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TITLE: THE CHEMISTRY AND PROCESSABILITY OF CRUDE OIL ASPHALTENES AS STUDIED BY ULTRACENTRIFUGATION

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The Chemistry and Processability of Crude Oil Asphaltenes
As Studied by Ultracentrifugation^a

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ABSTRACT

From the number of crudes of this study, there appears to be a positive correlation between the total quantity of crude oil hetero atoms (S, N, Ni, and V) which are precipitated under conditions of ultracentrifugation and the degree of that particular crudes difficulty of hydroprocessing. Because of its powerful ability to separate colloidal material from suspensions and because of the known colloidal nature of asphaltenes, the ultracentrifuge was employed to effect the separation of crude oil constituents, and to thus provide information relating to the hydrocracking of resids. Asphaltenes vary greatly in their response to hydrocracking with some being remarkably refractive while others are readily destroyed. By studying the chemical nature of the asphaltene/colloid fractions, a correlation between this chemical constitution and processability was observed. The observation of Liesegang band-like phenomena is also reported along with chemical analyses of these bands.

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INTRODUCTION

The existence of colloids in crude oil has been previously confirmed by experiments with the ultracentrifuge (1, 2, 3, 4, 5, 6). The importance and variety of implementations for such petroleum colloids has been called upon for such diverse areas as secondary and tertiary reservoir recovery, petroleum biogenesis, and resid hydroprocessing. This latter area was of interest because of the colloidal nature of asphaltenes, their solubilizing agents, and the fact that during high severity hydrocracking of resids, asphaltenes precipitate on the catalyst, in reactor effluent lines, and perhaps most importantly in certain product blends. Asphaltenes differ widely in the manner in which they respond to hydrogen processing, i.e., some are remarkably refractive whereas others are quite readily destroyed. These differences are difficult to relate to asphaltene analytical chemistry because: (1) the chemistry of asphaltenes is both complex and ambiguous, and (2) defining such properties as reactivity under process conditions is most difficult. Because of these problems and the fact that other analytical

techniques had not thrown much light on the nature of petroleum's colloidal constituents per se, the ultracentrifuge was employed for the present studies. Indeed, the ultracentrifuge has been shown to be a powerful tool for studying self-association reactions (7) of the type which likely accompany fossil fuel asphaltenic systems (8, 9, 10, 11). Furthermore, the O'Grady and Wygant work (3) had shown in a study of the colloidal systems per se from two composite crudes, that there were distinct differences upon ultracentrifugation. One of the compositions, AP, was chosen because its vacuum resid was very difficult to process and the second, CY, was chosen because its vacuum resid was easy to process. From these studies, two important differences emerged: (1) there was more total precipitate with the refractive crude and (2) greater proportions of the crude oil hetero atoms concentrated in the precipitate from the refractive crude.

Because of these observations, the unique ability of the ultracentrifuge to study colloidal systems, and the fact that the ultracentrifuge had in the past been employed to only a limited extent, the present study was performed to provide analytical information which might relate to the processability of resids.

In the present study, several crude oils were ultracentrifuged and detailed analyses were performed on the resulting fractions. The crudes were selected as shown in Table I to attempt to correlate their hydroprocessability or surface chemistry interfacial phenomena effects with results from the ultracentrifuge study.

EXPERIMENTAL

A total of ten domestic and foreign crude oils were chosen for this study. Table I gives descriptions of the crudes and indicates why each was chosen for this study. (It should be recognized that each of these crudes may be collections of several crudes. Composite streams such as AB and CY actually contain several hundred crudes, and even crudes from one well could contain oil from several different strata.) A Spinco Model L-HT ultracentrifuge with an angle-head preparative rotor was used. Samples were run for 168 hours at 48,000 rpm (181,000 g's max.) at 25°C. This time was selected to insure an equilibrium separation. Two sampling techniques were used:

- 1) The best technique was to use a syringe to draw liquid out of the ultracentrifuge tubes to any discrete level desired.
- 2) Another technique was to simply pour off the supernate and then allow the precipitate to drain by inverting the tube at a 45° angle for 15 minutes. A glass rod was placed inside the tube along the wall to improve drainage.

When the tubes of most crudes were removed from the ultracentrifuge there was an obvious darkening toward the bottom of the tubes as shown in Figure 1. The top was light and straw-colored; the bottom was black/brown. However, some of the heavier, more viscous crudes did not show these distinct separations. When the product was separated into top, middle, and precipitate fractions with a syringe, the split between top and middle was based upon a distinct difference in the viscosities of the two layers. The precipitate was

always distinct from the layer above it. The separation technique used for each sample is included with the product analyses and although somewhat arbitrary, the separation technique afforded good reproducibility on a weight percent basis for duplicate samples.

