BERC/RI-76/11

TREATMENT OF WASTE LUBRICATING OIL USING BERC/ERDA SOLVENT

By
Custom Refining Company

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TREATMENT OF WASTE LUBRICATING OIL USING BERC/ERDA SOLVENT

Bench-and-pilot-scale investigations performed for U. S. ERDA, Bartlesville Energy Research Center by Custom Refining Company, Adams City, Colorado under order no. BE-76-P-1601

Principal investigators:

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MR. R. J. SLUSKI

June 25, 1976

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LIST OF ILLUSTRATIONS

LIST OF TABLES

INTRODUCTION

For the past several years, Custom Refining has been investigating several rerefining methods which would be compatible with economic and environmental conditions existing in the Denver area. The original concept for manufacturing was a continuous acid-clay process. However because of the environmental impact of acid sludges and the high cost of manufacturing the concept had to be abandoned. Other methods that were researched and showed little or no promise were caustic treatments and a patented solvent extraction method.

In an effort to find a rerefining method, Custom Refining contacted the Bartlesville Energy Research and Development Administration (BERC/ERDA). Custom was allowed to perform some preliminary investigations using the BERC/ERDA solvent system and clay treatment for the rerefining of waste oil. Once these investigations showed promise BERC/ERDA awarded a contract to Custom Refining.

The objectives of the contract were: (1) A bench-scale study to investigate simultaneous solvent stripping and clay treatment, separate solvent stripping and clay treatment and the response to clay treatment as a function of temperature of the solvent extraction. (2) Investigate the recovery efficiencies of this rerefining method. (3) Determine the feasibility of producing a finished lubricating base stock from a pilot-scale study. This part also incorporate yields, product characteristics, performance of the equipment used and data for preliminary new plant design. (4) Report the potential market in the Denver area for a product of similar quality obtained from the pilot-scale study. (5) Investigate potential uses for by-products. The objectives of this contract have been met.

The following sections of the report include information pertaining to the collection of the waste crankcase oil; through a detailed description of the process, to the potential markets of such an oil.

SECTION I

BENCH-SCALE STUDY

Introduction

The objectives of the Bench-scale study were (1) Determine the feasibility of simultaneous solvent stripping (BERC's solvent system) (2) Find a suitable clay and suitable operation conditions that would properly bleach the solvent stripped oil. (3) Prepare infrared interpretations of the oils produced. (4) Investigate response to clay treatment as a function of the temperature of the solvent extraction. All the objectives of this part of the study were met. Also from preliminary analysis a suitable rerefined base stock can be produced via solvent and clay treatment.

Clay Treatment

Table 1 summarizes the various clays and conditions that were investigated in the course of this study. Besides the normal treating conditions of type of clay used, times, temperature and concentration two others played an important role in bleaching. These two were the temperature at which the oil solvent system was allowed to settle and the atmosphere under which the oil was treated with clay.

It was found that Filtrol-20 gave the best results with regard to color, odor and the amount of oxidation products removed when used at a 15 percent by weight concentration. At temperatures below 500°F very dark oils with high oxidation products concentrations (based on I. R.) were produced. Other clays that showed some positive results but far inferior to Filtrol-20 were Filtrol #4, Filtrol #6, Impact 150 and Impact 100 RR.

The rate of oxidation of the solvent treated oil is extremely fast at temperatures above 500°F. After 15 minutes at 550°F, the rate

TABLE 1

Summary of Clay Treatment

Sample No.	Temperature of Solvent Treatment	Clay	Wt. % Concentration	°F Temperature	Time Min.	Atmosphere	Color
7	55°	Filtrol-20	15	550°	180	N_2	3.0
8	85	Filtrol-20	15	550°	180	N_2	5.5
9	55	Filtrol-20	15	550°	60	N_2	5.5
10	55	Filtrol-20	15	550°	360	N_2	2.5
11	55	Filtrol-20	15	500°	360	N_2	5.5
12	55	Filtrol-20	15	550°	15	Air	6.5
13	55	Impact 150	15	550°	15	Air	7.0
14	55	Impact 100 RR	15	550°	15	Air	7.0
15	55	Filtrol-20	15	500°	15	Air	8+
16	55	Filtrol-20	10	500°	15	Air	Dark
17	55	Filtrol-20	10	550°	5	Air	Dark
18	55	Filtrol-20	10	550°	15	Air	Dark
19	55	Filtrol-20	10	550°	30	Air	Dark
20	55	Filtrol-20	10	550°	60	Air	Dark
21	55	JN T-13, simultaneous, clay & solvent stripping	15	450° End Point	-	Air	Dark

(Table 1 cont'd)

Sample No.	Temperature of Solvent Treatment	Clay	Wt. % Concentration	°F Temperature	Time Min.	Atmosphere	Color
22	55	JM T-21 simultaneous, clay & solvent stripping	15	450° End Point	–	Air	Dark
23	55	JM T-49 simultaneous, clay & solvent stripping	15	450° End Point	–	Air	Dark
24	55	JM T-49	15	550°	15	Air	Dark
25	55	JM T-21	15	550°	15	Air	Dark
26	55	JM T-13	15	550°	15	Air	Dark
–	55	JM T-49	15	450°	30	Air	Dark
–	55	JM T-21	15	450°	30	Air	DT
–	55	JM T-13	15	450°	30	Air	DT
–	55	Filtrol-20	15	450°	30	Air	DT
–	55	Filtrol-20	30	450°	30	Air	DT
–	55	Filtrol-20 R	15	450°	15	Air	Dark
–	55	Filtrol-20 R	15	450°	30	Air	Dark
–	55	Filtrol-20 R	15	450°	60	Air	Dark
–	55	Filtrol #6	15	550°	15	Air	8+
–	55	Filtrol #4	15	550°	15	Air	8+
–	55	Floridin-Refinex	15	550°	15	Air	Dark
–	55	Floridin Florex-Lum	15	550°	15	Air	Dark
–	55	Floridin Refinex	15	350°	60	Air	Dark
–	55	Floridin Refinex	15	450°	60	Air	Dark

(Table 1 cont'd)

Sample No.	Temperature of Solvent Treatment	Clay	Wt. % Concentration	°F Temperature	Time Min.	Atmosphere	Color
–	55	Floridin Refinex	15	450°	30	Air	Dark
–	55	Clarolite T-60	15	550°	15	Air	Dark
–	55	Clarolite BC	15	550°	15	Air	Dark
–	55	Mil White Hyac 50	15	550°	15	Air	Dark
–	55	Mil White Palex II	15	550°	15	Air	Dark
–	55	Mil White Palex III	15	550°	15	Air	Dark
–	55	IGS	15	550°	15	Air	Dark
–	55	IGB	15	550°	15	Air	Dark
–	55	Utah Standard	15	550°	15	Air	Dark
–	55	Utah Standard	30	450°	30	Air	Dark
–	55	Engelhard Attapulgus	15	550°	15	Air	Dark
–	55	Engelhard Attapulgus	15	450°	30	Air	Dark
–	55	Engelhard Bauxite	15	450°	15	Air	Dark
–	55	Filtrol-20	15	450°	60	Air	Dark
–	55	Filtrol-20	15	550°	60	Steam	Dark
–	55	Filtrol-20	15	550°	120	Steam	Dark
–	55	Filtrol-20	15	550°	180	Steam	Dark

of oxidation is faster than clay adsorption to the extent that only dark oils are produced when treated for longer periods in the presence of O_2. To combat oxidation an inert atmosphere (N_2) was placed over the heated clay oil slurry. Without oxidation much longer reaction times could and were used. If one plots (see Fig. 1) color vs. time, where 15 percent Filtrol-20 and 550°F were used 4 to 6 hours is a favorable reaction time period.

Temperature of the solvent treatment also proved to be an important variable. When a dehydrated oil was mixed and settled at 85°F for 7 days; solvent stripped, then clay treated using 15 percent by weight Filtrol-20, for 3 hours at 550°F under N_2, a 5.5 color oil was produced. However, at a 55°F solvent treat temperatures using the same clay conditions a 3.0 color was achieved.

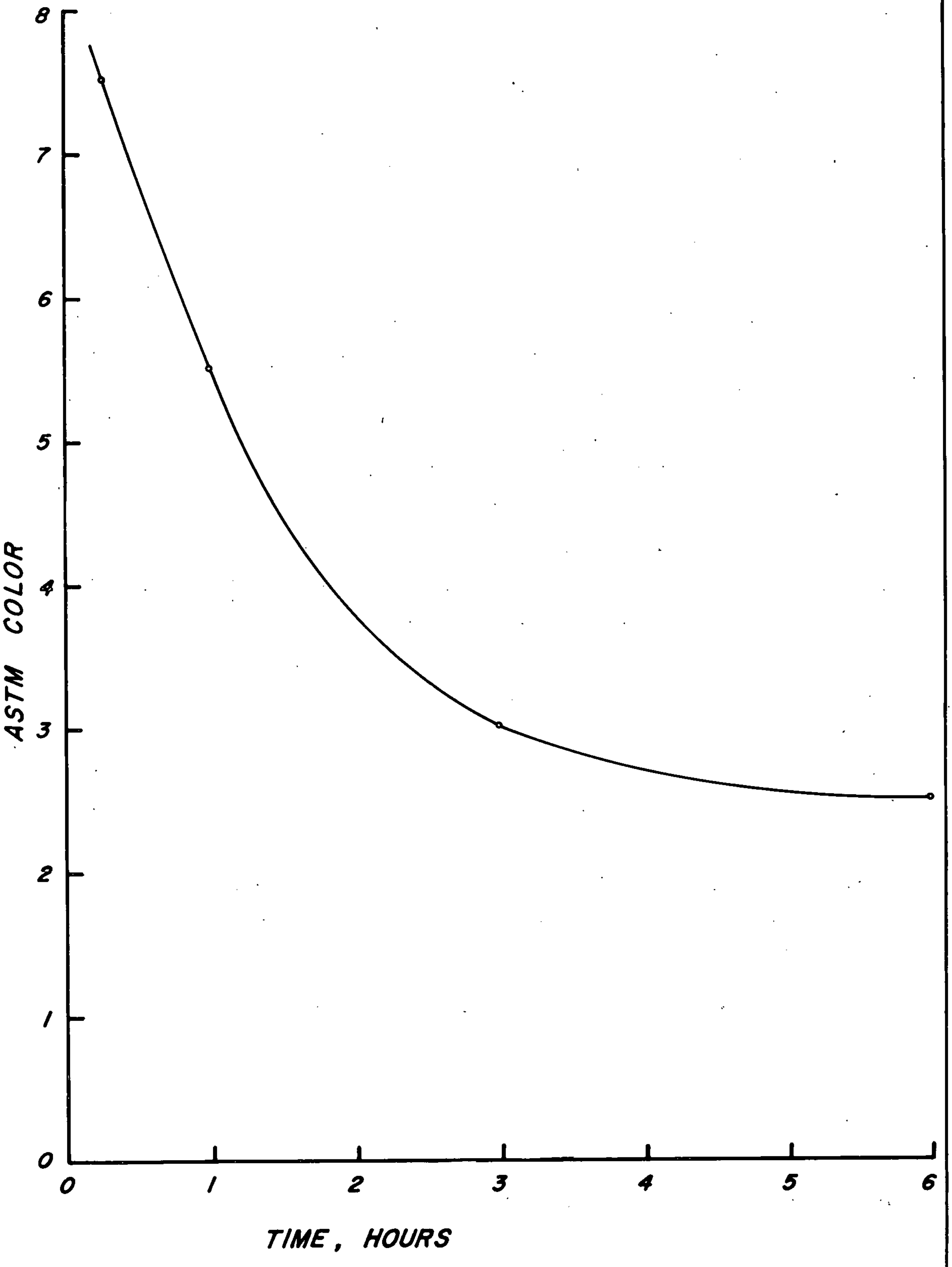
The above observations roughly correlates to the amount of sludge that settled out. The 85°F run yielded 9.0 percent and the 55° treat 20.0 percent sludge. This would indicate that at lower settling temperatures more oxidation products, additives, etc. fall out thus reducing the amount the clay has to adsorb. Also the I.R. confirms that there are less oxidation products in the 55°F solvent treated oil. More detail will be given in the infrared section.

