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Improving Low Temperature Properties of Synthetic Diesel Fuels Derived From Oil Shale

Alternative Fuels Utilization Program

November 1980

Prepared for:

U. S. Department of Energy

Assistant Secretary for Conservation
and Solar Energy

Office of Transportation Programs

Under Contract No. AC01-79CS50019

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Improving Low Temperature Properties of Synthetic Diesel Fuels Derived From Oil Shale

Alternative Fuels Utilization Program

November 1980

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FOREWORD

The research described in this report was performed at Exxon Research and Engineering Company, Products Research Division under Contract DE-AC-01-79CS50019. Dr. Ralph Fleming, U. S. Department of Energy, Washington, D. C., was contract technical monitor.

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Expert technical assistance was provided by Mr. H. S. Silakowski.

IMPROVING LOW TEMPERATURE PROPERTIES OF SYNTHETIC DIESEL FUELS DERIVED FROM OIL SHALE

ABSTRACT

The ability of additives to improve the cold flow properties of shale oil derived fuels boiling in the diesel fuel range was evaluated. Because a commercial shale oil industry did not exist to provide actual samples of finished fuels, a representative range of hydroprocessed shale oil fractions was prepared for use in the additive testing work.

Crude oil shale from Occidental Shale Company was fractionated to give three liquids in the diesel fuel boiling range. The initial boiling point in each case was 325°F (163°C). The final boiling points were 640°F (338°C), 670°F (354°C) and 700°F (371°F). Each fraction was hydrotreated to three different severities (800, 1200 and 1500 psi total pressure) over a Shell 324 nickel molybdate on alumina catalyst at 710-750°F to afford 9 different model fuels.

A variety of commercial and experimental additives were evaluated as cold flow improvers in the model fuels at treat levels of 0.04-0.4 wt.%. Both the standard pour point test (ASTM D97) and a more severe low temperature flow test (LTFT) were employed. Reductions in pour points of up to 70°F and improvements in LTFT temperatures up to 16°F were achieved.

It is concluded that flow improver additives can play an important role in improving the cold flow properties of future synthetic fuels of the diesel type derived from oil shale.

I. SUMMARY

I.1 Purpose and Scope

A potentially major problem in the use of synthetic fuels from oil shale is low temperature flow. This research was designed to investigate the low temperature flow characteristics of fuels of the No. 2 diesel type, and to evaluate the potential of additives for improving such properties. The program was limited to estimating the magnitude of the cold flow problem in several different hydroprocessed shale liquids boiling in the diesel fuel range and determining whether existing flow improver additives of the wax crystal modifier type are capable of combatting it.

I.2 Method of Approach

Since no commercial shale industry exists it was necessary to prepare a range of representative hydroprocessed shale distillates to serve as model fuels. This was done by distilling crude shale oil into three fractions in the No. 2 diesel fuel boiling range. These were 325-640°F; 325-670°F and 325-700°F. These were hydroprocessed to three different severities (800, 1200 and 1500 psig total pressure) at 1.0 LHSV (liquid hourly space velocity) and 700°F over a nickel molybdate on alumina catalyst. This afforded nine different model fuels for study.

A total of 37 additives, both commercial and experimental, were evaluated at various treat levels. Two methods were used, pour point depression and a more severe low temperature flow test (LTFT). The effects of treat level and processing history were investigated to determine their effects on additive response. The additives were evaluated on a double blind basis.*

*The additives are identified in Appendix IV.8 this report..

I.3 Results

The hydroprocessed shale distillates (additive free) had pour points ranging from 0°F for the narrowest boiling fraction to +20°F for the wide cut. These were not affected by hydroprocessing severity. Several additives were found to be quite effective in improving the low temperature flow of the test liquids. The most effective of those tested (on an as-received basis) were Tretolite 79-36029, Tretolite 78-36021, Exxon Paradyne 25 and Amoco PC9-154, although a number of others also showed considerable promise. At the 0.4% treat level, reductions in pour points of up to 70°F for the broad and mid boiling range fuels and up to 60°F for the narrow boiling fuel were achieved. Thus, the treated fuels were fluid to as low as -60°F to -70°F. At treat ratios of 0.04 wt.% reductions of 20°F or more were observed. In the LTFT improvements in lowest pass temperatures of 16°F for the broad and mid range fuels were found and up to 9°F for the narrow cut fuel. This is in the range normally encountered with petroleum-derived middle distillates but treat levels, in the case of shale liquids, were somewhat higher. The most effective additives in the LTFT were Amoco PC9-155, Tretolite 78-36030, Tretolite 78-36021, Exxon Paradyne 25, Rhom & Haas Acryloid 154 and Rhom & Haas Acryloid 150. Broad boiling range fuels were generally more responsive to the test additives. Hydroprocessing severity had little effect on additive effectiveness.

I.3.1 Conclusions

Based upon the results described above the following conclusions may be drawn.

- Because of their waxy nature, future hydroprocessed shale liquids will present low temperature flow problems; finding ways to surmount these difficulties could be important in developing synthetic fuels derived from shale.
- Shale liquids were responsive to flow improver additives of the wax crystal modifier type. Improvements in cold flow properties, comparable to those obtained in petroleum-derived fuels, can be achieved with current additives but higher treat levels may be necessary.
- Shale liquids with broad boiling ranges are more responsive to flow improvers than those with narrow ranges.
- Hydroprocessing severity, within the range studied (800-1500 psi total pressure) has only minor effects on additive response.
- Since the use of additives improves the low temperature flow properties of a fuel, it offers the possibility of widening the boiling range of useful fuels and thus, potentially increases the maximum theoretical yield of such fuels.

I.3.2 Recommendations for Additional Research

The results described above were obtained with additives, both commercial and experimental, which were designed for use with petroleum-derived fuels. Since wax crystal modifiers are quite specific in their action, additional research is needed to develop new additives especially tailored for hydroprocessed shale liquids. To this end the following specific research is recommended.

- Continue to expand studies of the effects of fuel properties, especially as modified by processing history, on response to various additives.
- Synthesize and evaluate optimized additives in actual shale liquids.
- Field evaluation of best additives and additive packages using actual diesel vehicles.

II. INTRODUCTION

II.1 Background and Objectives

It is likely that the coming years will see middle distillate fuels derived from shale oil supplement those now obtained from petroleum. Because of their origin the properties of these synthetic fuels can be expected to differ somewhat from more conventional materials. Shale liquids, for example, are quite waxy by nature because of a high normal paraffin content. In addition, it is anticipated that shale liquids will require considerable hydroprocessing to reduce their nitrogen and sulfur content. This will tend to increase the wax content by converting olefins to saturated hydrocarbons. It is known that middle distillate fuels rich in normal paraffins present low temperature flow problems. These problems may be even greater in shale liquids than in conventional fluids. Therefore, this program was undertaken to investigate the low temperature flow properties of hydroprocessed shale liquids with particular emphasis on the use of additives to improve them.

The major objectives of this research were:

- (1) To estimate the magnitude of cold flow problems in various hydroprocessed shale liquids.
- (2) To determine whether actual shale-derived liquids in the diesel fuel boiling range would respond to low temperature flow improvers.
- (3) To measure the response of different shale liquids to various additives in order to draw correlations between fuel properties and their sensitivity to flow improver additives.

II.2 Cold Flow Problems in Petroleum Fluids

The problem of cold flow in petroleum fuels has been studied extensively for a number of years.¹⁻⁵ It is generally agreed that poor flow at low temperatures is caused by wax crystals which form at temperatures below their saturation point. Such crystals, which are due mainly to normal paraffins, tend to grow slowly in an interlocking network of sheets or plates.¹⁻³ These plates can plug fuel lines and filters and render engines, pumps and even pipelines inoperable, sometimes even at fairly high temperatures.¹⁻³ The tendency for a given fuel to form such crystals depends upon the amounts and types of the normal paraffins it contains. As little as 1% n-paraffins can cause a noticeable increase in the cloud and pour point of a fuel.¹⁻³ Knepper and Hutton¹ showed that the pour point of petroleum fuels increased significantly as the concentration and/or average molecular weight of the normal paraffins increased. These results, and others, have been interpreted as support for two different modes of wax formation, independent crystallization and "solid solution" formation. The former predominates in cases where the molecular weight distribution of the n-paraffins is broad while the latter assumes greater importance when the distribution is narrow.²

II.2.1 Improving Cold Flow Properties of Hydrocarbon Fuels

Two methods have been used to improve the low temperature flow properties of petroleum crude oils and distillate fuels. These are large volume dilution with a lighter fuel, typically kerosene, and the use of additives.^{1,2,4} In the case of transportation diesel fuels the former method has been used almost exclusively until rather recently. Dilution with kerosene, however, increases fuel costs and has an adverse effect on fuel economy. In addition, recent trends toward using a broad

boiling range fuel as possible renders the dilution method relatively ineffective. As mentioned above, such methods may be even less useful in the case of diesel fuels derived from shale.

Cold flow improvers, also called pour point depressants and, more recently, wax crystal modifiers, have been in common use for some time in crude oils, lubricating oils and burner fuels.^{1,4,5} Lately there has been increased interest in these additives for diesel fuels as well. Unfortunately, such additives can be quite selective in their action; those that are effective in crude oils often work poorly or not at all in middle distillate fuels.^{1,5,6} This is apparently due to the mechanism of wax crystal modifiers as discussed below.

II.2.2 Mode of Action of Cold Flow Improver Additives

Considerable research has been devoted to an understanding of the mechanism by which wax crystal modifiers work in order to design better ones for specific purposes.¹⁻⁶ The following is only a brief summary.

It is important, first, to understand what cold flow improvers or wax crystal modifiers do not do. In general, such additives do not:

- Reduce the cloud point
- Reduce the total amount of wax that crystallizes from the fuel
- Alter the physical properties of the fuel other than pour point and cold flow rate

On the other hand, some additives are extremely effective at improving the cold flow of hydrocarbon fuels; pour point depressions of

as much as 50°F with treat levels as low as 0.05 wt.% can often be achieved.^{1,5,6} Since wax crystal modifiers do not prevent the formation of wax it appears that they instead inhibit the growth of crystals, probably by co-crystallization.^{1,4} This results in the formation of many tiny crystals which will not clog fuel filters or fuel lines. This process is represented schematically in Figure 1.^{6,7} It appears that the selectivity of the various additives depends upon their ability to co-crystallize with the particular paraffins in the fuel. Thus, research is required to develop the best structure for each type of fuel.