Chemical analyses of the fractions resulting from ultracentrifugation were performed using the following techniques:

- 1) Sulfur (ppm, X-ray fluorescence)
- 2) Nitrogen (Kjeldahl)
- 3) Carbon, hydrogen (combustion)
- 4) Oxygen (Schutze-Unterzaucher)
- 5) Heptane insolubles (ASTM D-893)
- 6) Nickel/Vanadium (Amperometry, Colorimetry)
- 7) Mass spectral type analysis (ASTM D-2786, ASTM D-3239)
- 8) High performance liquid chromatography (14)

The ultracentrifugation of resids per se appears to be limited because of the long settling times required by high viscosity materials. In fact three of the crudes that were used, Magrip, Jobo, and Cyrus, were diluted with virgin naphtha to reduce their viscosity and improve separation. The poor or incomplete separations indicated for some of the other crudes could have probably been improved if these crudes had been diluted.

Complete mass balances were not obtained in this study and for mass balance purposes all losses were assigned to the lightest fraction due to its volatility. The "spontaneous" formation of Liesegang-like bands or ring in the samples was observed upon standing after removal from the ultracentrifuge.

Results and Discussion

General

Table II provides insight into the chemical and physical properties of the crudes studied. As may be seen, these crudes represent both high and low sulfur stocks (Anse La Butte, 0.11 wt percent; Winkelman Dome, 4.38 wt percent) and a wide range of API gravities, (AB, 38.7⁰; Jobo, 14.1⁰) and as such represent certain extremes of crude.

Table III presents the relative fractions of material in the top, middle, and precipitate fractions resulting from ultracentrifugations of the crudes of this study. (In those cases where the separation was made by decanting, the overhead material is listed as the middle fraction.) Table IV shows analytical results of interest for the precipitate. The amount of precipitate varied from 0.8 wt percent of the crude with Anse La Butte to about 27 wt percent with Magrip.

The total weight of the ultracentrifuge precipitate relative to the total weight of asphaltene in the crude also varied considerably (Table IV) with (precipitate wt)/(asphaltene wt.) ratios ranging from a low value of 0.25 in Jobo to greater than 3 in the AB composite. These ratios may provide insight leading to further studies into the solubilizing agents of the particular crudes. Most of the samples that had low (wt of precipitate)/(wt of asphaltene) ratios in the crude were heavy, viscous crudes that gave incomplete separations. The top layer showed substantial amounts of material boiling above 1000⁰F even though it was usually quite clear. The naphtha (360⁰F) was concentrated slightly in the top fraction as would be expected, but the middle fractions also contained substantial amounts of naphtha.

Asphaltenes are generally thought to exist in a colloid structure (1-6) wherein the asphaltene molecule is surrounded and interacts with molecules broadly classified as maltenes. To assume that the colloidal structure is the same in the resid as it is in the crude may not be completely correct. However, data from this study (below) and in previous work (1) have shown that a substantial fraction of the non-asphaltene part of the colloid is high molecular weight material such that light ends probably have a negligible effect.

Concentration of Hetero Atoms

The quantity of hetero atoms (S, N, Ni, V) which concentrated in the precipitates (Table IV) may relate to the difficulty of hydroprocessing. Precipitates from three crudes, AB, Magrip, and Anse La Butte, contained a high proportion of the total hetero atoms in the crudes. Two of these crudes, AB and Magrip, were known to be difficult to hydroprocess (Table I). There is no information on hydroprocessing the Anse La Butte. This concentrating effort may be due to any one or combination of the following: (1) the colloidal suspensions of these crudes may be relatively unstable, and the heavier molecules that normally contain the hetero atoms were not held in suspension as they were with the other crudes, (2) for some reason there was a higher concentration of hetero atoms in the heavier molecules of these three particular crudes, or (3) the heavier molecules of these three crudes may have had a more compact structure that increased their density and the amount precipitated. All three of these possibilities point to the materials being more difficult to hydroprocess.

Asphaltene Content

Precipitates from AB and CY crudes were separated into oils, resins, and asphaltenes by liquid chromatography (Table IV). Contrary to expectations,

there were fewer asphaltenes and more resins in the AB precipitate than in the CY precipitate. These data were analyzed further as shown in Table V where the amounts of resins and asphaltenes in the precipitates are compared to those in the crudes. Proportionately more resins were precipitated from the AB crude than the CY crude, 24 percent of the total resins for AB vs. 7 percent for CY. This may result from: (1) the AB colloids having contained more resins than the CY colloids, (2) some of the resins in AB were more dense than those in CY crude, or (3) some of the resins in AB crude may have been only held weakly in solution. The CY crude contained about 1.8 times as many asphaltenes as the AB crude. Ultracentrifugation brought down the same proportion of asphaltenes, about 45 percent, in both AB and CY, leaving slightly over half of the asphaltenes which were not precipitated. This suggests that: (1) all the asphaltenes may not exist in colloids, (2) not all the colloids were precipitated by the ultracentrifuge, (3) asphaltenes may not all have had the same molecular density, or (4) some of the asphaltenes may have been held very strongly in solution.