Simultaneous solvent stripping clay treatment did not show promise. In order that the solvent system would not be contaminated with water, only water free clays (JM-T21, JM-T13, JM-49) could be used. Even with slow distillation rates allowing for longer treating times the oils did not bleach sufficiently. It was concluded that this system would not work due to the type of clay that had to be used and the low (bottoms distillation end point 460°F) treating temperatures achieved.

Another variable that was investigated to improve color was steam injection. Dry steam was injected into a 15 percent Filtrol-20 clay oil slurry. The injection was started at 250°F and continued during treating at 450°F and 550°F respectivly. In addition steam was also injected during cool down until 250°F was reached. All oils produced were dark in color and up to 50 percent of the oil was lost due to steam distillation at 550°F for 3 hours.

FIGURE 1

AFFECT OF CLAY TREATMENT TIME ON COLOR OF FINISHED OIL



Infrared Analysis

Figure 2A and 2B show the comparision between the pilot plant dehydrated, solvent treated and clay treated oils. The dehydrated oil contains oxidation, fuel dilution and additive products. The oxidation products can be classified into carboxylic acids, carboxylates and resins. Fuel dilution shows up as aromatics and the major additives are succinimide dispersants and polybutenes.

The I. R. for the solvent stripped oil reveals that all of the alcohols have not been removed as evidenced by the strong OH peak at 3.0 microns. Also remaining after solvent treatment, although in lesser amounts than in the untreated oil, are the oxidation resins (7.7 - 10.0 microns). One can not determine if the acids have been effectively reduced since the alcohols and succinimides absorb in the same region as the acids.

The clay treated oil infrared scan shows that the oxidation products and additives have been effectively removed. The only major peak in question is at 6.25 microns. Furthur analysis would be required to determine if this peak is due to fuel aromatics or carboxylates. If carboxylates are present it may be possible to convert these to their original acid state. Once in the acid state they could be removed in the solvent and/or both clay treatment steps.

In comparing the BERC/ERDA solvent clay treated oil (Figures 2A and 2B) with an off the shelf sample of a rerefined product (Figures 3A and 3B), one finds an improvement in the BERC oil with regard to the removal of additives and residual oxidation products. The rerefined sample can be assumed to be from an acid-clay process due to the rerefinery that it came from.

Infrared Figures 4A and 4B compares several clay treated oils with time as a variable. Each sample was reacted at 550°F with 15% Filtrol-20 for 1,3 and 6 hours. Also shown is the final product achieved in the pilot plant. After 1 hour under the above conditions the majority of the oxidation products (7.7 - 10 microns) have been removed. Still remaining, however, are the succinimide dispersances and not until 6 hours are they effectively removed.

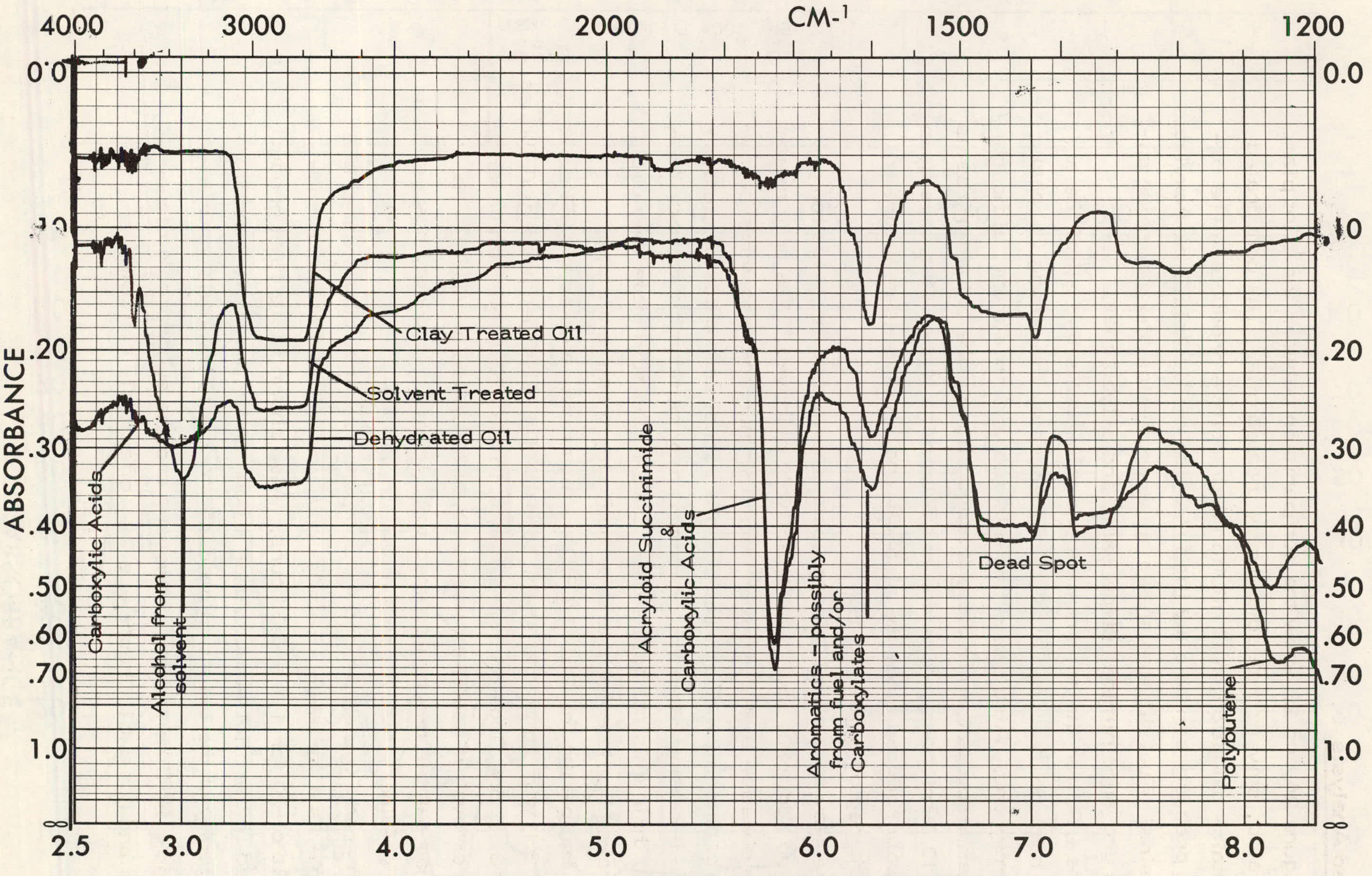


FIGURE 2A

CURVE NO.

CONC.

CELL PATH

REFERENCE 150 vis @ 100°, 95 V. I.

SCAN SPEED

SLIT

OPERATOR

DATE

REMARKS

NO. PR 1132 (337-1209)

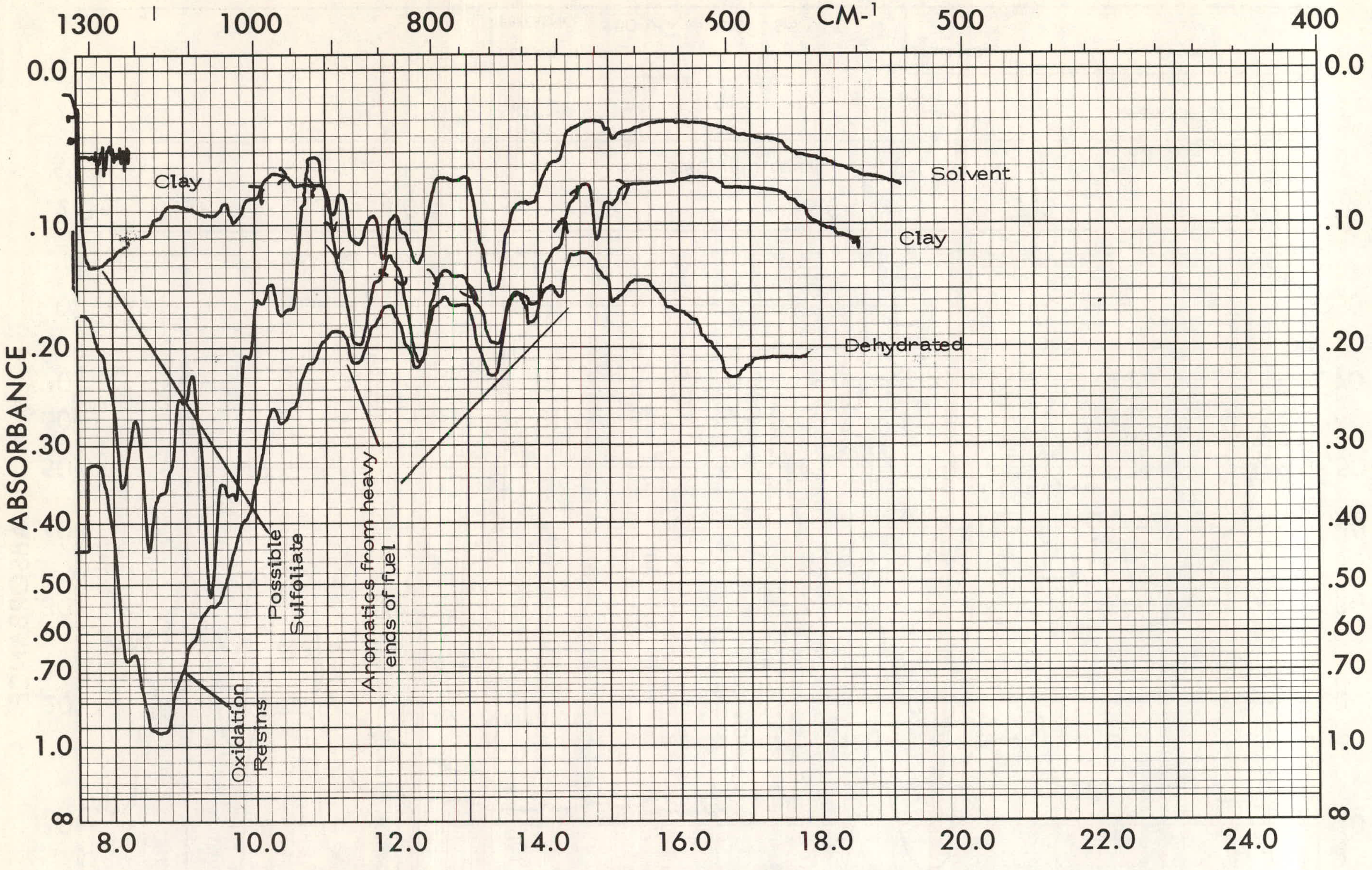


FIGURE 2B

CURVE NO.
CONC.
CELL PATH
REFERENCE 150 vis @ 100°, 95 V. I.

