on Ash and Lead Reduction

The additives are group I and II metal compounds and are highly reactive and more ionic in nature. The reaction between DAP and additive metals goes to completion and is least dependent on time and temperature. The same is true for the reaction between TEA and acids. The reaction between oxidation products and TEA occurs even at low temperature within a short period of time. As seen from the Table 28, a reaction time of 15 minutes is sufficient to reduce the ash and lead content to 0.12 wt% and 10 ppm, respectively. A further increase in reaction time does not improve the ash and lead reduction.

As discussed in the previous chapter, the lead content of DAP-treated oil depends on reaction temperature and residence time. but with the addition of TEA, high lead reduction was obtained at low temperature due to the following reasons: (i) neutralization of acids by TEA causes the precipitation of lead compounds, and these neutralization reactions occurs at low temperature; and (ii) TEA flocculates the particulates lead along with reaction products and impurities. Table 29 shows the effect of the reaction temperature on ash and lead reduction. The ash and lead content is reduced between 85 to 95% at 80°C, while there is not much difference in ash and lead content with further increase in temperature.

Although ash and lead reduction is least dependent on reaction temperature and time, a recovery of oil is greatly influenced by settling temperature and time. The viscosity of oil depends on the temperature and is lower at higher temperatures to facilitate the separation of sludge from oil. Figures 28 and 29 show the effect of settling temperature and time on oil recovery. The oil recovery is based on the volume % of recovered oil with an ash and lead content below 0.15 wt% and 10 ppm, respectively. It can be seen from these figures that 90% of the oil is recovered at 80°C (settling time 24 hours), which is very high considering the fact that used motor oil contains roughly 5 to 8% of sludge and additives.

Effect of Water on the Demetalization of Oil

The presence of water is absolutely necessary for the reaction to occur between phosphate ions and metals.

It should be noted that a large quantity of water increases the load on the separation unit and on the wastewater treatment plant. To evaluate the effect of water on the demetallization reaction, various concentrations of aqueous solution were reacted with waste oil. In all these experiments, the amount of DAP and TEA was kept constant. As seen from Table 30, too much dilute solution reduces the oil recovery. This may have been caused by the poor separation of the reaction products, or it may be that a large quantity of water inhibits the flocculating power of TEA. It was found that a concentration of aqueous solution between 20% to 30% essentially provided the same level of oil recovery. A further increase in the concentration of DAP solution was not possible due to the recrystallization of DAP by the addition of TEA.

TABLE 28. EFFECT OF REACTION TIME ON ASH AND LEAD REDUCTION

Reac. Time (min.)	Ash Content wt%		Red. %	Lead Content ppm		Red. %
	Before	After		Before	After	
7	0.86	0.45	48	100	45	55
15	0.85	0.12	86	105	10	90
30	0.89	0.11	88	109	8	93
45	0.85	0.10	88	104	6	94
60	0.89	0.10	89	108	5	95

DAP: 1 wt%, TEA: 0.5 wt%; Reaction Temperature: 80°C
Settling Temperature: 75°C; Settling Time: 24 Hrs.

TABLE 29. EFFECT OF REACTION TEMPERATURE ON ASH AND LEAD REDUCTION

Temp. (°C)	Ash Content wt %		Red. %	Lead Content ppm		Red. %
	Before	After		Before	After	
50	0.85	0.45	47	75	30	60
80	0.89	0.11	88	109	6	94
100	0.89	0.13	85	108	8	93
120	0.89	0.11	87	114	6	95

DAP: 1 wt%, TEA: 0.5 wt%; Reaction Time: 1 hr.
Settling Temperature: 75°C; Settling Time: 24 hrs.

TABLE 30. EFFECT OF WATER ON OIL RECOVERY

Aqueous Solution (wt%)	Ash Content wt%		Red. %	Lead Content ppm		Red. %	Recovery (vol%)
	Before	After		Before	After		
10	0.87	0.10	89	102	9	91	71
15	0.85	0.10	88	104	10	90	77
20	0.89	0.11	88	107	9	92	89
25	0.85	0.09	89	103	7	93	89
30	0.89	0.11	88	108	6	94	88

DAP: 1 wt.%; TEA: 0.5 wt.%; Reaction Temperature: 80°C
Settling Temperature: 75°C; Settling Time: 24 Hrs.

Note:

The amount of DAP is same for all the run but concentration of aqueous solution is different.

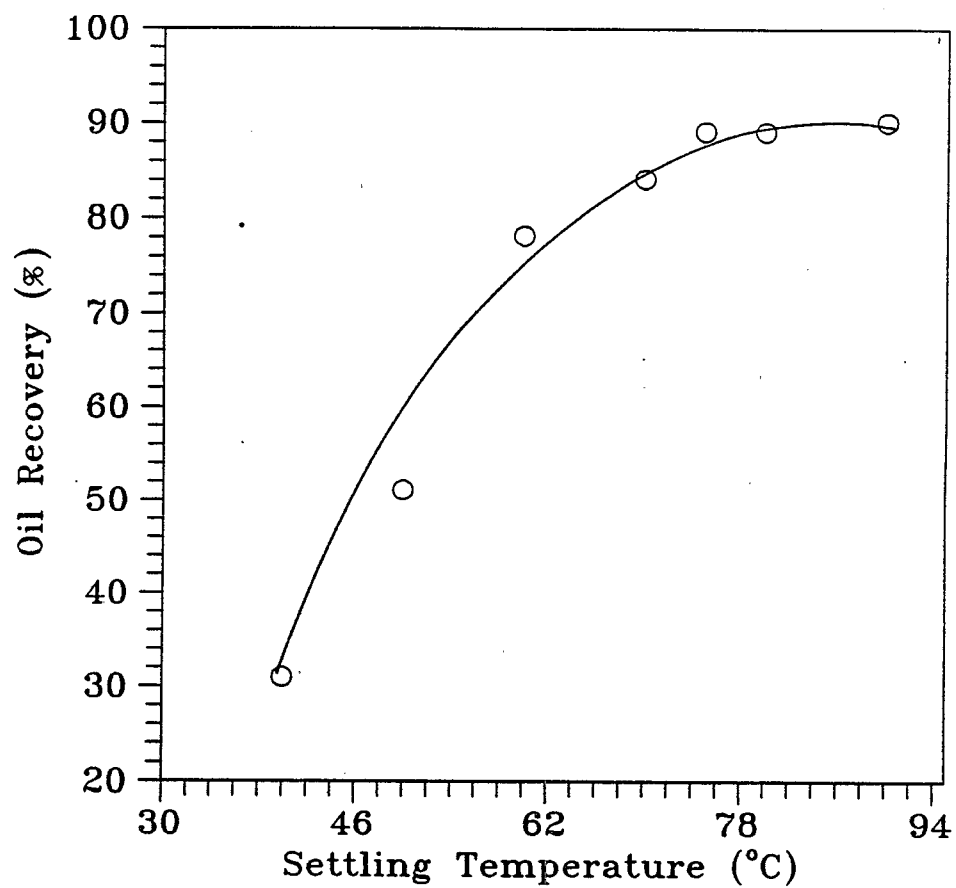


Figure 28. Effect of Settling Temperature on Oil Recovery.
(DAP: 1 wt.%; TEA: 0.5 wt.%; Settling Time: 24 hrs.)

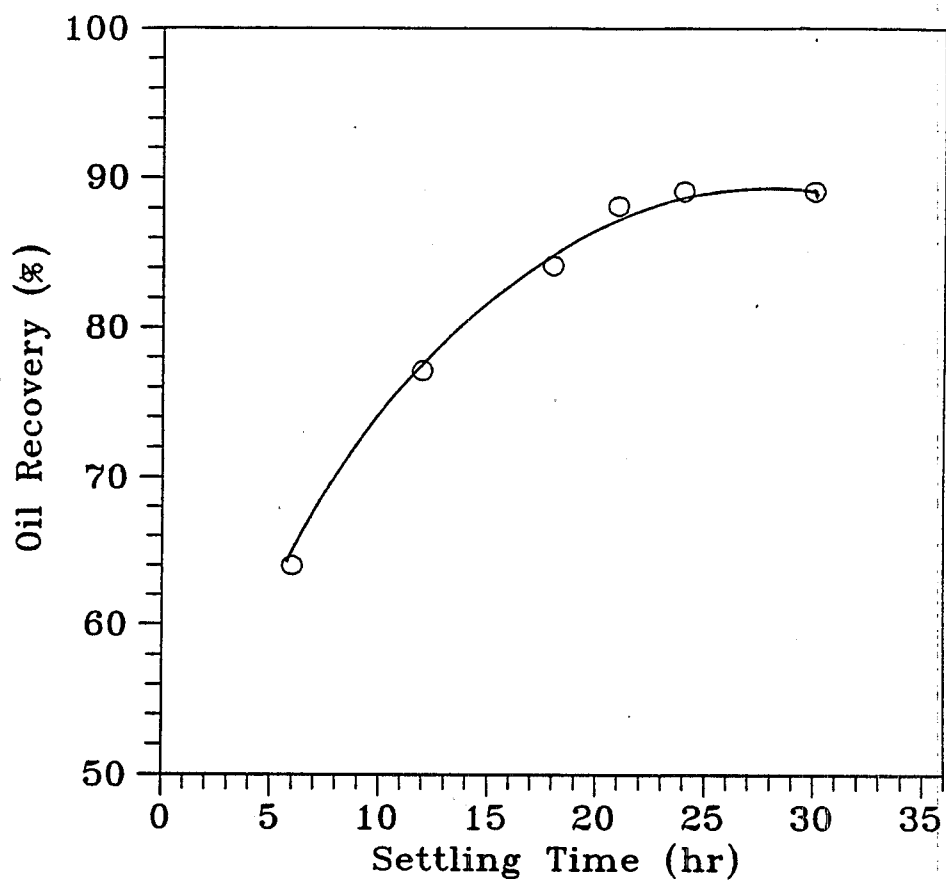


Figure 29. Effect of Settling Time on Oil Recovery.
(DAP: 1 wt.%; TEA: 0.5 wt.%; Settling Temperature: 80°C)

MECHANISM OF METALS REMOVAL

The organometallic additives in waste oil react with DAP in the interfacial region, as shown in Figure 30. The hydrophilic metallic parts are oriented toward the aqueous phase, while the organic chain is oriented toward the oil phase. The anion (PO_4^{3-}) in the aqueous solution forms salts with the metals in the oil.

