4.0 FISCHER-TROPSCH WAX CHARACTERIZATION PROGRAM (TASK 2)

Analytical techniques were developed by the Allied-Signal Engineered Materials Research Center, UOP's prime subcontractor in this program, which were capable of providing detailed molecular characterization of Fischer-Tropsch waxes. Some of the raw data and procedural information used to characterize the wax are attached as Appendix A.

4.1 DESCRIPTION OF WAXES

The molecular structures of four Fischer-Tropsch waxes were characterized using the analytical procedures developed in this program. The first wax was commercially produced in an Arge fixed-bed reactor. The other waxes were produced in pilot plants at Air Products and Chemicals, Inc., Union Carbide Corporation and Mobil Research and Development Corporation.

The Air Products wax was produced with a promoted cobalt catalyst at approximately 500°F, 1.0 CO/H_2 feed ratio and 300 psig reactor pressure (11). The Union Carbide wax was produced with promoted cobalt catalysts during a series of pilot plant runs at approximately 465-500°F temperature, 1.0 CO/H_2 feed ratio and 300 psig reactor pressure (12). The Mobil Wax was produced in a bubble column reactor at approximately 535°F, low H_2/CO ratio of 0.7 (1.4 CO/H_2), 165 psig and a precipitated iron catalyst (13).

4.2 BULK WAX ANALYSIS

Physical properties of these waxes have been obtained (Table 4.1) that provide useful information on the bulk characteristics of each material. Significant differences between these waxes have been observed, suggesting that the average molecular weight of each wax decreases in the following order: Mobil, Arge, Union Carbide and Air Products. For example, the specific gravity, initial boiling point, melting point and acetone insoluble content of the Mobil and Arge wax are higher than those of the Union Carbide and Air Products waxes.

4.2.1 Bulk Wax Analysis: GPC

Carbon number distributions for the waxes have been determined using a Gel Permeation Chromatography (GPC) technique. Average carbon numbers for each wax were also determined. GPC data showed large differences in the carbon number distribution range of each wax (Figure 4.1). The GPC technique called for dissolving each wax sample in an ortho-dichlorobenzene solvent followed by separation of the wax components over styrene divinylbenzene packing in a Waters ALC/GPC Model 150C chromatograph. Eluants were analyzed with a differential refractometer.

4.2.2 Bulk Wax Analysis: NMR

Quantitative NMR techniques were developed using a General Electric NT-300 instrument to determine hydrocarbon types, degree of branching and average molecular weight of the Fischer-Tropsch waxes. Carbon-13 NMR spectra showed that the major component in the commercial wax is linear paraffins (Figure 4.2). The largest resonance (29.8 ppm) indicates the presence of internal methylene carbons in linear paraffins longer than six carbon numbers. The other resonances (14.15, 27.8 and 32.8) arise from terminal n-propyl groups.

Average carbon numbers for the waxes were determined with the NMR data by comparing the peak area of the terminal propyl signals to that of the internal methylene peak. With the GPC analysis, average carbon numbers were determined by converting peak area percentage to component weight percent using correlations developed with paraffin standards of various carbon numbers. Relatively good agreement was observed between the average carbon numbers determined by these two methods (Table 4.2). As expected from physical properties and carbon number distribution data, the Mobil and commercial Arge wax have the highest average carbon number, followed by the Union Carbide and Air Products waxes.

The degree of branching was indicated by peaks from tertiary carbons (37.8 ppm) and methyl carbons (19.9 ppm). Other peaks appeared from methylene carbons in the branched molecules (24 to 29 ppm). Quantitative spectra from the Arge (Figure 4.3), Union Carbide (Figure 4.4), Air Products (Figure 4.5) and Mobil (Figure 4.6) on an expanded scale (21X) show peaks characteristic of terminal dimethyl groups, indicating that most of the branching occurs at the terminus of the molecule. Smaller peaks (33 ppm) are observed with the Union Carbide wax indicating internal methyl branching. Similar resonances are not observed with the other wax spectra; however, these signals may be masked by the base of other resonance peaks.

Ethers and alcohols are indicated by peaks (64 ppm) from oxy substituted methylene carbon. The locations of these signals indicate that the main oxygenates present are primary aliphatic alcohols. Unsaturated wax components are also suggested (110 and 140 ppm), but the peaks are broad and generally buried in the base line in all samples except the Air Products wax. This lack of resolution made quantification of the unsaturated components extremely difficult.

The percentage of total carbons in the wax that is branched has been determined by comparing the integrated area of the tertiary and methyl carbons to those of the terminal _n_-propyl and internal methylenes. This factor can be converted to the percentage of branched chain molecules by multiplying by the average carbon number (Table 4.3). Quantification of the alcohol and olefin was not feasible, because of the extremely low concentrations of these components.

4.2.3 Bulk Wax Analysis: IR

IR spectra of the waxes (Figures 4.7-4.10) were very similar, with long chain paraffins being the major component. Common IR absorption characteristics are carbon-hydrogen stretching (3100-2750 cm^{-1}) and methylene group bending (1467-1460 cm^{-1}). Faint alcohol bands (3700-3400 cm^{-1}) from O-H stretching, carbonyl absorption (1740 cm^{-1}), C-D stretching (1000-1300 cm^{-1}) and substituted vinyl groups (900-1000 cm^{-1}) are also indicated in the spectra. Although MS analysis could not differentiate between cycloparaffins and mono-olefins, both IR and NMR data showed mono-olefins to be the more abundant species in the commercial wax.

IR spectra were acquired during wax characterization using a Perkin-Elmer 580B Dispersive Infrared Spectrometer. Quantification of the wax components in each sample could not be achieved. The absence of pure component models and the insolubility of the waxes made it difficult to obtain samples of the same size for analysis.

4.3 WAX SEPARATION INTO FRACTIONS

Separating the Fischer-Tropsch waxes into relatively narrow carbon number fractions is an important step in developing MS techniques for characterizing the higher molecular weight components. In this fashion, the required hydrocarbon type matrix information, based on fragment ion peaks, can be directly obtained, and will be accurate for a particular carbon number range. Fragment ion peaks are strongly affected by the molecular weight of the sample being analyzed with the sensitivity of detection increasing with higher molecular weights.

4.3.1 Wax Separation: Distillation

To obtain these fractions, the Arge wax was first distilled using a modified ASTM D 1160 method designed to minimize thermal cracking by applying a carefully staged heat up and stirring procedure during the wax distillation. Thermal decomposition, however, was observed during the wax separation using this procedure, as seen by analysis of the separated wax fractions (Table 4.4). During the distillation procedure, thermal cracking was observed by the appearance of lower carbon number range materials in the distilled fractions, especially at cut points above 997°F.

4.3.2 Wax Separation: Solvent Solubility Procedure

As an alternative to distillation, a solvent separation procedure was developed that separated the wax into three carbon number fractions (Figure 4.11): acetone soluble (C_{13}-C_{42}), acetone insoluble (C_{34}-C_{80}) and cyclohexane insoluble (C_{50}-C_{250}). Each wax sample was separated into the above three fractions (Table 4.5) using this technique. The largest amounts of acetone insolubles are present in the Mobil wax, followed by the Arge, Union Carbide and Air Products. This is consistent with the physical properties and average carbon number of each wax material. However, despite a high acetone insoluble content, the Mobil wax has higher acetone soluble and lower cyclohexane insoluble content than the commercial Arge wax. Mobil wax was prepared in a Fischer-Tropsch synthesis reactor at a low H_2/CO ratio of 0.7. Hence, Mobil wax is much more olefinic and has a higher concentration of oxygenates compared to the Arge wax. Also, Mobil wax has a considerably higher degree of branching. These differences in chemical composition of the Mobil wax might account for the higher solvent solubility. As discussed later, IR absorbances have shown greater selectivity of branched and oxygenated compounds in the soluble fraction over the insoluble fraction.

Although the solvent separation technique was used, it was not ideal because of the relatively broad range of carbon numbers in the separated fractions. To achieve narrower carbon number fractions, a preparative GPC column was acquired and tested. This method was not successful because of the low wax solubility and high solvent volume required to obtain very small fractions. Efforts, therefore, were directed at developing MS techniques using the acetone soluble fractions (Table 4.5) and the lower molecular weight distillation fractions that did not decompose during separation (cuts 1 and 2, Table 4.4).

4.4 ANALYSIS OF WAX FRACTIONS

Four fractions of the acetone soluble Arge wax and distillation cuts were obtained using silica gel chromatography and were designated paraffins, olefins and oxygenates (Table 4.6). The paraffin and olefin fractions were eluted with hexane. The more polar oxygenates were desorbed from the column in a relatively sharp band with a 50/50 mixture of dichloromethane and methanol. Attempts were also made to separate the acetone insolubles. Extremely low solubility of these materials resulted in only poor separation and sample recovery. Molecular sieve separations, to obtain normal and branched paraffin fractions, and $AgNO_3$ separations to obtain paraffin and olefin fractions, were also unsuccessful.

4.4.1 Analysis of Wax Fractions (MS/EI)

The Kratos MS-30 high resolution spectrometer was used for analyzing the acetone soluble wax fractions. This instrument employs a standard electron impact (EI) source operated at high ionizing voltages. Samples were quantitatively introduced into the instrument through a specially designed all glass system operated at approximately 662°F. At these conditions, the acetone soluble material was the only fraction that could be vaporized into the MS instrument for analysis.

The instrument was set up according to a procedure described in ASTM D 2786 method. This is a low resolution MS method for determining hydrocarbon types of gas oil saturates including paraffins, cycloparaffins and monoaromatic type in average carbon number ranges from C_{16} to C_{32}. The relative amount of each type present was determined using fragment ion peak summation values most characteristic of that hydrocarbon type.