SCAN SPEED
SLIT
OPERATOR
DATE
REMARKS

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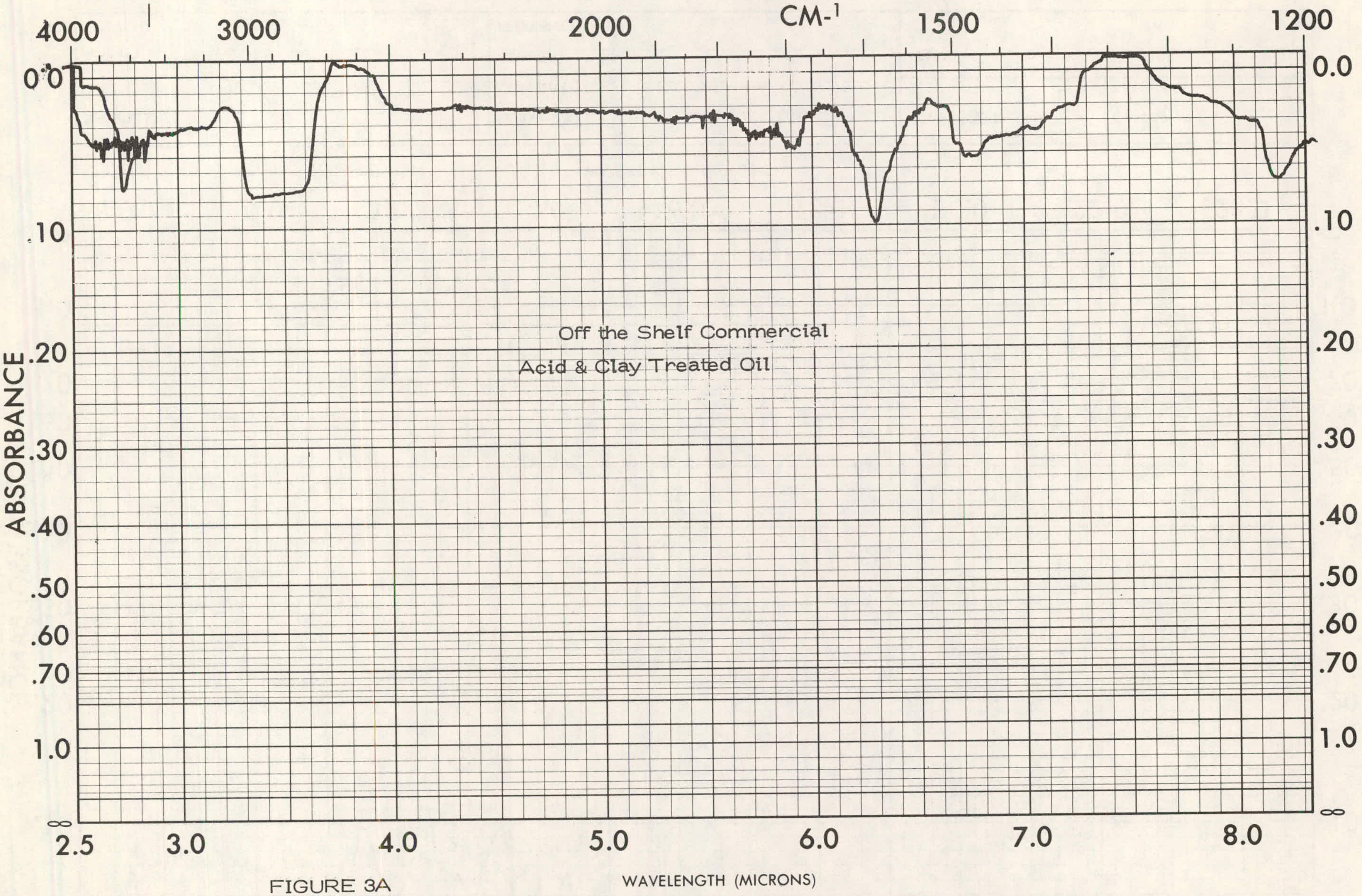


FIGURE 3A

SAMPLE

ORIGIN

SOLVENT

CURVE NO.

CONC.

CELL PATH

REFERENCE 150 vis @ 100°F, 95 V.I.

SCAN SPEED

SLIT

OPERATOR

DATE

REMARKS

No. PR 1132 (337-1209)

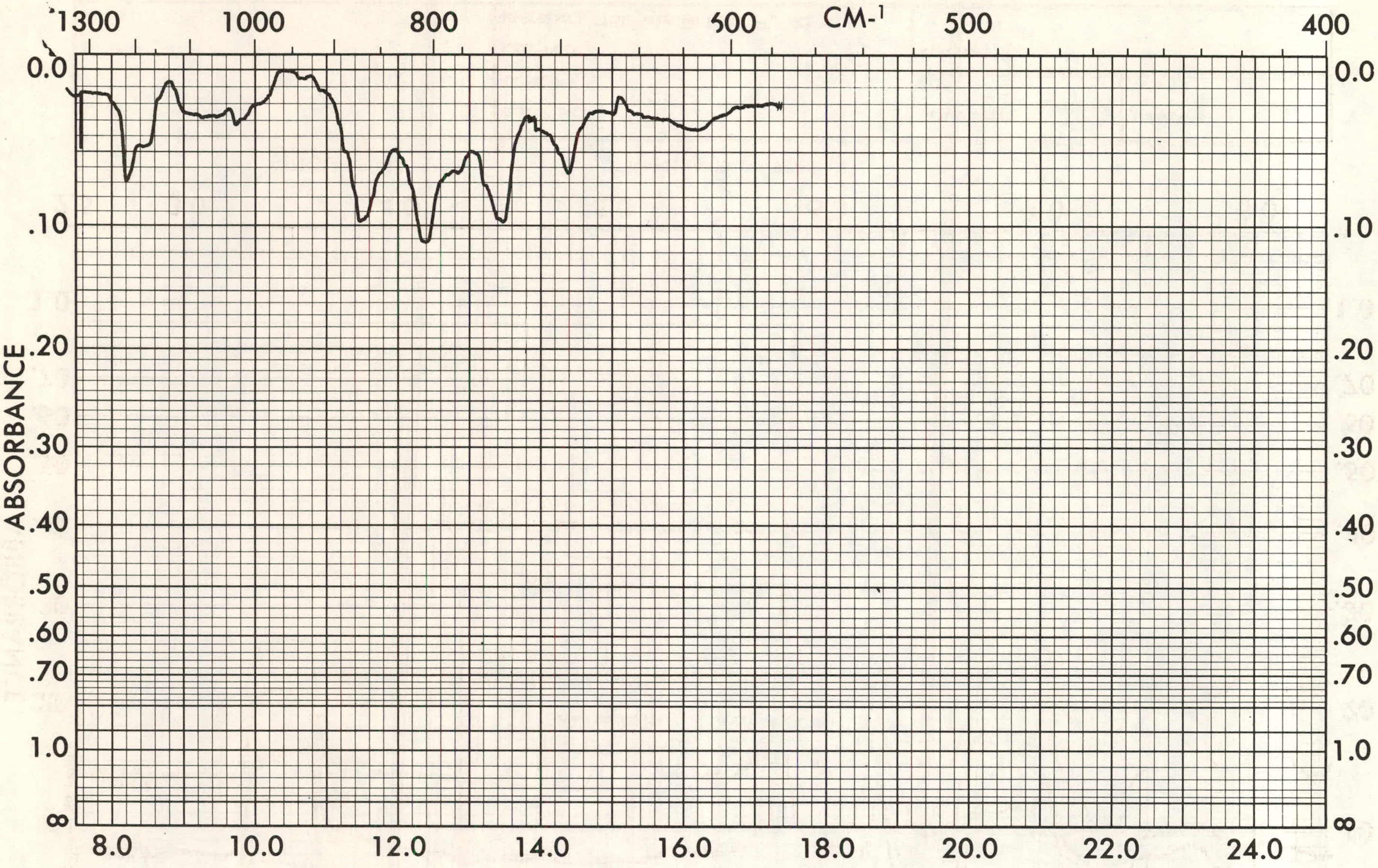


FIGURE 3B

SAMPLE	CURVE NO.	SCAN SPEED	OPERATOR
	CONC.	SLIT	DATE
ORIGIN	CELL PATH	REMARKS	
SOLVENT	REFERENCE		

CHART NO. PR 1133 (337-1210)

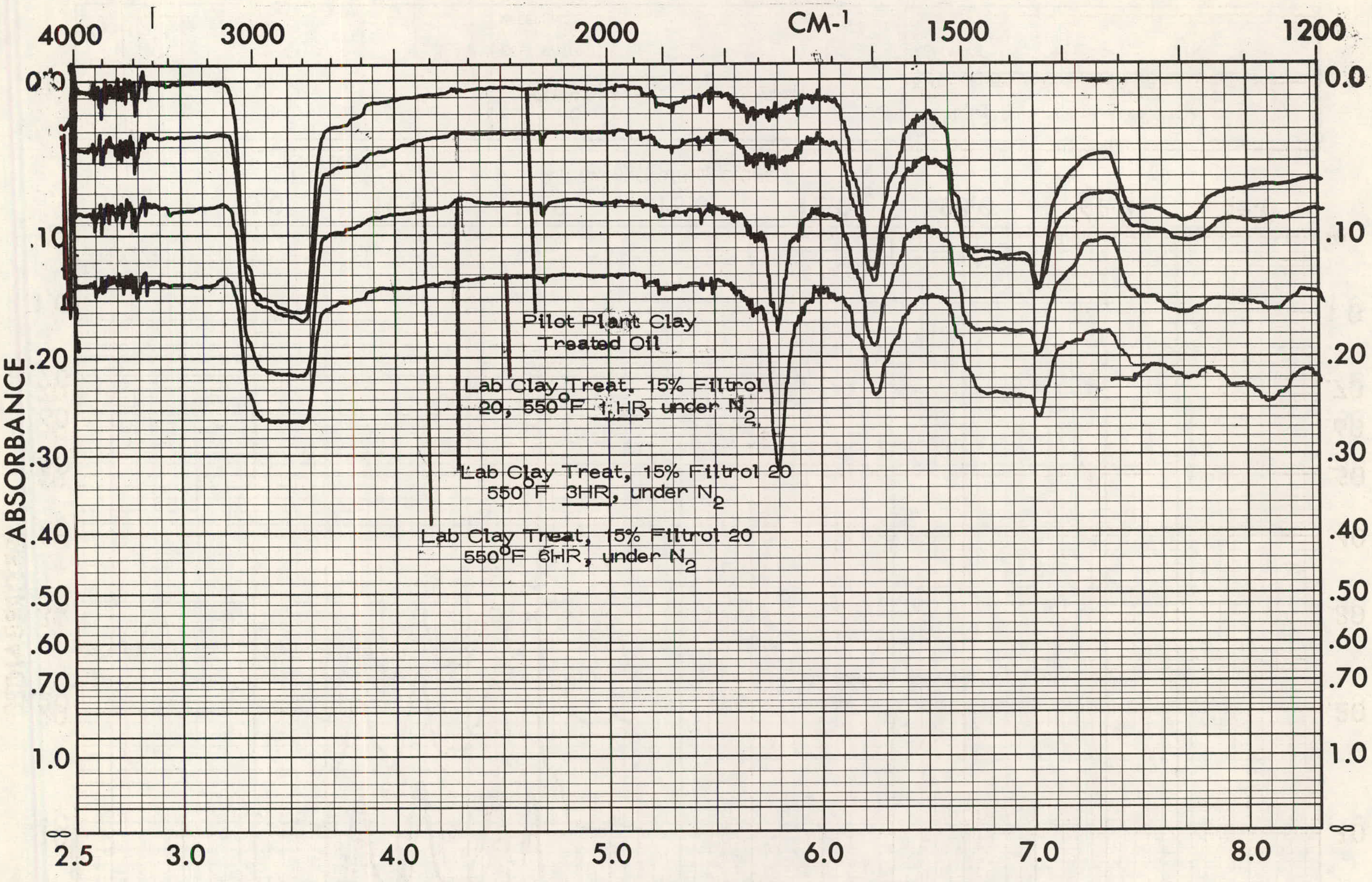


FIGURE 4A

CURVE NO.
CONC.
CELL PATH
REFERENCE 150 vis @ 100°F, 95 V. I.
SCAN SPEED
SLIT
OPERATOR
DATE
REMARKS

No. PR 1132 (337-1209)

