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International Coal Refining Company
Allentown, Pennsylvania

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TABLE OF CONTENTS

Note

Articles in this Supplement were previously withheld from publication to avoid premature disclosure of inventions. The article on page 49 was published prior to June 1984 (DOE/OR/03054-61, Development of SRC-I Product Analysis) and is not republished here. Pagination has not been altered, since this could invalidate any cross-references.

RHEOLOGY AND STABILITY OF SRC RESIDUAL FUEL OILS - STORAGE EVALUATION

K. C. Tewari*

In Air Products' ongoing study to characterize the rheology and stability of various SRC residual oils, single-phase blends of 50 wt % HSRC and TSL SRC in 1:1 mixtures of 1st- and 2nd-stage process solvents were subjected to storage stability tests at 150°F in nitrogen and air atmospheres. Using viscosity as an indicator, it was observed that the blends studied increased in viscosity with storage time in an air atmosphere; the viscosity increase began after a 4-week storage period. The increase in HSRC blend viscosity was significantly greater than that of the TSL SRC blend. A 60-day air-stored blend will require a pumping temperature about 10°F higher than that specified for an unaged blend in order to have the same viscosity. The viscosity increase under nitrogen storage was relatively insignificant. Nitrogen blanketing appears to be important in maintaining the specified viscosity characteristics of the blends during storage at the 150°F storage condition tested.

A loss of volatiles undoubtedly occurs during high-temperature storage under laboratory conditions. Such losses contribute to an increase in the viscosity of the blend. In commercial practice, volatile losses are expected to be significantly lower.

Solvent extraction data and analysis of separated fractions suggest that during storage under the above conditions, some oxidative polymerization of pentane-soluble oil components forms higher molecular weight pentane insolubles (asphaltenes and benzene insolubles). Asphaltenes are also involved in the increase in viscosity and do chemically change.

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*Corporate Research Services Department, Air Products and Chemicals, Inc. (APCI).

INTRODUCTION

Heavy distillates and residual fuel oils, representing a significant proportion of the products from SRC-I liquefaction, exhibit properties that qualify them as power-generating fuels for use in combustion turbines and boilers. SRC residual oils are defined as homogeneous, single-phase blends of SRC distillate oils (400-850°F boiling range) and solid SRC, which is the 850°F+ boiling range product derived from the first and second stages of the SRC-I coal liquefaction process.

Air Products is conducting a laboratory evaluation for International Coal Refining Company (ICRC) to characterize the rheology and stability of various SRC residual fuel oils. Correlating viscosity of heavier-grade fuel oils with temperature is important because the correlation indicates the relative ease of pumping and atomizing the oil. Specifically, the objectives of this program are to provide the temperature-viscosity characteristics of various blends of SRC residual oils prepared in the laboratory, to investigate the storage stability of selected blends, and to develop data that will support future investigations designed to evaluate the potential of these residual oils as viable utility fuels.

To date, the variation of viscosity with temperature has been determined for several combinations of the following SRC materials (Tewari et al, 1982):

Solids (850°F+ boiling range)

- LSRC (light SRC) - intermediate stream derived from the Kerr-McGee deashing process
- HSRC (heavy SRC) - first-stage SRC product recovered from the SRC-I process after Kerr-McGee deashing
- TSL SRC - two-stage liquefaction or hydrocracked SRC

Liquids

- Middle oil - 400-650°F SRC-I distillate fraction
- Heavy oil - 650-850°F SRC-I distillate fraction

In the temperature ranges and solid concentrations studied, the various blends behaved like a Newtonian liquid; that is, viscosity of the fluid was independent of shear rate, within experimental accuracy. However, experimental shear rates were low compared with typical shear rates recorded during liquid pumping; consequently, additional studies will be necessary to truly characterize the Newtonian behavior of these blends. It was determined that the flow characteristics of SRC residual oils at a given temperature and composition depend on the average molecular weight of the solid and the amount of low-boiling materials in the liquids used in the blends. The optimum compositions of the blends were defined based on certain criteria. These criteria were selected as reasonable upper limits that would allow the blends to be handled by conventional fuel handling equipment: at $\leq$ 225°F, the viscosity must be below 1,000 centipoise (cP) to facilitate pumping; at $\leq$ 325°F, the viscosity must be below 30 cP to properly atomize the fuel. The pumping and the atomizing temperatures of the blends were found to depend on the type and content of the solid, and increased in the order LSRC < TSL SRC < HSRC.

ICRC then evaluated the viscosity/temperature/composition data, and selected the following two SRC residual oil blends for storage stability tests:

	Composition (wt %)			
	HSRC	TSL SRC	Process solvent 1st-stage	Process solvent 2nd-stage
SRC blend	50	-	25	25
TSL SRC blend	-	50	25	25

This report discusses stability data obtained after subjecting these SRC and TSL SRC blends to a 60-day storage stability investigation.

RESULTS AND DISCUSSION

Component Characterization

The 1st- and 2nd-stage SRC-I solid and liquid samples were acquired through ICRC from the Wilsonville Pilot Plant. The identification, ultimate analysis, and heating value for each sample are listed in Table 1. To provide information on the amounts of materials as a function of boiling points, the standard ASTM D2887 simulated distillation method was applied to both process solvent samples. The results are summarized in Table 2.

Preparation and Physical Characteristics of Single-Phase Blends

HSRC and TSL SRC solids were pulverized to a fineness of 100% through 140 mesh, approximately 105 μm. Single-phase blends were prepared in a three-necked round-bottomed flask (500 mL), equipped with a thermometer and a glass stirrer. A requisite amount of pulverized solid was gradually added to the preheated liquids with constant stirring. To assure complete dissolution and homogeneous mixing, the solid was added slowly over a 4-hr period at a 200 ± 5°F blending temperature, which was maintained for at least 12 hr.

A modified ASTM D2887 simulated distillation technique was used to obtain the boiling point distribution of the volatile fraction of both SRC and TSL SRC blends (Tables 3 and 4).

Tables 5 and 6 summarize, respectively, the viscosities of the SRC and TSL SRC blends at specified temperatures and at various shear rates. Viscosity measurements were made with a Brookfield viscometer. The range of applied shear rates varied with the viscosity of the blend and the spindle used. In the reported temperature ranges, each blend behaved like a Newtonian liquid, within experimental error. Figure 1 summarizes the relationship of viscosity with temperature for each blend; the viscosity values are at the highest shear rate applied. The temperatures required for the blends to reach viscosities of 30 cP (atomizing) and 1,000 cP (pumping) are as follows:

Blend	Temperature (°F) at: 30 cP	1,000 cP
SRC	300	202
TSL SRC	268	167

The density-versus-temperature data for the blends are listed in Table 7. Densities were determined using a pycnometric procedure.

Storage Stability Test

In an initial 15-day stability test, in which SRC and TSL SRC blends were stored in open beakers at 150°F, an approximate 50% increase in blend viscosity occurred in both nitrogen and air atmospheres. The results were therefore discarded. In a subsequent 60-day test, a beaker containing approximately 100 mL of the blend was placed in a 30-oz wide-mouth glass bottle, which was capped after flushing with the desired gas, and then stored in an isotherm oven. All openings in the nitrogen oven were sealed to prevent an excess consumption of nitrogen; the air oven openings were not sealed. The 150°F temperature of the oven and atmosphere was maintained by the slow circulation of the gas.

Any degradation of the unstirred blend with storage time is expected to occur largely at the surface exposed to the applied atmosphere. Therefore, at specified intervals, each blend was removed from the storage bottle and mixed thoroughly. A 10-mL aliquot of representative sample was then extracted to measure viscosities at three specified temperatures used to monitor the blend deterioration with time. The blends were viscous at the storage temperature. In fact, the SRC blend required heating to almost 200°F to transfer it into the preheated thermocel for viscosity measurements.

Tables 8-11 and Figures 2 and 3 show the changes in viscosity that occurred at the three temperatures when the blends were stored at 150°F in air and nitrogen. Using viscosity as an indicator, it is obvious that the blends studied deteriorate or age with storage time. Storage in the unsealed air oven had a significant effect in increasing the viscosity of the blend, whereas storage in the sealed nitrogen oven had only a small effect. This suggests that nitrogen blanketing and/or sealing of the storage vessel is important in maintaining the viscosity characteristics of the blend during storage at the 150°F storage condition tested.