Some additional generalizations, taken from research on petroleum-based fuels, which may aid in development additives for shale liquids include the following:^{1,5-7.}

- Fuels with high cetane index tend to be more responsive to flow improver additives.
- Fuels with wide boiling ranges are more responsive than those of narrow ranges.
- Fuels with relatively high final boiling points are more responsive to flow improver additives.

II.3 Task Statement and Description

The major objectives of this program were to study the low temperature flow properties of several hydroprocessed shale distillates boiling in the diesel fuel range and to evaluate the potential of additives for improving these properties. The scope of the research did not encompass either a process variable study of the hydroprocessing of shale liquids or the development of an additive especially for shale liquids. Rather the program was designed to determine whether the concept of using flow improver additives on a

FIGURE 1. FLOW IMPROVERS - HOW DO THEY WORK?

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variety of shale-derived distillates was valid and to serve as a starting point for future development work. In order to meet these objectives the following tasks were performed.

- (1) Procurement, Distillation and Hydrotreating of Shale Oil
- (2) Procurement, Repackaging and Coding of Additives
- (3) Evaluation of Additive Response
- (4) Characterization of Samples
- (5) Preparation of Reports

Detailed descriptions of the tasks follow.

II.3.1 Task (1) Procurement, Distillation and Hydroprocessing of Shale Oil

Because a commercial shale oil industry does not exist to provide actual samples of finished fuels, it was decided to prepare a representative range of hydroprocessed shale oil fractions to use for the additive testing. Nine drums of crude shale liquid from the Occidental Shale Oil Co. (in situ process) were supplied by DOE. These were blended into a single sample and vacuum distilled into three fractions in the diesel fuel boiling range (325-750°F on an atmospheric pressure basis). Each of these fractions were hydrotreated to three different severities to yield nine different samples of simulated synthetic diesel fuel. No attempt was made to do process variable studies. The objective of this task was simply to provide nine samples with different properties for evaluation of additive response.

II.3.2 Task (2) Procuring, Repackaging and Coding of Additives

A computer based library technical and patent literature search was carried out to identify known producers of cold flow additives. All (27) producers of cold flow additives identified in this search were contacted by mail and asked to participate in this program. The samples that were supplied by these manufacturers were forwarded, unopened, to U. S. Testing Company of Hoboken, New Jersey for coding. Both commercial and experimental additives were included.

Coding was included in this task to avoid any possible conflict of interest which might arise from the fact that Exxon experimental additives as well as those from other commercial suppliers were to be used in this program. Thus, all additives were tested on a double-blind basis. Arrangements were made with an outside laboratory, U. S. Testing Company, Inc. of Hoboken, New Jersey, to repackage, code and provide Exxon Research and Engineering Company with coded samples for testing. This repackaging was done according to the following protocol:

"ER&E will purchase and have delivered to U. S. Testing Company up to 50 additives. U. S. Testing will repackage and code these additives and send them back to ER&E in a coded form. U. S. Testing will agree not to analyze any additive they receive. U. S. Testing agrees not to reveal to ER&E the identity of the coded additives until after the draft of ER&E's final report has been accepted by the U. S. Department of Energy (DOE). At that time, U. S. Testing will send a letter type report to ER&E for inclusion in the final report to DOE, identifying which additive corresponds to the code designation".

In addition, U. S. Testing retained, on a confidential basis, sufficient of the original sample on each additive to permit retesting if needed.

The identification of additives is shown in Appendix IV.

II.3.3 Task (3) Evaluation of Additive Responses

Two methods were used; the common pour point test (ASTM D97) and a more severe test, the low temperature flow test (LTFT) developed by Exxon. The latter has been made available to industry sources. It has been shown to give results which can readily correlate with field tests using actual diesel engines. The test is described in Appendix III of this report. Pour points were measured both because, for some purposes, this is the evaluation method of choice and since it afforded a rapid, inexpensive way to reduce the number of additives for low temperature flow testing. All additives were evaluated as pour point depressions. About 2/3 were employed in the LTFT.

II.3.4 Task (4) Characterization of Samples

The shale liquids produced in Task (1) were characterized by means of the following tests:

- ASTM distillation
- Gravity
- Total wt. % S
- Total wt. % N
- ASTM Color
- Cloud Point
- Pour Point
- Viscosity at 100°F
- Ash, wt. %
- Compound type distribution (paraffins, aromatics, polars)
- Distribution by carbon number of straight chain paraffins (by gas chromatography) up to approximately C₃₀ range.

II.3.5 Task (5) Preparation of Reports

In addition to this Final Report, 11 monthly letter-type reports were prepared and submitted.

III. RESULTS AND DISCUSSION

III.1 Task (1) Procurement, Distillation and Hydrotreatment of Shale Oil

Nine 55 gallon drums of oil shale were obtained from Occidental Oil Shale Co. They were immediately blended into a single sample at a temperature of 100°F. The composite sample was dark in color but quite uniform and free of water or sludge. It was waxy in appearance and set up to a semi-solid at temperatures below 40°F. A 15 gallon portion was removed for characterization (Task 4). The major portion of the remainder was shipped to the Imperial Oil Company Ltd. at Sarnia, Ontario for distillation. Of several stills available the one at Sarnia afforded the most efficient operation and best delivery time. Three fractions were taken in the diesel fuel boiling range (325-750°F). These all had the same initial boiling point (325°F) and three different final boiling points (A, 640°F; B, 670°F; C, 700°F; corrected to atmospheric pressure). These were chosen to represent a narrow, medium and wide-cut No. 2 diesel fuel. A summary of the distillations is shown in Table 1. Details of the distillation are given in Appendix I.

Each fraction was hydrotreated to three different severities using the Shell Oil Company #324 nickel molybdate on alumina catalyst. This was recommended by DOE personnel as representing an especially active, commercial type catalyst. A summary of average processing conditions is shown in Table 2. Details are given in Appendix I. The distillation and hydrotreating afforded nine samples according to the sample preparation matrix shown in Figure 2. These samples were prepared to provide a variety of different model fuels within the broad diesel fuel range, in order to evaluate additive response under different conditions.

TABLE 1

DISTILLATION OF CRUDE SHALE OIL¹

<u>Fuel Designation</u>	<u>Sample No.</u>	<u>Boiling Range °C (°F) (2)</u>	<u>wt. % Yield (3)</u>	<u>Overhead °API</u>	<u>Density</u>	<u>wt. % Yield (3)</u>	<u>Pot Residue</u>		<u>% Loss</u>
							<u>°API</u>	<u>Density</u>	
A	A-90-79	IBP-338 (640)	31.4	31.5	.8676	68.2	20.4	.9310	0.4
B	A-92-79	IBP-354 (670)	38.0	30.5	.8730	61.6	19.8	.9347	0.4
C	A-93-79	IBP-371 (700)	45.4	29.7	.8773	54.2	19.2	.9384	0.4

(1) Distillation carried out by Imperial Oil Ltd.; crude shale oil obtained from Occidental Shale Oil Co.

(2) IBP = 325°C (163°F) in each case.

(3) Based on crude charged to still.

TABLE 2.
AVERAGE CONDITIONS FOR HYDROPROCESSING

Fuel (1)	LHSV	CC/HR	Hydrogen Flow Rate (2) SCFH	Total Pressure MPa (PSI)	Catalyst Bed Temperature			Product Identification
					Top °C (°F)	Mid °C (°F)	Bottom °C (°F)	
A	1.0	300	9.98	10.10 (1470)	400 (752)	375 (707)	365 (695)	A-1
A	1.0	300	9.97	8.30 (1204)	400 (752)	375 (707)	370 (698)	A-2
A	1.0	300	9.98	5.65 (820)	405 (761)	376 (709)	365 (695)	A-3
B	1.0	300	9.99	10.35 (1501)	395 (743)	377 (710)	365 (695)	B-1
B	1.0	300	10.00	8.30 (1204)	392 (738)	374 (706)	360 (680)	B-2
B	1.0	300	9.99	5.50 (799)	395 (743)	380 (716)	360 (680)	B-3
C	1.0	300	9.94	10.34 (1500)	384 (723)	375 (707)	384 (723)	C-1
C	1.0	300	9.94	8.27 (1200)	358 (676)	375 (707)	384 (723)	C-2
C	1.0	300	9.94	5.52 (801)	358 (667)	375 (707)	384 (723)	C-3

(1) Fuel designations: A = IBP - 338°C (640°F);
B = IEP - 354°C (670°F);
C = IEP - 371°C (700°F).

(2) LHSV - liquid hourly space velocity; SCFH - standard cubic feet per hour.

FIGURE 2
SAMPLE PREPARATION MATRIX

Final BP Distillation (1) (feed identification)	Hydroprocessing Conditions (2)		
	Total Pressure		
	1500 psig (severe) or 1	1200 psig (medium) or 2	800 psig (mild) or 3
640°F (A)	X	X	X
670°F (B)	X	X	X
700°F (C)	X	X	X

(1) Initial BP = 325°F in all cases.

(2) Temp. = 710-750°F; 1.0 LHSV in all cases (See Table 2).

III.2 Task (4) Characterization of Samples*

The crude, distilled and hydroprocessed shale was characterized by normal methods used for middle distillate fuels.