Triethanol amine ($\text{C}_6\text{H}_{15}\text{NO}_3$) reacts with organic acids to form neutralization products. TEA has three hydroxyl groups and one amino group. In general, the hydroxyl group is viewed as serving to reduce the vapor pressure and increase the water solubility, while the amino group provides the necessary alkalinity in water solution to cause the neutralization of acids. A typical reaction between tertiary amines and carboxylic acids is as follows⁵³:



Based on the above reaction, tertiary amines react with carboxylic acids to form salts, which are highly complex and insoluble in the oil and aqueous phase. TEA also reacts with a wide variety of peroxides and forms insoluble products. Due to the neutralization of organic acids by TEA, the heavy metal oxides (e.g. lead oxide) which are soluble in these acids also precipitate with the agglomeration of metal hydroxyl phosphates and neutralization products from the oil. Lead particulates are entrained in the agglomeration of reaction products and are removed along with the sludge. The flocculating power of TEA facilitates the separation of impurities from the used oil.

Solid-Liquid Separation

In precipitating the impurities and reaction products from the oil, three separation techniques, including filtration, centrifugation, and constant temperature settling, were studied. A detailed discussion related to these separation techniques follows.

Filtration

Solid-liquid separation is much better by filtration, compared with any separation techniques. Filtration is very cumbersome to operate, needs frequent supervision, and increases the cost of the process due to high temperature requirement.

It appears that a combination of separation techniques may be better for overcoming the problem associated with filtration. Sedimentation, which precedes filtration, removes the bulk of impurities from used oil, which in turn improves the filtration rate and is less troublesome from an operational point of view. The ash content of clarified oil (0.1-0.12 wt%) was further reduced (0.05-0.08 wt%) by filtration. Hence, the process scheme for the pilot plant should include sedimentation before any other separation techniques.

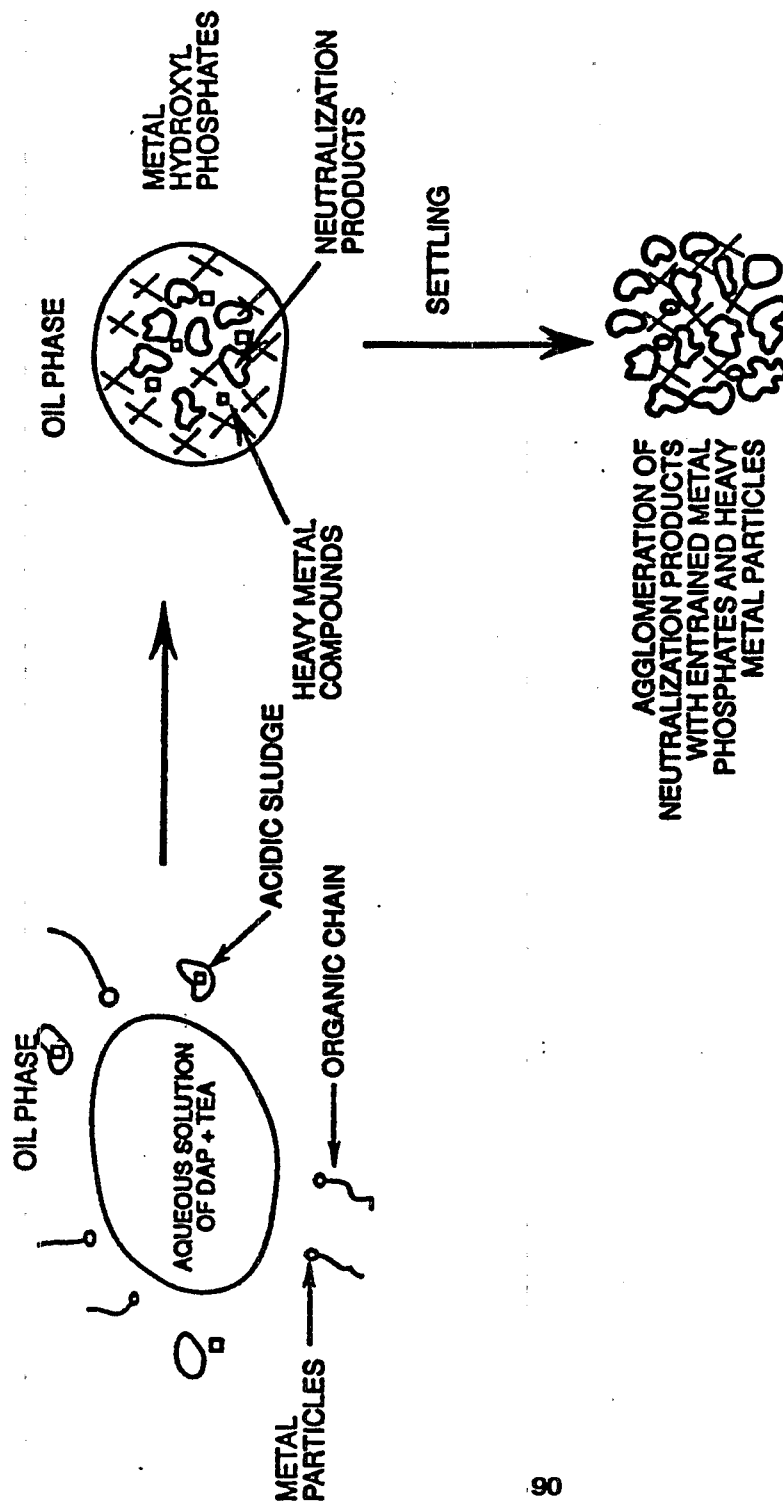


Figure 30. Proposed Mechanisms for Metal Removal.

Centrifugation

It increases the mass forces on particles and thus extends sedimentation to finer particles that are normally stable in the gravity field. In sedimenting centrifuge, the centrifugal acceleration is much larger than the acceleration due to gravity. Centrifugal force overcomes the brownian diffusion forces, which in gravity sedimentation hinder or prevent the settling of very fine particles. As the separation efficiency is mainly affected by the behavior of the smallest particles in the system, it is common to assume that centrifugation might work better, in terms of separating the fine particles, in comparison with gravity sedimentation. However, in terms of ash and lead reduction, both separation techniques i.e., centrifugation and sedimentation, work equally well (Table 31).

In order to verify the results, several samples of waste oils were sent (after the treatment) to a commercial centrifuge manufacturer for their evaluation. The oil was centrifuged under the force of 8,000 G (acceleration was 8,000 times more than gravity). The ash and lead content of the oil after centrifugation were in the same range as that obtained through gravity sedimentation. This indicates that flocculation increases the particle sizes, which facilitate the separation of impurities from oil. Hence, gravity sedimentation takes longer than centrifugal sedimentation, but the overall separation of the solids in terms of ash and lead reduction is the same.

TABLE 31. EFFECT OF DIFFERENT MODES OF SEPARATION ON ASH CONTENT

Samples	Ash Content wt%		Red. %	Lead Content ppm		Red. %
	Before	After		Before	After	
1	0.89	0.11	88	104	9	91
2	0.89	0.12	87	105	10	90
3	0.89	0.10	89	104	9	91

DAP: 1 wt.%; TEA: 0.5 wt.%; Temp: 80°C; Time: 30 Min.

Note:

Sample 1 was allowed to settle at 75°C for a day.

Sample 2 was centrifuged in the lab.

Sample 3 was sent to the Sanborn Inc. for their evaluation.

The major advantages of centrifugation over gravity sedimentation are high throughput capacity and smaller size of the equipment. However, centrifuges are high maintenance items and can handle only a certain amount of solids. Since waste oils contain high concentrations of solids, commercial centrifuge systems include a combination of a decanter (for the separation of coarse particles) and a high-speed centrifuge (for the separation of fine particles). This increases the cost of the process significantly; hence, centrifuge was not considered for the separation of impurities from used oil.

Gravity Sedimentation

The results obtained so far suggest that gravity sedimentation performs just as well in separating solids (reaction products) from waste oil. The clarified oil has a low metals content, as can be seen in Table 32. In addition to additive metals, lead was also significantly reduced by gravity separation.

The efficiency of gravity sedimentation depends on temperature, time, settling area, and particles size. Settling area and time are interrelated, because a large settling area requires less time for particles to settle, and vice versa. Temperature is an important factor, because the viscosity of liquid is reduced at higher temperature, which reduces the viscous force. Particle size, especially for fine particles, affects the effect of gravity separation. But in the case of TEA-treated oil, particles sizes are much larger due to flocculation, and hence a nearly complete separation of solids is achieved by gravity sedimentation.

CONCLUSIONS

(1) The organometallic additives in waste oil react with DAP in the interfacial region and form metal phosphates.

(2) Triethanol amine is very effective in neutralizing acids and flocculating impurities from used oil.

(3) Lead is present either in particulates or in oxide form, and its removal is least dependent on temperature and time.

(4) Lead particulates are entrained with the sludge, and are removed along with the reaction products, while neutralization of acids cause the precipitation of lead oxide from used oil.

(5) More than 85% of the metals are removed at 80° under atmospheric pressure.

(6) Reaction conditions of this process are very mild as compared to other waste oil recovery processes.

(7) Solid-liquid separation by gravity sedimentation is comparable with other separation techniques, and produces specification grade fuel oil.

(8) This method of treatment can be used as a pretreatment for the Distillation-Hydrogenation process.

**TABLE 32. METAL CONTENTS OF USED OIL PROCESSED BY
CHEMICAL TREATMENT**

Metal Conc.	Used Oil (ppm)	Processed Oil Sedimentation	Filtered	Sludge
K	119	9	9	231
Ca	1570	157	120	12297
Mg	905	11	7	7187
Ba	150	2	2	1160
Zn	1805	92	44	13500
P	1367	240	180	26623
Pb	150	<2	<2	1264
Cu	338	268	236	400
Fe	225	9	5	1106
Mn	9	<1	<1	73
Mo	11	<1	<1	52
Al	24	20	18	120
Cr	5	<1	<1	30
B	5	<2	<2	33
Si	34	5	3	57
Total	6710	815	625	64143

DAP: 1 wt.%; TEA: 0.5 wt.%; Temp: 80°C; Time: 30 min.
Settling Temp: 75°C; Settling Time: 24 hrs.