Several changes to the method, however, were required to allow analysis of the wax materials. First, the resolution of the instrument was increased to separate the oxygenated components from the hydrocarbon fragment ions. Second, the sensitivity coefficients of the ASTM matrix were adjusted to more adequately reflect the equilibrium distribution of the components characteristic of Fischer-Tropsch waxes. The silica gel fractions were used to determine the applicable sensitivity coefficients for the MS technique. Third, accurate masses were used instead of nominal masses to obtain matrix coefficients for the different hydrocarbon types. New peak summation values had to be derived for the oxygenated types.

MS analyses using this matrix determined the concentrations of each hydrocarbon type in the acetone soluble fraction of each wax (Table 4.7). This analysis showed that the Mobil and Arge wax had the highest concentrations of oxygenates (10-12 wt-%) while the highest paraffin concentrations were in the Air Products and Union Carbide waxes.

4.4.2 Analysis of Wax Fractions (MS/FAB)

The fast atom bombardment technique was employed for determining the molecular weight distributions and component types present in the Fischer-Tropsch waxes. This technique was used with a high performance Kratos MS-50 mass spectrometer operating at 10,000 resolution and a source potential of 8 kV. The FAB gun created a beam of fast xenon atoms (6-8 kV) at a source pressure of 5×10^{-5} torr. Under these conditions, a high flux atom beam was produced and aimed at a sample deposited on a probe tip target. Operating conditions were optimized to achieve maximum sample sensitivity.

FAB is a soft ionization surface analysis technique, which makes it possible to desorb ionized molecular ions of large organic molecules intact from a liquid matrix. Typically, samples to be analyzed are dissolved in a suitable matrix, such as glycerol, and placed on the probe tip. As the sample is depleted at the surface, it is replenished by other sample molecules from the matrix. This procedure allows for reproducible spectra to be obtained over an extended period of time.

Because of the poor solubility of these waxes, no suitable liquid matrix was found in which these waxes could be dissolved. When these waxes were analyzed directly as solids with the probe, no desorption of ions occurred. Preliminary experiments with the acetone soluble fraction, however, were undertaken with the standard Kratos FAB probe tip being manually heated prior to the sample being placed on the probe tip for analysis. These experiments proved the feasibility of utilizing a heated FAB probe tip. Accordingly, a resistance type heated probe was designed and built for analysis of the wax samples.

This heated FAB probe has two advantages. First, the lower concentration sample components in individual solvent extracted fractions are easier to detect because they are not diluted in a liquid matrix. Second, because the samples are not dissolved in a liquid matrix material, the interpretation of the data is less complicated, as the sample spectrum does not contain extraneous ion peaks or adducts from the liquid matrix material.

The positive-ion spectrum obtained with the heated probe in the molecular weight region of the acetone solubles from the commercial wax showed an array of abundant ion peaks. The advantage of using this technique was clearly seen when comparing the spectrum of this same sample taken under standard EI source conditions (Figure 4.12). The molecular weight distribution from EI spectra was composed mainly of lower molecular weight fragment ions. The cleaner appearance of the EI spectrum was due to the lower sensitivity of EI for the oxygenated components present in the sample.

FAB techniques were developed to obtain accurate masses of the wax materials by utilizing the n-paraffins, known to be the most abundant species in the wax, as the mass internal standards. These components produce relatively intense spectral peaks representing carbon numbers spaced apart by only 14.0156 atomic mass units, and are ideal standards for identifying unknown masses falling between the peaks. The accurate mass values were calculated for the (M-H)+ molecular ion peaks from C_{15}- C_{100} and stored in the computer as reference masses. Using these masses, the hydrocarbon and oxygenated types were identified as well as their carbon number range.

To determine the relative responses between the different compound types in the waxes, silica gel fractions (Table 4.6) were blended together to obtain a sample comprised of 50% paraffins, 40% cycloparaffins/mono-olefins and 10% oxygenated types. The relative intensity for each of these types in the major seven-carbon number range (C_{20}-C_{26}) for this sample showed that the monocycloparaffin/mono-olefin and oxygenates have much larger instrument responses than the paraffinic types (Figure 4.13). Accordingly, this makes these components easier to detect at the low concentration levels in the wax samples.

Carbon number distributions for each compound type detected and their relative abundances are shown for three acetone soluble waxes (Figures 4.14-4.16). Corrections were made to the C_{17} and C_{18} peak intensities, due to the small amount of fragmentation that occurred from the higher molecular weight components present. In most cases the carbon number range for the paraffins present in each wax was from about C_{17} through C_{35} and was in good agreement with GC data. The olefins and both single and double oxygenated paraffinic species were also detected in each wax. Air Products wax showed only a trace amount of detectable dioxygenates, while the rest of the waxes contained relatively large concentrations of these heteroatom species. Union Carbide wax had the dioxygenates skewed toward the lower carbon number values.

The concentrations of the paraffins, CyP/MO and single oxygenated types were seen to vary between samples, and attempts to relate these differences even qualitatively with the quantitative MS data were not feasible. This was expected, since the FAB is a qualitative surface ionization technique and, therefore, it is impossible to reproduce peak intensities, since the ionization reaction occurring on the probe tip cannot be controlled. Nevertheless, the MS/FAB technique allowed us to determine the presence of oxygenated compounds, number of heteroatoms present and their molecular weight range.

When the acetone insolubles were analyzed, however, no molecular ion peaks could be detected in the spectrum. The major reason for this was attributed to the very wide carbon number range for these fractions of about 50-75 carbon atoms as compared with only about a 35 carbon atom spread for the acetone soluble fractions. Also, the decrease in molecular ion sensitivity associated with higher molecular weight may result in an instrument response, at 10,000 resolution, not great enough for analyzing the insoluble fractions. Increasing the instrument sensitivity by a factor of five and operating at 2000 resolution still did not produce detectable molecular ion peaks.

4.5 ANALYSIS OF TOTAL WAX

Quantitative characterization of the total waxes was attempted using MS analyses of acetone soluble fractions combined with IR, NMR and GPC data for the acetone soluble as well as total waxes. Infrared spectroscopy data for the separated fractions from the commercial Arge wax showed greater selectivity of branched and oxygenated compounds in the acetone soluble fraction over the acetone insoluble fraction (Table 4.8). When the total IR absorbances (normalized) for all oxygenate compounds were compared, it was seen that the concentration of all oxygenate compounds in the acetone soluble fraction was greater than that in the total wax by a factor of two. Also, the olefin fraction was equally distributed between the acetone soluble and the insoluble fraction. Based on all these observations, the composition of total wax was predicted (Table 4.9). The Mobil and Arge commercial wax are much higher in oxygenated species while the Air Products and Union Carbide wax are more paraffinic. The Mobil wax has more olefins, oxygenates and branched molecules than any of the other waxes.

4.6 FINDINGS AND CONCLUSIONS

4.6.1 Comparison of Analytical Data

A direct comparison between MS and the other analytical techniques used cannot be made, since the total waxes could not be completely vaporized into the MS. Nevertheless, a rough quantitative characterization of the total wax was attempted, because this information may provide a better perspective for predicting hydrocracking processibility. This was accomplished by using the quantitative MS analyses of the acetone soluble fractions combined with IR, NMR and GPC data on the acetone solubles as well as the total waxes. The following comparison of the data was made for supporting this kind of analytical approach.

It was necessary to know the selectivity of dissolution between the various species during solvent separation. Comparison of the solvent separated fractions from the commercial Arge wax by IR (Table 4.8) indicated that some selectivity differences occur for the molecules having more -CH_3 groups (branching) in the acetone soluble over the acetone insoluble fractions. This is consistent with NMR data (Table 4.3), which also shows more branching as a percent of total carbon in the Arge wax acetone solubles. These molecules have a greater acetone solubility over their n-paraffin analogs. Comparison of the long chain -CH_2 group absorbances in these fractions also indicates that solubility of the branched paraffins is greater than the n-paraffins. However, IR cannot give information on the average carbon number or the molecular weight range of the wax. These data can be obtained from GPC and GC analyses that provide both average carbon number and carbon number range on the total wax. NMR can also provide data on the average carbon number of the total wax as well as the degree of branching.

The determination of the oxygenated compounds in the total wax was more difficult due to the presence of many different species at relatively low concentration levels. The approach taken was to quantitatively determine the total oxygenated types (both single and diheteroatoms) by MS in the acetone soluble fractions and to relate their concentration to the total wax. The IR analysis indicated some selectivity difference for the oxygenates over the insoluble fractions during the solvent separation of the commercial wax with acetone. This was seen by an increase in the absorbance ratios for the -OH, alcohols/acetals, aromatic oxygenates and esters functionalities. NMR also showed the presence of aliphatic (mainly primary) alcohols, but due to their low concentrations quantification was difficult. More importantly it was seen by both NMR and IR that aliphatic alcohols were present in all the fractions, which suggests their existence in the higher carbon number range. Comparison of the total IR ratios of aliphatic alcohol functionalities showed that there was approximately a two-fold increase in the acetone solubles over the total wax.

The IR analyses for the olefin functional group indicates no real differences between the acetone soluble and insoluble fractions. There was a slight drop in the olefin ratio for the cyclohexane insolubles, but upon comparison with the total sample one may infer very little selectivity, if any, had taken place.

No discrimination could be made between the olefins and cycloparaffins with the MS analysis, but the presence of olefins was detected by both NMR and IR. An attempt was made to quantify the olefins present by NMR in the acetone fraction of the commercial wax and an estimate of 4 wt-% (Table 4.3) was obtained. This compares favorably with the 5.2 wt-% obtained by MS and, therefore, the data suggest that olefins and not the cycloparaffins are the more prevalent species present in the commercial wax. The MS analysis of the acetone fractions for the total waxes in Table 4.7 shows an increase in the concentration of CyP/MO over the commercial wax. These changes in concentrations also generally follow the changes in ratios seen with IR analysis in Table 4.8 which also implies that the major type for CyP/MO are the mono-olefins.