III.2.1 Characterization of Crude Shale Oil

The inspections for the crude shale oil, as received but blended into a single sample are shown in Table 3. A gas chromatographic trace of the crude shale oil, showing the normal paraffin distribution is given in Figure 3. Figure 4 illustrates a similar analysis for two petroleum based crudes, a typical waxy (paraffinic) crude from Libya and an aromatic crude from Venezuela. The Libyan crude contains more than 60% saturates and less than 30% aromatic and polar compounds while the Venezuelan crude has these figures approximately reversed.⁸ This distribution is evidenced by the large paraffin "spikes" and small aromatic "envelope" shown by the Libyan crude (Figure 4A) while the paraffin peaks rise only slightly above the envelope for the Venezuelan oil (Figure 4B). The crude shale oil exhibits somewhat different properties. Although the liquid has an aromatic and polar content of 55% (Table 3) it still exhibits a well resolved normal paraffin trace (Figure 3). The distribution of paraffins is also quite interesting. A bimodal distribution, typical of shale oil,⁹ with peaks at C_{17} and again at C_{29} is observed. Also typical is the large peak due to the C_{17} paraffin and the predominance of odd-carbon hydrocarbons in the C_{21} - C_{30} range.⁹ This is not shown by most petroleum-derived crudes.^{8,10}

*This task, while number (4) chronologically, is best described at this point.

TABLE 3
INSPECTIONS ON CRUDE SHALE OIL

Analysis	Result
Physical Properties	
Pour Point	+40°F
API Gravity (60°F)	24.0
Specific Gravity	0.9100 g/cc
Viscosity at 100°F	29.8 c _{ST}
Ash	.014%
Elemental Analysis*	
C	86.87%
H	12.01%
N	1.19%
S	0.69%
Fe	45 ppm
V	10 ppm
As	28 ppm
Compound Type Analysis	
% Saturates	43.8
% Aromatics and Polars	55.0
ASTM Distillation (760 mm)	
IBP	159°C 318°F
10 pct recovered	291°C 550°F
20	327°C 621°F
30	361°C 683°F
40	393°C 740°F
50	424°C 797°F
60	457°C 854°F
70	491°C 916°F
80	531°C 988°F
End Point	565°C 1050°F

*Based on separate analyses and rounded; may not total exactly 100%.

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610114 SHALE LIQUID CRUDE
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FIGURE 3. CRUDE OCCIDENTAL SHALE OIL

FIGURE 4. G.C. FINGERPRINTS OF TWO TYPICAL PETROLEUM-DERIVED CRUDE OILS

← CHART

A. Waxy Libyan Crude Oil

B. Aromatic Venezuelan Crude Oil

This well resolved chromatogram is a good indication of the large quantities of n-paraffins (relative to other saturates such as naphthenes) present in the shale. These compounds are responsible for its very waxy nature. The Venezuela crude, shown in Figure 4, has a gravity of 23.8, close to that of the shale oil but a pour point of -45°F . The Libyan is a 41 gravity crude with a pour point of -5°F despite its relatively waxy nature.⁸ The shale oil has a pour point of $+40^{\circ}\text{F}$ (Table 3). This is undoubtedly due to its exceptionally high n-paraffin content.

III.2.2 Characterization of Unprocessed Shale Distillates

Inspections on the three distilled shale fractions are given in Table 4. Each sample had the same initial boiling point (325°F , 163°C). The final boiling points, 640°F (388°C), 670°F (354°C) and 700°F (371°C) were chosen to represent narrow, medium and broad range diesel fuels. The major influence of final boiling point on physical properties is on specific gravity and pour points. Viscosity also increases but only moderately. Surprisingly, the sulfur and nitrogen contents are virtually unchanged in going from the crude oil (Table 3) to any of the distilled samples. This suggests that nitrogen and sulfur compounds are fairly evenly distributed over the entire boiling range. Similar observations have been reported by McKay *et al.*¹¹ and Frost *et al.*¹² for many types of shale liquids. The distribution of saturate, aromatic and polar compounds is also nearly constant in each fraction. The very high percentage of polars in all fractions, as compared to typical petroleum derived oils is noteworthy, however.

TABLE 4. INSPECTIONS ON UNTREATED SHALE DISTILLATES

Property	Distillation Cuts		
	A. 325-640°F	B. 325-670°F	C. 325-700°F
Yield ⁽¹⁾	31.4%	38.0%	45.4%
API Gravity (60/60°F)	31.5	30.5	29.7
Specific Gravity	.9100	.8676	.8773
Color ⁽²⁾	Black	Black	Black
Pour Point (°F)	+10	+20	+25
Viscosity (C _{ST} @ 100°F)	4.51	5.24	5.47
Ash	.01%	.01%	.01%
Elemental			
%C	84.84	84.67	82.53
%H	11.61	11.75	12.36
%N	1.18	1.28	1.22
%S	0.62	0.62	0.62
Fe (ppm)	16	23	250
V (ppm)	<1	3	2
Compound Type			
% Saturates	45.4	43.1	43.6
% Aromatics	30.8	31.5	31.1
% Polars	21.9	24.6	24.1
ASTM Distillation (760 mm)	°F		
IBP	326.1	353.2	356.5
10 pct recovered	431.9	442.3	446.8
20	466.5	478.7	484.3
30	492.3	506.2	513.8
40	515.5	530.5	545.1
50	541.4	559.5	573.4
60	565.0	578.5	598.6
70	583.4	602.5	624.0
80	609.0	624.5	651.2
90	645.4	648.9	683.3
FBP	787.2	707.5	736.9

(1) Based on crude charged to still.

(2) To dark for ASTM Color test.

Gas chromatograph traces of the three unprocessed distillates are shown in Figure 5. The increasing contribution of heavier wax fractions is apparent progressing from fractions A-C.

III.2.3 Characterization of Hydrotreated Distillates

The three distilled fractions, described in Section II.2.2, were each hydroprocessed to three different severities to yield nine different model fuels. Hydroprocessing conditions are discussed in Section III.1. These nine fuels were characterized according to typical diesel fuel tests. The inspections are given in Table 5. The wax contents of the various samples are shown in Table 6. Also shown are average inspections for typical petroleum-derived diesels to serve as a basis for comparison. A gas chromatography (GC) trace for fuel B-2 is given in Figure 6 while a similar trace for a commercial No. 2 diesel fuel is shown in Figure 7.

Superficially, at least, the hydrotreated shale distillates resemble a commercial No. 2 diesel fuel. The major differences lie in the higher wax contents. This is illustrated by the data in Table 6 and by comparing Figures 6 and 7. The sharp spikes in the GC traces are due mostly to normal paraffins. It is evident that they rise higher above the "envelope" (aromatics, naphthenes, and some branched paraffins) in Figure 6 and 7. As expected from these high wax contents the cloud and pour points of the samples were also rather high.

FIGURE 5. GAS CHROMATOGRAPHIC TRACES OF DISTILLED SHALE OIL FRACTIONS

TABLE 5. INSPECTIONS ON HYDROTREATED SHALE DISTILLATES

Boiling Range Total Pressure (PSI)	Hydrotreated Samples									Typical Petroleum No. 2 Diesel Fuel (1)
	A. 325-640°F A-1 1500	A-2 1200	A-3 800	B. 325-670°F E-1 1500	B-2 1200	B-3 800	C. 325-700°F C-1 1500	C-2 1200	C-3 800	
API Gravity	43.0	43.0	42.1	41.9	41.9	40.6	40.8	37.1	36.8	36.2
Color (ASTM)	1.5	1.0	1.0	1.0	0.5	0.5	1.5	5.5	3.5	0-1.5
Cloud Point (°F)	+6	+6	+4	+18	+14	+18	+26	+28	+26	-20-+40
Pour Point (°F)	0	0	0	+10	+10	+10	+20	+20	+20	-60-+20
Cetane Index ⁽²⁾	60.0	59.5	57.0	60.5	60.2	57.5	60.0	55.5	54.8	49.1
Viscosity (C _{ST} , 100°F)	2.24	1.95	1.90	2.39	2.39	2.35	2.80	3.12	3.06	2.60
Elemental Analysis										
%C	81.94	85.47	85.81	85.55	85.58	84.66	86.47	86.65	86.50	---
%H	12.92	14.00	13.73	13.85	13.48	13.99	13.96	13.42	13.1	---
S (ppm)	49	---	44	67	68	46	56	122	103	100-1000
N (ppm)	480	---	240	340	300	360	420	3,900	4,100	10-300
Compound Type										
% Sats	84.9	84.0	76.0	83.1	82.3	80.4	84.4	71.5	70.8	---
% Arom	15.1	13.8	21.8	14.7	16.6	19.2	15.2	27.7	29.0	---
% Polars	0.5	0.3	0.5	0.7	0.7	0.3	0.3	0.3	0.3	---
% Ash	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1

TABLE 5. INSPECTIONS ON HYDROTREATED SHALE DISTILLATES (Continued)

Hydrotreated Samples										Typical Petroleum No. 2 Diesel Fuel ⁽¹⁾
Boiling Range	A. 325-640 ^o F			B. 325-670 ^o F			C. 325-700 ^o F			
Total Pressure (PSI)	A-1	A-2	A-3	B-1	B-2	B-3	C-1	C-2	C-3	
	1500	1200	800	1500	1200	800	1500	1200	800	
ASTM Distillation										
IBP (°F)	233	233	234	237	236	237	238	239	241	
10%	320	310	317	352	350	356	362	383	385	
50%	482	480	486	502	498	506	515	530	529	
90%	605	604	607	629	623	629	651	654	652	
FBP	702	715	718	752	724	737	770	756	753	

(1) Averaged values for No. 2 Diesel (type T T-Eastern Region) from U. S. Bureau of Mines survey; see E. M. Shelton, BETC/PPS-78/5 (1978).

(2) Estimated using ASTM D976; this method is in common use for petroleum diesels but may not be strictly applicable to fuels from alternate sources.

TABLE 6. WAX CONTENTS OF HYDROTREATED SHALE DISTILLATES

<u>Sample</u>	<u>Final Boiling Point (°F) (1)</u>	<u>Total Hydrotreating pressure (psi)</u>	<u>Total</u>	<u>% Paraffins Wax Fraction (2)</u>
A	640	NT (3)	32.3	5.62
A-1	640	1500	48.5	6.72
A-2	640	1200	47.5	4.92
A-3	640	800	51.4	6.30
B	670	NT (3)	36.9	6.10
B-1	670	1500	42.2	6.35
B-2	670	1200	43.0	6.09
B-3	670	800	44.5	6.40
C	700	NT (3)	30.5	8.17
C-1	700	1500	41.9	8.00
C-2	700	1200	39.8	8.35
C-3	700	800	42.3	8.18
Commercial Diesel (4)		---	37.3	3.00

(1) Initial boiling point = 325°F for all shale liquids.