Worth noting is the fact that the results of the current work are not in total agreement with results reported in the literature (2). Particularly, for Bachaquero crude oil the quantity of "saturates" was reported as constant for the top, middle and bottom fractions. This was not the case for all crudes in the present study.

Sulfur

Since asphaltenes are known to be rich in sulfur, it was somewhat surprising that there is not more concentrations of sulfur in the precipitates (Table IV). In fact, Rocky Point, Winkelman Dome, and Jobo actually showed decreases in the weight percent sulfur in the precipitate relative to the crude. Additional support of this unexpected result with Jobo was obtained

from sulfur analyses of three separate 1000+⁰F resin and asphaltene fractions from Jobo resid which showed slightly less sulfur in the asphaltenes than in the resins.

Additional support for asphaltene solubilization by non-asphaltene molecules can be obtained from the sulfur analysis on three different Rocky Point asphaltene-rich samples. The ultracentrifuge precipitate contained 3.0 percent sulfur; a gel permeation chromatography sample of nominally greater than 80A size molecules showed 4.4 percent sulfur; and a heptane precipitate asphaltene showed 6.6 percent sulfur.

Metals: Nickel and Vanadium

As given in Table II, the crudes studied represented metal concentrations ranging from less than 1 ppm to greater than 100 ppm. For most samples, the vanadium/nickel ratio was greater than 1.0. Interestingly, the data of Table III show that the V/Ni ratio for many of the samples was larger in the crude than in the precipitate. This implied a difference in the sedimentation values of the Ni and V containing molecules as fewer of the vanadium-containing molecules were precipitated. Differences in the density of the molecules or more pronounced solvation of vanadium compounds as opposed to the nickel compounds may explain this. Recent work (10) has shown evidence of association of vanadyl porphyrins; whether or not this would increase the molecular density is not clear.

It is interesting to note that Winkelman Dome and Rocky Point, two crudes studied for their relation to tertiary recovery, had high V/Ni ratio in their precipitates. By the same token, Anse La Butte, which was studied for the same reason, yet having diametrically opposed surface chemistry, exhibited the lowest V/Ni ratio.

Electron Microscopy

The size of the colloidal particulates in petroleum undoubtedly affects the behavior of a crude during processing. For example, diffusion into and out of the pores of a catalyst is affected by the size of the diffusing particles. To explore particle size in the present work, samples were studied by electron microscopy (EM). An RCA-EMU was used for the study. This early model instrument had an effective working resolution of 100Å. Relative to published EM studies of asphaltenes (11), the present work was limited by instrumental resolution. However, certain worthwhile observations were obtained and are reported here. Only the precipitates were examined, and two sample preparation methods were used. The first method was to prepare samples of the precipitate which had been deasphalted with n-heptane. The second method was to simply prepare a benzene solution of the precipitate.

In most cases the particles fell into two classes: a background, and an upper layer of particles. Most of the background particles were of a size from 0.01 to 0.05 microns. Atop this "background" material were particles and particle clusters. These ranged in size from 2 microns to as large as 13 microns. Diamond-shaped platelets and/or Ries microislands (12) were also observed on certain of the samples. In CY there existed puckered lamella of poorly crystallized paraffin wax which had folds or creases at their centers. The monolayer thickness of the AB precipitate was 15-50Å thick. Certain objects were thought to be inorganic. Differences in the materials are shown in the scanning electrons microscopy photographs of Figures 2 and 3. Figure 2 presents the agglomerated material of an AB heptane asphaltene viewed at 200X and Figure 3 presents a 500X Magrip sample which illustrates almost plane-like cleavages.

Mass Spectral Type Analyses of Crude

Because ultracentrifugation is known to fractionate samples on the basis of viscosity, density and particle size, it was desirable to determine chemical types that give the composites observed. Thus, mass spectral type analyses relative to these fractions are given in Table VI. Observations of interest are described below:

Low Paraffin Content -- In the context of this paper, crudes with less than 15 estimated weight percent paraffins are called low paraffin and may have been biologically altered. Winkelman Dome, Rocky Point, and Jobo are in this category. Relative to the crude, both Winkelman Dome and Jobo concentrated paraffins in the top layer to a considerable extent. However, within the limits of experimental error there was no such concentration in the Rocky Point sample. (The Jobo value may be misleading in that naphtha was added to the crude to reduce its viscosity for ultracentrifugation).

High Paraffin Content Crudes -- For the purpose of this discussion, high paraffin crudes were those with greater than 15 weight percent paraffins. Again, there was a tendency for the concentrating of paraffins in the top layer while at the same time depleting the concentration of aromatics relative to the crude.