Based on all of the above data, it is believed that the MS data for the total paraffins in the acetone solubles closely represents that of the total waxes. Using IR data, the concentration of the oxygenates in the total wax was estimated to be about one half of that present in the acetone fraction. Using this basis, the total oxygenates in the acetone fraction were reduced by one half and the remainder of the types normalized to 100%. The estimated composition of the total wax is shown in Table 4.9. The Air Products sample was the only one that does not show a significant change since the acetone solubles represent 90% of the sample.

4.6.2 Conclusions

Although good analytical data were obtained for comparing the composition of Fischer-Tropsch waxes, there was difficulty in completely characterizing the higher molecular weight species present in the "insolubles" fractions. Nevertheless, an estimated quantitative characterization of the total wax was attempted and is shown in Table 4.9.

The Union Carbide and Air Products waxes have the highest concentrations of paraffins at about 90 wt-%, and they also have a high degree of branching (13 and 44%). NMR analyses indicated that most of the branching occurs at the terminus of the molecule. The Arge commercial wax has the lowest amount of branching with only 2.3% of the molecules being branched. One explanation for the lower branching in the Arge waxes would be due to the iron catalyst as compared with the cobalt catalyst system used in producing the Union Carbide and Air Products waxes. This may also be a factor in the lower average carbon number seen for these waxes.

The lowest concentration of olefins/cycloparaffins (5.2 wt-%) was present in the commercial Arge wax. Air Products wax had 7.0 wt-% and Union Carbide wax had 6.1 wt-%. Mobil wax had by far the largest concentration of olefins/cycloparaffins with 20.6 wt-%. This observation is consistent with the low H_2/CO ratio of 0.7 used in the Mobil Fischer-Tropsch synthesis reactor. Both NMR and IR suggests that most of the olefins are vinyl substituted. It was also believed that the average carbon number would be similar to the paraffins for each wax, but it is difficult to establish this for the olefins/ cycloparaffins present.

The diolefins and aromatic types were present in too low a concentration to be characterized. However, the mass spectral fragment ions detected suggest long chain alkylbenzenes.

Comparison of the total oxygenated species present for the waxes in Table 4.9 shows that the Mobil wax had the highest concentration with 10 wt-%, followed by Arge wax with 6 wt-%, and the rest of the waxes in the range of 2-3 wt-%. The IR spectra also show that the aliphatic alcohols are one of the major oxygenates present, and NMR data suggest that primary alcohols would be the major oxygenate present in each wax. MS/FAB analysis shows that in addition to the single oxygenated species, double oxygenated components are also present and extend through the entire carbon number range to about C_{35}. The IR spectra suggest that esters are the major dioxygenates present in these waxes.

Table 4.1

Bulk Properties of Fischer-Tropsch Waxes

Analysis Type	Commercial Arge Wax	Union Carbide	Air Products	Mobil	Petroleum Feeds A	Petroleum Feeds B
API	22.3	29.9	39.0	20.4	23.5	23.7
Specific Gravity	0.9200	0.8767	0.8299	0.9317	0.9129	0.9117
IBP, °F	597	547	417	518	586	602
Carbon, wt-%	85.2	85.3	85.2	84.4	85.1	86.2
Hydrogen, wt-%	14.7	14.7	14.8	15.3	12.3	13.0
Elemental Oxygen, wt-%	0.1					0.1
Sulfur, ppm	80	<100	<100	4	10860	2500
Nitrogen, ppm	16	0.1	10	3	1700	300
Aniline Point, °F	293	258	239	298	189	215
Melting Point, °F	220	196	156	203		
Viscosity, cSt @ 250°F	7.59	3.70	2.31	12.44	7.64	4.99
Conradson Carbon, wt-%	<0.1	<0.1	<0.1	<0.1	0.40	0.05
n-C_7H_{16} Insolubles, wt-%	24.4	0.44	<0.1	22.6		

Table 4.2

Comparison of NMR and GPC Average Carbon Number Data

Wax	GPC	NMR
Commercial Arge Wax	43	47
Air Products	26	23
Union Carbide	29	28
Mobil	48	51

Table 4.3

Branching by NMR

Wax	Ave. Carbons	% Branched Molecules	(% Total C)	% of Alcohols	Olefins
Commerical Arge Wax	47	2.3	(0.05)	9.4	4*
Air Products	23	44	(1.9)	P	P
Union Carbide	28	13	(0.45)	P	P
Mobil	51	31	(0.61)	P	P
Arge Wax Breakdown					
Total Wax	47	2.3	(0.05)	9.4	4*
Acetone Solubles	22	2.2	(0.10)	P	P
Total Insolubles	51	2.3	(0.05)	P	P

P-Present

*-Estimate

Table 4.4

Distillation of Fischer-Tropsch Arge Wax

Cut Number	Weight Percent	Boiling Range, °F	Carbon Number Range
1	9.0	IBP-752	C_{11}-C_{32}
2	9.1	752-865	C_{17}-C_{40}
3	8.8	865-914	C_{12}-C_{56}
4	9.0	914-955	C_{21}-C_{56}
5	8.4	955-997	C_{27}-C_{62}
6	8.5	997-1,036	C_{24}-C_{71}
7	8.5	1,036-1,072	C_{16}-C_{80}
8	4.9	1,072-1,074	C_{6}-C_{80}
Bottom	33.8	1,074+	C_{9}-C_{250}
Total	100.0		

Table 4.5

Solvent Separated F-T Waxes

Feedstock	Acetone Soluble	Acetone Insoluble Wt-%	Cyclohexane Insoluble
Arge Commercial Wax	28	41	31
Air Products	90	9	1
Union Carbide	56	25	19
Mobil	41	54	5

Table 4.6

Silica Gel Separation of Arge Wax Fractions

Fraction No.	Solvent	Expected Composition	Wt-% Cut 1	Wt-% Cut 2	Wt-% Acetone Solubles
1	10 mL *n*-hexane	Paraffins	85.1	90.0	86.0
2	10 mL *n*-hexane	Olefins	5.3	2.9	
3	130 mL *n*-hexane	Olefins	0.6	0.2	
4	50 mL 50/50 CH_3OH/CH_2Cl_2	Oxygenates	9.0	6.9	14.0
		Totals*	100.0	100.0	100.0

Table 4.7

Mass Spectrometry - EI
Comparison of the Acetone Solubles for Four F-T Waxes

HRMS Types Analysis - Wt-%*

Composition	F-T Wax: Commercial Arge Wax	Air Products	Union Carbide	Mobil
Paraffins	82.4	89.7	88.8	57.5
CyP/MO	5.2	7.0	6.1	20.6
DiCyP/DO/MCyMO	0.1	0.2	0.1	1.2
Aromatics	0.3	0.2	0.5	0.7
Oxygenates	12.0	2.9	4.5	20.0

---

* Estimated accuracy ± 10% relative. Tenths shown only for normalization purposes.

Table 4.8

Qualitative Comparisons of IR Functional Group Absorbances

Proposed Functionality	Commercial Arge Wax				Air Products	Union Carbide	Mobil
	Acetone Solubles	Acetone Insolubles	Cyclohexane Insolubles	Total	Total	Total	Total
CH_2	16.8	16.6	21.3	20.2	11.2	8.81	16.7
CH_3	0.155	0.090	0.060	0.121	0.204	0.122	0.130
Long Chain-CH_2	0.243	0.504	0.576	0.515	0.244	0.375	0.421
Olefinic	0.019	0.018	0.013	0.017	0.020	0.023	0.058
Asymmetric Aromatic							
Aromatic Breathing/CH_2	0.028	0.037	0.049	0.039	0.028	0.036	0.040
OH	0.160	0.054	0.049	0.061	0.020	0.029	0.058
Aliphatic Alcohol/Acetal	0.070	0.029	0.022	0.030	0.020	0.008	0.023
Ester/Alcohol	0.053	0.010	0.003	0.030	0.040	0.027	0.031
Aliphatic Ether	0.002	0.006	0.001	0.005	0.005	0.004	0.000
Ester/Alcohol	0.033	0.028	0.028	0.025	0.002	0.010	0.039
Esters	0.012	0.002	0.008	0.007		0.008	0.009
Ketone/Aldehyde	0.015	0.010	0.005	0.012	0.004	0.008	0.037
Carboxylate			0.001				

Data reported as absorbance area relative to the CH_2 functionality.

Table 4.9

Composition of Total Fischer-Tropsch Waxes

Wax Identification	Commercial Arge Wax	Air Products	Union Carbide	Mobil
	Wt-% Hydrocarbon Types			
Paraffins	88.0	89.7	90.5	64.6
Mono-olefins (major type)	5.6	7.0	6.2	23.2
Diolefins (major type)	0.1	0.2	0.1	1.4
Monoaromatics	0.3	0.2	0.5	0.8
Oxygenates (aliphatic alcohols major type)	6.0	2.9	2.7	10.0
	% Branched Molecules			
	2.3	44.0	13.0	31.0
	Average Carbon Number			
	43	26	29	48