(2) Arbitrarily defined as normal paraffins > n-C17.

(3) NT = not hydrotreated.

(4) Sample of No. 2 diesel fuel from Exxon-Bayway, New Jersey.

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FF = 0

DIESEL FUEL REFERENCE
Inst: 11 Ch: 0 Tray # 24

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Colors, gravities and viscosities of the hydroprocessed shale distillates were generally similar to commercial diesels. Nitrogen, and especially sulfur contents, were quite low due to the efficient hydrotreating. With the exception of fuel C, even the least severe treatment reduced both the sulfur and nitrogen levels by 98% as compared to the distilled but not hydrotreated samples (compare data in Table 4).

The estimated cetane indices for all processed samples were very high, well above those normal for No. 2 diesels. These values were estimated from API gravity and boiling range data by ASTM #926 and it is not yet known whether this technique is applicable to fuels derived from oil shale. However, high cetane numbers are to be expected from fuels with such large normal paraffin contents. The cetane indices tended to increase slightly with increasing hydroprocessing severity.

III.2.3.1 Effects of Hydrotreating Severity on Fuel Properties

The severity of hydrotreating conditions had less influence over the properties shown in Table 5 than the boiling range. With the exception of the very heaviest samples, C-2 and C-3, the gravities, viscosities, colors, elemental analyses and even pour points are quite similar whether the samples were exposed to 800 or 1500 psi total hydrogen pressure. As expected the amount of saturates relative to aromatics increases somewhat but, in most instances, not dramatically. On the other hand, in comparison with untreated samples (Table 4), the aromatic contents of the three distillates were reduced by half by even the mildest hydrotreating. Even more striking is the effect of the polar fractions (mostly N, S, O containing compounds). These were reduced from >20% to <1% of the total in all treated samples.

The nitrogen and sulfur levels of the untreated distillates A and B were reduced by >98% in the case of nitrogen (1.3% to ~300 ppm) and 99% for sulfur by mild hydrotreating. Increased hydrogen pressure beyond 800 psi had virtually no additional effect for these samples. In the case of the heaviest distillate, C, however, only the severe treat produced low N and S values. Apparently, heavier N and S compounds are less responsive to hydrotreating.

The wax contents of the various hydrotreated distillates (Table 6) were not affected significantly by hydrotreating conditions. For any given boiling range, the waxy contents are similar regardless of hydrogen pressure. However, the amount of waxy hydrocarbons is, of course, higher in the higher boiling range distillates.

III.3 Task (2) Procurement, Repackaging and Coding of Additive Samples

Since additives from a variety of suppliers, including Exxon, were included in this program, precautions were taken to avoid any possible conflict of interest. This was done by setting up a "double blind" evaluation program. An outside laboratory, United States Testing Co. Inc., was retained to repackage and return all test additives to Exxon Research and Engineering Co. in coded form. The code was not to be revealed until testing was concluded. The protocol for this is given in Section II.3.2.

A search of both open literature and patent literature was conducted to identify potential additive suppliers. A total of 27 were located. All were contacted by mail and invited to participate in the testing program by providing potentially useful additives. Nine positive responses were received which provided 37 samples for evaluation. The other 18 potential suppliers did not respond. All additive samples were delivered, unopened, to U. S. Testing. These were immediately repackaged, coded and returned to Exxon Research. Sufficient samples were retained by U. S. Testing to permit re-testing if needed. The suppliers of the 37 test additives are listed in Table 7. It should be emphasized that many of these materials had not been previously tested as flow improvers. However, both because of the blind testing and since little is known about the response of shale liquids to flow improvers no attempt was made to be selective. All 37 additives were evaluated as pour point depressants in the preliminary tests. All additives are identified in Appendix IV.

III.4 Task (3) Evaluation of Additive Response

Two test methods were used, the common pour point test (ASTM D97) and a newly developed low temperature flow test (LTFT). The former is a

TABLE 7. SUPPLIERS OF TEST ADDITIVES

<u>Supplier</u>	<u>Number of Samples</u>
Amoco Chemicals Corp.	2
Chevron Chemical Co.	2
Exxon Chemical Company (Paramins Technology Division)	3
Ethyl Corp.	1
GAF Inc.	10
Lubrizol Corp.	3
Petrolite Corp. (Tretolite Div.)	7
Rohm and Haas Co.	5
Texaco Inc.	4

standard test used for determining the lowest temperature that a petroleum product has some fluidity. For some purposes, such as storage and pumping this is the most critical property. Thus, low pour points are always desirable.¹⁻⁵ In addition, since the ASTM D97 test is rapid and inexpensive, it afforded a good method for eliminating inactive additives. It must be emphasized that there is no direct correlation between the pour point of a fuel and its behavior in the LTFT test. However, if an additive has no or a very small effect on pour points it is safe to say it will impart little or no improvement in the LTFT test.

The low temperature flow test (LTFT) was developed by Exxon Research and has recently been made available to the industry. It has a major advantage in that there is a good correlation between laboratory test results and field tests with actual diesel engines.⁶ Details of the test procedure are given in Appendix III. Briefly, it involves cooling the test fuel to the test temperature at a rate of 2°F/min and then determining its filterability through a screen of given mesh size at a vacuum of 6 in. of mercury. For the purposes of this program a fuel was considered to have "passed" if 80% or more passed through a 40 μ screen in 60 seconds or less. The critical parameter is the lowest temperature at which this occurs (lowest pass temperature).

III.4.1 Evaluation of Test Additives as Pour Point Depressants

The cloud points and pour points for each of the hydrotreated distillates are given in Table 8. It is apparent that these increase significantly with increasing final boiling point but that changes in hydroprocessing severity have relatively little effect (see Section II.2.3). For the

TABLE 8. CLOUD AND POUR POINTS FOR HYDROTREATED SHALE LIQUIDS

<u>Designations</u>	<u>Boiling Range °F</u>	<u>Hydrotreating total pressure (psi)</u>	<u>Cloud Point⁽¹⁾ °F</u>	<u>Pour Point⁽²⁾ °F</u>
A-1	325-640	1500	+6	0
A-2	" "	1200	+6	0
A-3	" "	800	+4	0
B-1	325-670	1500	+18	+10
B-2	" "	1200	+14	+10
B-3	" "	800	+18	+10
C-1	325-700	1500	+26	+20
C-2	" "	1200	+28	+20
C-3	" "	800	+26	+20

(1) ASTM D2500.

(2) ASTM D97.

initial testing samples A-2, B-2 and C-2 were chosen. All additives were tested at the 0.4 wt.% level in these fuels and at the 0.04 wt.% level in fuel B-2. In addition, selected additives were tested in other samples and at intermediate treat levels. The pour points were determined using ASTM method D97.

Complete screening results are given in Appendix II. Results for the additives showing most promise are summarized in Tables 9-11. The response of most distillates tested to a number of these additives was excellent.

Table 9 shows the response of A-2 to the 11 best additives tested at the 0.4 wt.% level. Similar results for hydrotreated distillates B-2 and C-2 are shown in Tables 10 and 11 respectively. In addition, results at a low treat level (0.04 wt.%) in B-2 are given in Table 10. A somewhat larger group is shown in Table 10 since B-2 was the primary model fuel and care was taken not to miss any promising additives. A total of 24 were effective in this initial test. All of these were used in the LTFT work described in Section III.4.2.

Pour point depressions of up to 70°F were attained in these tests at the 0.4 wt.% treat level. Even at a level of 0.04 wt.% some additives depressed the pour point of B-2 by nearly 30°F. As expected many additives showed greater response in the broad range distillate, C-2, than in A-2. It appears that many of the additives have considerable potential as pour point depressants of shale liquids of these types.

TABLE 9. EFFECTS OF 0.4 WT. % OF VARIOUS ADDITIVES
ON THE POUR POINT OF HYDROTREATED DISTILLATE A-2⁽¹⁾

<u>Additive⁽²⁾</u>	<u>Pour Point (^oF)⁽³⁾</u>	<u>Pour Point Depression (^oF)</u>
None	0	---
3-10-30-1	-45	45
-7	-45	45
-9	-45	45
-16	-60	60
-17	-60	60
-23	-65	65
-30	-50	50
-31	-50	50
-32	-50	50
-33	-50	50
-36 ⁽⁴⁾	-40	40

(1) See Tables 5, 6 and 8 for characteristics of hydrotreated distillate A-2.

(2) Code supplied by U. S. Testing Co; additives identified in Appendix IV.

(3) ASTM D97.

(4) Additive 36 is included here because of its excellent response to LTFT tests as well as in pour point depressant tests with other fuels.

TABLE 10. EFFECTS OF MOST PROMISING ADDITIVES
ON POUR POINT OF HYDROTREATED DISTILLATE B-2⁽¹⁾

Additive ⁽²⁾	Treat Level (wt. %)			
	0.4		0.04	
	Pour Point (°F) ⁽³⁾	Pour Point Depression (°F)	Pour Point (°F) ⁽³⁾	Pour Point Depression (°F)
None	+10	---	+10	---
3-10-30-1	-40	50	-5	15
-2	-35	45	-5	15
-3	-20	30	-5	15
-4	-30	40	-5	15
-5	-35	45	-5	15
-8	-25	35	0	10
-9	-50	60	0	10
-10	-20	30	+5	5
-11	-20	30	+5	5
-12	-30	40	-10	20
-13	-30	40	-10	20
-14	-20	30	0	10
-16	-45	55	-10	20
-17	-55	65	-15	25
-23	-60	70	-15	25
-24	-30	40	+5	5
-25	-40	54	-5	15
-26	-25	35	-10	20
-30	-45	55	-5	15
-31	-45	55	-10	20
-32	-50	60	-5	15
-33	-45	55	-10	20
-35	-25	35	0	10
-36	-55	65	-5	15

(1) See Tables 5, 6, and * for characteristics of hydrotreated distillate B-2.

(2) Code supplied by U. S. Testing Co; additives identified in Appendix IV.

(3) ASTM D97.