Although the blends were stored in closed glass bottles of the same size, some loss of volatiles undoubtedly occurred during high-temperature storage. A major loss of lighter components was observed during mixing and transfer of material to a viscometer cell, and during viscosity measurements at high temperatures. Such losses contribute to an increase in the viscosity of a given blend. However, since the storage conditions, transfer procedure, and the temperatures of viscosity measurements were the same, except for the difference in the sealing of the ovens, the loss of material and its impact upon viscosity should be constant for the same blend stored under air and nitrogen. Therefore, the fact that the blends in the air storage oven had larger increases in viscosity clearly implies that oxygen may have had a specific deleterious effect. Viscosity increase of the blend under storage in the nitrogen atmosphere oven should be considered insignificant. It should be noted that the sampling technique used for viscosity measurements constantly reduced the sample size of the stored blend. The increased percent volatile loss due to the increase in surface/volume ratio of the stored blend during the latter half of the storage period contributed significantly to an increase in viscosity of the blend.

Evaluation of the viscosity data (Figures 2 and 3) suggests that the viscosity increase in both SRC and TSL SRC blends in an air environment begins after a 4-week storage period at the 150°F storage condition tested. A comparison of viscosity-temperature data for aged and unaged blends is shown in Figure 4. To maintain the same pumping characteristics, 60-day air-stored TSL SRC and SRC blends will require temperatures about 10 and 15°F higher, respectively, than those specified for unaged blends.

To quantify the weight loss during storage and viscosity measurements, about 16 g of freshly prepared SRC blend was stored at 150°F for 47 days in closed and open 1-oz glass vials. The weight loss data determined at specified intervals are listed in Table 12. Both closed and open vials showed a significant weight loss during the first 10 days of storage. In open vials, the loss of material after 10 days increased rectilinearly with storage time, while in closed vials the loss became insignificant after 20 days. An average of nine determinations showed a 0.2 wt % loss during viscosity measurements at 200°F and a total loss of 0.9 wt % during measurements at all three temperatures (i.e., 200, 250, and 310°F).

It should be noted that the viscosity difference (Figure 2) between the unaged and 5-day aged SRC blend was due to the fact that the viscosity of the unaged blend was measured immediately after it was prepared at 200°F, while the aged sample stored at 150°F required preheating to almost 200°F to transfer it into a preheated viscometer thermocel. Therefore, the viscosity increase was due mainly to the loss of material during the storage and transfer process. This loss and its impact upon viscosity were the same for all measurements performed on aged samples stored at 150°F, and are a function of the number of previous measurements made on the samples.

Solvent Separation

Solvent extraction was performed to separate the blends into oils (pentane solubles), asphaltenes (benzene solubles, pentane insolubles) and benzene-insoluble fractions. The weight percent distribution of the fractions in unaged and air-aged blends is summarized in Table 13. The solvent analysis data for the blends are instructive as to the overall mechanism of the noted degradation. The blends stored in an air environment showed significant increases in the amount of asphaltenes and/or benzene-insoluble materials, and corresponding decreases in oil components. The average molecular weight of these fractions increased in the order oils < asphaltenes < benzene insolubles. Thus, it appears that oxidative polymerization of SRC blend stored in air for 68 days caused the formation of and increase in large-molecular-weight benzene insolubles. The chemical portion of the viscosity increase in TSL SRC blend stored in air for 72 days was due mainly to this oxidative polymerization of oil components to form higher molecular weight asphaltene components.

Characterization of the Solvent-Separated Fractions

Benzene Insolubles. The amounts of this fraction separated from unaged and aged TSL SRC blends were insufficient to perform any analysis. The elemental distribution of benzene insolubles in unaged and air-aged SRC blend, listed in Table 14, shows no noticeable change. Infrared spectra of the two solid samples were also identical.

Asphaltenes. The elemental distribution, number average molecular weight, and the distribution of heteroatoms, oxygen, and nitrogen in asphaltenes are summarized in Table 15. The number average molecular weight was determined by vapor pressure osmometer in solvent pyridine at 87°C. Near infrared (NIR) analysis was used to determine the weight percent of oxygen as OH (hydroxyl) and nitrogen as NH or NH_2. Infrared spectra of the samples showed the absence of the carbonyl (C=O) absorption band, indicating that oxygen in each of the four samples analyzed was present in the form of phenolic (OH) and ether (-O-) linkages. Nitrogen existed mainly as basic nitrogen, $-\ddot{N}=$.

The number average molecular weight of asphaltenes derived from the TSL SRC blend was higher than that derived from the SRC blend. The measured high molecular weight values of asphaltenes derived from air-aged blends corresponded well with the observed viscosity increases of the aged blends.

Each asphaltene fraction was further evaluated by high-resolution proton magnetic resonance (NMR) at 200 MHz. Complete solubility of the asphaltene samples in solvent THF-d_8 ensured that total samples were evaluated. The contribution of solvent impurities to the asphaltene aliphatic proton signals was quantitatively estimated and subtracted from the aliphatic proton integration. Tetramethylsilane was used as an internal standard. To calculate the hydrogen distribution, the hydrogen on the NMR spectra was divided into the following four types: aromatic and phenolic hydrogen, H_a, 6-9 ppm; hydrogen attached to α carbons, 2-5 ppm; hydrogen bound to β or farther from aromatic rings, except for terminal methyl, H_β, 1.1-2 ppm; and hydrogen in terminal methyl, H_γ, 0.3-1.1 ppm. The NMR proton distribution and weight percent distribution of absolute hydrogen are listed in Table 16. Structural parameters of average molecules in each sample were calculated from elemental composition, molecular weight, and proton NMR spectra using modified Brown and Ladner equations. Their definitions and formulae are:

- Number of aromatic carbons:

$$C_A = C - \frac{1}{2}(H_\alpha + H_\beta) - \frac{1}{3} H_r \qquad (1)$$

- Fraction of aromatic carbons (= aromaticity):

$$f_a = \frac{C_A}{C} \qquad (2)$$

- Total number of rings:

$$R = \frac{2C - H + 2}{2} - \frac{1}{2} C_A \qquad (3)$$

- Number of aromatic clusters:

$$n = \frac{1}{3}(C_{AP} - \frac{1}{2} C_A) \qquad (4)$$

where

$$C_{AP} = H_a + \frac{1}{2} H_\alpha$$

- Number of aromatic rings:

$$R_A = \frac{1}{4}(C_A - 2n) \qquad (5)$$

- Number of naphthenic rings:

$$R_N = R - R_A \qquad (6)$$

Values of C and H were derived from the empirical formula of each asphaltene sample. The results are summarized in Table 17.

It should be noted that the number of average structural units per molecule, n, and the aromaticity, f_a, of asphaltenes in original and air-aged blends remain nearly constant. The effect of aging is to increase, per average asphaltene molecule, the numbers of aromatic carbons, the aromatic ring numbers, and the naphthenic ring numbers. This suggests that the observed increase in the average molecular weight of the asphaltene fraction in the air-aged blend is mainly due to the variation of types of unit structures.

Although the ultimate analysis data (Table 15) would indicate that asphaltenes in air-aged and unaged blends are essentially the same, the molecular weight and NMR structural analysis data definitely show that asphaltenes are involved in the aging process and do chemically change.

Pentane-Soluble Oils. The elemental distribution, number average molecular weight, and the distribution of heteroatoms, oxygen, and nitrogen for the oil fractions separated from unaged and aged blends are summarized in Table 18. The number average molecular weight was determined by vapor-pressure osmometer in solvent methylene chloride at 37°C.

The behavior of the oil components is also noteworthy. While the molecular weight of oils in aged and unaged blends remained the same, the oxygen content of the oil fraction in the aged SRC blend decreased. This decrease is associated with the decrease in the total amount of oil components in the air-aged blend (Table 13), and may imply that oxygen-containing species in the oil are preferentially reacting to form higher molecular weight components (i.e., asphaltenes and benzene insolubles), or are preferentially evaporating.

The NMR spectrum of the oil fraction was taken at 25°C as CD_2Cl_2 solution. The NMR proton distribution and weight percent distribution of absolute hydrogen are listed in Table 19. The calculated structural parameters of average molecules in each sample are summarized in Table 20. In addition to some increase in numbers of naphthenic rings per average molecule of oil components in the air-aged blend, the structural parameters of oil in aged and unaged blends remained identical. To characterize further, the boiling-point distribution of each oil sample was determined using the standard (ASTM D2887) gas chromatographic simulated distillation method. Tables 21-24 summarize the boiling point distribution by area percent. For each oil sample, the ASTM 1160 distillation correlation derived from D2887 data is also shown.