SECTION VIII PILOT PLANT

Based on the bench-scale studies, the Chemical Engineering Department of Auburn University has developed a pilot plant to reprocess waste oils into specification grade fuel oil. The pilot plant (Figure 31) has the capacity to treat 5 gallons/min. of used oil. The pilot plant studies will be very useful in determining the feasibility of the process. It will also identify engineering problems so they can be corrected before any future upgrading of the facility takes place. The plant is divided into three sections, namely demetallization, separation and sludge treatment.

DEMETALLIZATION

Waste oil is preheated to 85°C and is reacted with DAP and TEA in the demetallation unit (Figure 32). The demetallization unit is equipped with a dual turbine type agitator with 45° pitch blades. The additive metals in used oil react with DAP to form metal hydroxyl phosphates, while TEA neutralizes the acids and flocculates the impurities from used oil. The reaction is carried out for 30 minutes. After the reaction, demetallized oil is transferred to the agglomeration unit. Agitation in the demetallization unit is very vigorous so the reaction is not mass transfer limited, while agitation is very slow in the agglomeration unit to facilitate the agglomeration of metal hydroxyl phosphates, neutralization products and heavy metals. Both tanks are well insulated to maintain the temperature during the reaction. Demetallized oil passes through a lamella clarifier to separate solids and impurities.

Lamella

The unit is shown in Figure 33, and is a development of the Axel Johnson Institute for Industrial Research in Sweden.⁵⁴ It consists of a series of inclined plates in close proximity to one another so that the effective area becomes the horizontal projected area of each plate. The incoming slurry is introduced either directly into the feed box or into a flash mix and flocculation tank. The slurry is introduced to the lamella plates through a bottomless rectangular feed curtain, from which it flows to the plates, as shown in Figure 33, exiting at the top of the tank through flow distribution orifices. The solids settle against the inclined surfaces of the plates and slide downwards into the sludge hopper, where additional densifying is achieved by the action of a low-amplitude vibrator located inside the hopper.

The unit at the AWORL does not have a flocculation tank or vibrator, and slurry is directly introduced into the feed box. The lamella clarifier offers an advantage in that it increases the settling area and decreases the settling distance for the solids. The distance is reduced to the separation between

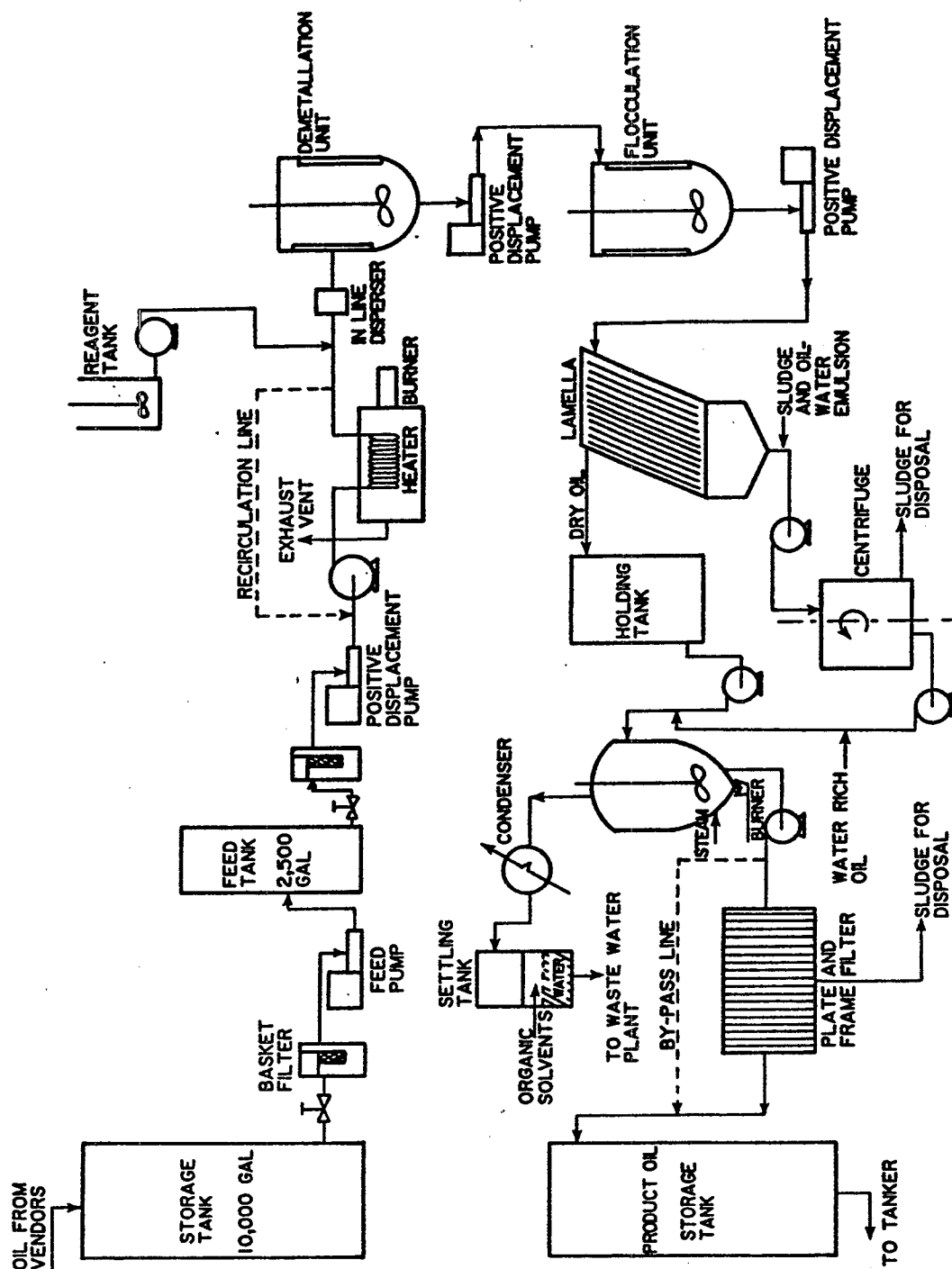


Figure 31. Flow Sheet for Waste Oil Recovery Pilot Plant.

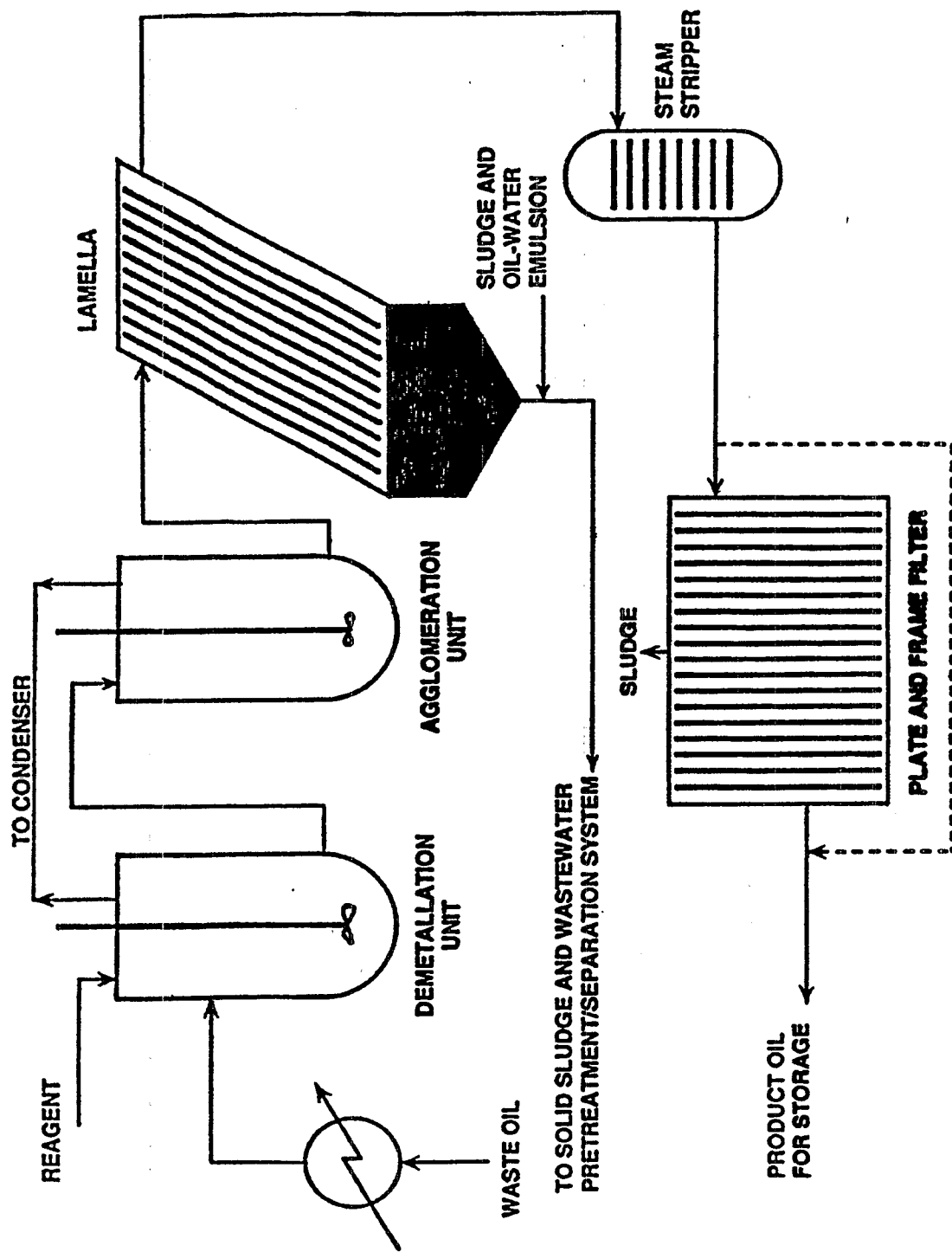


Figure 32. Flow Sheet for Demetallization Section.