TABLE 11. EFFECTS OF SELECTED ADDITIVES ON POUR POINT
OF HYDROTREATED DISTILLATE C-2 (0.4 wt. % TREAT LEVEL)⁽¹⁾

Additive ⁽²⁾	Pour Point (^o F) ⁽³⁾	Pour Point Depression (^o F)
None	+20	---
3-10-30-9	-35	55
-14	-35	55
-15	-40	60
-16	-40	60
-23	-40	60
-25	-35	55
-30	-50	70
-31	-45	65
-32	-50	70
-33	-50	70
-35	-30	50
-36	-50	70

(1) See Tables 5, 6 and 8 for characteristics of hydrotreated distillate C-2.

(2) Code furnished by U. S. Testing Co; additives identified in Appendix IV.

(3) ASTM D97.

III.4.1.1 Effects of Additive Concentration on Pour Point Depression

The effects of additive concentration on pour point depression are illustrated by the curves shown in Figure 8 as well as data in Table 12. An excellent (#23), moderate (#1) and relatively ineffective additive (#10) are shown in Figure 8. In general, it appears that higher levels of the additives are required in the shale liquids than are normally used in petroleum-derived fuels.^{5,6} From the limited data available so far it appears that optimum treat levels may range from 0.1-0.2 wt.%.

III.4.1.2 Effects of Fuel Compositions on Additive Responses in Pour Point Tests

In general, broad boiling range petroleum based fuels are more responsive to wax crystal modifiers than those with narrow ranges (see Section II.2.2). This was also observed in the shale liquids used in the present program (Table 12, Figure 9). The broad range distillate C-2 (325-700°F) was generally more responsive than A-2 (325-640°F). The effect was more marked with some additives than others. Noteworthy are #15 and #36 (Table 12, Figure 9). Additive #15 shows a 60°F depression in C-2 compared with a 20°F depression in A-2 (0.4 wt.% treat level). For additive #36 the corresponding values are 70°F and 40°F, respectively. This is illustrated graphically in the case of #36 in Figure 9. This is important since it illustrates the potential of wax crystal modifiers in extending the useful boiling range of synthetic fuels. Thus, with as little as 0.04% of a good additive, model fuel C-2 has a lower pour point than the untreated narrow cut distillate A-2. The yield of C was 45% as compared to 31% for A (see Table 4).

FIGURE 8. EFFECTS OF ADDITIVE CONCENTRATIONS ON POUR POINT OF SHALE LIQUID B-2

TABLE 12. EFFECTS OF ADDITIVE CONCENTRATION
ON POUR POINTS OF VARIOUS HYDROPROCESSED SHALE DISTILLATES(1)

Hydroprocessed Distillate	Additive ⁽²⁾	Wt. %	Pour Point (°F)	Pour Point Depression (°F)	
A-2	3-10-30-15 -23	0.4	-20	20	
		0.40	-65	65	
		0.20	-55	55	
		0.10	-35	35	
		0.04	-20	20	
	-36	0.40	-40	40	
		0.20	-45	45	
		0.10	-30	30	
		0.04	-10	10	
	B-1	3-10-30-10	0.20	-10	20
3-10-30-23		0.20	-45	55	
B-2	3-10-30-1	0.40	-40	50	
		0.20	-15	25	
		0.10	-10	20	
		0.04	-5	15	
	-10	0.40	-20	30	
		0.20	-5	15	
		0.10	-5	15	
		0.04	+5	5	
	-23	0.40	-60	70	
		0.20	-50	60	
		0.10	-30	40	
		0.04	-15	25	
	C-2	3-10-30-15	0.40	-40	60
			0.20	-30	50
			0.20	+10	10
			0.04	+10	10
-23		0.40	-40	60	
		0.20	-50	70	
		0.10	-30	50	
		0.04	-10	30	

TABLE 12. EFFECTS OF ADDITIVE CONCENTRATION
ON POUR POINTS OF VARIOUS HYDROTREATED SHALE DISTILLATES⁽¹⁾(Continued)

<u>Liquid</u>	<u>Additive⁽²⁾</u>	<u>Wt. %</u>	<u>Pour Point (°F)</u>	<u>Pour Point Depression (°F)</u>
C-2	3-10-30-36	0.40	-50	70
		0.20	-45	65
		0.10	-30	50
		0.04	-5	25

(1) Characteristics of fuels in Tables 5, 6 and 8 ; Pour Points by ASTM D97.

(2) Code furnished by U. S. Testing Co; additives identified in Appendix IV.

FIGURE 9. EFFECTS OF BOILING RANGE OF DISTILLATE
ON ADDITIVE RESPONSE IN POUR POINT TEST

Hydroprocessing severity, on the other hand, appears to have little or no effect on the response of the model fuels to the additives. Thus, hydrotreated distillates B-1 and B-2 gave very nearly the same response to additives #10 and #23 (Table 12). The sample B-1 was hydrotreated at 1500 psi while B-2 was treated at 800 psi.

III.4.2 Response of Various Additives in the Low Temperature Flow Test

This test is much more severe than pour point evaluations. It also requires more effort and is more time consuming. Details of the test are given in Appendix III. The main virtue in this method lies in the good correlation between laboratory and field tests.^{4,6}

The results of preliminary LTFT tests on untreated test fuels are given in Table 13. The higher boiling range fuels had significantly higher pass temperatures, indicative of their increased wax content. However, the pass temperature was affected in only a minor way by the severity of hydroprocessing (Table 13).

B-2 was chosen as the primary test fuel. All additives capable of depressing the pour point of B-2 by 30°F or more at the 0.4 wt.% treat level were employed in these preliminary tests. A total of 24 additives met these requirements. These are shown in Table 10, Section III.4.1.

The results of the initial screening in B-2 are shown in Appendix Table III.1. In these severe tests an improvement of >5°F is considered good. Several additives were retested to confirm the original value and to determine their effectiveness at lower treat levels. The results for these best additives are shown in Table 14. An improvement of 16°F was obtained for additive #36, suggesting that this distillate mixture would be operable

TABLE 13. LTFT RESULTS WITH MODEL FUELS

<u>Hydroprocessed Distillate</u>	<u>Fuel⁽¹⁾ Boiling Range (°F)</u>	<u>Hydrotreat Pressure (psi)</u>	<u>LTFT Results Lowest Pass Temp. (°F)⁽²⁾</u>
A-2	325-640	1200	+5
B-1	325-670	1500	+14
B-2	325-670	1200	+14
B-3	325-670	800	+16
C-2	325-700	1200	+26

(1) For characteristics of hydroprocessed distillates see Tables 5, 6, and 8.

(2) Lowest temperature at which 80% or more of fuel pass 40 μ screen in 60 seconds or less under vacuum of 6 inches of mercury.

TABLE 14. EFFECTIVENESS OF SELECTIVE ADDITIVES IN IMPROVING LOW TEMPERATURE FLOW PROPERTIES OF HYDROPROCESSED DISTILLATE B-2⁽¹⁾

Additive ⁽²⁾	Treat Level (wt.%)	Lowest Pass Temp. (°F) ⁽³⁾	Improvement Over Base Fuel (°F)
None	---	+14	---
3-10-30-1	0.4	+5	9
	0.25	+5	9
	0.1	> +5	---
-12	0.4	+5	9
	0.25	+5	9
	0.1	+5	9
-13	0.4	+5	9
	0.25	> +5	---
-17	0.4	+5	9
	0.25	> +5	---
-23	0.4	+5	9
	0.25	+5	9
	0.1	> +5 ⁽⁴⁾	---
-35	0.4	+2	12
	0.25	> +5	---
-36	0.4	-2	16
	0.25	+5	9
	0.1	+5	9

(1) B-2 fuel: Boiling range 325-670°F; hydrotreating total pressure: 1200 psi; cloud point: +14°F; pour point: +10°F. Complete screening of additives is given in Appendix III.

(2) Coded by U. S. Testing Company; additives identified in Appendix IV.

(3) Lowest temperature at which 80% or more pass 40 μ filter in 60 seconds or less; details of test given in Appendix III.

(4) Near pass at 5°F.

at 0°F or slightly below. Additive #35, at a treat level of 0.4 wt.%, gave a 12°F improvement. At low treat levels (0.1 wt.%) additives #12 and #36 gave the largest response. For these additives 9°F improvements in lowest pass temperature were achieved at the 0.1% treat level.

Table 12 shows the results of LTFT testing in hydrotreated distillate A-2. As expected, the response in this material, since it has a lower boiling range, is less. Nevertheless, some additives showed a 9°F reduction in lowest pass temperature. This would permit the use of A-2 at temperatures down to -4°F.

The response of the broadest material with the broadest boiling range, C-2, is greater than either of the others (Table 16). An improvement of from +26°F to +10°F was observed for additive #23. At a treat level of 0.25 wt.% an improvement of 14°F (nearly 16°F) was achieved. Almost as good results were obtained with additive #36.

III.4.2.1 Effects of Fuel Composition on Response of Additives in LTFT Tests

The broad boiling range distillates were more responsive to additives in the LTFT tests (Tables 14-17). Thus, several additives were capable of lowering the pass temperature of fuel C-2 or C-1 by 14-16°F while most additives could only reduce the pass temperatures for A-2 or A-3 by 4-9°F. Fuels B-2 and B-3 showed intermediate responses. On the other hand, hydro-processing severity had little or no influence on the response of the model fuels (compare results with B-2 to B-3 and C-1 to C-2). These observations are similar to those made during pour point testing (Section III.4.1).

TABLE 15. EFFECTIVENESS OF SELECTED ADDITIVES IN
IMPROVING LOW TEMPERATURE FLOW OF HYDROPROCESSED DISTILLATE A-2(1)

Additive(2)	Treat Level (wt.%)	Lowest Pass Temp. (°F)(3)	Improvement Over Base Fuel (°F)
None	---	+5	---
3-10-30-1	0.4	-2	7
-12	0.4	-2	7
-16	0.4	-4	9
	0.25	0	5
	0.1	+2	3
-17	0.4	0	5
-23	0.4	-4	9
	0.25	0	5
	0.1	+2(4)	3
-36	0.4	-14(4)	9
	0.1	+2	3

(1) A-2 fuel: boiling range: 325-650°F; hydrotreating total pressure: 1200 psi; cloud point: +6°F; pour point: 0°F.