A capillary gas chromatography (CGC) analysis method was used to identify individual components and to determine area percent distribution relative to boiling ranges in each of the oil samples. CGC conditions used are given in Table 25. The chromatograms are shown in Figures 5-8 and the numbers on the chromatograms correspond to the most likely components listed in Table 26. The area percent distribution relative to boiling ranges is shown in Table 27.

CONCLUSIONS

° The blends studied increased in viscosity with storage time under an air environment. The viscosity increase began after a 4-week storage period.

° Although apparently large (40-70%), the viscosity increases are relatively small when the small temperature increase required to maintain a pumpable and atomizable fluid is considered. When stored at 150°F, a 60-day air-stored blend will require a pumping temperature about 10°F higher than that specified for an unaged blend.

° Loss of volatile components during high-temperature storage contributed to an increase in blend viscosity. The viscosity increase was also due to the oxidative polymerization of pentane-soluble oil components to form higher molecular weight pentane insolubles. Asphaltenes were also involved in the aging process.

° The viscosity increase under nitrogen storage was relatively insignificant.

° When blends are stored at 150°F, blanketing with nitrogen helps decrease the rate of viscosity increase.

° It is apparent that both evaporation and chemical reactions are involved in the viscosity increases. Additional investigation will be required to determine the relative importance of each.

LITERATURE CITED

Tewari, K. C., P. J. Persico, and D. R. Lennon. 1982. Rheology and stability of SRC residual fuel oils. SRC-I quarterly technical report, Supplement. April-June 1982. DOE/OR/03054-8 (Suppl.). International Coal Refining Co., Allentown, Pa.

Table 1

Properties of Fuel Oil Blend Components

Component:	HSRC	TSL SRC	Process solvent (1st-stage)	Process solvent (2nd-stage)
Identification				
Run no.	227	2-234 BMB	227	235
Wilsonville no.	67782	74256	67785	78378
ICRC no.	903-053	936-082	907-053	936-102
Ultimate analysis (wt %)				
C	86.80	88.80	87.87	89.18
H	5.80	7.06	7.83	9.70
N	2.11	1.67	0.88	0.57
O	4.33	2.14	2.82	0.46
S	0.88	0.33	0.60	<0.10
Ash	0.08	-	-	-
H/C	0.802	0.954	1.069	1.305
Heat of combustion (Btu/lb)	15,619	16,432	17,105	18,047

Table 2

Boiling Point Distribution by ASTM D2887

1st-Stage Process Solvent[a]

% dist.	Temperature (°F)	% dist.	Temperature (°F)
IBP	403	60	623
5	446	70	651
10	471	80	687
20	510	90	739
30	542	95	782
40	574	99	854
50	599	FBP	875

[a] C_4 and lighter: 0.2%; C_3: 0.1%

2nd-Stage Process Solvent[a]

% dist.	Temperature (°F)	% dist.	Temperature (°F)
IBP	424	60	692
5	475	70	729
10	508	80	775
20	558	90	843
30	591	95	900
40	620	99	997
50	655	FBP	1,029

[a] C_4 and lighter: 0.0%; C_3: 0.0%

Table 3

Boiling Point Distribution of Volatile Fraction of SRC Blend by Modified ASTM D2887[a]

% dist.	Temperature (°F)	% dist.	Temperature (°F)
IBP	398	60	694
5	468	70	744
10	507	80	815
20	556	90	902
30	595	95	955
40	623	99	1,001
50	657	FBP	1,007

[a] Nonvolatile residue: 29.74 wt %; C_4 and lighter: 0.0%; C_3: 0.0%

D1160 Correlation from D2887

% dist.	Temperature (°F)	% dist.	Temperature (°F)
IBP	383	50	662
5	515	60	706
10	548	70	775
20	587	80	821
30	618	90	883
40	634	95	980

Table 4

Boiling Point Distribution of Volatile Fraction of TSL SRC Blend by Modified ASTM D2887[a]

% dist.	Temperature (°F)	% dist.	Temperature (°F)
IBP	411	60	724
5	464	70	781
10	501	80	850
20	554	90	931
30	602	95	980
40	636	99	1,024
50	677	FBP	1,029

[a] Nonvolatile residue: 20.5 wt %; C_4 and lighter: 0.0%; C_3: 0.0%

D1160 Correlation from D2887

% dist.	Temperature (°F)	% dist.	Temperature (°F)
IBP	369	50	686
5	501	60	748
10	542	70	810
20	586	80	861
30	628	90	914
40	650	95	1,004

Table 5

Variation of Viscosity with Temperature in an SRC Blend

Temperature (°F)	Shear rate (sec^{-1})	Viscosity (cP)
200	4.08	1,088
	10.20	1,087
	20.40	1,086
210	4.08	665
	10.20	663
	20.40	664
250	15.84	122
	39.60	121
	79.20	120
270	15.84	64.8
	39.60	64.1
	79.20	64.0
310	39.60	24.8
	79.20	24.6

Table 6

Variation of Viscosity with Temperature in a TSL SRC Blend

Temperature (°F)	Shear rate (sec^{-1})	Viscosity (cP)
160	2.04	1,463
	4.08	1,463
	10.20	1,460
170	4.08	854
	10.20	855
	20.40	851
180	10.20	548
	20.40	545
220	15.84	110
	39.60	110
	79.20	109
250	39.60	47.0
	79.20	46.9
270	39.60	29.3
	79.20	29.1

Table 7

Blend Density as a Function of Temperature

Blend	Temperature (°F)	Density (g/mL)
SRC	180	1.0938
	230	1.0697
	270	1.0532
	310	1.0392
TSL SRC	160	1.0725
	180	1.0607
	230	1.0474
	270	1.0284

Table 8

Aging Characteristics of SRC Blend Stored at 150°F in Air Atmosphere

Temperature (°F)	Shear rate (sec^{-1})	Viscosity (cP) after storage time (days)						
		0	5	10	19	32	45	60
200	2.04	-	1,329	1,400	1,425	1,638	1,813	2,575
	4.08	1,088	1,331	1,394	1,406	1,638	1,813	2,575
	10.20	1,087	1,320	1,388	1,393	1,633	1,808	2,575
250	7.92	-	134	141	143	158	166	203
	15.84	122	133	139	140	157	166	200
	39.60	121	132	139	139	156	167	200
	79.20	120	-	-	-	-	-	-
310	39.60	24.8	25.8	26.5	26.8	28.3	29.3	34.0
	79.20	24.6	25.4	26.3	26.0	27.9	29.3	33.3

Table 9

Aging Characteristics of SRC Blend Stored at 150°F in Nitrogen Atmosphere

Temperature (°F)	Shear rate (sec^{-1})	Viscosity (cP) after storage time (days)						
		0	5	10	20	32	45	60
200	2.04	-	1,325	1,388	1,400	1,475	1,588	1,860
	4.08	1,088	1,325	1,388	1,381	1,469	1,588	1,860
	10.20	1,087	1,313	1,380	1,378	1,450	1,585	1,850
250	7.92	-	134	139	141	148	154	175
	15.84	122	133	139	139	146	153	174
	39.60	121	132	138	138	143	153	172
	79.20	120	-	-	-	-	-	-
310	39.60	24.8	25.5	26.3	26.8	27.0	28.3	30.5
	79.20	24.6	25.3	26.0	26.0	26.8	28.3	30.5

Table 10

Aging Characteristics of TSL SRC Blend Stored at 150°F in Air Atmosphere

Temperature (°F)	Shear rate (sec^{-1})	Viscosity (cP) after storage time (days)						
		0	5	10	19	32	45	59
160	2.04	1,463	1,538	1,600	1,688	1,925	2,038	2,363
	4.08	1,463	1,538	1,600	1,688	1,919	2,038	2,363
	10.20	1,460	1,538	1,588	1,665	1,890	2,020	2,330
220	7.92	-	-	-	-	139	143	153
	15.84	110	114	116	122	133	138	151
	39.60	110	114	115	121	133	138	151
	79.20	109	113	114	118	-	-	-
270	39.60	29.3	30.8	31.3	32.0	33.5	34.3	36.5
	79.20	29.1	30.3	31.3	31.0	32.8	34.0	36.4