FIGURE 4.1

CARBON NUMBER DISTRIBUTIONS
GPC ANALYSIS

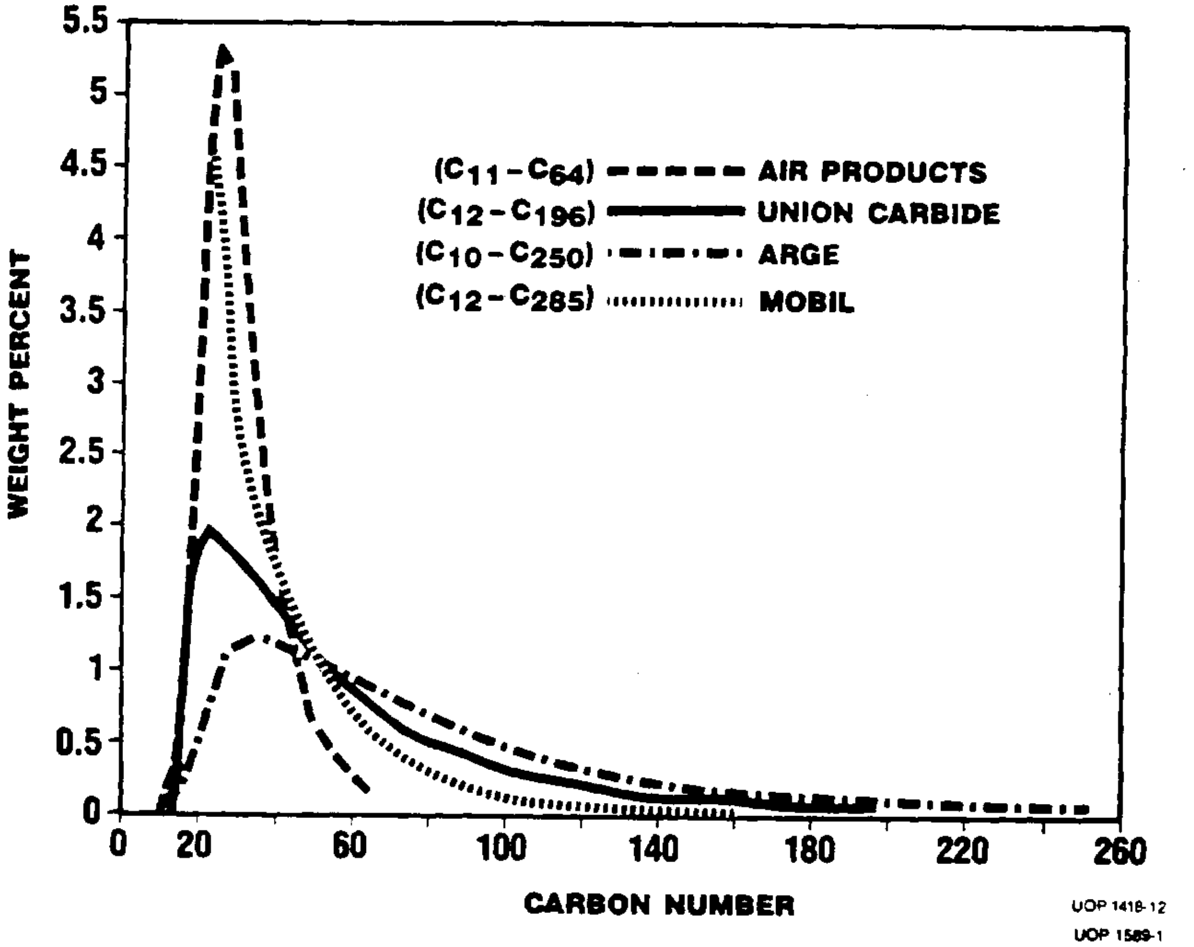
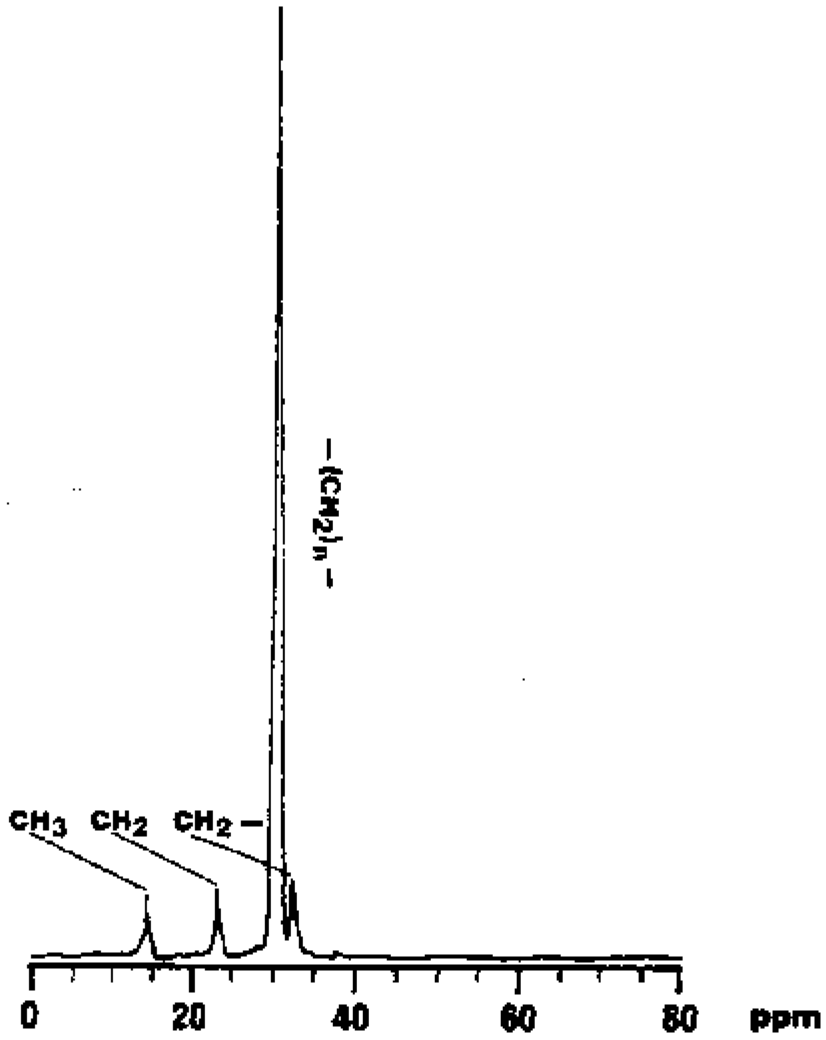


FIGURE 4.2

COMMERCIAL ARGE WAX

C_{13} NMR SPECTRUM



UOP 1545-48
UOP 1589-2

FIGURE 4.3

COMMERCIAL ARGE WAX

C_{13} NMR SPECTRUM

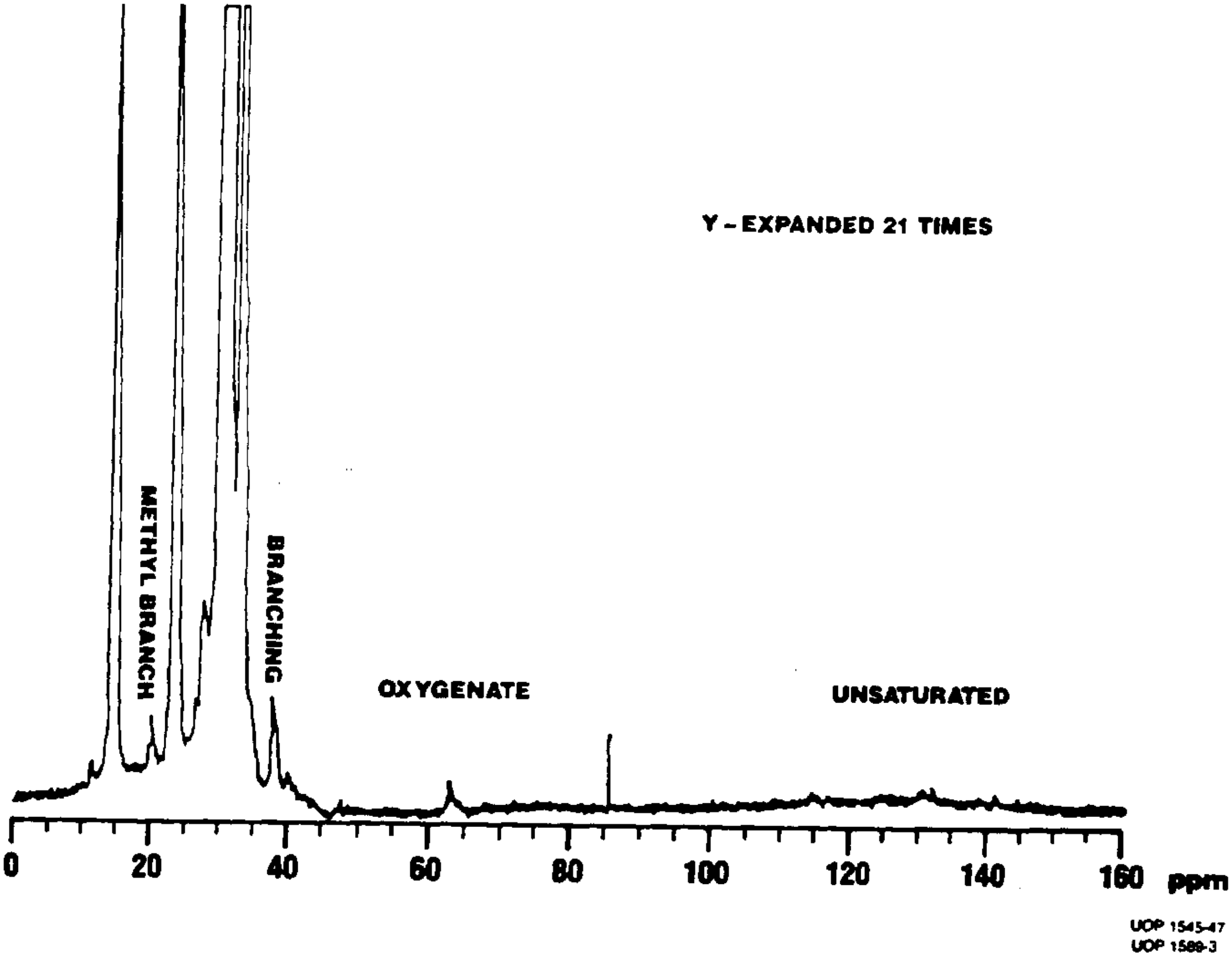
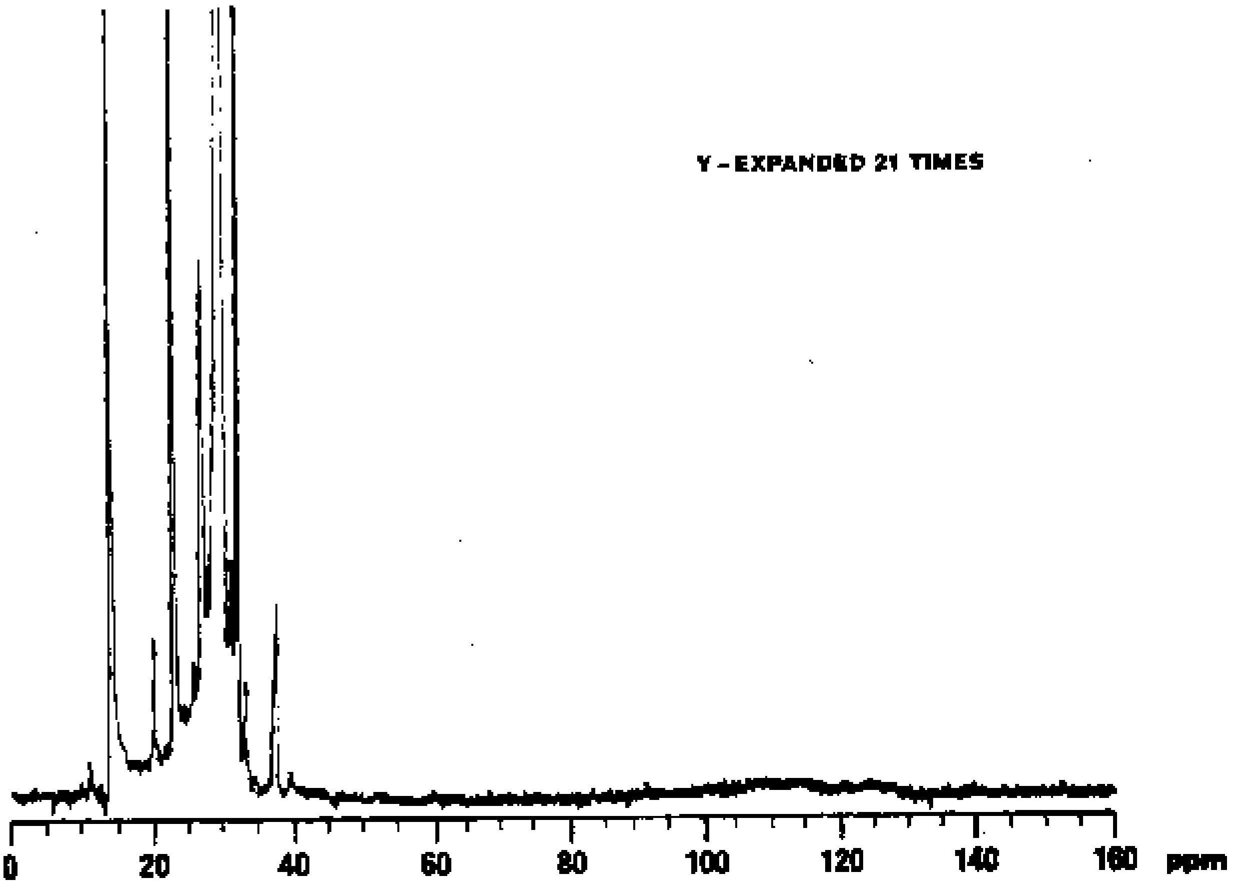