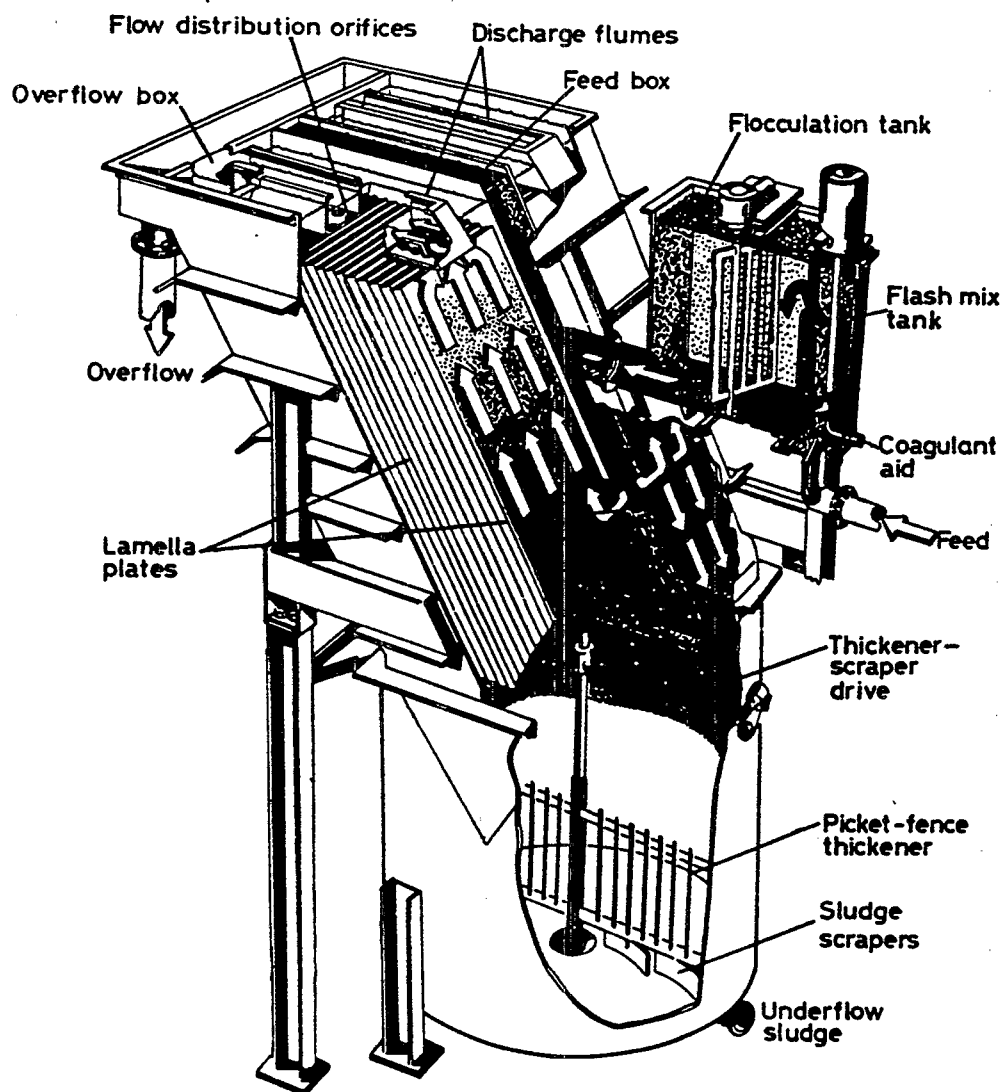


Figure 33. Lamella Clarifier.

the two plates. This unit is finding wider usage beyond its original coal and metallurgical applications. They are now used extensively in the treatment of gas scrubber effluents, mill scale solutions and fly ash suspensions. This unit has been in use for the past several years at AWORL, mainly for removing water and suspended solids from used oil.

The demetallized oil (a mixture of oil, water, reaction products, etc.) is passed through a lamella clarifier to separate the impurities. Another advantage of the lamella clarifier is that settled solids are washed in water before they are removed from the bottom. The clarified oil from the top is steam-stripped or flash-vaporized to remove light hydrocarbons, chlorinated solvents and water from the oil. Depending on the ash and lead content of oil, it is either filtered or bypassed and stored in a product tank. This oil can be used as a specification grade fuel oil or as a feedstock to the refinery.

Sludge Treatment

The bottoms (solids, water, and oil) from the lamella clarifier is transferred to the skim tanks, where loose oil from the top is sent back to the feed tank for reprocessing (Figure 34). Water from the skim tanks is treated in a waste water treatment plant, while oily solids from the bottom are washed with light distillate or Stoddard solvents. The oil-solvent mixture is either centrifuged or filtered to remove inorganic solids and neutralization products. The solids are dried and stored in the aggregate bin. Research is presently being conducted on how to use these solids as an asphalt aggregate.

RESULTS

At this point, 7,000 gallons of waste oil had been reprocessed at the pilot plant. The used oil was a mixture of different kinds of lubricating oils from Fort Rucker, Alabama. Since this project was funded by DoD, which is very interested in developing technology to convert used oil generated at their facilities into specification grade fuel oil, the oil selected for the pilot plant studies was from Fort Rucker. This oil was similar to the kinds typically generated at many DoD facilities.

Before the pilot plant evaluation, the oil was treated in a laboratory to determine the ash and lead reduction achievable by this treatment. The predictive demetallization test provides a quantitative measurement of ash and lead reduction possible by the above process. Waste oil from Fort Rucker was treated with a solution of DAP (1 wt.%) and TEA (0.5 wt.%) at 80°C for an hour. The oil was allowed to settle overnight at 75°C. The ash content of the clarified oil was reduced to 0.1 wt.% from 0.48 wt.%.

Table 33 shows the metals content of the oil processed at the pilot plant. As seen from this table, the ash and lead content of the processed oil is reduced to less than 0.1 wt.% and 100 ppm respectively, while pentane insolubles are negligible due to the flocculation of impurities by TEA.

The problem encountered during the pilot plant studies was in removing the chlorinated solvents from the used oil. Waste oils from DoD invariably contain small amounts of solvents due to improper mixing. The objective of this project is to remove the chlorinated solvents from used oil and to reduce

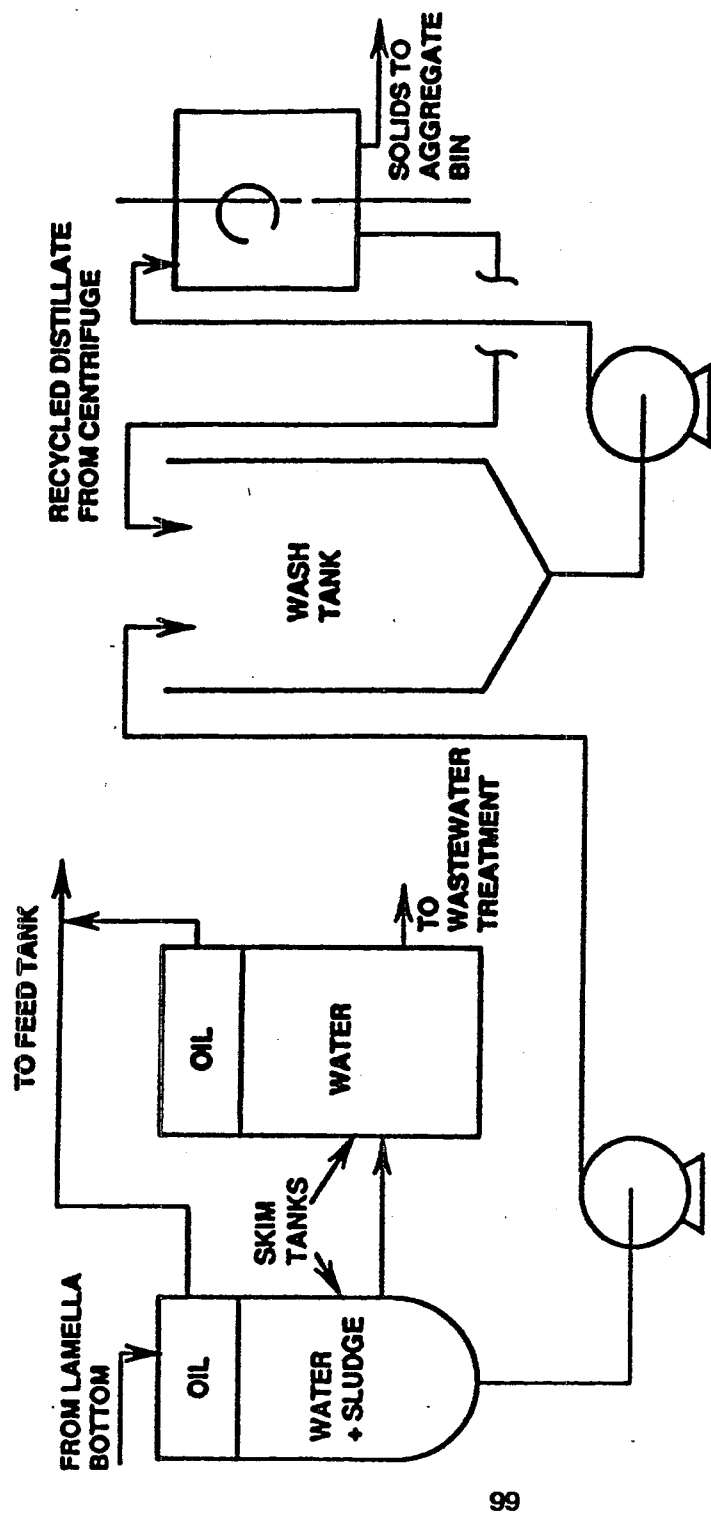


Figure 34. Solid Sludge and Waste Water Pretreatment System.

TABLE 33. METALS CONTENT OF OIL PROCESSED AT PILOT PLANT

	Used Oil	Processed Oil
Ash Content, wt. %	0.48	0.092
Pentane Insolubles, %	0.201	0.018
Metal Content (ppm)		
K	19	5
Ca	500	76
Mg	210	10
Zn	375	10
Ba	251	10
P	700	150
Cu	40	32
Fe	74	18
Mn	4	<1
Mo	3	<1
Al	35	5
Co	<1	<1
B	2	<1
Si	5	1
Pb	140	41
As	<1	<1
Cd	2	<1
Cr	3	<1
Total	23603	360

ash and lead content. The project was very successful in ash and lead reduction, and in converting waste oil to specification grade fuel oil.