Table 11

Aging Characteristics of TSL SRC Blend Stored at 150°F in Nitrogen Atmosphere

Temperature (°F)	Shear rate (sec^{-1})	Viscosity (cP) after storage time (days)						
		0	5	10	19	32	45	59
160	2.04	1,463	1,525	1,563	1,600	1,663	1,663	1,825
	4.08	1,463	1,525	1,556	1,588	1,625	1,663	1,825
	10.20	1,460	1,523	1,550	1,580	1,615	1,640	1,825
220	7.92	-	-	-	-	-	-	128
	15.84	110	114	115	116	116	118	127
	39.60	110	114	114	114	114	117	125
	79.20	109	113	113	113	114	116	-
270	39.60	29.3	30.3	30.8	31.8	31.8	31.3	33.3
	79.20	29.1	29.9	30.4	30.6	30.6	30.9	33.3

Table 12

Loss of Volatiles During Storage

Storage time (days)	% weight loss Closed vial	% weight loss Open vial
9	0.35	1.19
23	0.52	1.93
38	0.57	2.63
47	0.66	2.99

Table 13

Solvent Analysis Data for the Blends Stored in Air at 150°F

		Yield (wt %)		
Sample	Storage time (days)	Oils	Asphaltenes	Benzene insolubles
SRC blend	0	59.3	30.4	10.3
	68	49.0	33.7	17.3
TSL SRC blend	0	67.6	31.8	0.6
	72	59.1	40.4	0.5

Table 14

Ultimate Analysis of Benzene Insolubles in SRC Blend

Benzene insolubles in:	Elemental distribution (wt %)					
	C	H	O	N	S	Ash
Unaged SRC blend	86.31	5.11	5.00	2.46	0.92	0.20
Air-aged SRC blend (68 days)	86.04	5.23	5.13	2.42	0.92	0.26

Table 15

Analysis of Asphaltene Fractions

	Sample separated from:			
	SRC blend		TSL SRC blend	
Analysis	Unaged	Air-aged (68 days)	Unaged	Air-aged (72 days)
Elemental (wt %)				
C	86.33	86.09	87.42	87.74
H	5.78	5.86	6.23	6.17
O	4.54	4.82	3.67	3.54
N	2.36	2.32	2.19	2.09
S	0.99	0.91	0.49	0.46
Molecular weight ($\bar{n}$M wt)	505	625	800	935
Near infrared				
Wt % O as OH	1.34	1.52	0.63	0.62
Wt % N as NH	0.23	0.29	0.23	0.25
Wt % N as NH_2	0.46	0.52	0.26	0.35

Table 16

Distribution of Hydrogen in Asphaltene Fractions

Asphaltene in:	Area % NMR spectra				Wt % hydrogen			
	H_a	H_α	H_β	H_r	H_a	H_α	H_β	H_r
Unaged SRC blend	47.8	33.1	13.4	5.7	2.76	1.91	0.78	0.33
Air-aged SRC blend (68 days)	36.2	39.9	17.2	6.7	2.12	2.34	1.01	0.39
Unaged TSL SRC blend	38.8	37.6	17.4	6.2	2.42	2.34	1.08	0.39
Air-aged TSL SRC blend (72 days)	39.3	34.0	21.1	5.6	2.42	2.10	1.30	0.35

Table 17

NMR Structural Parameters of Average Asphaltene Molecule

Asphaltene in:	Structural parameters				
	C_A	f_a	R_A	R_N	n
Unaged SRC blend	29.0	0.80	6.5	1.7	1.4
Air-aged SRC blend (68 days)	33.6	0.75	7.8	3.0	1.3
Unaged TSL SRC blend	43.6	0.75	9.7	2.9	2.3
Air-aged TSL SRC blend (72 days)	51.4	0.75	11.7	3.1	2.3

Table 18

Analysis of Pentane-Soluble Oil Fractions

Analysis	Oils in: SRC blend Unaged	Oils in: SRC blend Air-aged (68 days)	Oils in: TSL SRC blend Unaged	Oils in: TSL SRC blend Air-aged (72 days)
Elemental (wt %)				
C	88.35	88.38	88.79	88.78
H	8.50	8.35	8.66	8.55
O	2.02	1.86	1.56	1.48
N	0.70	0.73	0.72	0.94
S	0.43	0.38	0.27	0.25
Molecular weight ($\bar{n}$M wt)	235	235	250	255
Near infrared				
Wt % O as OH	0.67	0.68	0.47	0.50
Wt % N as NH	0.18	0.20	0.18	0.20
Wt % N as NH_2	0.08	0.06	0.06	0.09

Table 19

Distribution of Hydrogen in Oil Fractions

Oils in:	Area % NMR spectra				Wt % hydrogen			
	H_a	H_α	H_β	H_r	H_a	H_α	H_β	H_r
Unaged SRC blend	27.5	29.2	31.2	12.1	2.34	2.48	2.65	1.03
Air-aged SRC blend (68 days)	26.7	30.6	32.5	10.2	2.23	2.56	2.71	0.85
Unaged TSL SRC blend	29.9	26.7	30.3	13.1	2.59	2.31	2.62	1.14
Air-aged TSL SRC blend (72 days)	24.2	31.0	33.8	11.0	2.07	2.65	2.89	0.94

Table 20

NMR Structural Parameters of Average Oil Molecule

Oils in:	Structural parameters				
	C_A	f_a	R_A	R_N	n
Unaged SRC blend	10.5	0.60	2.1	1.0	1.1
Air-aged SRC blend (68 days)	10.5	0.60	2.1	1.2	1.0
Unaged TSL SRC blend	11.4	0.61	2.2	0.8	1.2
Air-aged TSL SRC blend (72 days)	11.0	0.58	2.2	1.2	1.1

Table 21

Boiling Point Distribution of Oil Fraction of Unaged SRC Blend by ASTM D2887[a]

% dist.	Temperature (°F)	% dist.	Temperature (°F)
IBP	417	60	707
5	475	70	752
10	510	80	804
20	559	90	884
30	604	95	943
40	633	99	1,012
50	667	FBP	1,022

[a] C_4 and lighter: 0.0%; C_3: 0.0%

D1160 Correlation from D2887

% dist.	Temperature (°F)	% dist.	Temperature (°F)
IBP	402	50	673
5	513	60	723
10	549	70	765
20	589	80	804
30	628	90	865
40	645	95	956

Table 22

Boiling Point Distribution of Oil Fraction of Air-Aged SRC Blend by ASTM D2887[a]

% dist.	Temperature (°F)	% dist.	Temperature (°F)
IBP	432	60	713
5	489	70	757
10	523	80	811
20	567	90	888
30	609	95	944
40	637	99	1,008
50	672	FBP	1,017

[a] C_4 and lighter: 0.0%; C_3: 0.0%

D1160 Correlation from D2887

% dist.	Temperature (°F)	% dist.	Temperature (°F)
IBP	410	50	676
5	530	60	730
10	561	70	772
20	595	80	812
30	631	90	869
40	647	95	958

Table 23

Boiling Point Distribution of Oil Fraction of Unaged TSL SRC Blend by ASTM D2887[a]

% dist.	Temperature (°F)	% dist.	Temperature (°F)
IBP	197	60	721
5	454	70	777
10	496	80	847
20	551	90	930
30	601	95	984
40	634	99	1,033
50	674	FBP	1,040

[a] C_4 and lighter: 0.0%; C_3: 0.0%

D1160 Correlation from D2887

% dist.	Temperature (°F)	% dist.	Temperature (°F)
IBP	289	50	683
5	496	60	745
10	518	70	807
20	585	80	858
30	629	90	913
40	649	95	1,008

Table 24

Boiling Point Distribution of Oil Fraction of Air-Aged TSL SRC Blend by ASTM D2887[a]

% dist.	Temperature (°F)	% dist.	Temperature (°F)
IBP	417	60	723
5	473	70	777
10	509	80	843
20	560	90	921
30	607	95	970
40	640	99	1,014
50	678	FBP	1,019

[a] C_4 and lighter: 0.0%; C_3: 0.0%

D1160 Correlation from D2887

% dist.	Temperature (°F)	% dist.	Temperature (°F)
IBP	380	50	686
5	510	60	744
10	549	70	803
20	591	80	852
30	632	90	903
40	653	95	993

Table 25

GC Conditions

GC	Perkin-Elmer 3920
Integrater	SP-4100
Column	15-m, 0.8 i.d., SE-52 glass capillary
Carrier Gas	Helium at 2.2 cm^3/min
Detector	FID
Detector temperature	275°C
Injector temperature	300°C
Detector range	X1
Detector makeup flow	30 cm^3/min
Oven temperature	50 to 275°C at 4°C/min
Split ratio	55 to 1
Sample size	0.2 µl
Integrator attenuation	X64