(2) Coded by U. S. Testing Company; additives identified in Appendix IV.

(3) Lowest temperature where 80% or more of the fuel mixture passes 40 μ screen in 60 seconds or less under a vacuum of 6 inches of mercury.

(4) Near pass at 0°F.

TABLE 16. EFFECTIVENESS OF SELECTED ADDITIVES IN IMPROVING LOW TEMPERATURE FLOW OF HYDROPROCESSED DISTILLATE C-2⁽¹⁾

Additive ⁽²⁾	Treat Level (wt.%)	Lowest Pass Temp. (°F) ⁽³⁾	Improvement Over Base Fuel
None	---	+26	---
3-10-30-1	0.4	> +12 ⁽⁴⁾	---
-12	0.4	> +12 ⁽⁴⁾	---
-15	0.4	> +12 ⁽⁴⁾	---
-16	0.4	+12 ⁽⁵⁾	14
	0.25	> +14 ^(4,6)	---
-17	0.4	> +12 ⁽⁴⁾	---
-23	0.4	+10	16
	0.25	+12 ⁽⁴⁾	14
-33	0.4	> +12 ⁽⁴⁾	---
-35	0.4	+12	14
-36	0.4	+12 ⁽⁷⁾	14
	0.25	+14 ⁽⁸⁾	12

(1) C-2 fuel: boiling range 325-700°F; hydrotreating total pressure: 1200 psi; cloud point: +28°F; pour point: +20°F.

(2) Coded by U. S. Testing Company; additives identified in Appendix IV.

(3) Lowest temperature at which 80% or more of fuel mixture passed 40 μ filter in 60 seconds or less under a vacuum of 6 inches of mercury.

(4) Highest temperature tested.

(5) Near pass at +10°F.

(6) Near pass at +12°F.

(7) Near pass at 10°F.

(8) Near pass at +12°F.

TABLE 17. EFFECTS OF SELECTED ADDITIVES ON COLD
FLOW PROPERTIES OF VARIOUS FUEL SAMPLES

Designation	Fuel ⁽¹⁾ Boiling Range (°F)	Hydrotreating Pressure (psi)	Additive ⁽²⁾	LTFT Results ⁽³⁾	
				Low Pass (°F)	Improvement Over Base Fuel
A-3	325-650	800	None	+4 ⁽⁴⁾	---
			3-10-30-16	-4	8
			-23	0	4
			-36	-4	8
B-3	325-670	800	None	+16	---
			3-10-30-12	+8	8
			-35	+4 ⁽⁵⁾	12
			-36	+4 ⁽⁵⁾	12
C-1	325-700	1500	None	+26 ⁽⁴⁾	---
			3-10-30-16	>+12 ⁽⁶⁾	---
			-23	>-12 ⁽⁶⁾	---
			-36	-10 ⁽⁷⁾	16

(1) For fuel characteristics see Tables 5, 6 and 8.

(2) Codes furnished by U. S. Testing Company; 0.4 wt.% treat level.

(3) Lowest temperature at which 30% or more pass 40 μ filter in 60 seconds or less; details of test in Appendix III.

(4) Estimated.

(5) Near pass at +3°F.

(6) Highest temperature tested: neither #15 nor #23 passed at 12°F.

(7) Near pass at +8°F.

IV. CONCLUSIONS AND RECOMMENDATIONS

IV.1 Conclusions

Based upon the results described above the following conclusions may be drawn.

- Because of their waxy nature, future hydroprocessed shale liquids will present low temperature flow problems; finding ways to surmount these difficulties will be important in developing synthetic fuels derived from shale.
- Shale liquids are responsive to flow improver additives of the wax crystal modifier type. Improvements in cold flow properties, comparable to those obtained in petroleum-derived fuels, can be achieved with current additives but higher treat levels may be necessary.
- Shale liquids with broad boiling ranges are more responsive to flow improvers than those with narrow ranges.
- Hydroprocessing severity, within the range studied (800-1500 psi total pressure) has only minor effects on additive response.
- Flow improver additives have the potential for contributing to the development of shale derived middle distillate fuels in at least two ways:
 - (1) By improving the cold flow properties of synthetic fuels thus rendering them operable over a wider range of ambient conditions.
 - (2) By extending the boiling range of useful fuels, thus, potentially increasing the yield of the middle distillate fraction.

IV.2 Recommendations for Additional Research

The results described above were obtained with additives, both commercial and experimental, which were designed for use with petroleum-derived fuels. Since wax crystal modifiers are quite specific in their action

additional research is needed to develop new additives especially tailored for hydroprocessed shale liquids. To this end the following specific research is recommended.

- Continue and expand studies of the effects of fuel properties, especially as modified by processing history, on response to various additives.
- Synthesize and evaluate optimized additives in actual shale liquids.
- Conduct field evaluation tests of best additives and additive packages using actual diesel engines.

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APPENDICES

I. Sample Processing

- A. Distillation
- B. Hydroprocessing

II. Pour Point Screening Tests

III. Low Temperature Flow Tests (LTFT)

- A. Description of Test Methods
- B. Results of LTFT Screening Tests

IV. Identification of Additives

I.A DISTILLATION OF SAMPLES

The crude shale liquid from the Occidental Oil Shale Co.'s in situ process was blended into a single sample. A portion of this was delivered to Imperial Oil Co. Ltd.'s laboratories in Sarnia Ontario for distillation. Of several possible stills, this one afforded the most accurate distillation cuts and best delivery time.

Three fractions were produced, each nominally within the diesel fuel boiling range (325-750°F). Each fraction had the same initial boiling point (325°F). The three final boiling points were as close as possible to 640°F, 670°F and 700°F to represent a narrow, medium and wide cut diesel.

Distillation data follows.

APPENDIX TABLE I.1 DISTILLATION DATA FOR FUEL A⁽¹⁾

<u>Wt.</u> <u>(g)</u>	<u>Charge⁽²⁾</u>		<u>Operating Conditions</u>					<u>Temp.</u> <u>°C</u>	<u>Overhead</u>			
	<u>Vol.</u> <u>(cc)</u>	<u>Density</u> <u>(g/cc)</u>	<u>Pot</u> <u>Start</u>	<u>Temp (°C)</u> <u>Finish</u>	<u>Pressure (KPA)</u>		<u>Vol.</u> <u>(cc)</u>		<u>Yield⁽³⁾</u> <u>(%)</u>	<u>Density</u> <u>(g/cc)</u>		
179,120	196,317	.9124	233	274	14	14	i-328	56090	64650	31.4	.8675	

(1) Distillation performed at Imperial Oil Co. Ltd., Sarnia, Ontario.

(2) Crude shale liquid from Occidental Oil Shale Co.

(3) Wt. basis; based on charge to still.

TABLE I.2 DISTILLATION RECORD FOR FUEL A

Cut No.	Time	Vol. cm ³	Tot. Vol. cm ³	Cum. Vol. %	Temp. Obs'd °C	Corr.	Vap. Temp. Corr'd °C	Abs. Press. kPa	Atm. Equiv. Temp. °C	Pot Temp. °C
1	11 ³⁵	INT			71	0	71			214
2	1 ⁴⁴	2000	2000	1.0	255	0	255			291
3	1 ⁵⁰	3000	5000	2.5	272	0	272			295
4	2 ⁰⁰	5000	10000	5.1	276	0	276			300
5	2 ¹⁰	5000	15000	7.6		0	283			305
6	2 ²⁵	5000	20000	10.1		0	289			311
7	2 ³⁵	4000	24000	12.2		0	294			315
8	9 ¹⁰	INT		VAC		0	181			225
9	9 ³⁵	5000	29000	14.8		0	204	14	278	233
10	10 ⁰⁷	5000	34000	17.3		0	217	14	292	241
11	10 ²⁰	5000	39000	19.9		0	226	14	307	247
12	10 ³⁵	5000	44000	22.4		0	234	14	312	253
13	10 ⁵⁰	5000	49000	25.0		0	240	14	317	258
14	11 ⁰⁵	5000	54000	27.5		0	247	14	325	264
15	11 ²⁰	5000	59000	30.1		0	254	14	332	270
16	11 ³⁰	4800	63800	32.5		0	258	14	338	274

FIGURE I.1
IMPERIAL OIL ENTERPRISES LTD, RESEARCH DEPT

SAMPLE NAME - Shale Liquid A

DESCRIPTION - A-90-79 *JS*

APPENDIX TABLE I.3 DISTILLATION DATA FOR FUEL B⁽¹⁾

<u>Charge⁽²⁾</u>			<u>Operating Condition</u>				<u>Overhead</u>				
<u>Wt.</u> <u>(g)</u>	<u>Vol.</u> <u>(cc)</u>	<u>Density</u> <u>(g/cc)</u>	<u>Pot Temp.(°C)</u>		<u>Pressure (KPA)</u>		<u>Temp.</u> <u>(°C)</u>	<u>Wt.</u> <u>(g)</u>	<u>Vol.</u> <u>(cc)</u>	<u>yield⁽³⁾</u> <u>(%)</u>	<u>Density</u> <u>(g/cc)</u>
			<u>Start</u>	<u>Finish</u>	<u>Start</u>	<u>Finish</u>					
178420	195679	.9118	189	273	9.0	9.0	i-354	67790	77652	38.0	.8730

(1) Distillation performed at Imperial Oil Co. Ltd.; Sarnia, Ontario.

(2) Crude shale liquid from Occidental Oil Shale Co.

(3) Wt. basis: based on charge to still.