Crudes of both high and low paraffin concentration showed a depletion of thiopheno type compounds in the top ultracentrifuge fraction relative to the total crude. Of those samples where more than one layer was studied, the thiopheno compounds increased going down the tube, and there was also a trend for the weight percent of the total crude which existed as sulfur in thiopheno compounds to increase.

For Winkelman Dome, Jobo, Rocky Point, Cyrus, and Sholom Alechem the weight percent of benzothiophenes was greater than that of dibenzothiophenes

in those fractions studied. For Magrip, Darius and CY the opposite was true, i.e., the dibenzothiophenes were present in a higher concentration.

As would be expected, the weight percent of the total crude existing as sulfur in thiopheno compounds increased with increasing density of the fractions of a given crude. Moreover, although exceptions existed, an increase in the weight percent of the total crude existing as sulfur in thiopheno compounds occurred as the density of the total crude increased. Since the importance of benzothiophenes and dibenzothiophenes has been pointed out previously (13), this "density/weight percent sulfur as thiopheno type compounds relationship" may be useful in a priori judgments on processing.

As with the paraffins, the noncondensed cycloparaffin concentration in the topmost layer was greater than in bulk crude. On a paraffin-free basis, the total cycloparaffin concentration in the top layer generally exceeded that in the whole crude.

Band Formation After Ultracentrifugation

An unusual phenomenon was observed for many of the samples. As a sample was removed from the ultracentrifuge head its color varied in a continuum from light at the tube top to deep brown or black at the bottom as shown in Figure 1. However, if the tube were allowed to stand a few minutes or was warmed to about 50°C (122°F) there was a coalescing of material within the tube such that discrete bands were formed. This "growing in" of bands is shown for the AB and CY in Figures 4 and 5 when viewed with black light and natural light respectively. The bands increased in number and became narrower over a few hours. Upon allowing to stand for a longer time, however, these bands completely dispersed and the sample reverted to its original state.

One explanation of this phenomenon, as suggested by Dr. H.E. Ries, Jr., of the Amoco Oil Company staff, is by way of a mechanism which is akin to the formation of so-called Liesegang bands (15). In this situation, diffusion, equilibrium product and electrostatic considerations would have been involved in the observed precipitation or flocculation. Yet another possibility was the precipitation or coalescing of certain paraffin waxes due to their non-solubility. Rather than trying to present a detailed explanation of exactly what happened in this experiment, the results are presented here for their own sake. Possibly more detailed interpretations can be developed at a later time.

A sample of the refractory AB crude was ultracentrifuged, and 10 bands that formed were separated. Certain of these bands were analyzed by GPC (14, 16) and by mass spectral type analysis. These results are shown in Table VII. From the GPC data, it is particularly interesting that even the lightest band contained a high proportion of molecules whose effective hydrodynamic volume would impede ready diffusion into typical Co/Mo alumina pores.

The mass spectral compositions of the various bands are given in Table VIII. The top layer is labeled AB-1. As might have been expected, in the mass spectral type analyses there was an increase in the amount of sulfur (as shown in the sulfur index) with increasing average molecular weight of the band. Thiopheno compounds, per se, did not appear until Band 5, although the least dense thiophenic compound, thiophene, had a density of 1.06g/cm^3 . Under these equilibrium conditions, all thiopheno compounds should have concentrated in the precipitate if only density considerations were involved. One must conclude that, not only density, but also solvation and association phenomena played an important role here in keeping the thiopheno compounds in solution.

Unlike the monocyclic paraffins whose concentration decreased towards the tube bottom, the monocyclic aromatics showed a slight increase toward the bottom of the tube. Likewise, the dicycloaromatic concentration increased toward the tube bottom whereas the dicycloparaffins showed a peak at Band 3 and decreased thereafter.

CONCLUSIONS

1. There were substantial differences in the amounts and compositions of the precipitates obtained from various crudes by ultracentrifugation.
2. In samples where equilibrium separations were obtained, the amount of precipitate was generally two-four times the amount of asphaltenes in the crude. This additional material was found to be primarily resins with some oils.
3. Not all the asphaltenes were precipitated during conditions of equilibrium ultracentrifugation at 181,000 g's.
4. The same percent (45) of the total crude oil asphaltenes were precipitated from AB and CY crudes. However, more of the total crude oil resins were precipitated from AB crude than from CY crude, 24 percent vs. 7 percent.
5. The amount of the total crude oil hetero atoms (S, N, Ni and V) concentrated in the precipitates seemed to correlate inversely with ease of hydroprocessing. Two crudes, AB and Magrip, whose resins are known to be difficult to hydroprocess, had high values of the total crude oil hetero atoms which were precipitated.
6. Differences were noted in the nickel- and vanadium-containing compounds as a greater fraction of the total nickel-containing compounds were precipitated.
7. An unusual phenomenon of band formation was observed in samples when they were removed from the ultracentrifuge.
8. There was enough interaction of resin/maltene/asphaltene systems that complete separation of these classes did not occur. This is in agreement with the work of Bunger, Cogswell, and Zilm (17) who reported overlapping

maltene/asphaltene chemical and physical functionalities and with others who have contributed to our knowledge of asphaltenes while at the same time pointing out the complex nature of these species (18, 19).