TABLE 26
COMPONENT TABLE

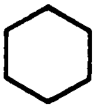
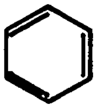
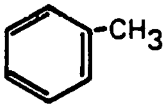
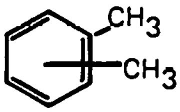
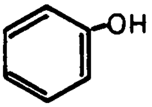
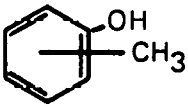
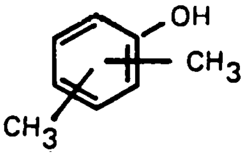
NAME	MW	BP (°F)	STRUCTURE
1. Pentane	72	97	$CH_3(CH_2)_3CH_3$
2. Hexanes	86	156	$CH_3(CH_2)_4CH_3$
3. Cyclohexane	84	178	
4. Benzene	78	176	
5. Heptane	100	209	$CH_3(CH_2)_5CH_3$
6. Toluene	92	232	
7. Octane	114	258	$CH_3(CH_2)_6CH_3$
8. Xylenes	106	280-284	
9. Phenol	94	328	
10. Methylphenol	108	348-366	
11. Dimethylphenols	122	412	

TABLE 26 (Continued)

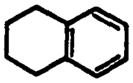
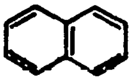
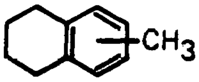
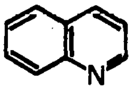
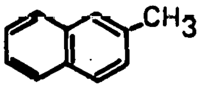
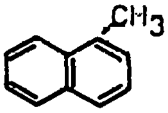
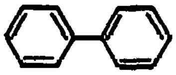
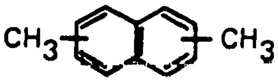
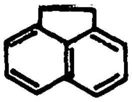
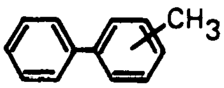
	NAME	MW	BP (°F)	STRUCTURE
12.	Tetralin	132	405	
13.	Naphthalene	128	424	
14.	Dodecane	170	421	$CH_3(CH_2)_{10}CH_3$
15.	Methyltetralin	146	–	
16.	Quinoline	129	460	
17.	2-Methylnaphthalene	142	466	
18.	1-Methylnaphthalene	142	472	
19.	Biphenyl	154	493	
20.	Tetradecane	198	488	$CH_3(CH_2)_{12}CH_3$
21.	Dimethylnaphthalenes	156	504-516	
22.	Acenaphthene	154	534	
23.	Methylbiphenyl	168	~514	

TABLE 26 (Continued)

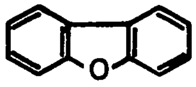
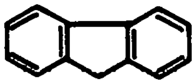
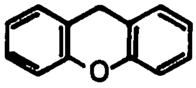
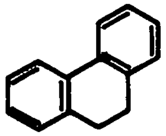
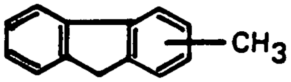
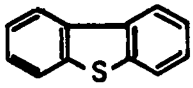
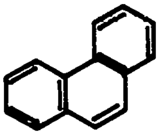
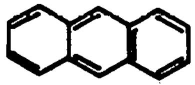
	NAME	MW	BP (°F)	STRUCTURE
24.	Dibenzofuran	168	549	
25.	Pentadecane	212	519	$CH_3(CH_2)_{13}CH_3$
26.	Fluorene	166	561	
27.	Hexadecane	226	548	$CH_3(CH_2)_{14}CH_3$
28.	Xanthene	182	594	
29.	9,10-Dihydrophenanthrene	180	551	
30.	Methylfluorenes	180	–	
31.	Heptadecane	240	576	$CH_3(CH_2)_{15}CH_3$
32.	Dibenzothiophene	184	600	
33.	Phenanthrene	178	644	
34.	Anthracene	178	644	
35.	Octadecane	254	602	$CH_3(CH_2)_{16}CH_3$

TABLE 26 (Continued)

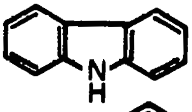
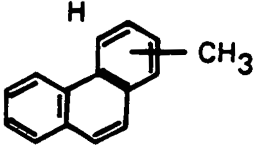
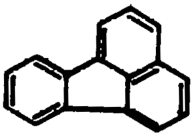
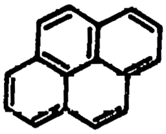
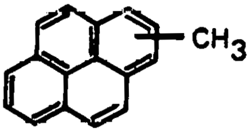
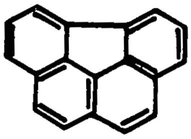
NAME	MW	BP (°F)	STRUCTURE
36. Carbazole	167	641	
37. Methylphenanthrenes	192	676	
38. Nonadecane	268	627	$CH_3(CH_2)_{17}CH_3$
39. Eicosane	283	641	$CH_3(CH_2)_{18}CH_3$
40. Fluoranthene	202	707	
41. Pyrene	202	739	
42. Heneicosane	297	674	$CH_3(CH_2)_{19}CH_3$
43. Docosane	311	606	$CH_3(CH_2)_{20}CH_3$
44. Methylpyrenes	216	–	
45. Tricosane	325	716	$CH_3(CH_2)_{21}CH_3$
46. Tetracosane	339	736	$CH_3(CH_2)_{22}CH_3$
47. Benzo(ghi)fluoroanthene	226	–	

TABLE 26 (Continued)

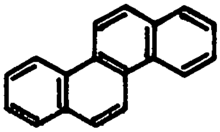
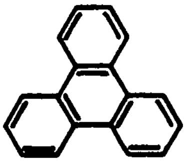
	NAME	MW	BP (°F)	STRUCTURE
48.	Chrysene	228	838	
	and/or			
	Triphenylene	228	838	
49.	Pentacosane	353	755	$CH_2(CH_3)_{23}CH_3$
50.	Hexacosane	367	774	$CH_3(CH_2)_{24}CH_3$
51.	Heptacosane	381	792	$CH_3(CH_2)_{25}CH_3$
52.	Octocosane	395	809	$CH_3(CH_2)_{26}CH_3$
53.	Nonocosane	409	825	$CH_3(CH_2)_{27}CH_3$
54.	Triacontane	413	841	$CH_3(CH_2)_{28}CH_3$

Table 27

Integrated Area Percent Relative to Boiling Range in Oils (Pentane Solubles)

Boiling range (°F)	Oils in: SRC blend Unaged	Oils in: SRC blend Air-aged (68 days)	Oils in: TSL SRC blend Unaged	Oils in: TSL SRC blend Air-aged (72 days)
IBP-350	0.08	0.07	0.13	0.07
350-450	1.55	0.73	1.42	1.15
450-550	14.54	12.38	13.36	14.29
550-650	23.73	22.86	21.18	22.30
650-750	24.30	23.66	22.08	22.22
760-FBP	35.80	40.30	41.83	39.97