To determine the effectiveness of different methods in removing the solvents, a small batch of used oil (700 gallons) was mixed with a known amount of 1,1,1-trichloroethane and tetrachloroethylene in a tank equipped with an agitator and a recirculation pump. The mixture (oil and solvents) at 275°F and 150 psi was flash-vaporized to the atmospheric pressure. The overheads were condensed and analyzed for chlorinated solvents. Since this used oil contained a large amount of light distillates (roughly 30 wt.%, with a boiling point of less than 250°F), this temperature and pressure were not found sufficient to vaporize the chlorinated solvents along with the light components. Mainly 1,1,1-trichloroethane (boiling point 165°F) was distilled off with light components, while tetrachloroethylene (boiling point 250 °F) remained in the oil. Hence, care should be taken in designing the capacity of a flash vaporization unit.

CONCLUSIONS

(1) The pilot plant studies demonstrated that this process is feasible and can convert waste oil to specification grade fuel oil.

(2) This process can also be used as a pretreatment for making lubricants out of used motor oils.

(3) This treatment has many applications in the field of oil purification and sludge treatment.

(4) This process was chosen by the Department of Health Services in California as an innovative process for waste oil reprocessing.

SECTION IX BURN TEST

It is well established that oil reclaimed as a result of the pilot plant studies can be analyzed in detail to ascertain whether it meets the "EPA specification for a used oil fuel" and whether it satisfies the ASTM specification for a No. 4 or No. 5 fuel oil. However, this analysis will not provide any insight as to the fate of particulates generated by the burning of reclaimed oil. ASTM specification for a No. 4 and No. 5 fuel oil allow an ash content of 0.1 wt.%; a goal of the developed process is to reduce the ash content of used oil to below 0.1 wt.%.

The particulates formed by burning used oil are derived from two sources: very fine (between 0.1 to 1 microns) insoluble residual particulates remaining in the reclaimed oil, and soluble metals bearing compounds (additives such as detergent/soaps, rust inhibitors, etc.). In general, the size of the particulates generated by the combustion of waste oils are assumed to be so fine that they are emitted completely from the stacks. This is believed particularly true for lead-bearing particulates (55). The overall objective of the burn test is to establish how particulate emissions of a reclaimed waste oil compare with those of a No. 5 fuel oil, each having nearly the same ash content (<0.1 wt.%).

Particulate emissions are very critical in high density population areas. In such areas, regulatory agencies usually prohibit or severely limit the burning of No. 6 fuel oil (e.g. this is true in Birmingham, Alabama). The main performance criteria of a burn test are the gaseous and particulates products of combustion (degree of pollution) and the condition of the boiler (amount of residue) after firing. The burn test will also establish the equivalency of treated oil with ASTM grade fuel oils, which will help the DoD obtain a future permit for air emission discharges.

The boiler trial burn is limited to particulate matter and lead because the DoD is mainly interested in particulate and lead emissions from the stack; whereas moisture, CO, CO₂, and O₂ are measured to determine the efficiency of the combustion process (i.e. burner in the boiler). The emission of other parameters such as HCl and SO₂ can be found by analyzing oil for the respective parameters (S and Cl content of the oil) prior to burning.

Roy F. Weston, Inc. (WESTON) was retained by the Chemical Engineering Department of Auburn University to conduct stack emission testing during the trial burn. Two series of emission tests will be conducted. The first series was conducted with the boiler burning No. 5 fuel oil, while the second series will be conducted on the reclaimed oil. Approximately 1,000 to 2,000 gallons of each type oil will be burned during the tests. The boiler at Fort Rucker, Alabama, is a typical industrial boiler found at many DoD facilities; hence, it was selected for burning the reclaimed oil. Figure 35 illustrates the proposed organization for the project.

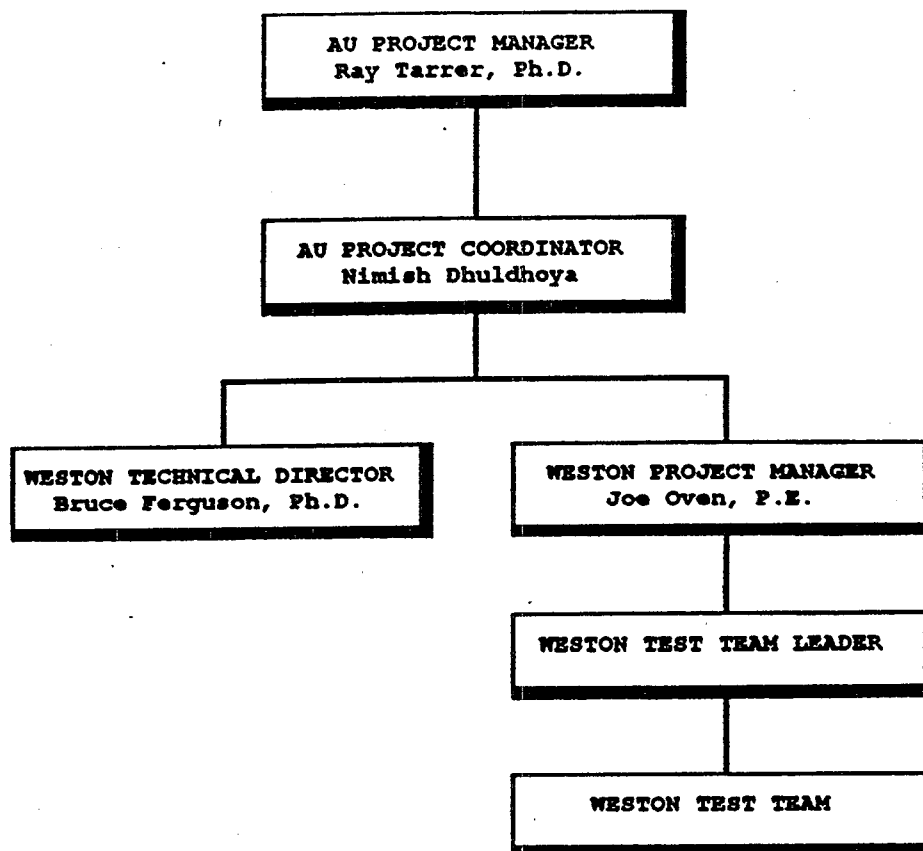


Figure 35. Project Organization Chart.

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APPENDIX A QUALITY ASSURANCE ACTIVITIES

The experimental results of oil demetallation as presented earlier were verified in accordance with the Quality Assurance Project Plan (QAPP). The procedures and results are described in detail later in this appendix.

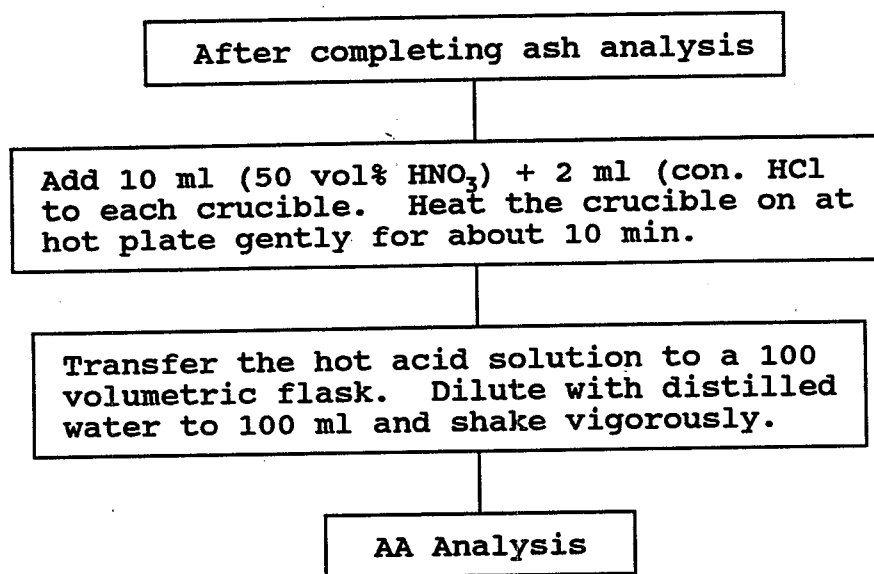
As mentioned earlier, the oil demetallation performance was evaluated in terms of ash and lead contents remaining in the treated oil. Thus, the reliability of ashing and lead-determining procedures as well as the AA calibration procedure was very important.

To determine the lead content of the oil sample, about 5g of oil sample was ashed first in a muffle furnace at 600°C for 12 hours. The ash (i.e., total ash-forming contaminants) content was determined as described in Figure A-1. Lead was assumed to remain in the ash. The ash was dissolved in an acid solution and then diluted to an appropriate concentration range for AA analysis as described in Figure A-2. The AA calibration procedure used is described in Figure A-3.

Since the oil sample was ashed in a muffle furnace at 600°C for 12 hours, it is questionable whether some of the lead is lost due to evaporation while ashing. To verify this, a known amount of organometallic lead compound (lead cyclohexanebutyric acid, $[C_6H_{11}(CH_2)_3COO]_2$ pb) was weighed in a crucible and ashed as described above. The lead content in lead cyclohexanebutyric acid is 37.8%. This compound was obtained from Kodak Laboratory and Specialty Chemicals. As shown in Table A-1, after ashing, the remaining amount of ash amounted to 38.97% of the original compound charged to the crucible. This percentage is close to the lead content of the original organometallic lead compound. Following the ashing, the ash was dissolved in an aqueous nitric acid solution as described in the QAPP and the lead content of the solution was determined using atomic absorption spectroscopy. The AA analysis showed that the lead content in the aqueous solution was 176 ppm which is very close to its estimated lead content (176.5 ppm) based on the known compound composition and amount of compound ashed (Table A-1). This observation suggests that the lead in the organometallic lead compound is not volatilized during ashing.

To determine the accuracy of lead analysis, a blind spiked oil sample was prepared. To prepare the blind spiked oil sample, a known amount of organolead standard, $[C_6H_{11}(CH_2)_3COO]_2$ pb, was first dissolved in an appropriate amount of xylenes (heated if necessary) and then blended with a specified amount of virgin SAE 10-30W motor oil. Regular procedures for ash and lead analyses as described in Figures A-1, A-2, and A-3 were followed. The results are given in Table A-2.

FIGURE A-1. LEAD ANALYSIS PROCEDURE (MODIFIED ASTM 2788-72).