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Table I

CRUDE OIL DESCRIPTIONS

<u>Crude</u>	<u>Description</u>
AB	Composite stream of sweet crude processed at Whiting. The vacuum resid is very difficult to hydroprocess.
CY	Composite stream of sour crude processed at Whiting. The vacuum resid is relatively easy to hydroprocess.
Darius	An Iranian crude typical of several high-sulfur, low asphaltene crudes.
Magrip	A Turkish crude obtained from Hydrocarbon Research Institute who reported difficulties in hydroprocessing the resid in their H-Oil unit.
Cyrus	A heavy, viscous, high-sulfur Iranian crude. Extensive resid hydroprocessing work has been carried out on this resid.
Jobo (Morichal)*	A heavy, asphaltic Venezuelan crude.
Anse La Butte (ALB)	Louisiana crude. Low sulfur. Low Nitrogen. Of interest for tertiary recovery.
Rocky Point	Wyoming crude from reservoir believed to be oil wet. Quite viscous.
Winkelman Dome	Wyoming crude from water wet reservoir. Quite viscous.
Sholom Alechem	Oklahoma crude. Medium low viscosity.

* This crude is actually from Phillips Petroleum's Morichal field that is located near, and is similar to, Amoco's Jobo field.

Table II

CHEMICAL AND PHYSICAL PROPERTIES OF CRUDE OILS

Crude Sample I.O.	AB	CY	Darius	Magrip	Sholom Alechem	Winkelman Dome	Rocky Point	Anse La Butte	Cyrus	Jobo (Morichal)
Elemental Analysis										
S wt. %	0.45	2.17	2.42	3.54	1.37	4.38	3.67	0.11	4.24	2.00
N	0.11	0.17	0.10	0.26	0.37	0.36	0.30	0.03	0.32	0.43
H	12.81	12.16	12.25	11.25	12.30	10.97	11.24	12.84	10.97	10.89
C	85.49	84.35	84.60	84.14	85.48	83.87	84.62	86.30	84.46	85.14
O	0.18	0.71	0.55	0.39	0.72	1.07	0.81	0.41	0.56	1.08
Total	99.04	99.56	99.92	99.58	100.24	100.65	100.64	99.69	100.55	99.54
H/C (atomic)	1.80	1.73	1.74	1.61	1.73	1.57	1.60	1.79	1.56	1.54
Metals, ppm										
Ni	5.4	14	7.3	55	45	28	13	0.94	59	82
V	12	34	17	82	71	109	41	0.00	133	138
V/Ni	2.2	2.4	2.3	1.5	1.6	3.9	3.2	0.00	2.3	1.7
Hot Heptane Insol. wt. %	1.1	2.0	0.7	15.5	1.4	---	---	---	---	---
Gravity, °API	38.7	29.2	33.7	21.7	28.9	14.9	16.7	35.6	18.8	14.1
Composition, wt. % (By Simulated Distillation)										
360-°F	23.7	20.6	25.5	12.7	16.6	3.7	3.7	24	8.1	1.6
650-°F	43.4	50.5	44.6	65.5	55.9	63.1	73.2	33.2	73.5	75.6
1000+°F	16.5	20.2	17.3	39.7	23.2	6.9	36.5	4.0	45.1	39.5
Liquid Chromatography, wt. %										
Oils	55.2	56.9	41.2	43.6	39.8	51.2	47.8	45.5	33.8	41.3
Resins	14.3	21.4	22.2	28.6	31.5	34.4	34.1	6.1	34.0	34.6
Asphaltenes	1.0	1.7	1.3	10.2	1.8	2.3	5.8	0.0	11.3	7.7
Loss*	29.5	20.0	35.3	17.6	26.9	12.1	12.7	48.4	20.9	16.4
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

*The liquid chromatography separation technique was developed for resids. The loss reported here is material boiling below about 500-600°F.