Figure 1
Viscosity as a Function of Temperature

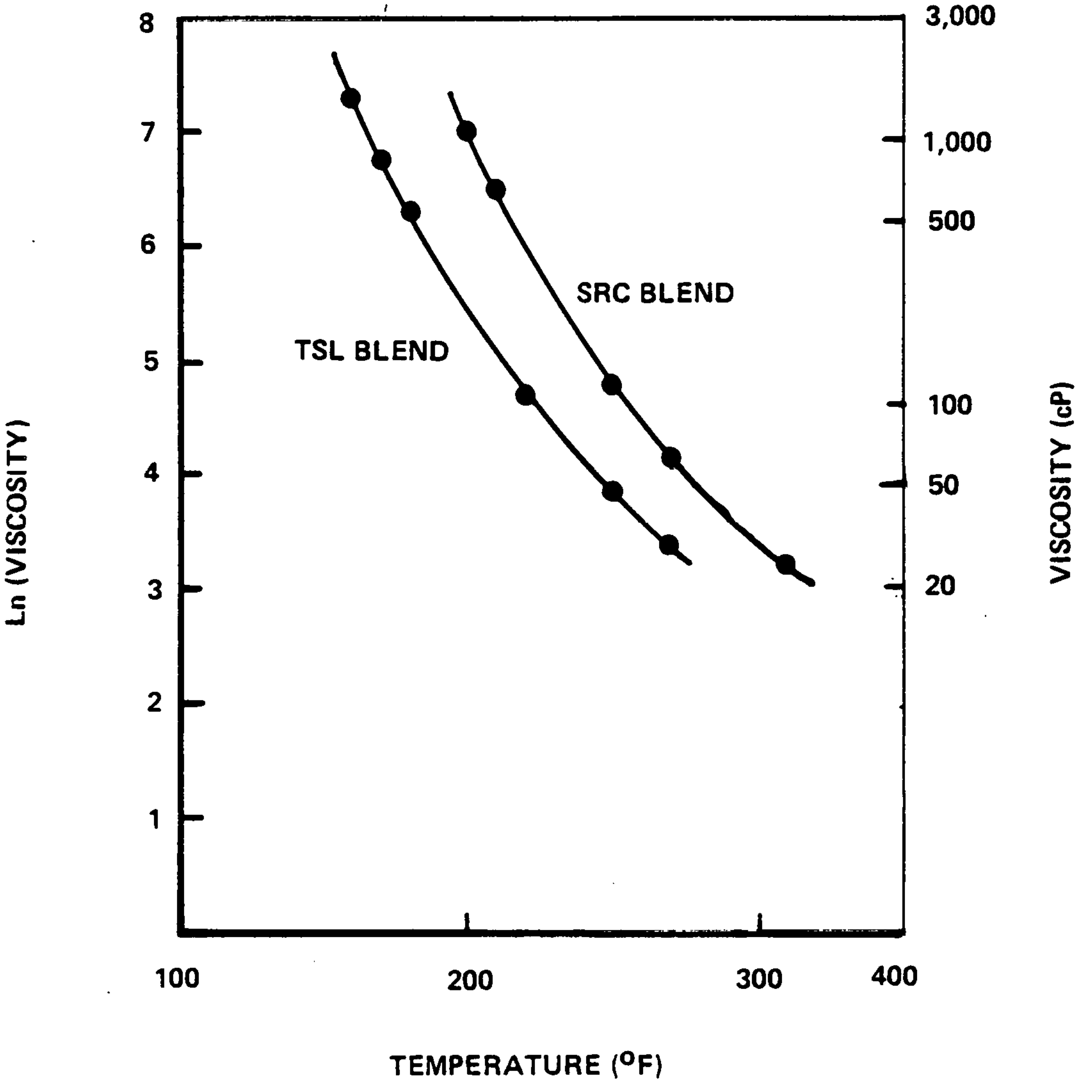


Figure 2
Viscosity Change on Storage of SRC Blend at 150°F in Air and Nitrogen Atmosphere

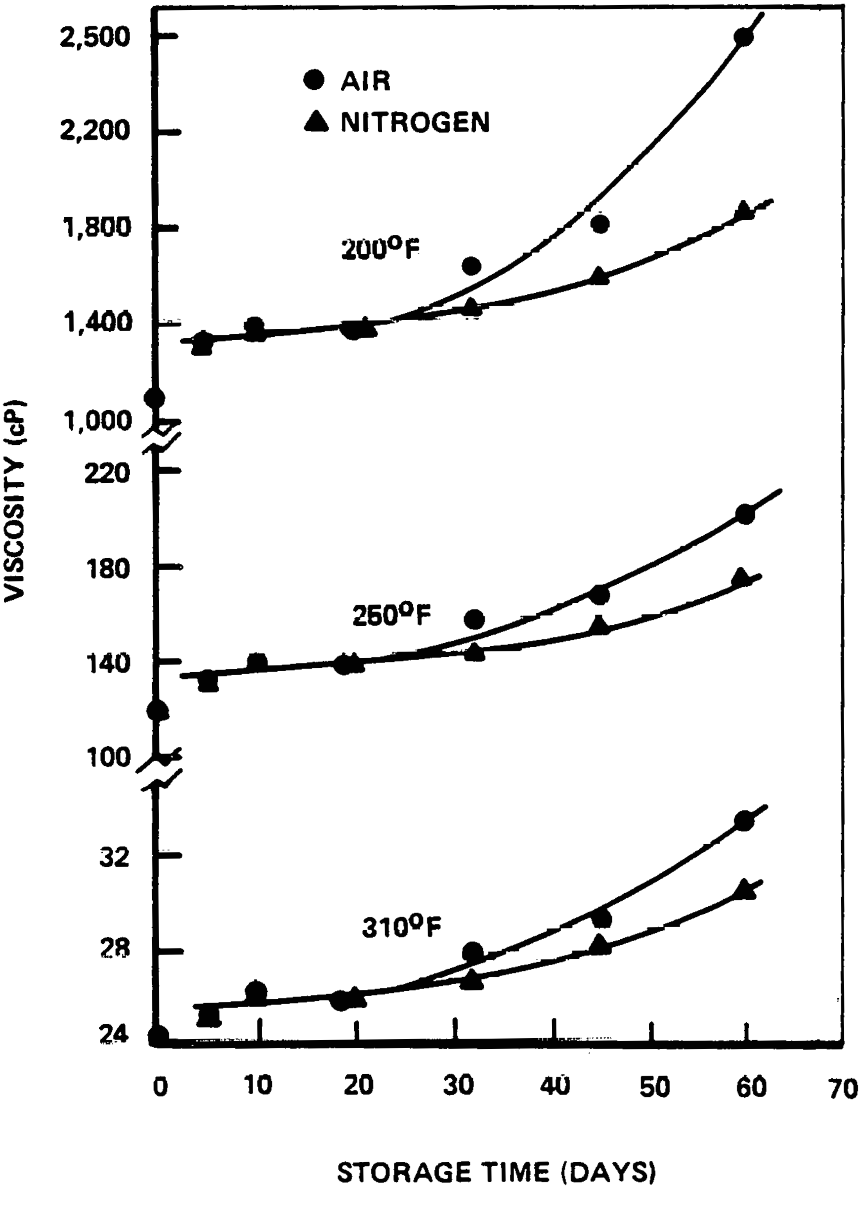


Figure 3
Viscosity Change on Storage of TSL Blend at 150°F in Air and Nitrogen Atmosphere