AA Spectrophotometer:	VARIAN AA-475
Lead hollow cathode lamp current:	5 MA
Wavelength:	217.0 NM
Spectral Band Pass:	1 NM
Optimum working range(ppm):	5-20
Working conditions (fixed)	
Fuel:	Acetylene
Oxidant (support):	Air
Flame stoichiometry:	Oxidizing

FIGURE A-2. ASH ANALYSIS PROCEDURE (MODIFIED ASTM D482-81).

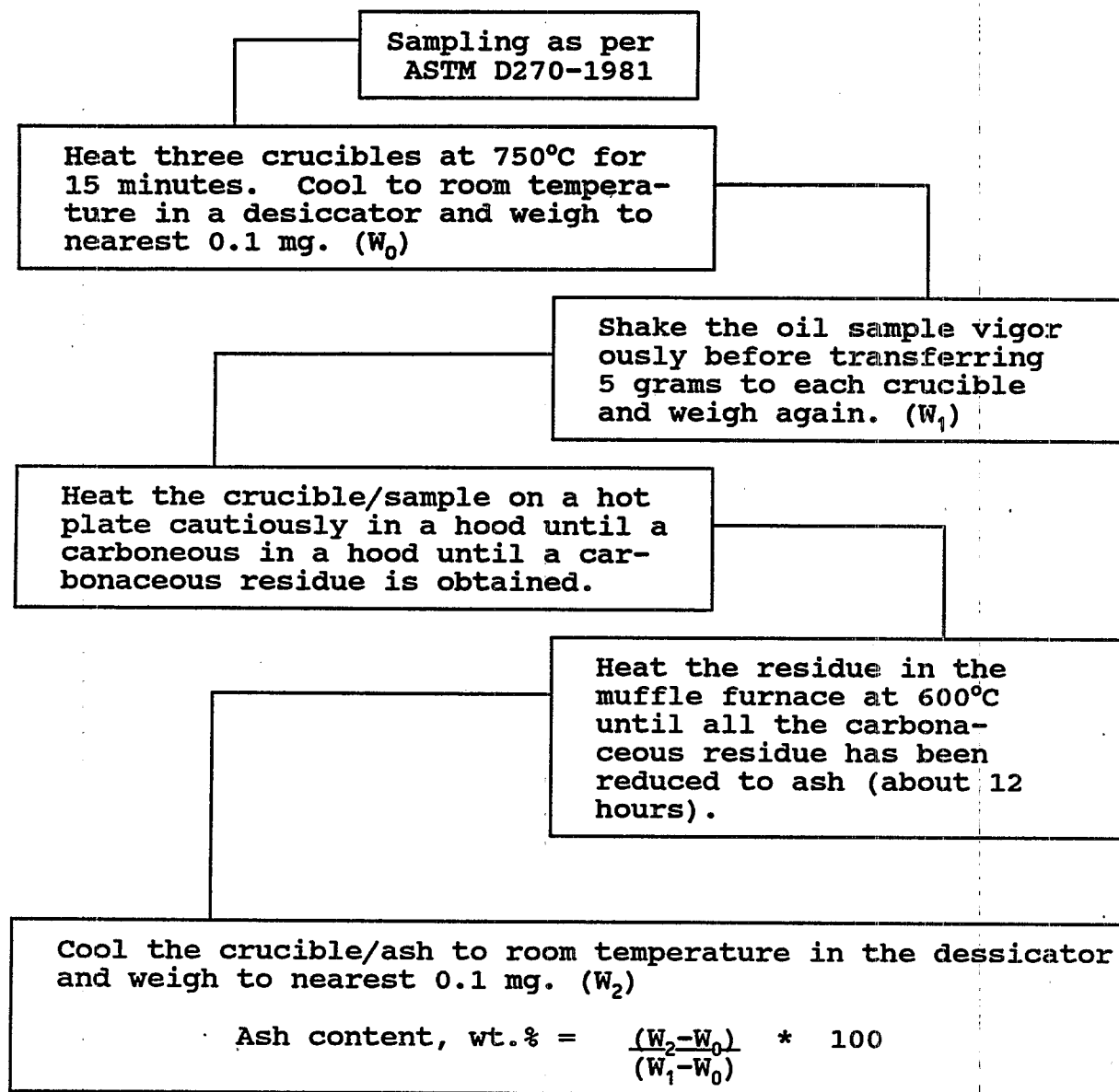


FIGURE A-3. AA CALIBRATION PROCEDURE.

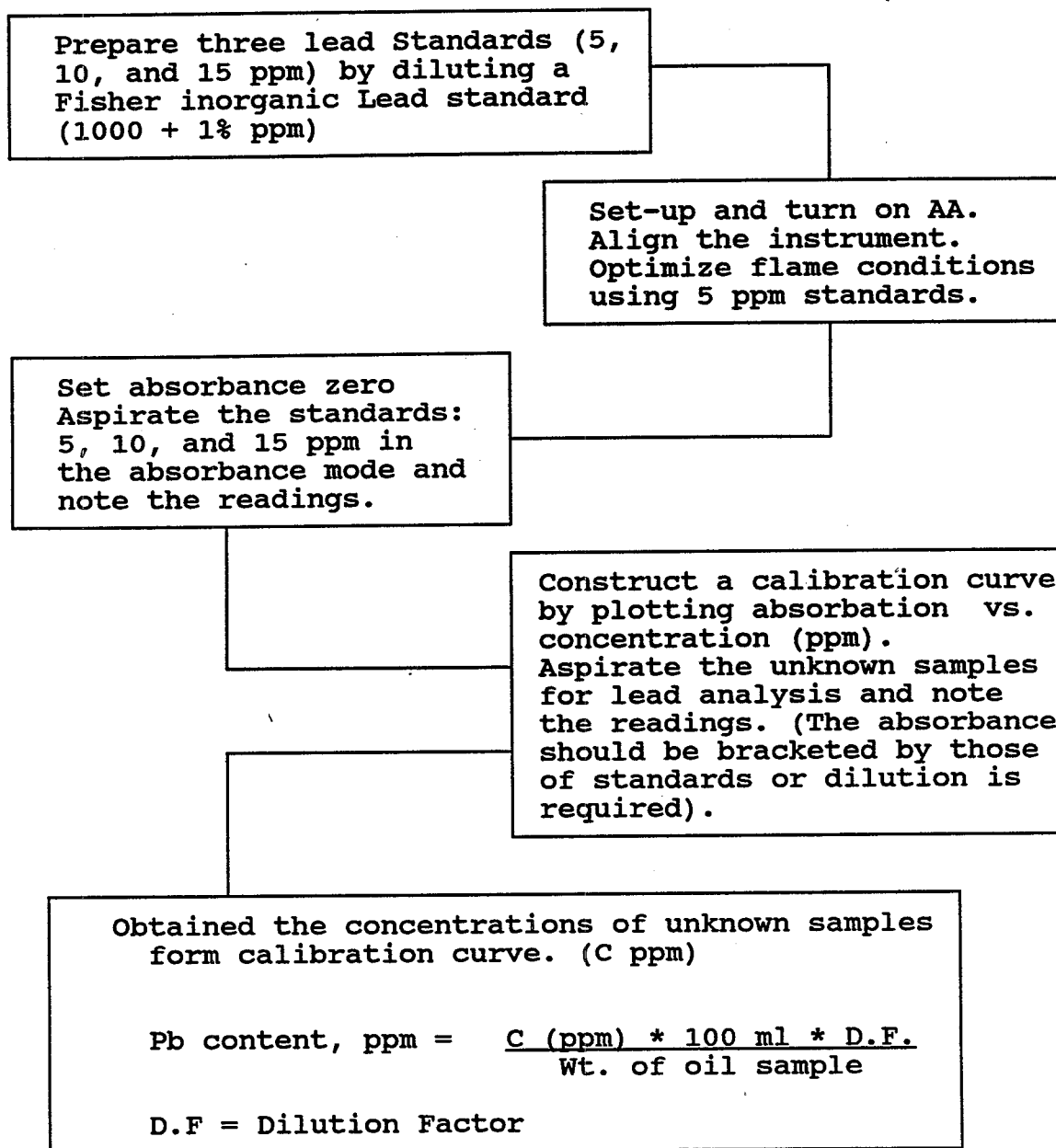


TABLE A-1. VOLATILITY TEST OF ORGANOMETALLIC LEAD COMPOUND* IN MUFFLE FURNACE AT 600°C FOR 12 HOURS.

Before Ashing:

Crucible weight	16.4060 g
Crucible/lead compound weight	16.4527 g
Lead compound weight	0.0467 g
Lead weight	0.01765 g

After Ashing:

Crucible/ash weight	16.4242 g
Ash weight	0.0182 g
Ash content	38.97%

Atomic absorption analysis:

Lead content	176 ppm in aqueous nitric acid solution
Theoretical lead content calculation	176.5 ppm in aqueous nitric by acid solution

* Lead cyclohexanebutyric acid
Structural formula: $[\text{C}_6\text{H}_{11}(\text{CH}_2)_3\text{COO}]_2 \text{ pb}$

Molecular weight: 545.68
Lead content: 37.8%

To determine the repeatability of ash and lead analyses, the blind spiked oil sample was poured into four crucibles; each crucible contained about 5g of spiked oil. As shown in Table A-2, the ash contents of the four oil samples were 0.568, 0.585, 0.582, and 0.594 wt.%, respectively. The resultant average measured ash content was 0.582 ± 0.011 (or $0.582 \pm 0.019\%$) weight percent, which was acceptable. The lead contents of the four oil samples were 230.7, 243.6, 231.9, and 242.1 ppm, respectively. The resultant average measured lead content was 231.1 ± 6.7 (or $231.7 \pm 2.9\%$) ppm, which was also acceptable.

Knowing the amount of organolead, xylenes, and motor oil used and the lead content in the organolead standard (37.8 wt.%), the lead content of the spiked oil could be calculated, assuming that no lead was present in the virgin motor oil. To confirm this assumption, the ash and lead contents of the virgin motor oil were measured. As shown in Table A-3, no lead was found in the motor oil. The true lead concentration in the spiked oil was 242.7 ppm as shown in Table A-2 as compared to the average measured value of 237.1 ± 6.7 ppm. The percent accuracy of lead determination was about 2.3%, which was acceptable.