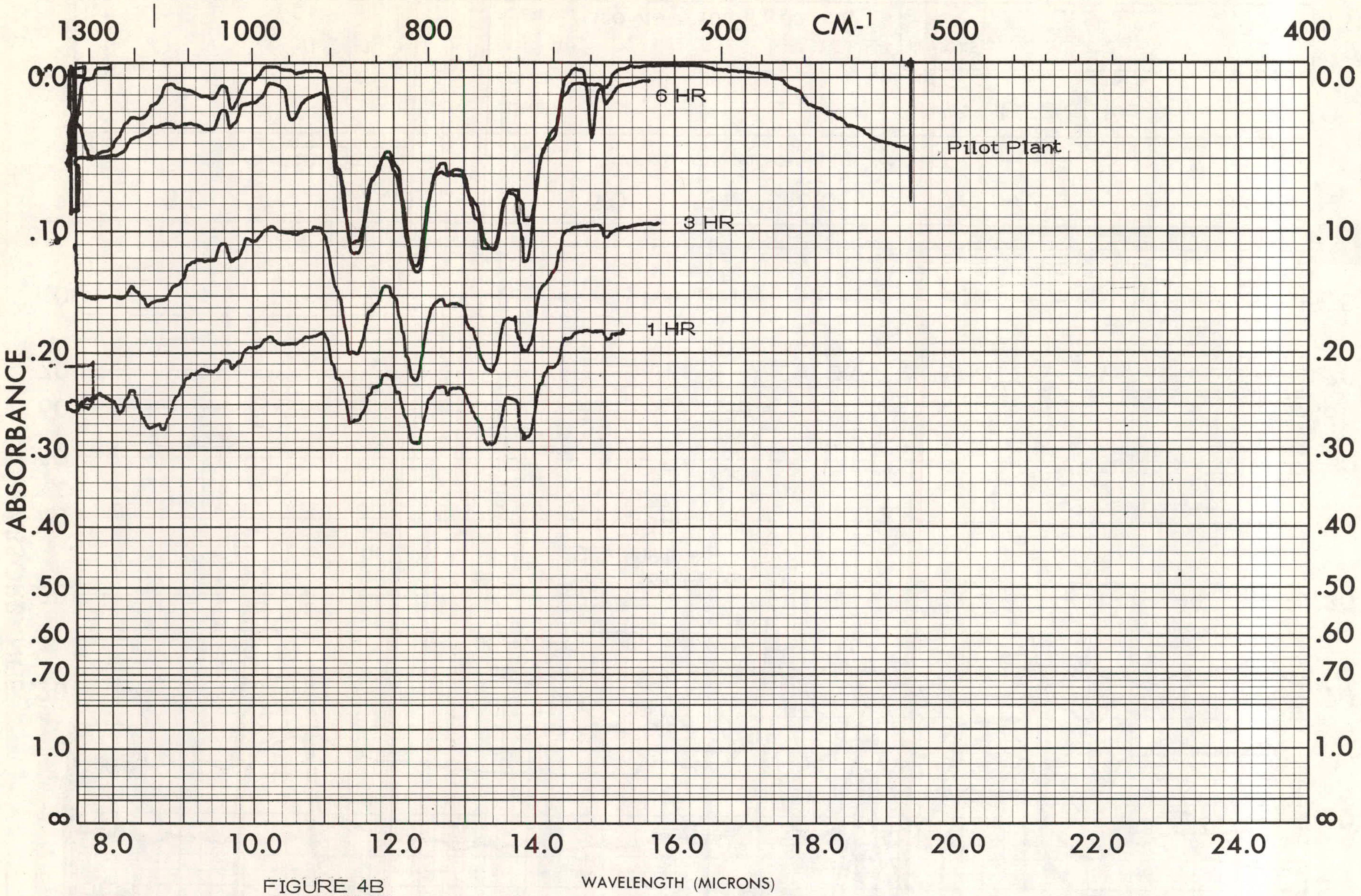


FIGURE 4B

CURVE NO.
CONC.
CELL PATH
REFERENCE

SCAN SPEED
SLIT

OPERATOR
DATE

REMARKS

CHART NO. PR 1133 (337-1210)

When one compares the infrared scans of oils solvent treated for 7 days at 55°F and 85°F (Figures 5A and 5B), the 55°F oil has settled out more oxidation resins then the 85°F oil. Once these oils have been clay treated (Figures 6A and 6B) with 15% Filtrol-20 @ 550°F for 3 hours under nitrogen the 55°oil still shows a reduction in the amount of resins and better color (3.0 vs 5.5).

Summary of Results

This part of the investigation found that for the production of an oil, with the lowest amount of resins, additives and the best color (ASTM 2·5) the following conditions were followed: (1) Dehydrate the oil to a 700°F end point. (2) Mix the oil and BERC/ERDA solvent system at 55°F and continue gravity settling for 7 days. (3) Decant and then solvent strip such that the distillation bottom end point is 500°F. (4) Clay treat the solvent stripped oil using 15 percent by weight Filtrol-20 for 6 hours at 550°F under a blanket of nitrogen. (5) Filter the oil clay slurry at 250°F.

Simultaneous solvent stripping clay treatment did not show promise. This system will in all probability not work due to the low clay treating temperatures achieved and the type of clay (water free) that had to be used.

The infrared analysis of the final product producted in the pilot plant shows that the residual additives and oxidation products have been removed. When one compares the BERC/ERDA oil to a acid-clay type of base stock, the BERC/ERDA oil shows an improvement in the amount of additives and resins remaining in the oil.

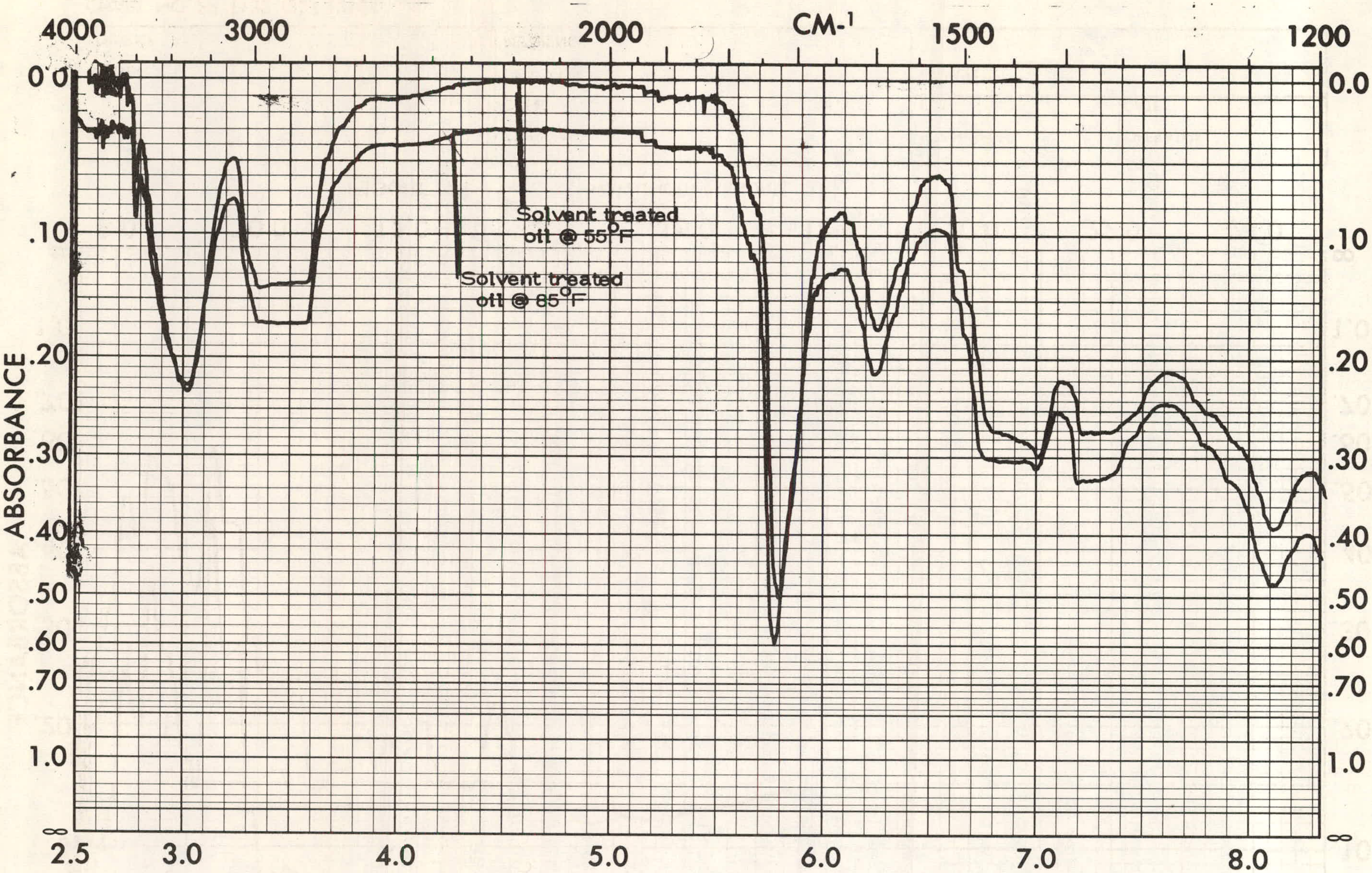


FIGURE 5A

ORIGIN

SOLVENT

CURVE NO.

CONC.

CELL PATH

REFERENCE 150 vis @ 100°F, 95 V. I.

SCAN SPEED

SLIT

OPERATOR

DATE

REMARKS

No. PR 1132 (337-1209)

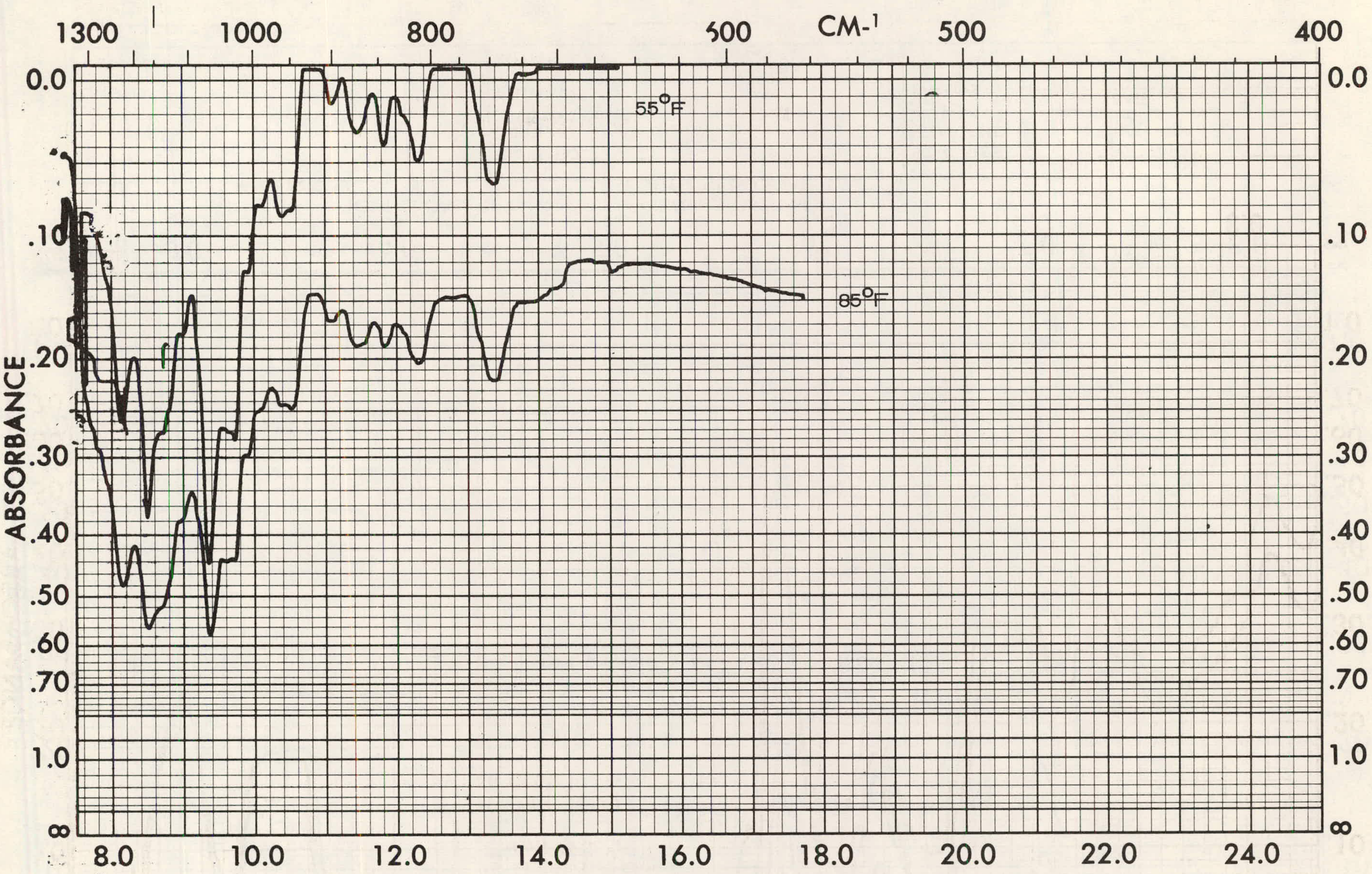


FIGURE 5B

SAMPLE	CURVE NO.	SCAN SPEED	OPERATOR
	CONC.	SLIT	DATE
ORIGIN	CELL PATH	REMARKS	
SOLVENT	REFERENCE		

CHART NO. PR 1133 (337-1210)