APPENDIX TABLE 1.4 DISTILLATION RECORD FOR FUEL B

Cut No.	Time	Vol. cm ³	Tot. Vol. cm ³	Cum. Vol. cm ³	Temp. Obs'd °C	Corr.	Vap. Temp. Corr'd °C	Abs. Press KPa	Atm. Equiv. Temp. °C	Pot Temp. °C
1	12 ³⁰	INT.			65	0	65			216
2	2 ⁵⁵	2000		1.0		0	250			290
3	3 ⁻	3000	5000	2.6		0	268			294
4	3 ¹⁴	5000	10000	5.1			179			300
5	3 ²⁰	5000	15000	7.7			286			305
5			Vac.							
7	8 ⁴⁰	INT.					63	9.0	134	189
8	9 ²⁰	2500	17500				170	9.0	257	205
9	9 ³⁰	2500	20000	10.2			180	9.0	267	208
10	9 ⁴⁵	5000	25000	12.8			190		279	214
11	10 ⁻	5000	30000	15.3			199		289	221
12	10 ¹⁵	5000	35000	17.9			207		298	227
13	10 ³⁰	5000	40000	20.4			213		304	237
14	10 ⁴⁵	5000	45000	23.0			220		312	238
15	11 ⁻	5000	50000	25.6			226	9.0	319	243
16	11 ¹⁵	5000	55000	28.1			223		326	250
17	11 ³⁰	5000	60000	30.7			239		333	255
18	11 ⁴⁵	5000	65000	33.2			246		341	261
19	12 ⁻	5000	70000	35.8			251		346	266
20	12 ¹⁰	5000	75000	38.3			256		352	271
21	12 ¹³	2400	77400	40.0			258		354	273

FIGURE I.2
IMPERIAL OIL ENTERPRISES LTD, RESEARCH DEPT

SAMPLE NAME - Shale Liquid B

DESCRIPTION - A-92-79 25

APPENDIX TABLE I.5 DISTILLATION DATA FOR FUEL C⁽¹⁾

Wt. (g)	Charge ⁽²⁾		Operating Conditions				Overhead				
	Vol. (cc)	Density (g/cc)	Temp. (°C)		Pressure (KPA)		Temp. (°C)	Wt. (g)	Vol. (cc)	yield ⁽³⁾ (%)	Density (g/cc)
			Start	Finish	Start	Finish					
179,050	196,241	.9124	194	272	5.5	5.5	L' -371	81100	92443	45.3	.8773

(1) Distillation performed at Imperial Oil Co. Ltd., Sarnia, Ontario.

(2) Crude shale liquid from Occidental Oil Shale Co.

(3) Wt. basis; based on charge the still.

APPENDIX TABLE I.6 DISTILLATION RECORD FOR FUEL C

Cut No.	Time	Vol. cm ³	Tot. Vol. cm	Cum. Vol. %	Temp. Obs'd °C	Corr.	Vap. Temp. Corr'd °C	Tensimeter °C	Abs. Press. kPa	Atm. Equiv. Temp. °C	Pot. Temp. °C
1	9 ⁻	INT			70	0	70				
2	11 ¹⁵	2000			70	0	248				290
3	11 ²⁰	3000	5000	2.5	70	0	259				293
4	11 ⁴⁰	5000	10000	5.1	70	0	272				300
5	12 ⁻	5000	15000	7.6	70	0	281				305
6	12 ¹⁵	5000	20000	10.2	70	0	289				311
7	12 ³⁰	5000	25000	12.7	70	0	296				316
8			Vac.			0					
9	8 ⁵⁵	INT.			154	0	154	155	5.5	250	194
10	9 ¹⁰	5000	30000	15.3		0	174	155	5.5	277	202
11	9 ²⁵	5000		17.8		0	184	155	5.5	287	208
12	9 ⁴⁵	5000	40000	20.4		0	193	155	5.5	297	216
13	10 ⁻	5000		22.9		0	200	155	5.5	305	222
14	10 ¹⁵	5000	50000	25.5		0	205	155	5.5	312	227
15	10 ³⁰	5000		28.0		0	213	155	5.5	318	233
16	10 ⁴⁵	5000	60000	30.6		0	219	155	5.5	327	239
17	11 ⁻	5000		33.1		0	226	155	5.5	335	244
18	11 ¹⁵	5000	70000	35.7		0	232	155	5.5	342	249
19	11 ²⁵	5000	75000	38.2		0	239	155	5.5	350	255
20	11 ⁴⁰	5000	80000	40.8		0	246	155	5.5	357	261
21	11 ⁵⁰	5000	85000	43.3		0	252	155	5.5	362	267
22	12 ¹⁵	7000	92000	46.9		0	258	155	5.5	371	272

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FIGURE I.3

IMPERIAL OIL ENTERPRISES LTD, RESEARCH DEPT

SAMPLE NAME - Shale Liquid, C (42381)

DESCRIPTION - A-93-79 26

I.B Hydroprocessing of Shale Liquids

The three distilled shale liquid fractions described above were hydroprocessed in the unit shown in Figure I.4. This unit was modified slightly for the present program to permit higher throughputs and higher total pressures. Modifications are shown in Figures III.5-III.8 and described below.

I.B.1 Hydroprocessing Unit - General Description (Figure I.4)

This unit is computer controlled and can be operated unattended.

The Hydroprocessor consists of a single sandbath containing the catalyst reactor shown in Figure 1.5-A.

The reactor is supplied with systems for H_2 and oil feeds. These can be at varying rates at any given reaction pressure between 0-100 psi (2000 psi as modified).

Hydrogen Feed System

Hydrogen is supplied to Hydroprocessor cells 3E and F from an external H_2 trailer. (There is also a parallel bottle feed system as backup and also for pressures higher than the trailer (800-1000 psi)).

H_2 enters unit from main trailer line to unit H_2 regulator. This provides 750 psi H_2 which is stepped down by regulator and mitey mite to either low pressure pretreatment or high pressure reaction H_2 (see modifications below).

H_2 is fed to a control loop consisting of a computer monitored orifice- ΔP cell and an air actuated, computer controlled research control valve.

Feed is pumped from the Milton Roy pump directly to the reactor.
Feed rate is controlled by the precalibration of the pump.

I.B.2 Modification of Hydroprocessor Made Especially for this Program

The hydroprocessor unit was upgraded to accept higher pressure running conditions.

1. All unit safeties and regulating systems are now capable of 2000# operation.
2. Newly designed reactor to accommodate higher weight catalyst charges (see Figure I.5).
3. New vapor-liquid separator, for higher pressure (Figure I.6).
4. New pump gearing system for liquid feed.
5. New feed line and safety shut off for H_2S/H_2 delivery.

Hydrogen

Hydrogen was delivered from high pressure cylinders.

Product

Product was collected in a 3 gallon safety can.

Gas Scrubbing

All H_2S flows and products were scrubbed through a 2 1/2 gallon 5 N NaOH scrubber.

FIGURE I.4 HYDROPROCESSING UNIT SCHEMATIC

REV. NO.	BY	DATE	DESCRIPTION
1	W. J. H.	10/1/68	DESIGN
2	W. J. H.	10/1/68	DESIGN
3	W. J. H.	10/1/68	DESIGN
4	W. J. H.	10/1/68	DESIGN
5	W. J. H.	10/1/68	DESIGN
6	W. J. H.	10/1/68	DESIGN
7	W. J. H.	10/1/68	DESIGN
8	W. J. H.	10/1/68	DESIGN
9	W. J. H.	10/1/68	DESIGN
10	W. J. H.	10/1/68	DESIGN

FIGURE I.5.A MODIFIED REACTOR SCHEMATIC

SEPARATOR

DESIGN PRESSURE 2000PSI
DESIGN TEMP 300°F

FIGURE I.6 MODIFIED LIQUID/VAPOR SEPARATOR SCHEMATIC

Safety Systems

All previous readout and control systems, as in the original unit, were in operation.

I.B.3 Hydroprocessing Conditions

See Table 2, Section III.1.

Catalyst was activated by pre-sulfiding using an H_2S/H_2 mixture according to manufacturers instructions.

II. POUR POINT DEPRESSION TESTS

The standard pour point test (ASTM D97) was used both as a screening tool to limit the number of additives for LTFT testing and because pour point depression is useful in its own right. Results of pour point screening tests with all additives studied are given in Tables II.1-II.3. Additional tests are presented in Section III.4.1.

TABLE II.1 EFFECTS OF 0.4 WT.% OF VARIOUS ADDITIVES
ON THE POUR POINT OF FUEL A-2(1)

Additive (2)	Pour Point ($^{\circ}\text{F}$) (3)
None	0
3-10-30-1	-45
-2	-35
-3	-35
-4	-25
-5	-35
-6	-5
-7	-45
-8	-30
-9	-45
-10	-30
-11	-30
-12	-35
-13	-35
-14	-15
-15	-20
-16	-60
-17	-60
-18	-5
-19	0
-20	0
-21	-5
-22	0
-23	-65
-24	-35
-25	-35
-26	-25
-27	-10
-28	-5
-29	0
-30	-50
-30	-50
-31	-50
-32	-50
-34	-10
-35	-30
-36	-35
-37	+5

(1) See Table 5, 6 and 8 (Section III.2.3)
for fuel characteristics.

(2) Coded samples from U. S. Testing; all sam-
ples tested on "double blind" basis.

(3) ASTM D97.

APPENDIX TABLE II.2 POUR POINT TESTS WITH VARIOUS ADDITIVES IN FUEL B-2⁽¹⁾

<u>Additive⁽²⁾</u>	<u>Pour Point (^oF)⁽³⁾ at Treat Level</u>	
	<u>0.4 wt.%</u>	<u>0.04 wt.%</u>
None	+10	
3-10-30-1	-40	-5
-2	-35	-5
-3	-20	-5
-4	-30	-5
-5	-35	-5
-6	+10	+10
-7	-15	+5
-8	-25	0
-9	-20	+5
-10	-20	+5
-11	-20	+5
-12	-30	-10
-13	-30	-10
-14	-20	0
-15	-15	+5
-16	-45	-10
-17	-55	-15
-18	+10	+10
-19	+10	+10
-20	+10	+10
-21	+10	+10
-22	+10	+10
-23	-60	-15
-24	-30	+5
-25	-40	-5
-26	-25	-10
-27	+10	+10
-28	+5	+10
-29	+10	+10
-30	-45	-5
-31	-45	-10
-32	-50	-5
-33	-45	-10
-34	0	+5
-35	-25	0
-36	-55	-5
-37	-5	0

(1) For characteristics of Fuel B-2 see Table 5, 6 and 8, Section III.2.3.