FIGURE 4.4

UNION CARBIDE WAX

C_{13} NMR SPECTRUM

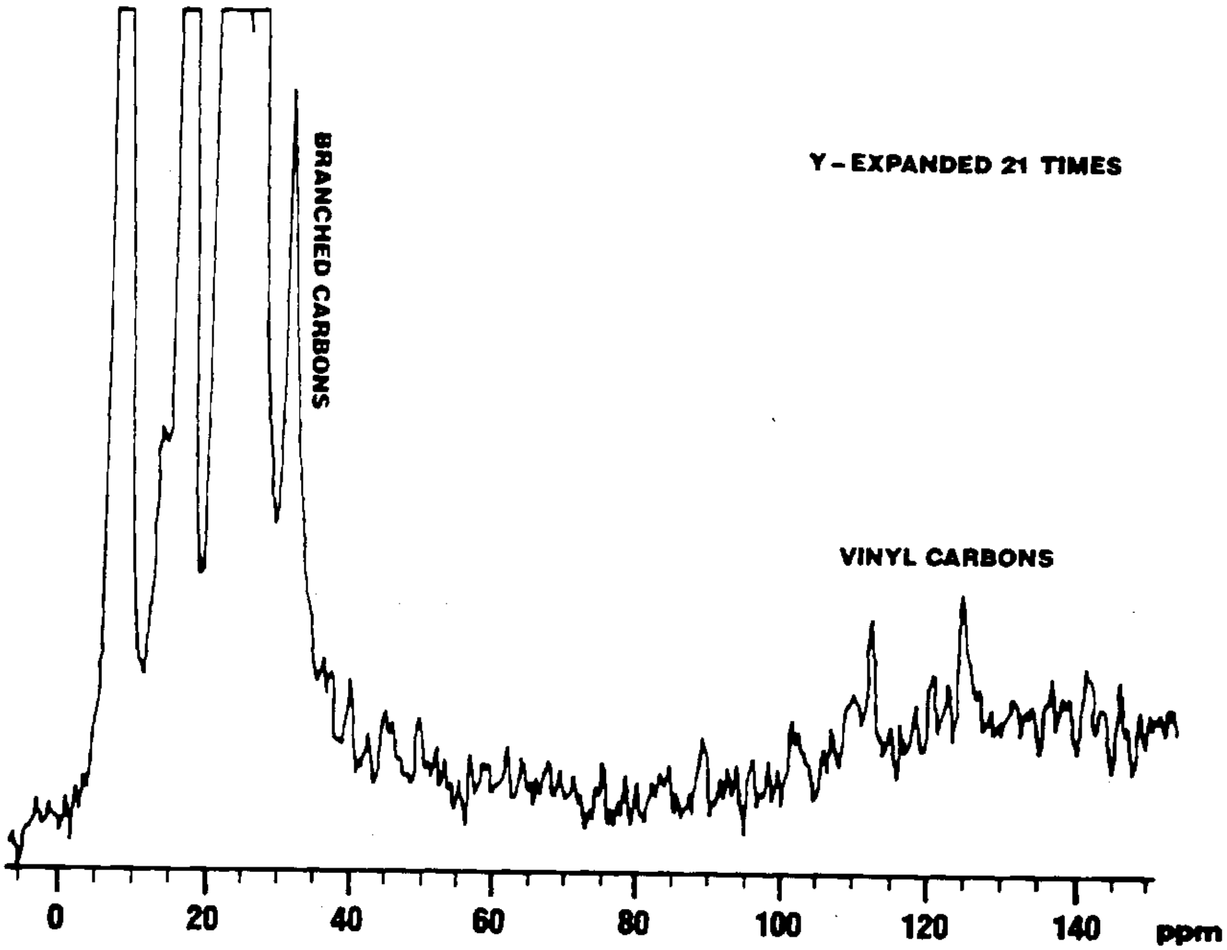


UOP 1545-49
UOP 1669-5

FIGURE 4.5

AIR PRODUCTS WAX

C_{13} NMR SPECTRUM



UOP 1545-48
UOP 1589-4

FIGURE 4.6

MOBIL WAX
C_{13} NMR SPECTRUM