Original

Table III
WEIGHT PERCENT OF SAMPLE IN TOP, MIDDLE, OR PRECIPITATE

Crude	AB	CY	Sholom Alechem	Magrip ¹	Rocky Point	Anse La Butte	Jobo ²	AB	Winkelman Dome
Sample Number	6	7	4	5	6	2	3	4	5
Separation Method	S	S	S	S	S	S	S	D	S-D
Composition ³ , wt. %									
Top	69.8	57.4	61.0	43.2		59.4	38.1		32.1
Middle	26.5	39.1	35.4	30.0	95.1	39.8	60.0	96.6 ⁴	66.2
Precipitate	3.7	3.5	3.6	26.8	4.9	0.8	1.9	3.4	1.7
Recovery	90.6	90.6	96.4	93.6	93.9	95.2	91.9	87.9	94.1

Separation Method: S = Syringe, D = Decanted

- ¹ Diluted with FRE-62, Whiting No. 2 Ultraformer Feed; 21.1 g. crude + 6.0 g. FRE-62.
- ² Diluted with FRE-62, Whiting No. 2 Ultraformer Feed; 50 cc crude + 19 cc, FRE-62, 57.6° API.
- ³ Normalized by assigning all losses to the top layer.
- ⁴ So-called middle fraction is actually top plus middle fraction.

PREPRINTS
New York Petrol. Chem.

Table IV

ULTRACENTRIFUGE PRECIPITATE ANALYSES

Crude	AB		CY		Shol. Asphaltene		Magrip ¹		Rocky Point		Anse La Butte		Jobo ²	AB	Winkelman Dome		CY
Sample Number	1	6	2	7	4	9	5	10	1	6	2	7	3	4	5	10	9
Separation Method	D	S	D	S	S	S	S	S	S	S	S	S	S	D	S-D	D	D
Quality of Separation	G	G	G	G	I	I	G	G	I	I	G	G	I	G	I	I	G
Precipitate																	
Elemental Analysis																	
S Wt%	1.69		4.67		2.37		6.21		2.99		0.65		1.37	1.40	3.72	3.28	
N	0.70		0.63		0.80		0.59		0.42		0.13		0.77	0.56	0.41	0.60	
O	0.99		1.31		1.85		0.85		16.71		1.77		2.72	1.66	0.92	2.46	
Total (C,H,N,O)	101.46		99.61		101.46		100.34		106.21		101.53		101.08	100.92	99.00	101.40	
H/C (Atomic)	1.42		1.34		1.57		1.27		1.69		1.45		1.48	1.44	1.54	1.48	
Metals, ppm																	
Ni	77		73		155		145		47		61		124	64	26	103	
V	137		161		141		200		52		0.3		86	179	80	124	
V/Ni	1.76		2.2		0.9		1.38		1.1		0.01		0.69	2.8	3.08	1.2	
Cu ³									80		1.3		14	1.3	5	23	
% Nitrogen in Precip/% Nitrogen in Crude																	
	6.7		3.7		2.2		2.3		1.4		4.3		1.8	5.3	1.1	3.5	
% Sulfur in Precip/% Sulfur in Crude																	
	3.8		2.1		1.7		1.8		0.8		5.9		0.7	3.1	0.8	1.5	
Concentration of Crude Oil Hetero Atoms % of Total in Crude																	
S	13.9		7.6				60.2		3.3		47.2		1.7	10.6	1.4	4.5	
N	24.4		13.1				77.5				38		4.4	17.9	1.9	10.5	
Ni	42.5		16.8		7.6		83.4		2.4		26.6		1.5	50.9	1.3	10.9	
V	52.8		18.5		13.1		90.2		6.5				3.8	40.3	1.6	22.1	
Weight of Precip/mt of Asphaltenes in Crude																	
	3.7		2.1		2.0		2.6		0.85				0.25	3.4	0.74	1.5	

Separation Method: S = Syringe, D = Decanted

Quality of Separation: G = Good Separation, Top Layer Clear; I = Incomplete Preparation, Top Layer Still Dark.

¹ Diluted with FRE-62, Whiting #2 Ultraformer Feed; 21.1 g crude + 6.0 g FRE-62.

² Diluted with FRE-62, Whiting #2 Ultraformer Feed; 50 cc crude + 19 cc FRE-62, 57.6°API.

³ May be present as a water soluble salt.

Precipitate HPLC Oils, Resins, and Asphaltenes: AB 17.2, 73.3, 9.5
CY 22.9, 67.1, 10.0

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Table V

CRUDE OIL AND PRECIPITATE ASPHALTENE
AND RESIN CONTENTS

	<u>AB</u>	<u>CY</u>	<u>CY/AB</u>
ASPHALTENES			
Crude Oil			
Liquid Chromatography, wt%	1.1	2.0	1.8
Solvent Insolubles, wt%	1.0	1.7	1.7
Precipitate			
Liquid Chromatography, wt%	0.5	0.9	1.8
(based on crude oil = 100%)			
Precipitate/Crude (Liq. Chrom.)	0.45	0.45	
RESINS			
Crude Oil			
Liquid Chromatography, wt%	14.3	21.4	1.5
Precipitate			
Liquid Chromatography, wt%	3.4	1.5	0.4
Precipitate/Crude	0.24	0.07	