To determine the precision of ash and lead analyses, a demetallated oil, treated with a metallic borohydride solution (i.e., SWS solution), was used in which eight aliquats (5g each) of this oil were analyzed for ash and lead contents. The ash and lead analysis results are given in Table A-4. The average measured ash content for this oil was 0.548 ± 0.009 (or $0.548 \pm 1.64\%$) wt.% and the average measured lead content was 74.99 ± 0.90 (or $74.99 \pm 1.20\%$) ppm. Both of them are acceptable.

In summary, the Quality Assurance Project Plan has been executed properly, and the results have been found to be satisfactory.

TABLE A-2. ACCURACY OF LEAD ANALYSIS PROCEDURE.

Crucible No.	1	2	3	4	Average
<u>Before Ashing:</u>					
Crucible wt., g	44.8785	44.0060	42.2435	42.4106	
Crucible/oil sample* wt., g	49.8643	49.0146	47.2462	47.4090	
Oil sample wt., g	4.9858	5.0086	5.0027	4.9984	4.9989±0.0097
<u>After Ashing:</u>					
Crucible/ash wt., g	44.9068	44.0353	42.2726	42.4403	
Ash wt., g	0.0283	0.0293	0.0291	0.0297	0.0291±0.0006
Ash content, %	0.568	0.585	0.582	0.594	0.582±0.011
<u>AA Analysis:</u>					
Pb content, ppm	230.7	243.6	231.9	242.1	237.1±6.7

*Lead-containing oil sample was prepared as follows:

Lead cyclohexanebutyric acid : 0.0321 g
 (Lead content: 37.8%)
 Xylenes : 4.0056 g
 SAE 30 hd motor oil : 45.9802 g
 Lead content (by calculation) : 242.7 ppm

Percent error: $\frac{(242.7 - 237.1)}{242.7} \times (100\%) = 2.31\%$

TABLE A-3. DETERMINATION OF ASH AND LEAD CONTENTS OF VIRGIN MOTOR OIL.*

Before Ashing:

Crucible weight	17.4812 g
Crucible/oil weight	= 22.4771 g
Oil weight	= 4.9959 g

After Ashing:

Crucible/ash weight	= 17.5123 g
Ash weight	= 0.0311 g
Ash content	= 0.62%

Atomic Absorption Analysis:

Lead content	= 0 ppm (nd)
--------------	--------------

* Motor oil used: Quaker State SAE-30HD
Refined from Pennsylvania Grade Crude Oil

TABLE A-4. PRECISION TEST FOR LEAD AND ASH ANALYSIS.

Sample No.	Ash Content (wt.%)	Lead Content (ppm)
1	0.551	75.26
2	0.541	75.04
3	0.555	75.26
4	0.549	75.10
5	0.540	74.89
6	0.543	73.84
7	0.541	73.84
8	0.567	76.68
Average	0.548 ± 0.009	74.99 ± 0.90

APPENDIX B
QUALITY ASSURANCE/QUALITY CONTROL PLAN
RECLAIMED OIL TRIAL BURN

Roy F. Weston, Inc. (WESTON) was retained by the Chemical Engineering Department of Auburn University to conduct emission testing on an oil-fired package boiler at Fort Rucker Army Base at Fort Rucker, Alabama.

Two series of tests were conducted for particulate, lead, and carbon monoxide emissions in the stack gas. The first test series was conducted during the burning of reclaimed oil from an experimental oil reclamation process being developed by Auburn University. The second test series was conducted during the burning of commercially available No. 5 fuel oil. The purpose of the tests was to compare the emission rates from the two fuel oils.

The emission testing was performed on July 25-26, 1990, by a WESTON test team comprised of Mr. Greg Sims, Mr. Arnold Seidl, Mr. William Kelly, and Mr. Jeff Hollingsworth. Mr. Joe Owen was the WESTON Technical Director and QA Officer.

Auburn University personnel collected boiler operational data and samples of each type of oil during testing. Oil analyses were conducted by Auburn University.

Dr. Ray Tarrer was the Auburn University Project Manager. Mr. Joe Hayes of Auburn University and Mr. Ron Leatherwood of Fort Rucker were the WESTON technical contacts at the plant.

The following section of this report details the emission test results. The section afterward outlines the sampling and analytical procedures used to conduct the testing.

RESULTS AND DISCUSSION

This section presents the results of the emission testing on the reclaimed fuel oil and the No. 5 fuel oil. Because all runs were being conducted on the same boiler, the runs were sequentially numbered from Run 1 through Run 7.

Runs 1, 2, 3, and 7 were conducted on the reclaimed fuel oil while runs 4, 5, and 6 were conducted on No. 5 fuel oil.

Comparison of Measured Emission-Reclaimed Fuel Oil and No. 5 Fuel Oil

Table B-1 presents a summary of results of the particulate, lead, and carbon monoxide (CO) emission testing on the package boiler at Fort Rucker, Alabama, performed on July 25-26, 1990. Results of the individual test series on each type oil are discussed in the following two sections.

Reclaimed Fuel Oil

Table B-2 summarizes the results of the particulate lead and carbon monoxide emission testing performed while the boiler was burning reclaimed fuel oil on July 25-26, 1990. A total of four runs (Runs 1, 2, 3, and 7) were conducted on the reclaimed fuel oil. After completion of Runs 1, 2, and 3, the client informed WESTON that the boiler was set at an incorrect air/fuel ratio during Run 1 and that a fourth run would be necessary to obtain three runs under optimum boiler conditions. It was mutually agreed upon to conduct the fourth run (Run 7) following the tests on the No. 5 fuel oil. Run 1 was voided. The mean particulate emission rate for Runs 2, 3, and 7 was 1.20 lb/hr and 0.061 lb/MMBTU. The mean lead emission rate was 0.04 lb/hr and 0.002 lb/MMBTU. The mean carbon monoxide emission rate was 108 ppm and 1.92 lb/hr.

Commercial No. 5 Fuel Oil

Table B-3 summarizes the results of the particulate lead and carbon monoxide emission testing performed while the boiler was burning No. 5 fuel oil on July 26, 1990. The mean particulate emission rate was 2.06 lb/hr and 0.135 lb/MMBTU. The mean lead emission rate was 0.05 lb/hr and 0.0031b/MMBTU. The mean carbon monoxide emission rate was 160 ppm and 2.76 lb/hr.

Sampling Procedures

Effective sampling procedures were used in conduction of the tests with the exception of the following deviations:

- The QA/QC plan indicated that each test run would be two hours in duration, to make sure that enough particulate would be collected on the EPA Method 5 sampling train filters. However, due to the heavy filter loading and high vacuum in the sampling train after the first run, it was decided to reduce the test run time. The test run sampling durations were 64 minutes (4 minutes per point) or 80 minutes (5 minutes per point) for various runs.
- After each test run, the EPA Method 5 sampling nozzle, probe, and filter holder were rinsed with 0.1 NHNO_3 following the acetone rinse. This was done to make sure all traces of lead were collected.
- Dr. Len Nelms replaced Dr. Bruce Ferguson as Technical Director and QA Officer in the project.
- Carbon monoxide sampling was done by collecting integrated samples in bags, followed by analysis in WESTON's laboratory. The sampling program described in the QA/QC plan anticipated on-line CO analysis. However, due to the calibration sensitivity of the CO analyzer and the open roof location, it was decided not to use the CO analyzer for testing in the field.

TABLE B-1. COMPARISON OF MEASURED EMISSION RATES.

	<u>Reclaimed Fuel Oil</u> MEAN TEST VALUE			<u>No. 5 Fuel Oil</u> MEAN TEST VALUE		
	1b/Hr	1b/MMBTU	ppm	1b/Hr	1b/MMBTU	ppm
Particulate	1.20	0.061	—	2.06	0.135	—
Lead	0.04	0.002	—	0.05	0.003	—
Carbon Monoxide	1.92	—	108	2.76	—	160

TABLE B-2. RECLAIMED FUEL OIL EMISSION DATA.

	RUN 2	RUN 3	RUN 7	MEAN
<u>Date</u>	07/25/90	07/25/90	07/26/90	—
<u>Time Begun</u>	1928	2055	1547	—
<u>Time Ended</u>	2038	2203	1707	—
<u>Stack Gas</u>				
Temperature, °F	335	348	343	342
Velocity, ft/sec	17.9	16.2	16.5	16.9
Moisture, %	13.4	13.6	12.9	13.3
Oxygen, %	4.5	4.5	3.2	4.1
Carbon Dioxide, %	12.5	12.5	13.0	12.7

TABLE B-2. RECLAIMED FUEL OIL EMISSION DATA (CONTINUED).

	RUN 2	RUN 3	RUN 7	MEAN
<u>Volumetric Flow Rate</u>				
At Stack Conditions ft ³ /min	7,580	6,890	7,000	7,160
At Standard Conditions* ft ³ /min	4,370	3,900	4,030	4,100
<u>Particulate</u>				
Isokinetic Sampling Rate, %	93	96	97	95
Concentration at Standard conditions*, gr/ft ³	0.035	0.033	0.035	0.034
Emission Rate, 1b/hr	1.29	1.10	1.19	1.20
Emission Rate, 1b/MMBTU	0.066	0.056	0.061	0.061
<u>Lead</u>				
Concentration at Standard conditions*, gr/ft ³	0.001	0.001	0.001	0.001
Emission Rate, 1b/hr	0.04	0.04	0.04	0.04
Emission Rate, 1b/MMBTU	0.002	0.002	0.002	0.002
<u>Carbon Monoxide^b</u>				
Concentration, ppm	86	72	165	108
Emission Rate, 1b/hr	1.64	1.22	2.90	1.92

*68°F and 29.92 inches of mercury.

^bCorrected for CO₂ in gas stream.