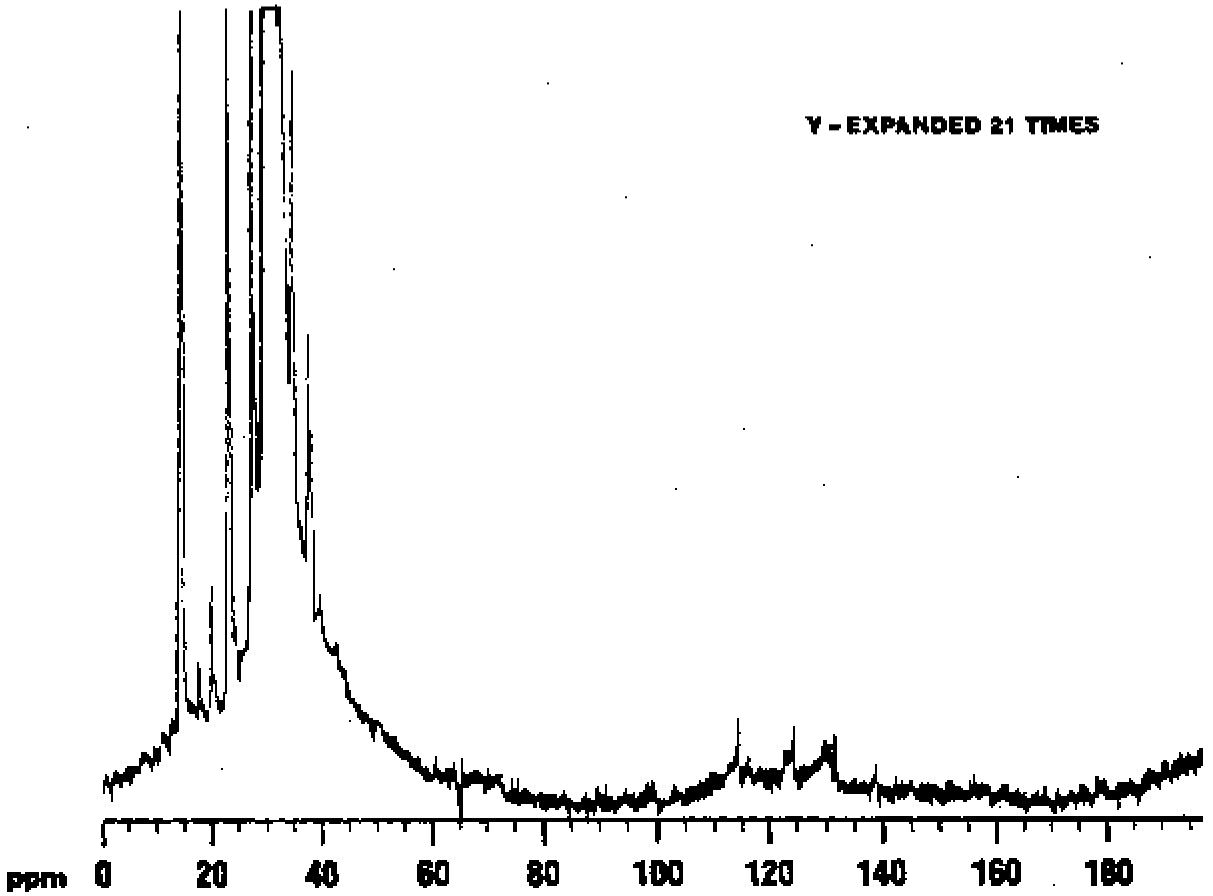


FIGURE 4.7

IR SPECTRUM ARGE WAX

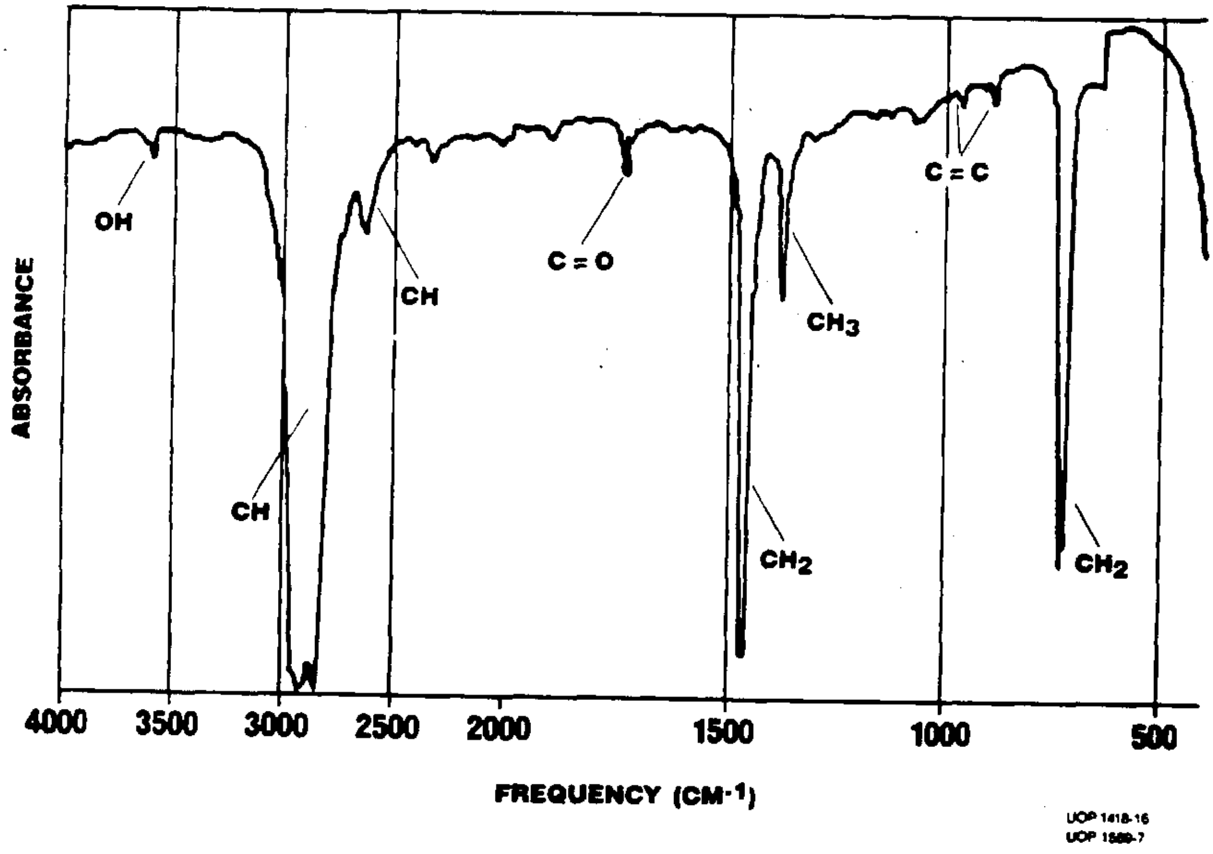
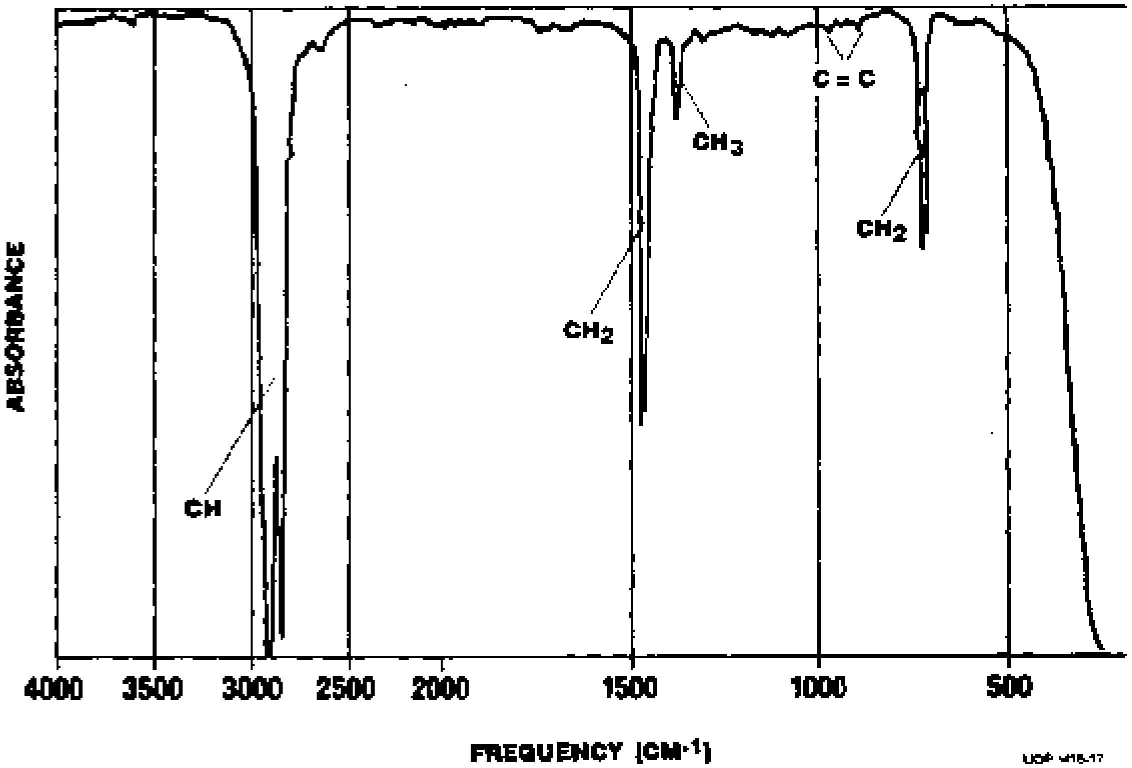


FIGURE 4.8

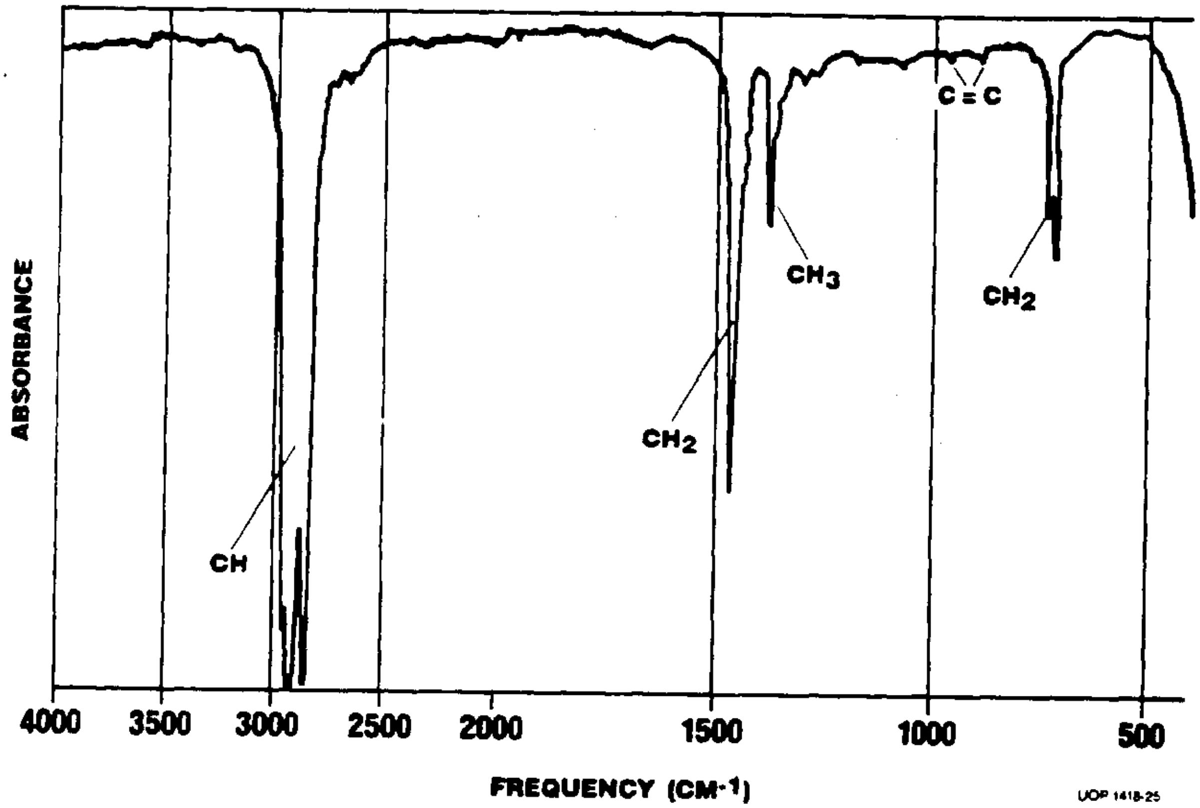
IR SPECTRUM
UNION CARBIDE WAX



UOP 418-17
UOP [illegible]