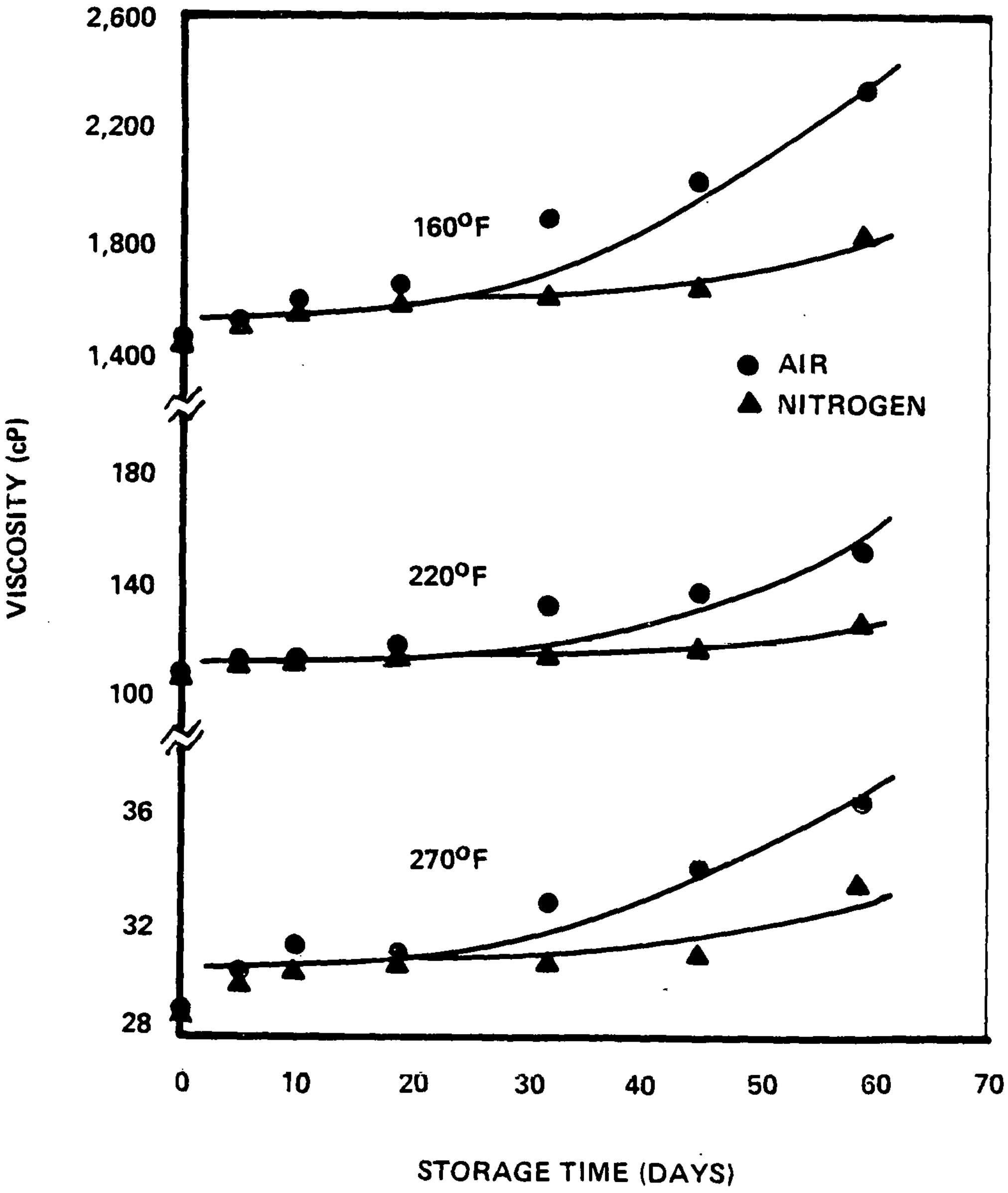
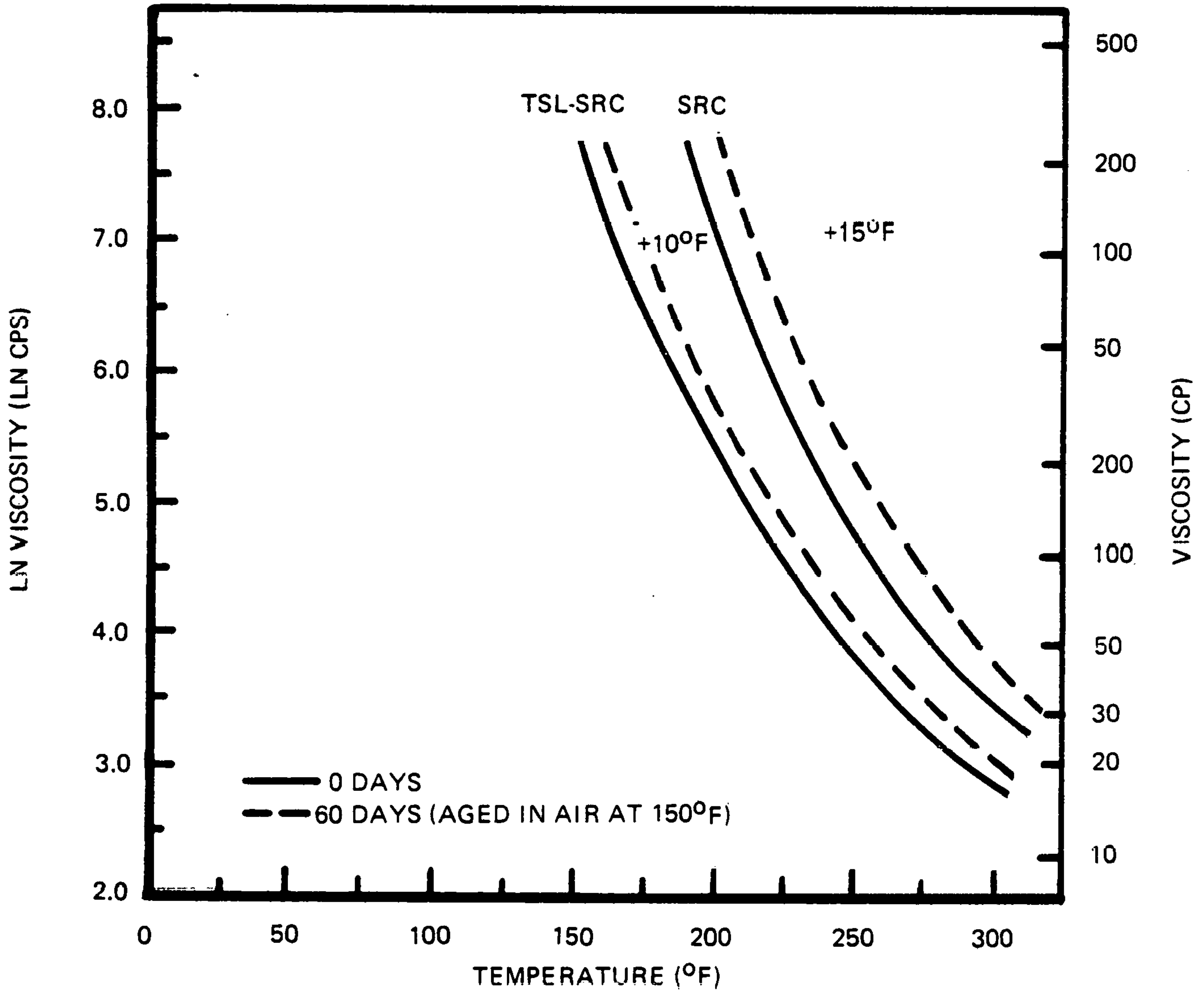


Figure 4
Temperature Increase Required to Achieve Original Blend Viscosity After 60-Day Aging*



*TEMPERATURE INCREASE REQUIRED TO BRING 60-DAY AGED BLENDS TO ORIGINAL VISCOSITY IS 10 AND 15°F, RESPECTIVELY, FOR TSL SRC AND SRC RESIDUAL OILS.

Figure 5
GC Chromatogram of Oils in Unaged SRC Blend

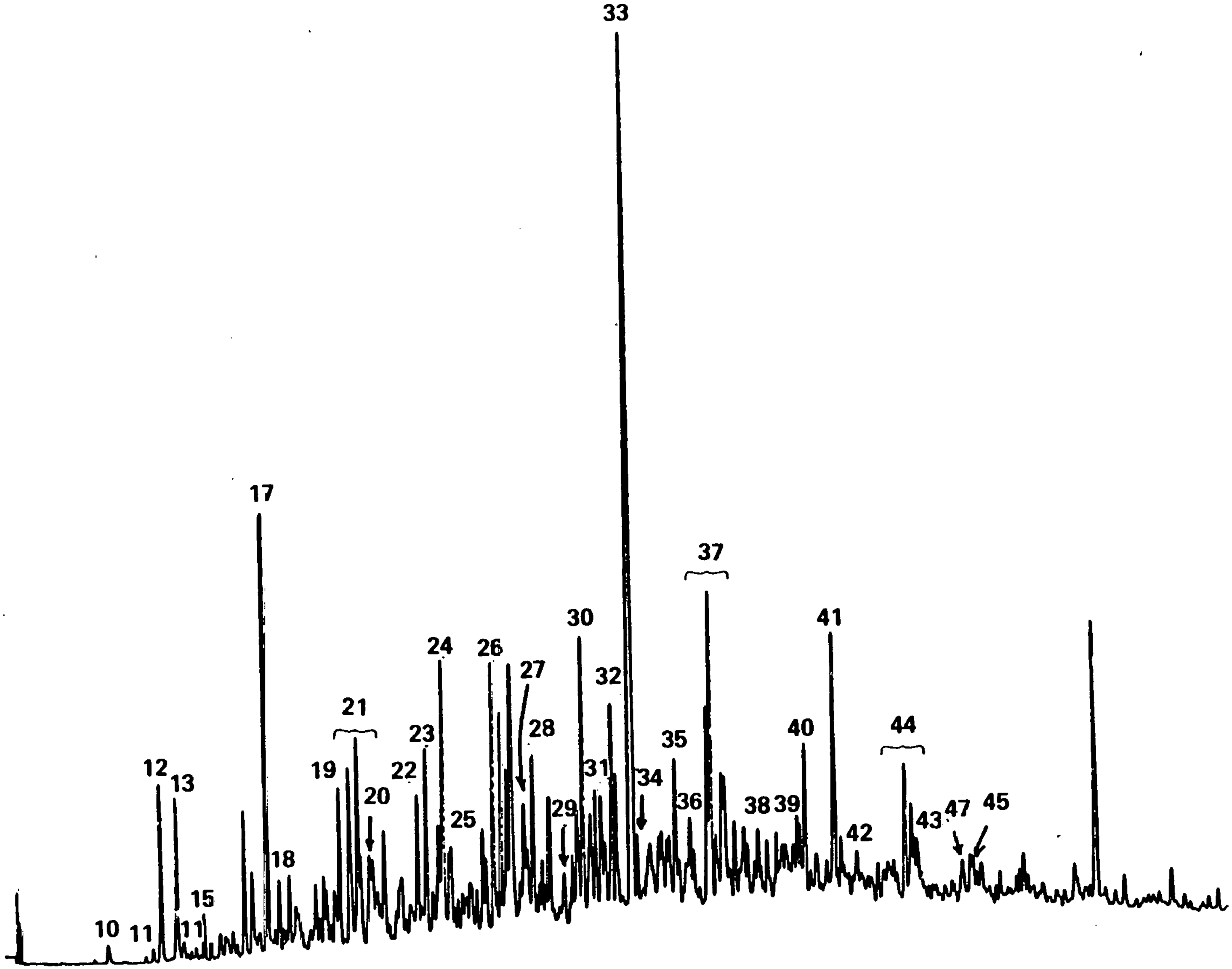


Figure 6
GC Chromatogram of Oils in Air-Aged SRC Blend (68 Days)