Table VI
 MASS SPECTRAL TYPE ANALYSES OF ULTRACENTRIFUGED CRUDES
 AND FRACTIONS FROM ULTRACENTRIFUGATION

Composition, wt%	Saturates	Paraffins	Noncondensed Cycloparaffins	Aromatics	Naphthalenes	Penanthrenes	Thiopheno (Total)	Dibenzothiophenis	Average Molecular Weight	Wt.% of Sample That Exists As Sulfur in Thiopheno Compounds
AB (Sept. '68)										
Crude	85.1	42.4	27.2	11.1	1.7	0.5	1.1	0.0	251	0.02
Top	85.7	42.2	28.4	14.3	1.6	0.8	1.0	0.0	229	0.00
Anse La Butte										
Crude	82.5	33.9	25.3	17.5	3.2	0.7	0.0	0.0	215	0.00
Top	84.0	34.6	25.9	16.0	3.0	0.5	0.0	0.0	188	0.01
Middle	80.7	29.6	25.2	19.3	3.4	0.8	0.2	0.1	229	0.02
CY (Dec. '68)										
Crude	74.6	35.7	24.2	25.4	4.0	1.1	2.6	1.5	322	0.26
Top	76.8	35.6	26.3	23.2	1.7	0.7	2.1	1.0	318	0.21
Cyrus										
Crude	64.7	26.3	20.2	35.3	3.1	1.9	5.6	2.3	362	0.5
Top	74.7	37.2	24.3	25.3	1.3	0.9	3.1	1.6	307	0.32
Darius										
Crude	75.4	49.3	13.3	24.6	1.1	1.0	3.9	2.3	298	0.42
Top	79.3	53.5	13.9	20.7	0.0	0.8	3.8	2.5	294	0.41
Middle	71.3	45.5	12.6	28.7	0.7	1.5	6.1	3.6	319	0.61
Jobo										
Crude	64.8	2.9	21.7	35.2	3.1	2.2	2.6	0.9	294	0.28
Top	74.5	17.0	25.4	25.5	2.1	1.6	0.9	0.4	251	0.12
Magrip										
Crude	72.3	40.3	14.6	27.7	1.3	1.2	5.4	2.6	382	0.45
Top	82.9	48.0	22.1	17.1	0.0	0.7	2.5	1.4	286	0.28
Middle	74.5	39.4	21.3	25.1	0.0	1.3	5.0	2.8	303	0.53
Rocky Point										
Crude	67.8	12.5	31.2	32.2	2.7	1.5	5.6	2.3	385	0.47
Top	65.1	12.7	29.5	34.9	2.5	1.6	6.0	2.4	374	0.52
Shalom Alechem										
Crude	75.4	26.0	30.3	24.6	2.6	0.8	1.4	0.5	320	0.18
Top	75.0	26.4	28.2	25.0	2.4	1.1	1.3	0.4	303	0.14
Middle	73.0	24.3	28.0	27.0	2.9	1.2	1.6	0.4	310	0.16
Winkelman Dome										
Crude	53.6	3.8	24.9	46.4	4.0	1.9	7.6	2.9	366	0.67
Top	56.0	6.3	25.5	44.0	3.3	2.0	6.7	2.5	359	0.60
Bottom	47.8	9.5	18.2	52.2	2.5	2.1	8.6	3.5	354	0.78

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Table VII

GEL PERMEATION ANALYSES OF BANDS WHICH FORMED
FOLLOWING ULTRACENTRIFUGATION OF AB CRUDE

<u>Band Number</u>	<u>Apparent Weight Average Hydrodynamic Diameter (A)</u>	<u>Apparent Number Average Hydrodynamic Diameter (A)</u>	<u>Primary Peak Maximum (A)</u>	<u>Secondary Peak Maximum (A)</u>	<u>Cumulative Weighth Percent At Maximum</u>
(Top)					
2	39	26	26	none	47.56
4	40	26	30	16	55.79
6	41	26	30	16	55.11
8	50	28	43	18	49.52
10	93	34	52	278(1)	58.17
(Bottom)					

(1) Typical peak maximum on asphaltenes.

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Table VIII
 MASS SPECTRAL TYPE ANALYSES OF BANDS OBSERVED
 IN ULTRACENTRIFUGE STUDIES

	Estimated Weight Percent							(Bottom) AB-8
	(Top) AB-1	AB-2	AB-3	AB-4	AB-5	AB-6	AB-7	
Paraffins	45.1	41.1	37.3	38.4	36.3	38.1	30.7	28.7
Noncondensed Cycloparaffin	28.0	27.5	26.0	27.0	26.7	26.6	23.7	24.1
Total Aromatics	12.5	14.9	17.6	17.2	19.0	19.2	26.0	27.4
Benzenes	6.1	6.7	6.0	7.0	7.4	8.5	7.6	6.5
Naphthalenes	1.3	1.7	2.2	1.9	2.2	2.1	3.4	3.8
Pyrenes	0.3	0.4	0.6	0.5	0.6	0.6	1.1	1.1
Benzothiophenes	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.2
Dibenzothiophenes	0.0	0.0	0.0	0.0	0.0	0.0	0.2	0.3
Average Molecular Weight	251	217	281	244	256	265	269	303
Sulfur Index	190	156	191	214	239	299	317	457

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Figure Captions

Figure 1. Photograph illustrating crude oil continuum immediately following removal from ultracentrifuge.