TABLE B-3. COMMERCIAL NO. 5 FUEL OIL EMISSION DATA

	RUN 4	RUN 5	RUN 6	MEAN
<u>Date</u>	07/26/90	07/26/90	07/26/90	—
<u>Time Began</u>	1005	1155	1350	—
<u>Time Ended</u>	1128	1317	1510	—
<u>Stack Gas</u>				
Temperature, °F	354	344	363	354
Velocity, ft/sec	16.8	16.0	16.9	16.6
Moisture, %	13.7	13.2	13.7	13.5
Oxygen, %	2.0	2.0	3.2	2.4
Carbon Dioxide, %	14.2	14.2	13.2	13.9
<u>Volumetric Flow rate</u>				
At Stack Conditions ft ³ /min	7,140	6,780	7,180	7,030
At Standard Conditions ^a ft ³ /min	4,020	3,890	4,000	3,970
<u>Particulate</u>				
Isokinetic Sampling Rate, %	98	96	97	97
Concentration at Standard Conditions ^a , gr/ft ³	0.061	0.064	0.057	0.061
Emission Rate, lb/hr	2.09	2.14	1.96	2.06
Emission Rate, lb/MMBTU	0.137	0.140	0.128	0.135

TABLE B-3. COMMERCIAL NO. 5 FUEL OIL EMISSION DATA (CONTINUED).

	RUN 4	RUN 5	RUN 6	MEAN
Lead				
Concentration at Standard Conditions ^a , gr/ft ³	0.002	0.002	0.001	0.002
Emission Rate, lb/hr	0.05	0.06	0.05	0.05
Emission Rate, 1b/MMBTU	0.003	0.004	0.003	0.003
Carbon Monoxide^b				
Concentration, ppm	177	213	91	160
Emission Rate, 1b/hr	3.10	3.61	1.59	2.76

^a68°F and 29.92 inches of mercury.

^bCorrected for CO₂ in gas stream.

Quality Control

Throughout the entire project, a high level of quality control was maintained to ensure the accuracy of the data. The test personnel are experienced in the use of the instrumentation, the procedures involved, and the quality control requirements. The following paragraphs briefly summarize the quality control associated with the project:

General. All data were recorded at the time of collection on preprinted data sheets. All samples were prepared for shipment, and chain-of-custody was maintained from the sampling technician to the analyst. Calculations were performed (where possible) with pre-programmed calculators. Data transfers were minimized, and all calculations were verified by a second person. The report was reviewed and approved by the Technical Director prior to transmittal. In general, all accepted quality control standards and practices recommended by the reference methods were followed.

Stack Gas Volumetric Flow. The stack was measured with a certified tape to an accuracy of 0.1 inch. The velocity and sampling traverse points were marked on the probe with heat resistant glass fiber tape.

The S-type pitot tubes used to measure the velocity pressures were visually inspected for damage prior to the test and damage was not indicated. The pyrometer used to measure the stack gas temperature and all thermocouples for intermediate measurements were calibrated with respect to standard thermometers. At the completion of the test, all equipment was visually inspected, and damage was not indicated.

Stack Gas Molecular Weight. Quality control on oxygen analyses by EPA Reference Method 3 involved the analysis of ambient air before sampling. If the measured concentration was less than 20.0 percent, the Orsat chemicals were changed before proceeding.

If the measured concentration was greater than 20.0 percent but less than 20.6 percent, the sample data were corrected for the low measurement. If the measured concentration was 20.6 percent or greater, no correction was made. The Method 3 train was leak-checked with a KNF Pump capable of producing a vacuum greater than 10 inches Hg.

WESTON also participated satisfactorily in the most recent EPA Audit Sample for Reference Method 3. Those data are on file at WESTON.

Moisture Content. Quality control of the moisture analysis involved the accurate measurement of the gas flow and the accurate determination of the moisture condensed in the sampling train. A calibrated triple beam balance was used to weigh the volume of water in each impinger before and after sampling. The silica gel was weighed, before and after its use, with the same balance to the nearest 0.1 gram. The sum of all differences in weights before and after sampling was considered to be the moisture collected.

Particulate and Lead Concentration. The dry gas meter used to measure the sample volume collected was calibrated before and after sampling. The calibration obtained was within the required

specifications each time. All thermocouples and other items used to calculate the mass emission rate were calibrated on a routine schedule.

WESTON participated satisfactorily in the most recent dry gas meter audit supplied by EPA. Those data are on file at WESTON.

WESTON used Class S 1-, 10-, 50-, and 100-gram weights to verify the accuracy of the balance for each used. The weight is weighed when the filters are tared and also at the final weighings. Any significant difference in weight indicates a problem with the balance, and the balance is repaired before proceeding.

The rate of sample collection was determined to be within 10 percent of the isokinetic rate. Those data indicate the validity of sample collection.

The particulate and lead analyses were performed according to the general procedures described in EPA Reference Methods 5 and 12. The particulate analysis was performed first on the probe wash samples by drying the samples in tared 250 ml beakers and weighing to a constant weight. The filter was then added to the beaker, dried, and weighed to a constant weight.

The lead analysis was performed using the same samples. The filter was removed, and the nitric acid impinger catch and probe wash made with 0.1N HNO_3 were added to the beaker, covered with a watch glass and taken to dryness. Next, the filter was cut into strips, added to the beaker, and digested according to EPA Method 12 Section 5.3.3. The final solution was filtered using a mixed cellulose ester membrane filter and diluted to 100 ml. The lead concentration was determined using a Perkin-Elmer 2380 Atomic Absorption Spectrophotometer.

Quality control procedures for this project consisted of duplicate analyses by separate analysts, analysis of spiked filter samples, spiked liquid samples and blank samples, and use of the method of standard addition. The following tables summarize the results of the quality control analyses performed for this project and shows that all guidelines have been met. The method of standard addition was performed by spiking a known volume of standard solution with an aliquot of Sample No. CE 800. The results showed an insignificant difference of two percent between the measured mass and the calculated mass of lead measured.

Two blank filters were analyzed along with a reagent blank which included the acetone from the particulate analysis, the 0.1N HNO_3 , and deionized water. All blank samples were found to be below the detection limit of 20 ug.

Carbon Monoxide. Samples were collected and conditioned in the field for laboratory analysis of carbon monoxide by NDIR techniques. Integrated samples were collected concurrently with and for the same sampling time as the particulate and lead sampling. At the time of collection, moisture was removed by a condensate trap. The samples were stored in Tedlar Bags prior to analysis. NBS traceable gases were used to calibrate the NDIR analyzer before and after analysis.

Quality Assurance Objectives

Table B-4 summarizes the QA objectives for measuring data in terms of precision, accuracy and completeness. Representativeness will be defined primarily by the sampling locations and correlation of sampling operations with process conditions.

Sampling Procedures

Preliminary test data will be obtained at the stack sampling locations. The sampling port locations and traverse points are selected in accordance with EPA Methods 1 and 2 as shown on Figures B-1 and B-2, respectively. Geometric stack measurements will be recorded and traverse point distances calculated. Prior to formal testing, a check for the presence or absence of cyclonic flow will be conducted at the stack test location. The cyclonic flow check must be negative to verify the test location is suitable for obtaining representative samples. Based upon the present ductwork and stack arrangement, WESTON does not expect to detect the presence of cyclonic flow at the stack sampling location. However, if cyclonic flow is detected, WESTON proposed to construct an "egg-crate" type flow straightening device and to lower it into position in the stack to alleviate the cyclonic flow condition. This device will be positioned such that the sampling port locations will not be affected.

A series of three test runs (on each type of oil) for each parameter will be conducted simultaneously at full load process conditions. The sampling ports illustrated on Figure B-1 will be used during testing. Two main ports will be used for Method 5 traversing. One smaller port, located approximately six inches above the plane of the main ports, will be used for the Method 10 stationary sampling probe. Each test run will be two hours long. The sampling condition for each specific sampling method will be followed to ensure that a quantitative recovery of each analyte is obtained from the source. Outlines of the various sampling procedures are detailed in the following text. The oil will be transported to Ft. Rucker by tanker truck, and fed to the boiler directly from the truck. This procedure will be used to avoid oil contamination if the reclaimed oil was pumped into Ft. Rucker's oil tanks.

The stack gas volumetric flow rate, molecular weight, and moisture content will be determined simultaneously by using EPA Methods 1-4 with the EPA Method 5 runs. The velocity of the gas stream will be determined by reading the instantaneous velocity head using an inclined manometer at each point with a calibrated S-type pitot tube. Stack gas temperatures will be determined by means of thermocouple and a calibrated pyrometer. Carbon dioxide and oxygen concentrations will be determined using a Fisher Brand Orsat with a 50 percent capacity. An integrated sample will be collected for the duration of each of the Method 1-5 Runs and subjected to analysis by the Orsat Method. The moisture content of the gas stream will be determined by weighing the impingers before and after each Method 1-5 Run.

The particulate and lead concentrations of the gas stream will be determined using EPA Methods 5 and 12 in the Method 5 sampling train. The filter will be of a low lead background, and the first two impingers will be changed with 100 ml of 0.1 N HNO_3 prior to each test run. Three test runs on each type of oil (each run being at least two hours long) will be performed. The gas stream will be sampled isokinetically at each sampling point by adjusting the sample flow rate to correspond to the measured velocity at each point. Following each run, the probe and nozzle will be washed with acetone to remove

TABLE B-4. SUMMARY OF DUPLICATE ANALYSES.

Lab No.	Run No.	% STD	% Accuracy
CE794	1	2	2
CE795	2	5	7
CE796	3	1	2
CE797	4	3	4
CE798	5	4	4
CE799	6	3	4
CE800	7	1	1

TABLE B-5. SUMMARY OF SPIKED SAMPLE RESULTS.

ID	Measured Mass (ug)	Actual Mass (ug)	% Diff
A Filter	100	100	0
B Filter	144	150	4
A Liquid	9.97*	9.90*	1
B Liquid	4.94*	4.98*	1

*Concentration in ug/ml.

the adhering particulate matter. The filter will be removed from the holder and stored in a petri dish until analyzed. The filter holder will then be rinsed with acetone, and this rinse will be added to the probe rinse. The first three impingers will be rinsed with 0.1 N HNO_3 , and this rinse will be transferred to the same sample container with the impinger contents. The containers will be sealed and labeled and liquid levels marked for transport to the laboratory.

The mean temperature of the stack gas and the dry gas meter will be used in calculating the final data. The mean isokinetic sampling rate and the stack gas velocity (volumetric flow) will be calculated from the mean of the square roots of the velocity pressure measured at each traverse point during the particulate sampling.

The concentration of carbon monoxide in the stack gas will be determined continuously by means of nondispersive infrared (NDIR) spectroscopy, in accordance with the analytical procedures identified in Method 10.