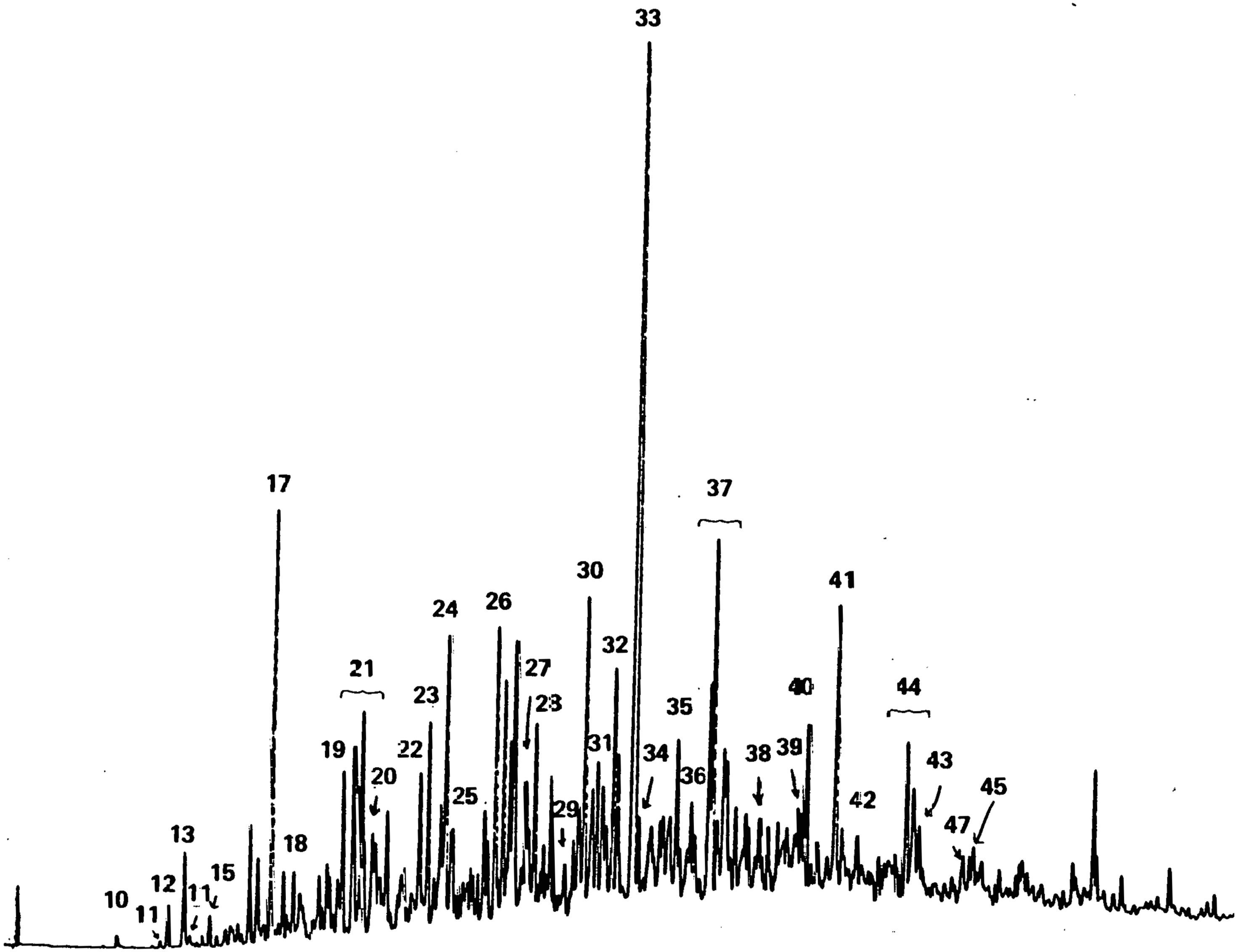


Figure 7
GC Chromatogram of Oils in Unaged TSL Blend

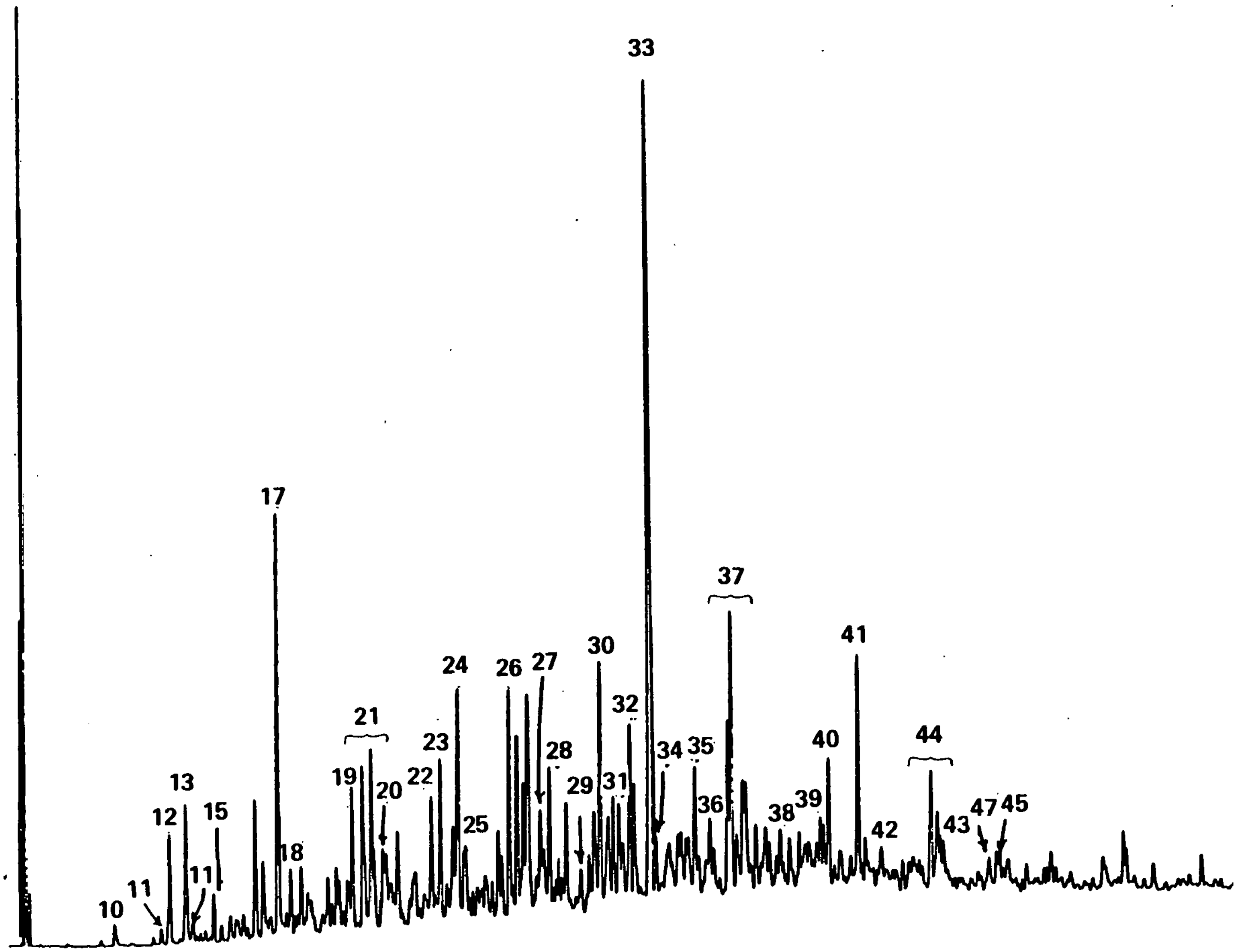


Figure 8
GC Chromatogram of Oils in Air-Aged TSL Blend (72 Days)