(2) Code furnished by U. S. Testing Co.

(3) ASTM D97.

APPENDIX TABLE II.3 POUR POINT TESTS WITH VARIOUS ADDITIVES IN FUEL C-2⁽¹⁾

<u>Additive⁽²⁾</u>	<u>Wt. %</u>	<u>Pour Point (°F)⁽³⁾</u>
None	---	+20
3-10-30-1	0.4	-20
-2	0.4	-25
-3	0.4	-15
-4	0.4	-20
-5	0.4	-10
-6	0.4	+20
-7	0.4	+15
-8	0.4	-25
-9	0.4	-35
-10	0.4	-25
-11	0.4	-15
-12	0.4	-20
-13	0.4	-5
-14	0.4	-35
-15	0.4	-40
-16	0.4	-40
-17	0.4	-35
-18	0.4	+15
-19	0.4	+15
-20	0.4	+15
-21	0.4	+15
-22	0.4	+15
-23	0.4	-40
-24	0.4	-10
-25	0.4	-35
-26	0.4	-20
-27	0.4	+15
-28	0.4	+15
-29	0.4	+15
-30	0.4	-50
-31	0.4	-45
-32	0.4	-50
-33	0.4	-50
-34	0.4	+15
-35	0.4	-30
-36	0.4	-45
-37	0.4	+5

(1) See Tables 5, 6, and 8, Section III.2.3 for fuel characteristics.

(2) Code furnished by U.S. Testing Co.

(3) ASTM D97.

III. Low Temperature Flow Test (LTFT) For Diesel Fuels

III.A Description of Method

Introduction

This test was developed by Exxon Research and Engineering Co. to determine the low temperature operability of diesel fuels in autodiesel equipment. Results obtained by this test correlate with those obtained at the 1970-71 Bemidji, Minnesota auto-diesel field test (see reference 4).

Scope

The method is applicable to all diesel fuels. Fuels passing the test are expected to provide satisfactory operability (free of wax plugging) in auto-diesel equipment at fuel temperatures equal to or higher than that of the test.

Summary of Method

The sample is brought to the desired test temperature by cooling it at a rate of 2°F per hour in a cold box. At that temperature the filterability of the test fuel through a screen of 40 micron openings at a vacuum of 6 inches of mercury is determined.

Low temperature operability of the test fuel at a given temperature is considered satisfactory if passage of the fuel through the screen is completed in less than 60 seconds.

Precision

Data not available yet.

Apparatus

(1) Cold Box (Low Temperature Bath) capable of providing a cooling rate of $2^{\circ}\text{F}/\text{hour}$ between 30°F and -20°F , with air circulation to provide uniform temperatures throughout the box.

(2) Temperature Controller, Rotax M-40, Cam. Set Controller, obtainable from Foxboro Co., Foxboro, Massachusetts, under catalog number M-40 is recommended. This controller has a range -30°F to $+70^{\circ}\text{F}$ and is equipped with a double pole, single throw switch wired so as to cut off power to the chart drive only.

(3) Temperature Controller Cam. Prepare the cam by marking the chart for 1°F drop in temperature for each 30 minutes ($2^{\circ}\text{F}/\text{hour}$ cooling rate). Cut the cam along a smooth curve through the points.

(4) Filtering Assembly, shown in Figures III.1 and III.2.

Procedure

1. Fill sample container (Figure 1) with 200 ml of clean, dry fuel to be tested.
2. Equip the filter with a screen of 40 micron openings, and place this filter and the tubing attached to it in the sample container. Cover the top of the bottle with aluminum foil to exclude contamination with condensed water.
3. Place the container into a cold box kept at a temperature at least 15°F above the WAP* of the test fuel.
4. Insert a thermometer or thermocouple in a separate bottle of fuel oil for recording test temperature and place it in the cold box next to the first bottle.
5. Close the cold box and start programmer to lower temperature at a rate of 2°F per hour.

*WAP = "wax appearance point" or cloud point.

6. When fuel temperature reached the desired last temperature, remove bottle containing test fuel and filter from the cold box.

7. Using the filter assembly, gently stir the oil to disperse settled wax crystals. Attach the filter assembly at B as shown in Figure 1.

8. Connect a vacuum system providing a suction equivalent to 6 inches of mercury. Open pinch-clamp "C" (Figure 1) and simultaneously start the timing with a stop watch.

9. Determine the time required for all of the fuel to pass through the filter.

Reporting

Report the time in seconds that was required for the filtration of the fuel.

The fuel is considered to have "passed the LTFT" if 80% of the fuel passed through the screen in 60 seconds or less.

III.B Results of Screening Tests

These are summarized in Table III.1.

FIGURE III.1

LOW TEMPERATURE FLOW TEST (LTFT)

Summary of Method

The sample is brought to the desired test temperature by cooling it at a rate of 2°F. per hour in a cold box. At that temperature the filterability of the test fuel through a screen of 40 micron openings at a vacuum of 6 inches of mercury is determined.

Low temperature operability of the test fuel at a given temperature is considered satisfactory if passage of the fuel through the screen is completed in less than 60 seconds.

FIGURE III.2
FILTER ASSEMBLY FILTERING

FIGURE III.3

FILTER DETAIL

APPENDIX TABLE III.1 LTFT SCREENING TESTS IN FUEL B-2 (0.4 WT.% LEVEL)⁽¹⁾

Additive ⁽²⁾	Lowest Pass (°F) ⁽³⁾	% Pass (Time in Sec)	Improvement Over Base Fuel (°F) ⁽³⁾
None	+14		---
3-10-30-1	+5	100 (<10)	9
-2	+10	100 (34.7)	4
-3	+10	100 (6.2)	4
-4	+10	100 (6.6)	4
-5	+10	100 (15)	4
-8	+10	100 (8.6)	4
-9	+10	100 (10.2)	6
-10	+10	100 (7.7)	4
-11	+10	100 (8.2)	4
-12	+5	100 (8.0)	9
-13	+5	100 (12.2)	9
-14	+10	100 (11.9)	4
-16	+10	100 (7.0)	4
-17	+5	100 (38)	9
-23	+5	100 (7.2)	9
-24	>10	---	---
-25	>10	---	---
-26	+10	100 (6.6)	4
-30	>10	---	---
-31	+10	100 (23.9)	4
-32	+10	100 (21.1)	4
-33	+5	85 (60)	9
-35	+2 ⁽⁴⁾	100 (9.1)	12
-36	-2	86 (60)	16

(1) See Table 5 for characteristics of fuel B-2.

(2) Code furnished by U. S. Testing Co.

(3) Lowest temperature at which 80% or better pass through 40 μ screening in 60 seconds. Highest temperature tested: +10°F.

(4) Near pass at 0°F.

APPENDIX IV. CODE DESIGNATIONS FOR ADDITIVES TESTED

<u>Code (1)</u>	<u>Manufacturer</u>	<u>Manufacturer's Designation</u>
3-10-30-1	Rohm & Haas	Acryloid Grade 154 Code 5-890-3 Lot 38248-8
3-10-30-2	Rohm & Haas	Acryloid Grade 155 Code 6-890-8 Lot 38100-5
3-10-30-3	Rohm & Haas	Acryloid Grade 156 Code 6-8911 Lot 38251-8
3-10-30-4	Lubrizol Corp.	Sample OS #16224M
3-10-30-5	Ethyl Corp.	Sample #3025-79 10/16/79 Hi-Tec E-672
3-10-30-6	Lubrizol Corp.	Sample OS #44980B
3-10-30-7	Lubrizol Corp.	Sample OS #49431
3-10-30-8	Texaco	34998-3B
3-10-30-9	Texaco	34998-3D
3-10-30-10	Texaco	3499A-3A
3-10-30-11	Texaco	34998-3C
3-10-30-12	Rhom & Haas	Acryloid Grade 150 Code 6-9011 Lot 339455
3-10-30-13	Rohm & Haas	Acryloid Grade 152 Code 6-9174 Lot 382117
3-10-30-14	Chevron	79-ARS-429 Sample OFA 414 8/8/79
3-10-30-15	Chevron	79-ARS-429 Sample OFA 416B 8/8/79
3-10-30-16	Amoco	PC9-155 Lube Oil Additive
3-10-30-17	Amoco	PC9-154 Lube Oil Additive
3-10-30-18	GAF	M-Pyrol (Methyl Pyrrolidone)
3-10-30-19	GAF	Gantrez ES-425 Butyl Half Ester of Gantrez AN 50% Solid in Ethanol

(1) Provided by U. S. Testing Company, Inc.

APPENDIX IV. CODE DESIGNATIONS FOR ADDITIVES TESTED (CONTINUED)

<u>Code (1)</u>	<u>Manufacturer</u>	<u>Manufacturer's Designation</u>
3-10-30-20	GAF	Polyvinylpyrrolidone (PVP) Type NP-K30
3-10-30-21	GAF	IGEPAL CO-530 Nonyl Phenoxy Polyoxyethylene Ethanol
3-10-30-22	GAF	IGEPAL CO-430 Nonyl Phenoxy Poly(ethyleneoxy) Ethanol
3-10-30-23	Exxon	Paradyne 25
3-10-30-24	Exxon	ECA 7963
3-10-30-25	Exxon	ECA 7973
3-10-30-26	GAF	Ganex V-216
3-10-30-27	GAF	IGEPAL DM-530
3-10-30-28	GAF	IGEPAL DM-430
3-10-30-29	GAF	IGEPAL CO-520 (Polyethyleneoxy) Derivative
3-10-30-30	Petrolite Corp. - Tretolite Division	76-47150
3-10-30-31	Petrolite Corp. - Tretolite Division	78-36010
3-10-30-32	Petrolite Corp. - Tretolite Division	79-36029
3-10-30-33	Petrolite Corp. - Tretolite Division	79-36016
3-10-30-34	Petrolite Corp. - Tretolite Division	79-36028
3-10-30-35	Petrolite Corp. - Tretolite Division	78-36030
3-10-30-36	Petrolite Corp. - Tretolite Division	78-36021
3-10-30-37	GAF	Ganex V-220

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