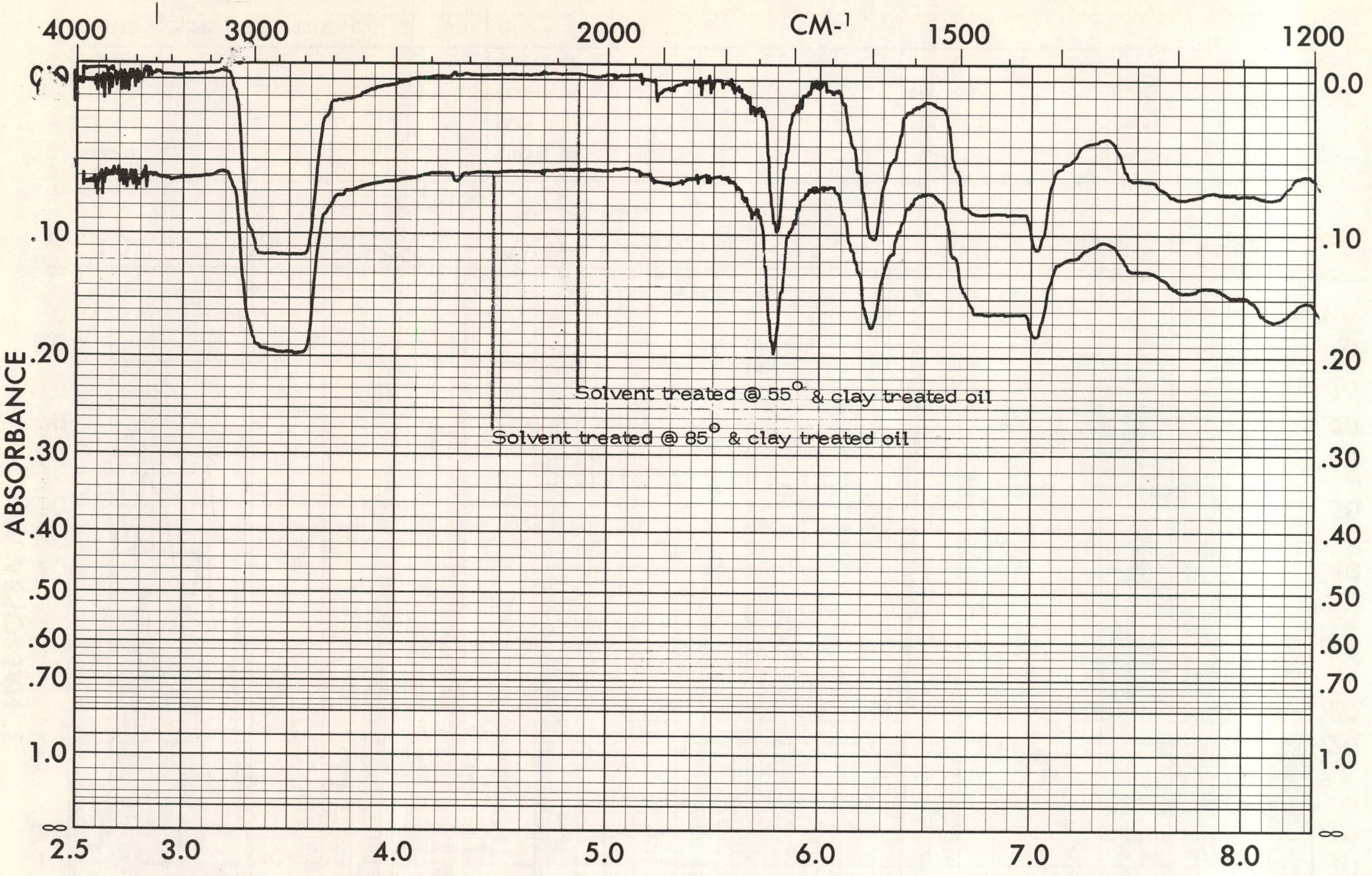


FIGURE 6A

ORIGIN

SOLVENT

CURVE NO.

CONC.

CELL PATH

REFERENCE 150 vis @ 100°F, 95 V. I.

SCAN SPEED

SLIT

OPERATOR

DATE

REMARKS

No. PR 1132 (337-1209)

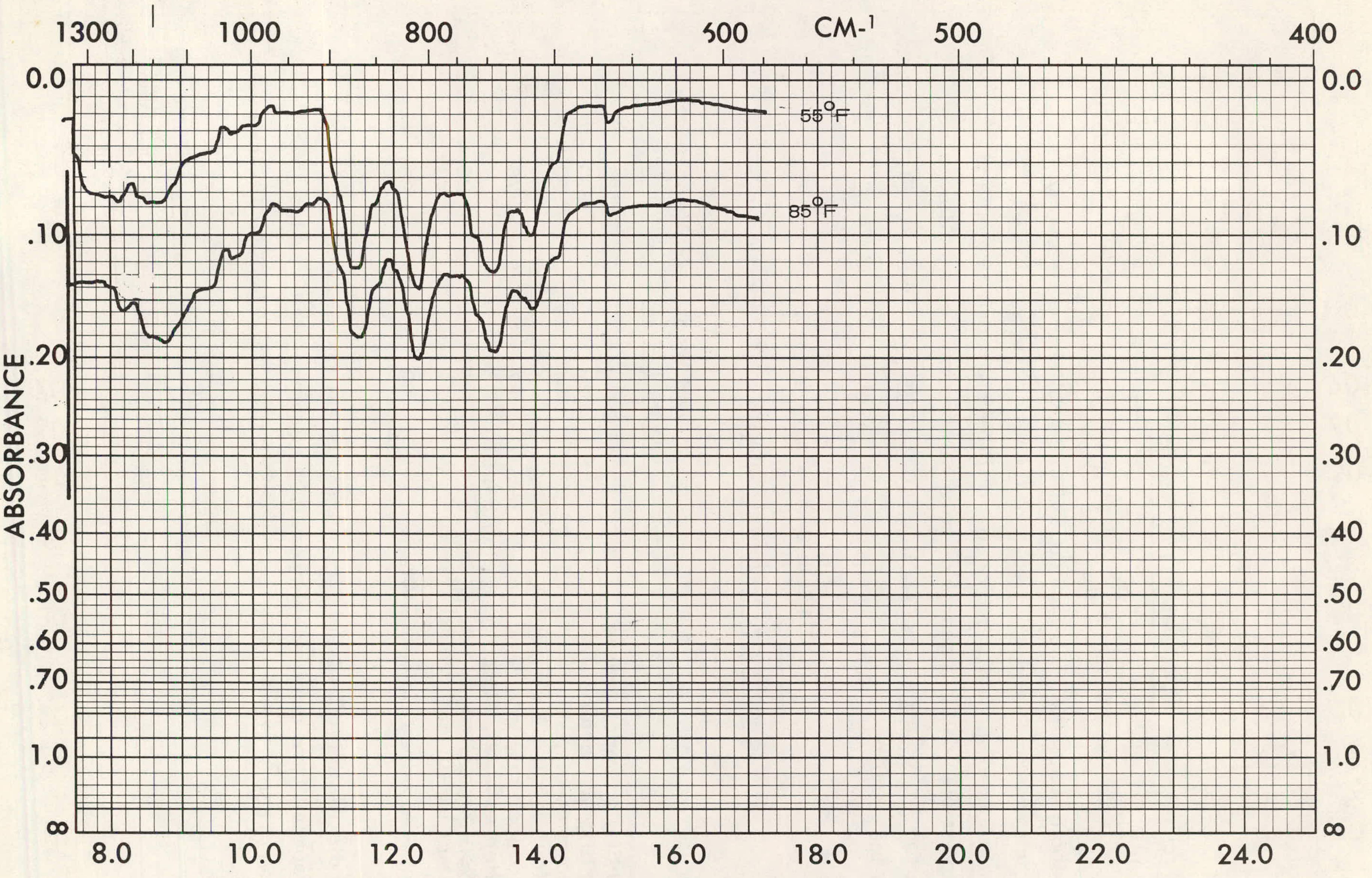


FIGURE 6B

SAMPLE

ORIGIN

SOLVENT

CURVE NO.

CONC.

CELL PATH

REFERENCE

SCAN SPEED

SLIT

OPERATOR

DATE

REMARKS

CHART NO. PR 1133 (337-1210)

SECTION II

MATERIAL BALANCE

A bench-scale study was conducted to establish the recovery efficiencies at a 55°F and 85°F solvent treatment temperatures. In each case approximately 830 grams of pilot plant dehydrated and fuel stripped oil and 2275 grams of solvent were mixed and allowed to settle for 7 days at the appropriate temperatures. Table 2 summerized the results.

Table 2

Laboratory Material Balance

	Solvent treat @ 85°F	Solvent treat @ 55°F
Starting solvent, grams	2272	2275
Starting oil, grams	829	830
Recovered oil, Wt. % (after settling & stripping)	91	80
Recovered oil, Wt. % (after settling, stripping & clay treat)	87	76
Solvent free Sludge, Wt. %	9	20
Solvent in Sludge, Wt. %	37	43
Total Recovered Solvent, Wt. %	98	98

The distillation of solvents from both the oil and sludges was carried out until the bottoms-temperature reached 460°F. Also 15% Filtrol-20 @ 550°F for 3 hours was used for clay treatment conditions.

SECTION III

PILOT SCALE STUDY

Introduction

The pilot scale study included four basic steps in the production of a finished lubricating oil base stock from waste crank case oil. First, the waste oil was vacuum distilled to remove water and fuel dilution; second, the bottoms from vacuum distillation were treated with BERC/ERDA solvent followed by two methods of sludge separation, gravity settling and centrifuging; third, solvent was removed from the solvent-oil mixture by atmospheric distillation; and fourth, the oil recovered from distillation of the solvent-oil mixture was clay treated and filtered to produce a finished lubricating oil base stock. The objectives of the pilot scale study were to (1) to determine the feasibility of producing a finished lubricating oil base stock employing the process outlined above, (2) to determine yields and product characteristics for each step of the process, (3) to obtain data relative to performance of the equipment used in the pilot study, and (4) to obtain preliminary design data for new plant construction. The objectives of the pilot scale study were successfully accomplished although as discussed later in this report, additional investigative work is recommended to facilitate the best possible plant design. The following sections of this report include information pertaining to the collection of waste crankcase oil used in this study and detailed descriptions of the process steps included in the pilot scale study.

Collection of waste crank case oil

A total of 8,200 gallons of waste crankcase oil was collected for this study. Of this amount 56 percent represented gasoline engine lubricating oil (service stations and automotive sales and service) and 44 percent represented diesel engine lubricating oil (truck repair, heavy equipment sales and service, and fleet sales and service). The oil collected is considered to be representative of feed stock to a re-refining plant, although the above percentages could vary considerably since it is considered impractical from a collection standpoint to separate waste oils by source or usage. The ash content on dehydrated oil (300°F at atmospheric pressure) amounted to 2.08 weight percent for gasoline engine lubricating oil and 0.87 weight percent for the diesel engine lubricating oil, resulting in a weighted average of 1.55 weight percent ash on the total waste oil collected. The oil collected was completely mixed by tank circulation prior to processing in the vacuum still.