FIGURE 4.9

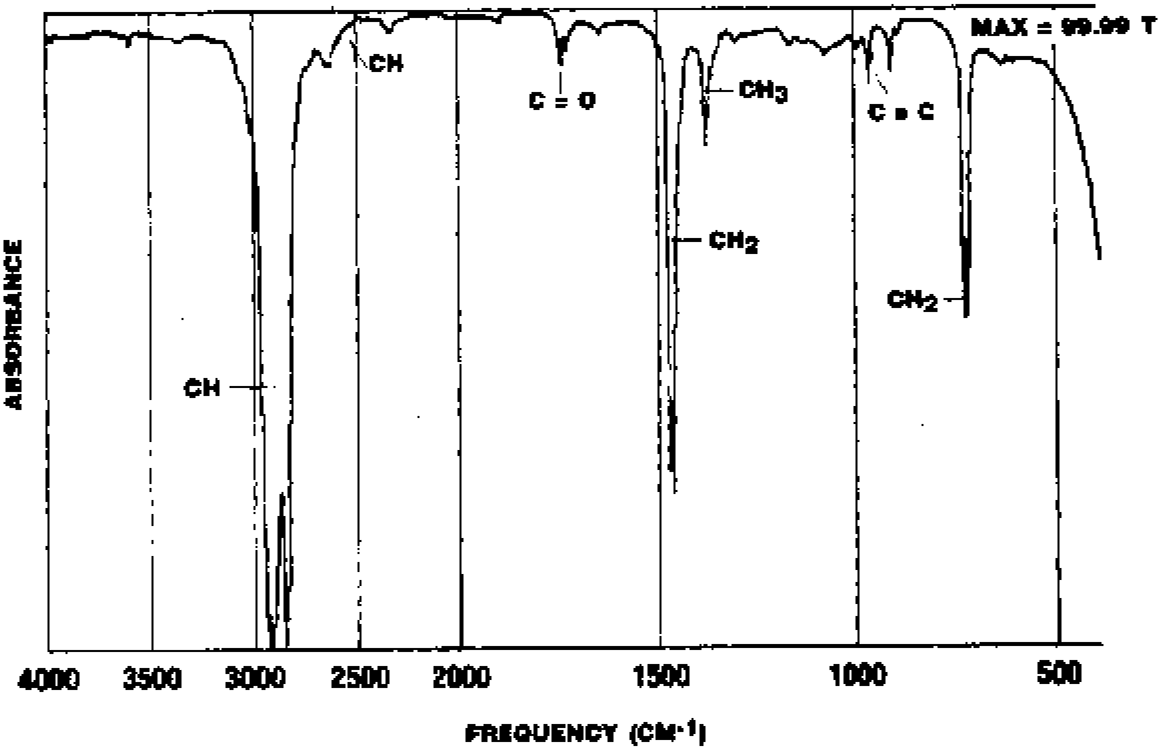
IR SPECTRUM
AIR PRODUCTS WAX



UOP 1418-25
UOP 1589-9

FIGURE 4.10

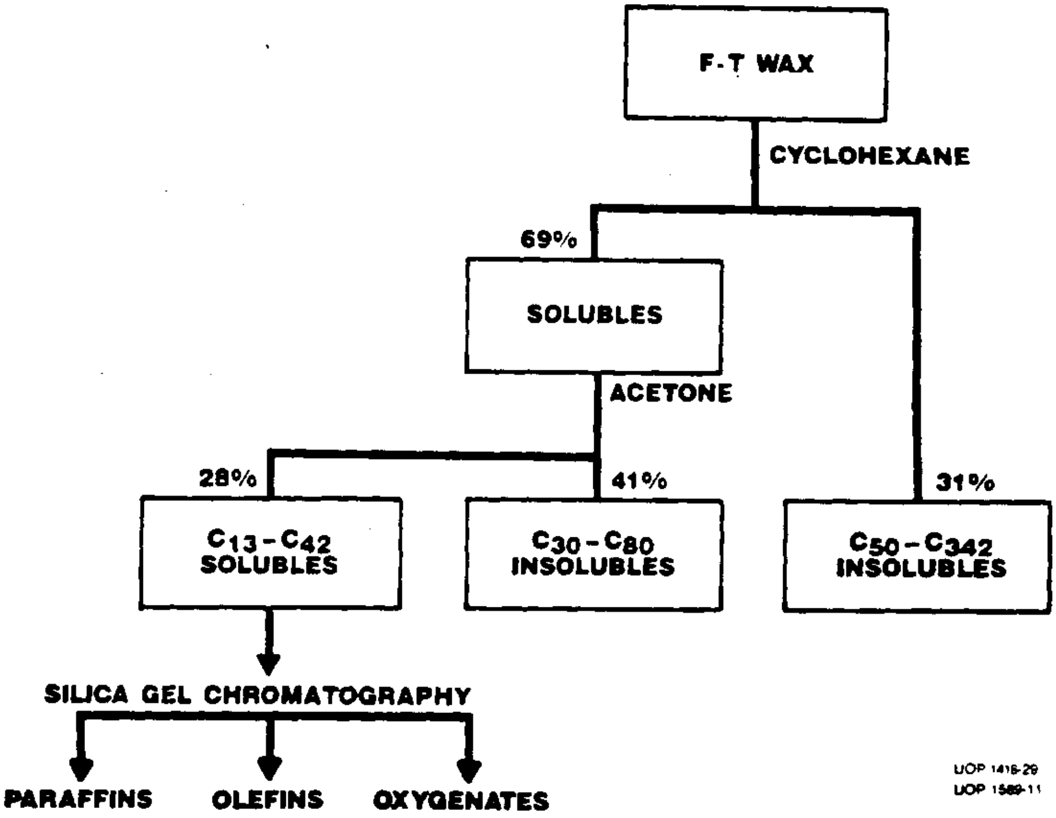
IR SPECTRUM
MOBIL WAX



UOP 1666-10

FIGURE 4.11

SOLVENT SEPARATION PROCEDURE

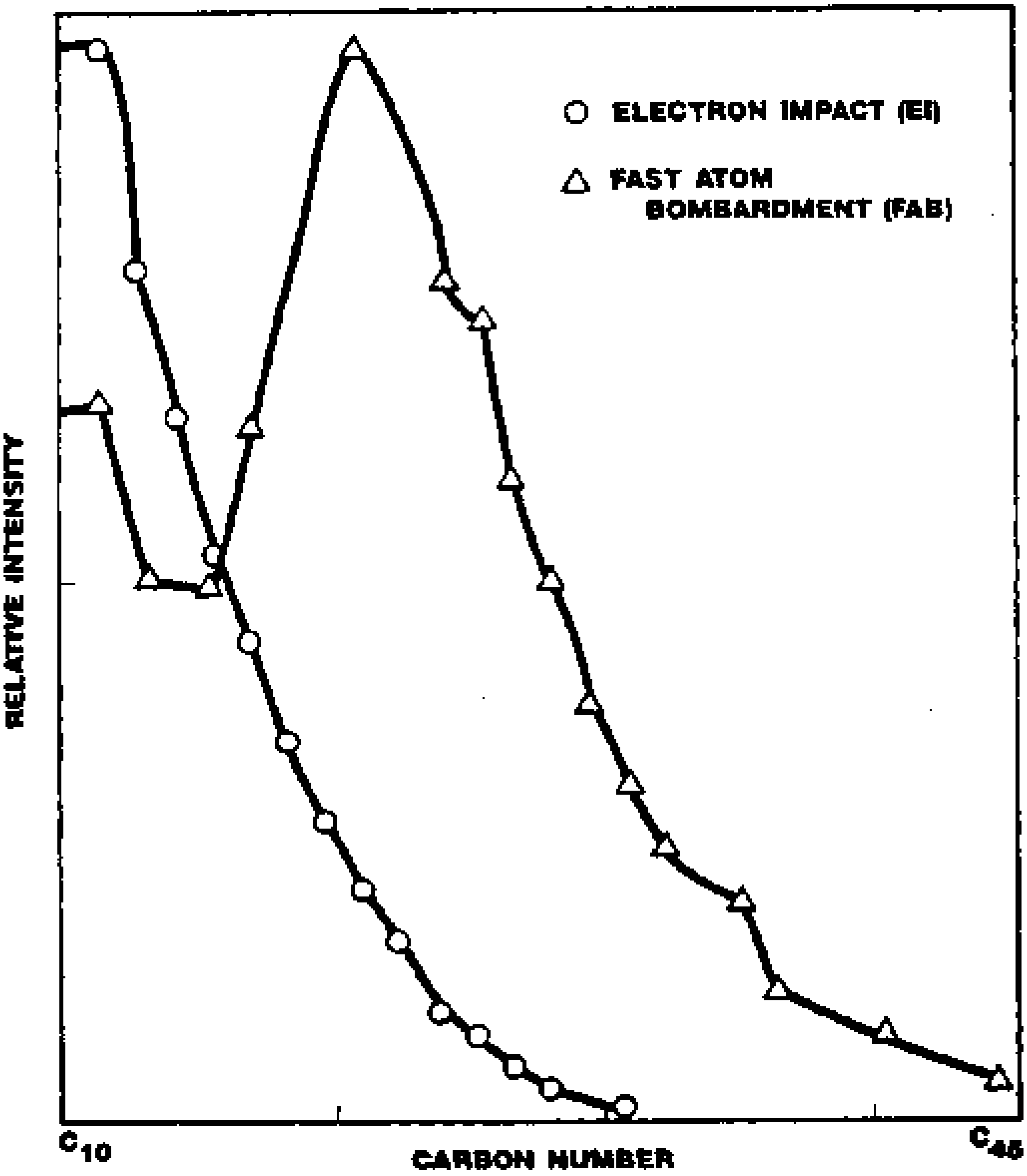


UOP 1416-29
UOP 1569-11

FIGURE 4.12

MASS SPECTROMETRY

ACETONE SOLUBLE ARGE WAX

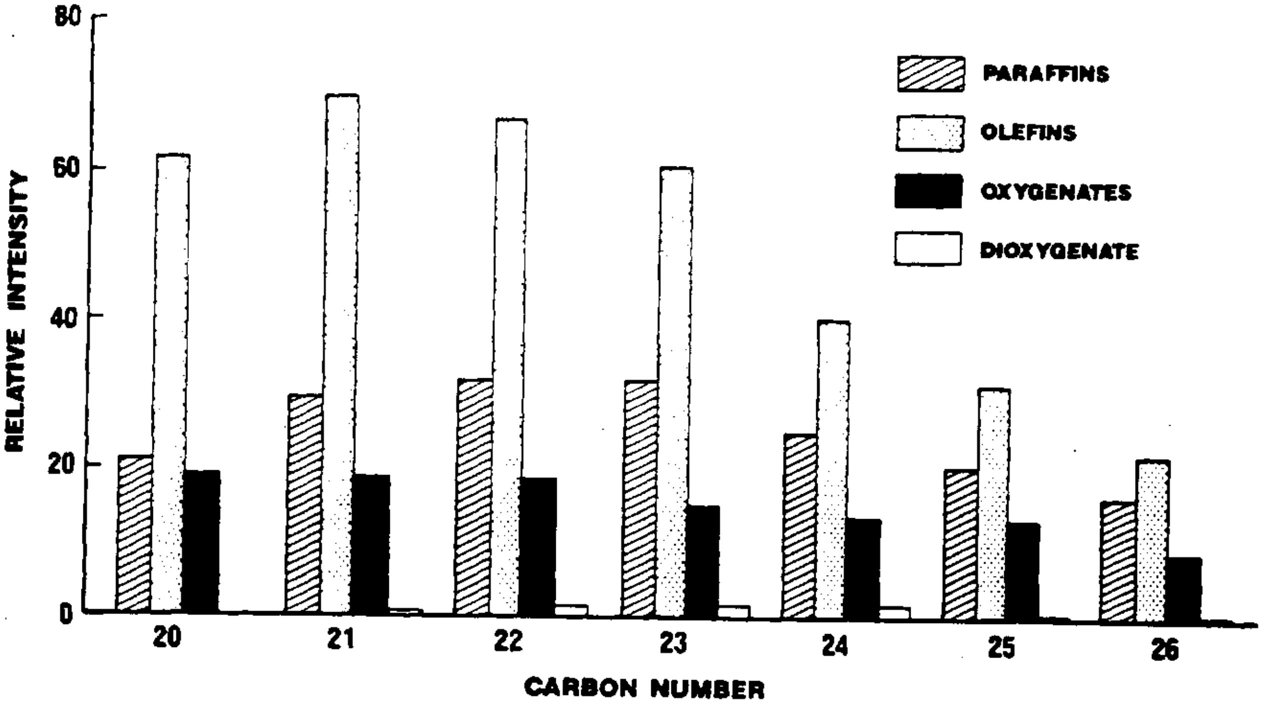