Vacuum distillation

The equipment used in the vacuum distillation step is shown schematically in Figure 7 which also gives the final operating conditions for the run. The system was charged with 2,456 gallons of oil from the fresh feed tank which contained the 8,200 gallons of waste lubricating oil collected for this study. After charging the system, oil circulation was established and the system was brought up to desired operating conditions which were maintained for a period equivalent to approximately 1.5 times the total volume of oil in the system at the prevailing oil circulation rate. Operating conditions were selected such that all of the 700°F end point distillate would be removed from the vacuum tower bottoms. Volumetric yields from the vacuum distillation are presented in the following table:

Table 3

Vacuum Distillation Yields

	Gallons	Volume %
Charge to system	2,456	100
Yields		
Water	30	-
*Water (loss to vacuum jets)	97	-
Total water	127	5.2
Distillate	604	24.6
Vacuum tower bottoms	1,725	70.2
Total Yield	2,456	100.0

* by difference

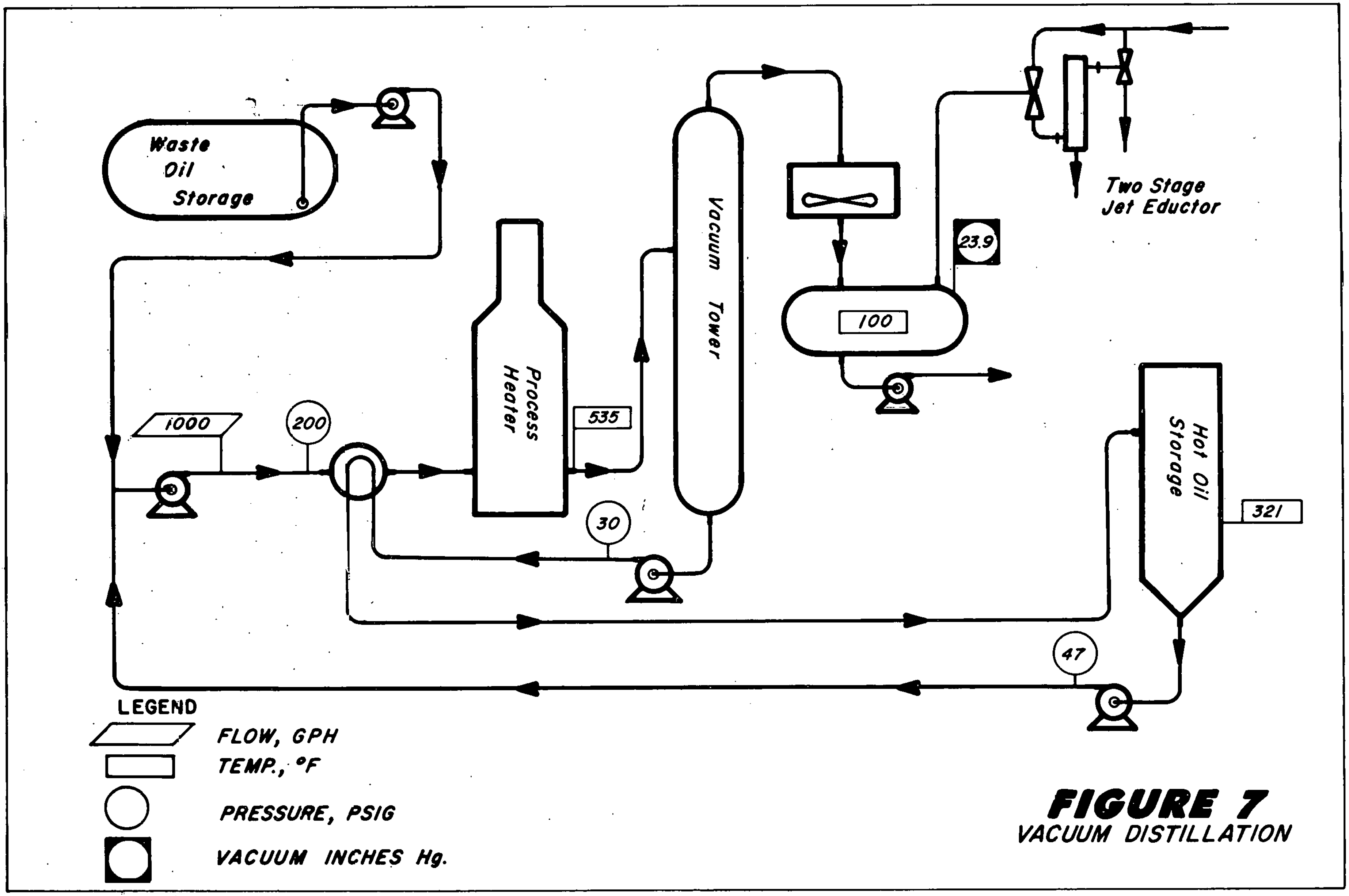


FIGURE 7
VACUUM DISTILLATION

A laboratory distillation of the distillate showed that about 45 percent of the distillate boiled above 700°F thus indicating a greater amount of distillate may have been removed than necessary. On the other hand, a substantial carryover of the oil boiling above 700°F would be expected since the vacuum tower is not equipped with bubble trays and separation is therefore equivalent to a single flash vaporization.

Tests on the products from distillation were as follows:

Table 4

Properties of Products from Vacuum Distillation

Test	Vacuum Tower Bottoms	Distillate	Water
pH	-	-	4.6
Gravity, API	25.6	31.5	-
*Distillation			
IBP, °F	-	333	-
10%	-	441	-
50%	-	695	-
90%	-	746	-
Viscosity			
cs @ 100°F	160.7	-	-
cs @ 210°F	16.5	-	-
Flash Point			
C.O.C. °F	460	-	-
Ash, wt. %	2.07	-	-

* corrected to 760 mm Hg

Solvent treating with BERC/ERDA solvent

BERC/ERDA solvent was mixed with vacuum tower bottoms in batches of approximately 400 gallons using a totally enclosed stirred tank mixer. After mixing, the batches were transferred to a cone bottom settling tank for sludge separation. An exception to this procedure was the batch that was centrifuged immediately after mixing in order to evaluate centrifuge performance. Figure 8 illustrates the equipment used in the solvent treating step.

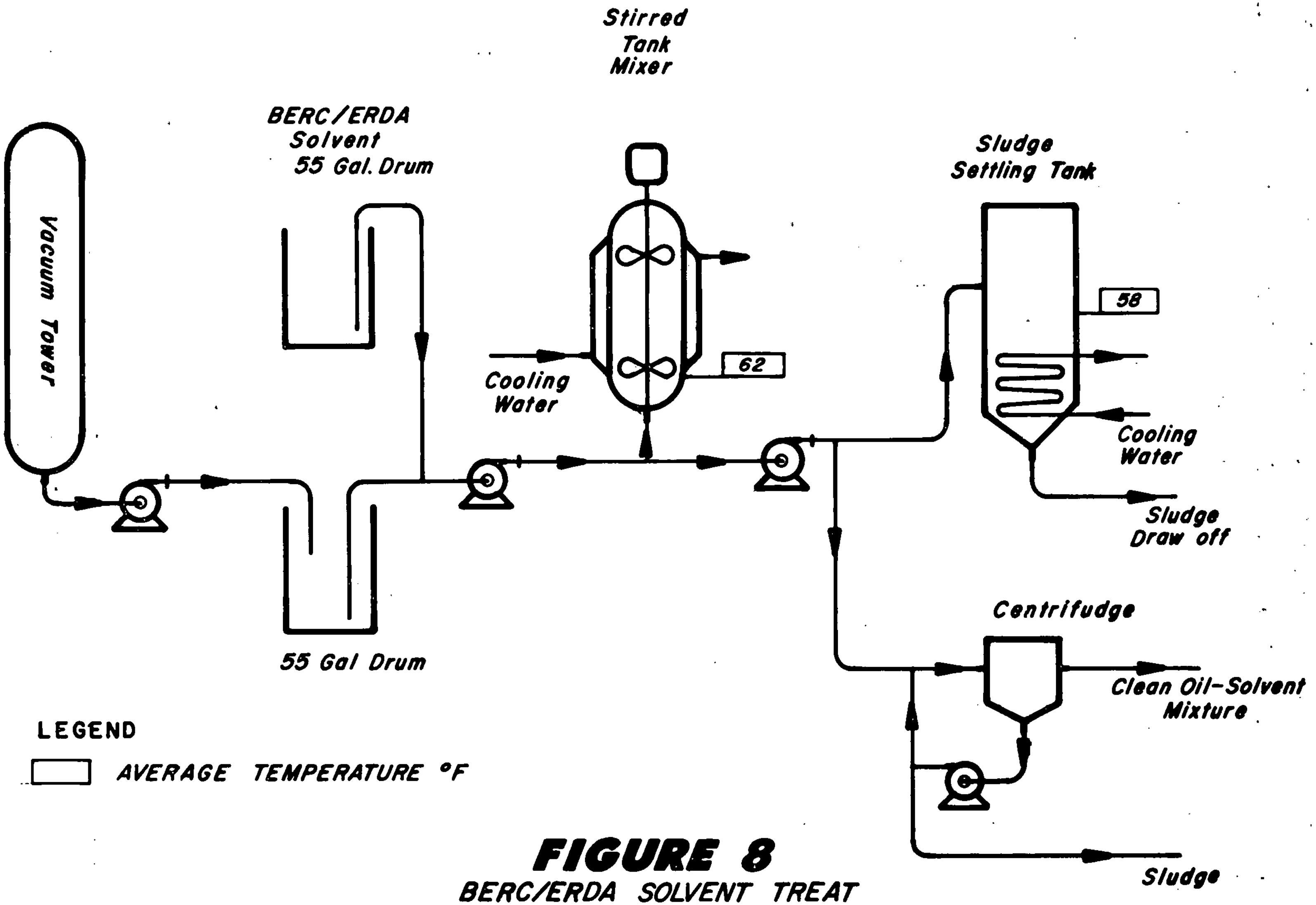


FIGURE 8
BERC/ERDA SOLVENT TREAT

Data pertaining to the mixing and settling of each batch are presented in the following table.

Table 5

Solvent Treats with BERC/ERDA Solvent

Batch No.	1	2	3	4	**5	Total
Vac. Twr. Btms, gals.	106	106	106	80	106	504
BERC/ERDA solvent, gals.	318	318	318	240	318	1,512
Total charge	424	424	424	320	424	2,016
Mixing Temp, °F	65	58	64	68	56	-
Mixing Time, Min.	20	20	20	20	20	-
Settling Time, Days	7.1	8.8	8.9	9.0	None	-
*Average settling time, Days	------------ 8.4 -----					
Average settling temp, °F	58					

* weighted average

** centrifuged

As indicated above the weighted average settling time for combined batch Nos. 1 through 4 was 8.4 days at an average settling temperature of 58°F. After settling a total of 120 gallons of sludge was drawn off the cone bottom tank. Laboratory distillation of the sludge to a liquid temperature of 500°F (515°F corrected to sea level) and atmospheric pressure gave the following yields:

Table 6

Yields from Sludge Distillation

	Volume %	Weight %
Charge to still	100.0	100.0
Overhead (solvent)	26.9	23.5
Bottoms (solvent free sludge)	72.1	75.7
Loss	1.0	0.8
Total	100.0	100.0

The foregoing data gives a solvent free sludge yield of 21.7 volume percent of the vacuum tower bottoms treated.

Characteristics of the settled sludge and solvent-free sludge are presented in the following table:

Table 7

Properties of Settled Sludge and solvent-free sludge

	Settled Sludge	Solvent Free Sludge
Gravity, API	20.3	13.8
Viscosity		
cs @ 70°F	190.9	-
cs @ 100°F	60.6	-
cs @ 210°F	-	76.3
cs @ 250°F	-	43.2
Flash point, COC, °F	-	455
Ash, Wt. %	-	8.47

Solvent treat batch no. 5 was centrifuged immediately after mixing using a De Laval AC-VO-1 solid bowl centrifuge with four 0.9 mm nozzles. Sludge recirculation was employed to concentrate the sludge, and a nitrogen purge system was used for explosion prevention. A clear solvent-oil mixture was produced at centrifuge feed rates varying from a low of 200 gph to a high of 1,100 gph which was the highest feed rate attempted. Sludge production amounted to 24 gallons which contained 52.6 volume percent solvent as determined by laboratory distillation to 500°F liquid temperature (515°F corrected to sea level) and atmospheric pressure. Solvent concentration in the sludge was high because of the lack of proper sludge recirculation controls. The yield of solvent-free sludge on vacuum flash bottoms treated amounted to 10.8 volume percent.

Samples of the solvent-oil mixture from the De Laval centrifuge were centrifuged again in the laboratory to confirm the samples were clear, and there was no sludge present. However, upon standing overnight at room temperature about 1.5 percent sludge had dropped to the bottom of the centrifuge tubes. This phenomenon was unexpected and suggests that sludge agglomeration may be time dependent. The sludge agglomeration phenomenon coupled with a rise in temperature of about 20°F in centrifuging would appear to account for the substantial difference in solvent-free sludge yield from settling as compared with centrifuging, 21.7 percent and 10.8 percent by volume respectively. It should be mentioned that the centrifuged solvent-oil mixture was allowed to settle six days before being combined with the gravity settled solvent-oil mixture for solvent recovery.