UOP 1545-30
UOP 1569-12

FIGURE 4.13

BLEND

F – T WAX COMPONENTS



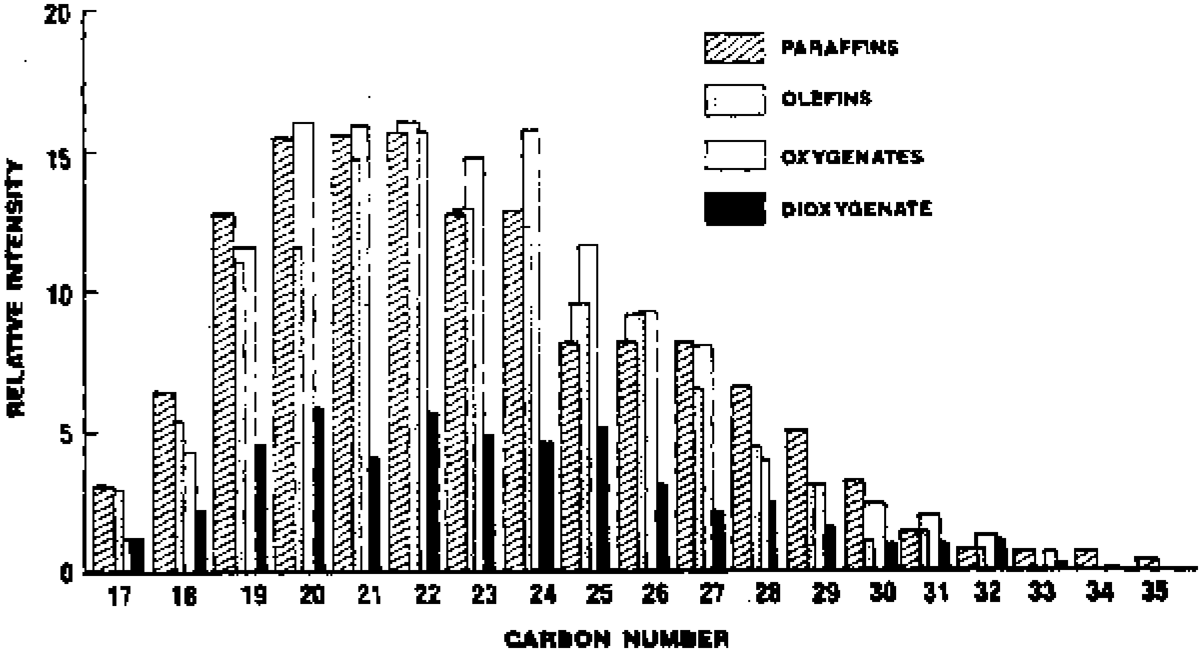
50% PARAFFINS, 40% OLEFINS, 10% OXYGEN

UOP 1545-33
UOP 1589-13

FIGURE 4.14

ARGE WAX

HIGH RESOLUTION FAB



ACETONE SOLUBLES

UOP 1565-36
UOP [illegible]-14

FIGURE 4.15

UNION CARBIDE F-T WAX

HIGH RESOLUTION FAB

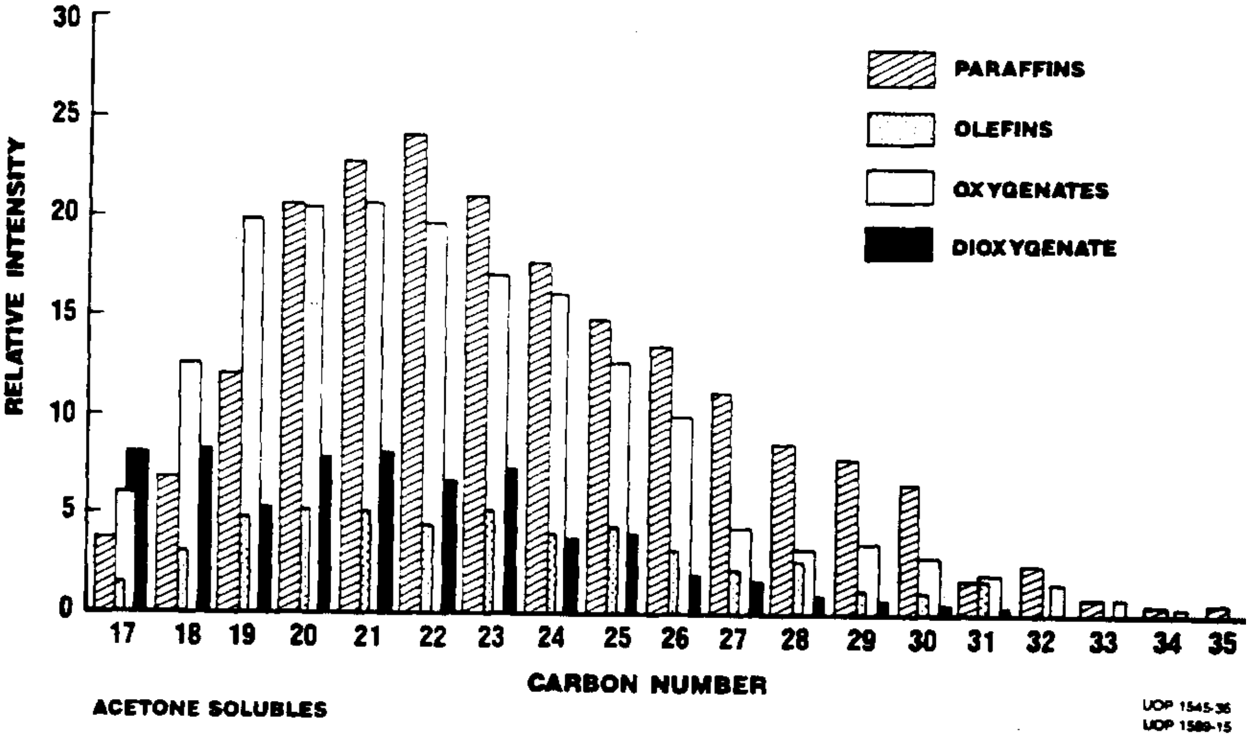


FIGURE 4.16

AIR PRODUCTS F—T WAX

HIGH RESOLUTION FAB