Solvent recovery

The third process step, that of recovering the solvent from the solvent-oil mixture, was accomplished by atmospheric distillation utilizing the equipment shown schematically in Figure 9. Also indicated on Figure 9 are the final operating conditions. The flash tower and heater were charged from the solvent-oil storage and solvent was distilled while maintaining circulation through the heater and increasing temperature. Solvent recovery was held to a maximum of about 300 gph as limited by the capacity of the overhead-aerial condenser. As solvent was recovered additional solvent-oil mixture was charged to the system until all of the solvent-oil mixture had been charged. A material balance for the solvent recovery step is presented in the following table:

Table 8

Solvent Recovery Yields

	Oil-solvent mixture		Oil		Solvent	
	gals.	vol. %	gals.	vol. %	gals.	vol. %
Charge to system	1823	100.0	393.3	100.0	1429.7	100.0
Solvent recovered					1423.0	99.5
Oil recovered			360.0	91.5		
Loss			33.3	8.5	6.7	0.5
Total			393.3	100.0	1429.7	100.0

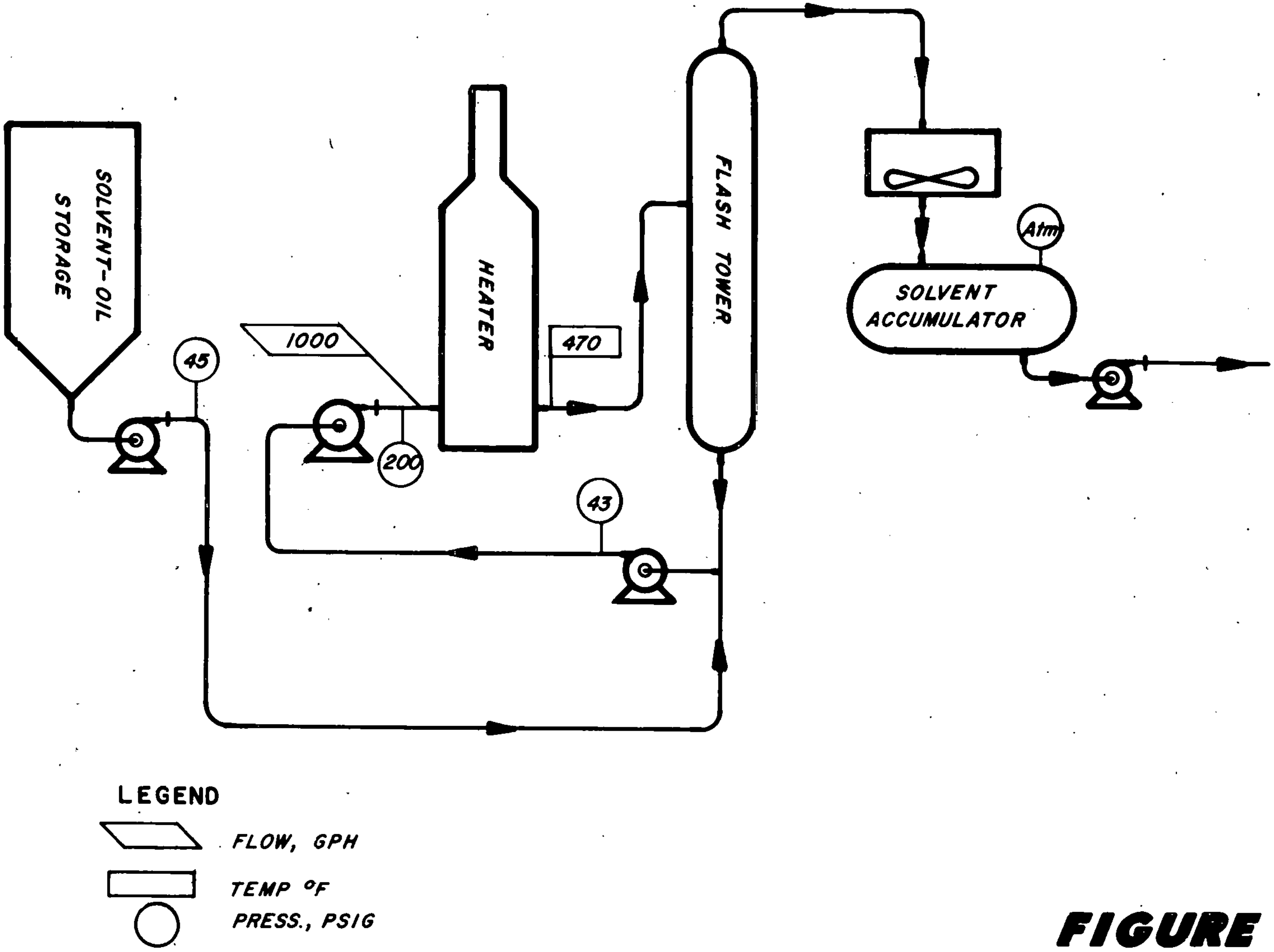


FIGURE 9

SOLVENT RECOVERY

The relatively high percentage of oil loss, 8.5 percent on charge was due to the amount of non-recoverable oil left in heater return bends, heater transfer line and other piping after the run was completed.

In the following table are presented the properties of the recovered oil.

Table 9

Properties of Solvent-Free Oil

Gravity, API	28.1
Viscosity	
cs @ 100°F	92.2
cs @ 210°F	10.8
Flash, C.O.C. °F	435
Ash, Wt. %	0.167
Color	8+

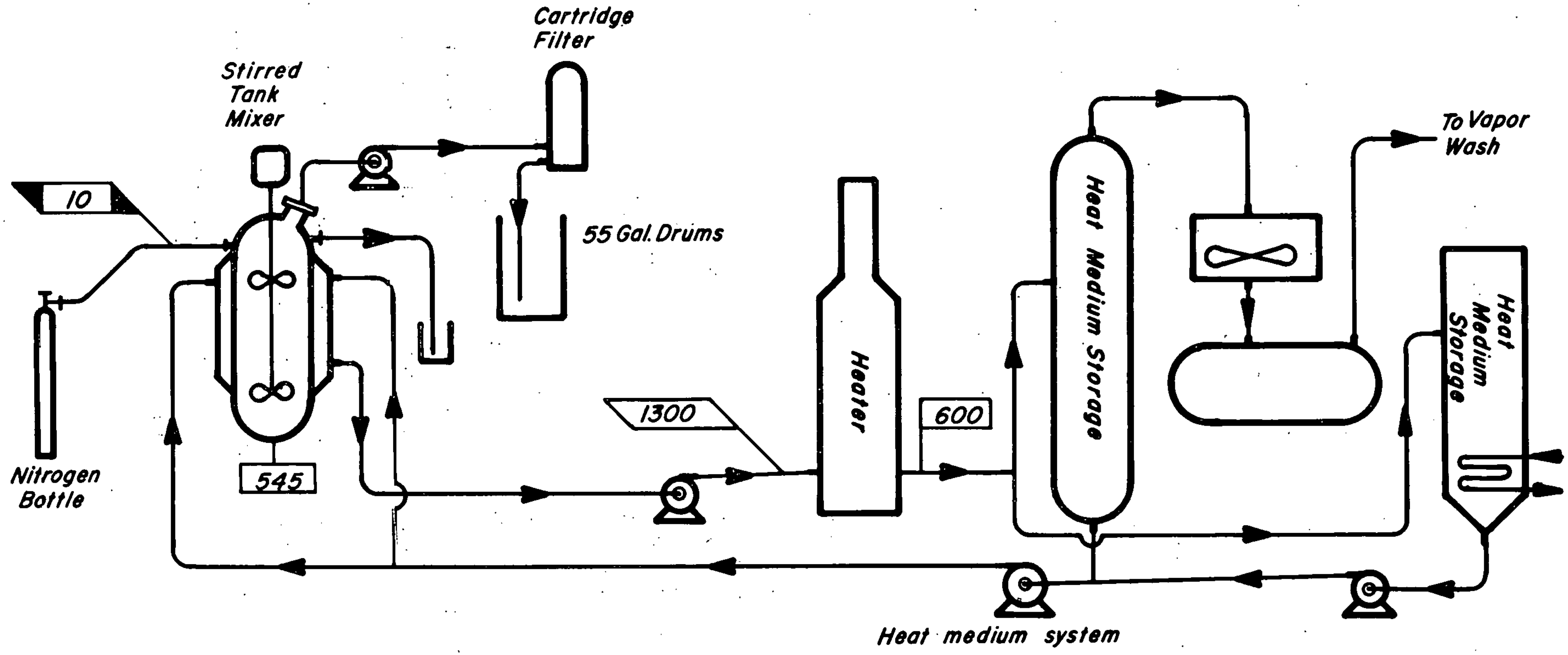
Following completion of the solvent recovery step, the solvent free oil was transferred to the stirred tank mixer for clay treating.

Clay Treating

A schematic presentation of equipment used in clay treating is given in Figure 10. Operating conditions at the time of maximum mixer temperature are also shown. After charging oil to the stirred tank mixer, heat medium circulation was started to bring the oil up to temperature. Clay was added at a mixer temperature of about 100°F and the temperature was increased gradually to remove moisture in the clay. Quantities of oil and clay charged were as follows:

	Volume gals.	Weight pounds	%
Solvent-free oil	350	2584	
Filtrol - 20 clay		388	
Wt. % clay on oil charged			15

Nitrogen purge of the vapor space in the mixer was started at a mixer temperature of about 300°F and was continued throughout the heating and cooling cycle. Treating time amounted to about six hours with



LEGEND

▱ FLOW, GPH

▰ FLOW, FT^3/Hr.

▭ TEMP., °F

FIGURE 10
CLAY TREATING

the oil-clay mixture between 530°F and 545°F. During the entire heating and cooling cycle a total of 5.8 gallons of a light oil was produced through the nitrogen purge effluent line. A time-temperature curve for the heating and cooling cycle is shown in Figure 11 with appropriate notations as to operations.

After the mixer was shut down, the oil-clay mixture was allowed to settle for one hour before filtering. The oil was filtered through a 5 micron cartridge type filter. The first filter cartridge plugged after a throughput of about 20 gallons. It was therefore decided to let the oil-clay mixture settle further before resuming filtration. After 5 days settling it was possible to filter 260 gallons of oil using three cartridges. The remainder of the oil in the mixer had a very high clay content and could not be filtered with available equipment.

Properties of the filtered oil are given in the following table:

Table 10

Properties of Clay Treated Oil

Gravity, API	29.8
Viscosity	
cs @ 100°F	62.9
cs @ 210°F	7.9
Flash point °F	395
Ash, Wt. %	0.005
Color	2.5

The flash point of the clay treated oil was somewhat lower than expected. Laboratory testing indicated that the flash point could be increased to 425°F by bubbling nitrogen through the oil at 300°F and atmospheric pressure. Accompanying the increase in flash point was a weight loss of 1.2 percent.

Unfortunately it was not possible to obtain a material balance on the clay treating step because of the inability to filter all of the oil in the stirred tank mixer. However, laboratory tests indicated that the volumetric oil loss for a 15 percent by weight clay treatment amounted to 5.0% by volume of the untreated oil.

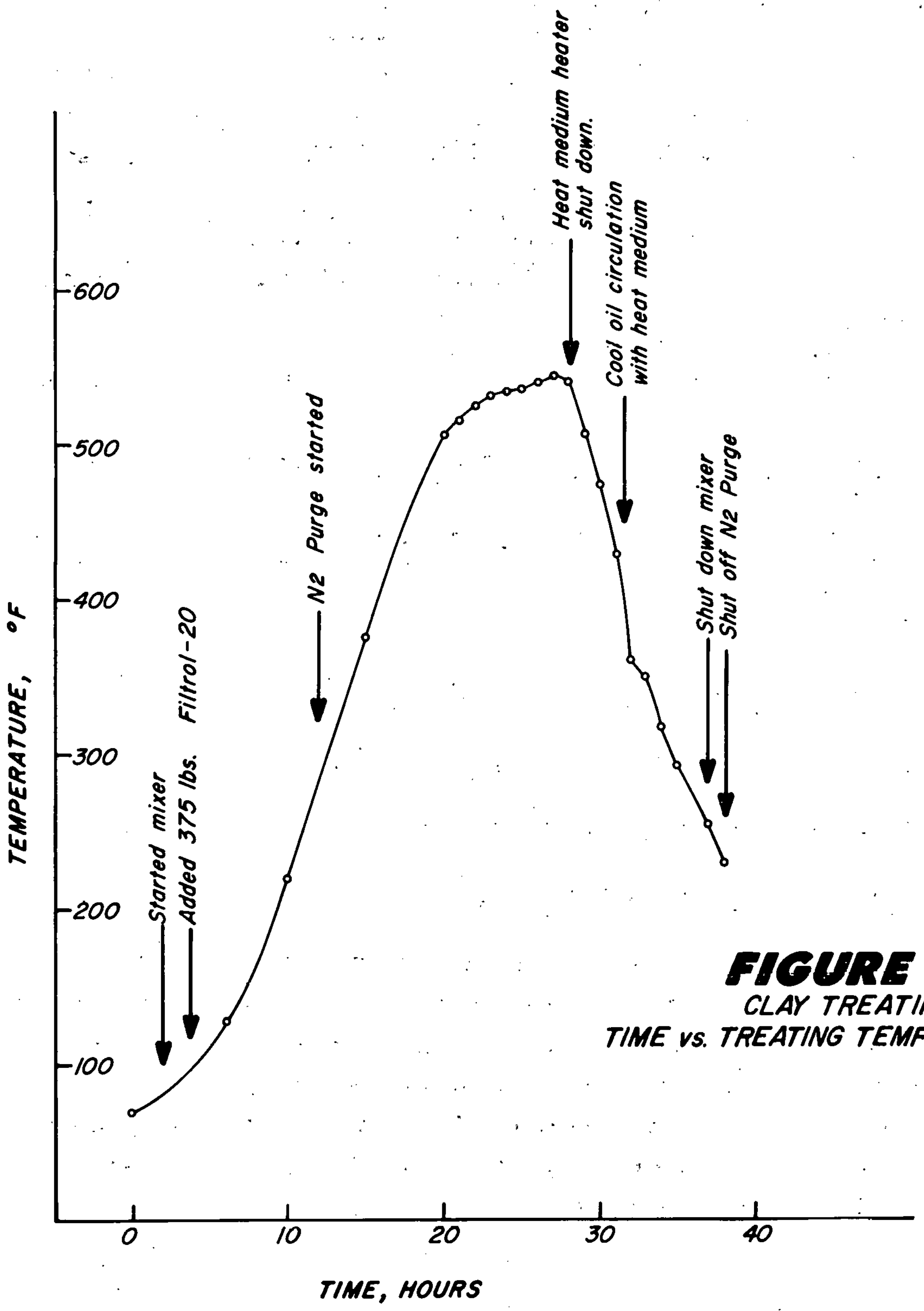


FIGURE 11
CLAY TREATING
TIME vs. TREATING TEMPERATURE

Summary of Results

In the following table is presented a summary of yield and property data for each of the steps involved in the pilot plant study:

Table 11

Summary of Yield and Property Data

	Step 1, vacuum distillation	Steps 2 & 3 solvent treating	Step 4 clay treating
Yield data			
Vol. % on vac. dist-btms.	100.0	79.8	*75.8
Vol. % on waste oil	70.2	56.0	*53.2
Property data			
Gravity, API	25.6	28.1	29.8
Density, 15°C	0.901	0.886	0.877
Viscosity			
cs @ 100°F	160.7	92.2	62.9
cs @ 210°F	16.5	10.8	7.9
Viscosity Index			
VI_E	118	111	
VI			99.4
**Characterization Factor	12.2	12.3	12.4
Flash, C.O.C., °F	460	435	395
Ash, Wt. %	2.07	0.167	0.005
Color	Black	8+	2.5

* computed from laboratory data using information from steps 2 and 3.

** computed from gravity and viscosity data

It will be noted that an overall volumetric yield of about 75 percent on distillate-water-free oil can be expected at the levels of solvent and clay treating employed. Higher yields may be expected at higher solvent treating temperatures and at lower percentage clay treatment levels provided commercially acceptable base oils can be produced. Laboratory work indicates a possible reduction in the amount of clay used. Sufficient data have not yet been obtained with regard to solvent treating temperature and sludge separation methods to specify optimum conditions in this regard. Further study is indicated in determining optimum sludge separation methods and solvent treating temperatures.

Both the solvent treating and clay treating steps resulted in a decrease in density, a reduction in viscosity and viscosity index, a reduction in flash point, a reduction in ash, and an improvement in color as would be expected from the removal of sludge, additives and higher molecular weight components from the oil.

The infrared for the final pilot plant oil shows that the oxidation products and additives have been effectively removed. The only major peak in question is at 6.25 microns. Further analysis would be required to determine if this peak is due to fuel aromatics and/or carboxylates. In comparing the BERC/ERDA solvent clay treated product with a commercial acid-clay-rerefined product, one finds an improvement in the BERC/ERDA oil with regard to residual additives and oxidation products.

All of the process equipment used in the pilot plant study functioned satisfactorily even though it was not designed specifically for the process steps involved. In all steps process rates were low because of limited capacity of the process heater. The addition of bubble trays in the vacuum tower would permit a sharper cut between lubricating oil and distillate fuel fractions. The DeLaval AC-VO-1 centrifuge performed satisfactorily, and it is believed that minimum solvent concentration in sludge can be effected with proper sludge recirculation controls. Explosion prevention equipment would need to be provided for centrifuges on a commercial unit.

SECTION IV

POTENTIAL MARKET

The original concept was to produce an oil which recycled the unreacted additives. However, we found that in order to do so, short clay treatment times are necessary, 15 - 60 minutes at 550°. At shorter time treatments, color and the amount of residual oxidation products were sacrificed.

Therefore it is felt that in the short run manufacturing would be geared for the production of an oil which would not recycle the additives. Over the long run, however, research should proceed in the direction of total recycling (base oil and additives).

Why one may ask recycle additives at all? The answer lies in two parts. First is economics. Additives as compared to base oil are much more expensive. And second, the treat dosage, in all probability will increase. This predicted increase in treat level is based on past historical trends, where over the past 15 years a greater percentage of the oil is additive and future trends where longer drain periods and better performances of all types of oils are predicted.

One of the largest untapped markets for a rerefined oil in this area is State and local government bid business. Currently the State specifications which also covers local government specifications do not restrict the use of a rerefined oil. The oil manufactured in the pilot plant with proper compounding and blending would meet the State specifications for automotive and hydraulic oils.

Retail automotive would be the easiest market to enter since rerefined oils are currently being sold in this area. The current oils being sold are packed in quart cans without any specification designation.

Railroads in this area are currently sending their engine oils out of this region to be rerefined. From preliminary work with a railroad engine oil it may be very possible to meet the current railroad specifications for rerefined engine lubes. If specifications can be met the railroad would save considerably both economic and service wise by not shipping out of this region.

The industrial market is another area where little or no rerefined oils are currently being used. A number of large users of oils, in the area, are very much interested in recyling their oils. To serve this market it would be best to segregate these from the automotive. From preliminary work this type of oil if segregated, would require lower treat levels of clay then the automotive. The majority of the oils being used are hydraulic and circulating types.

The mining industry is now a large market and potentially even larger as coal mining expands. Since this industry currently uses large amounts of diesel oils, segregation could be possible. Besides the off highway diesel type this industry uses flotation and hydraulic oils in large quantities.

Summary of Results

The pilot plant oil produced via BERC/ERDA solvent extraction and clay treatment could be used to fulfill the needs in the industrial, railroad, retail automotive, commercial automotive, mining, and state and local government bid markets. At the present time little if any of these markets are using a rerefined product. And it is strongly felt that the total demand far exceeds the supply for quality, properly compounded, recycled oils. Some of the products that could be blended from the pilot plant base stock are: (1) automotive which could range from no specification to one having SE/CD multigrade requirements. (2) railroad engine oils on a contract basis. (3) various industrial oils ranging from pure base stock to E. P. hydraulic oils.

SECTION V

POTENTIAL BY-PRODUCT USES

By products from the pilot study consisted of water, distillate, and sludge. Water from the vacuum distillation step must at least be treated to neutralize acidic bodies before disposal. Additional treatment may be required by local conditions. The distillate produced can probably be most economically utilized as plant fuel thus requiring only neutralization as produced. Of considerable interest is the solvent-free sludge produced from the solvent treating step since, unlike acid sludge from acid treating waste oils, the solvent-free sludge from the BERC/ERDA solvent process has the potential of commercial use.

For convenience the properties of the solvent-free sludge from the pilot scale study are presented in the following table:

Table 12

Properties of Solvent-Free Sludge

Gravity, API	13.8
Viscosity	
cs @ 210°F	76.3
cs @ 250°F	43.2
Flash point, C.O.C., °F	455
Ash, Wt. %	8.47

As produced the solvent-free sludge has a viscosity comparable to an MC-700 liquid asphalt and could probably be used without further treatment as a low cost dust pallative in road construction. The advantages and disadvantages of using the solvent-free sludge as a dust pallative are as follows:

Advantages

1. Low Cost

2. Demand for low cost dust pallative in rural areas could readily absorb limited production.

Disadvantages

1. Poor water-stripping characteristics.
2. Metal content of the sludge could in time become air-borne with dust from road surface.

With regard to the disadvantages, the addition of commercially available anti-strip additives would help minimize the water-stripping problem. However, use as a dust pallative may be neither the most desirable nor the most profitable use for the solvent-free sludge.

Preliminary laboratory tests indicate that the solvent-free sludge can be oxidized by air-blowing to produce a higher viscosity material containing substantially less oil. Such a material might be used for waterproofing concrete foundations or other hydraulic applications. Laboratory results from air-blowing the solvent-free sludge at 550°F for two hours gave a yield of 64 weight percent. The asphaltic material produced had improved coating characteristics, particularly with the addition of commercially available anti-strip agents. The oil contained in the solvent-free sludge acts as a flux during oxidation and it appears that much of the oil could be recovered from the oxidation process for use as fuel or possible retreatment with the BERC/ERDA solvent process.

Additional laboratory work is indicated in order to determine what types of products can be produced and the characteristics of these products with regard to performance and their effect on the environment. Accelerated weathering and leaching tests should provide information as to whether any portion of the metal content could become water soluble or water entrained as the result of using the material in hydraulic applications.

GENERAL SUMMARY AND CONCLUSIONS

From preliminary analysis, a quality rerefined base stock can be manufactured via BERC/ERDA solvent extraction and clay treatment. Both the solvent treating and clay treating steps resulted in a decrease in density, a reduction in viscosity and viscosity index, a reduction in flash point, a reduction in ash, and an improvement in color as would be expected from the removal of sludge, additives and higher molecular weight components from the oil.

The infrared for the final pilot plant oil shows that the oxidation products and additives have been effectively removed. In comparing the BERC/ERDA solvent clay treated product with a commercial acid-clay rerefined product, one finds an improvement in the BERC/ERDA oil with regard to residual additives and oxidation products.

The laboratory investigation found that for the production of an oil, with the lowest amount of oxidation resins, additives and the best color (ASTM 2.5) the following conditions can be followed: (1) Dehydrate the waste oil to remove 700°F end point distillates. (2) Mix the oil and BERC/ERDA solvent system at 55°F and continue gravity settling for seven days. (3) Decant and then solvent strip the oil such that the distillation bottoms end point is 500°F. (4) Clay treat the oil using 15 percent by weight Filtrol-20 for 6 hours at 550°F under a blanket of nitrogen. (5) Filter the oil clay slurry at 250°F.

An overall volumetric yield of about 75 percent on water-distillate-free oil can be expected at the levels of solvent and clay treating employed. Higher yields may be expected at higher solvent treating temperatures (greater then 55°F) and at lower (less then 15 percent) percentage clay treatment levels, provided that commercially acceptable base oils can be produced. Laboratory work indicates a possible reduction in the amount of clay used. Sufficient data, however, haven't yet been obtained with regard to solvent treating temperature and sludge separation methods to specify optimum conditions in this regard.

All of the process equipment used in the pilot study functioned satisfactorly even though it was not designed specifically for the process steps involved.

It is strongly felt, based on the data generated thus far, that the total market demand in this area far exceeds the supply for a rerefined product using the manufacturing scheme of BERC/ERDA solvent extraction and clay treatment. Some of the products that could be blended from this type of base stock are: (1) automotive oils which could range from no specification, to one having SE/CD multigrade requirements; (2) recyling railroad engine oils and (3) various industrial oils from pure base stock to E. P. hydraulic oils.

The solvent-free sludge could also be successfully marketed. The solvent-free sludge has a viscosity comparable to an MC-700 liquid asphalt and could probably be used without further treatment as a low cost dust pallative. Preliminary laboratory tests also indicate that the solvent-free sludge can be oxidized by air-blowing to produce a higher viscosity material. Such a material might be used for waterproofing concrete foundations or other hydraulic applications.