Figure 2. Crude oil AB heptane asphaltenic material as viewed at 200X with scanning electron microscope.

Figure 3. Magrip high molecular weight material as viewed at 500X with scanning electron microscope.

Figure 4. Examples of discrete band formation in AB and CY crudes as viewed with "black light" upon standing after removal from the ultracentrifuge.

Figure 5. Examples of discrete band formation in AB and CY crudes viewed with incandescent white light upon standing after removal from ultracentrifuge.

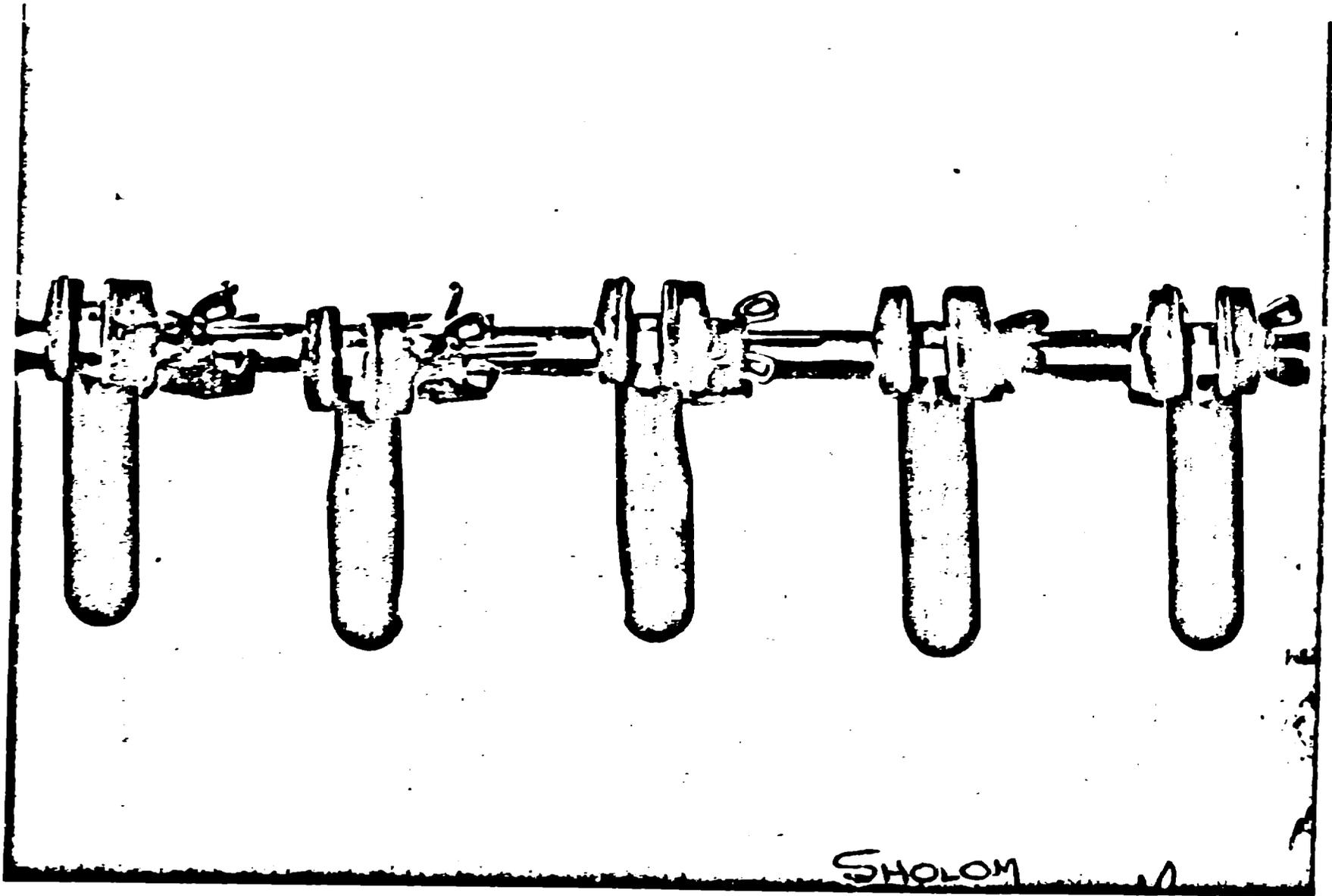
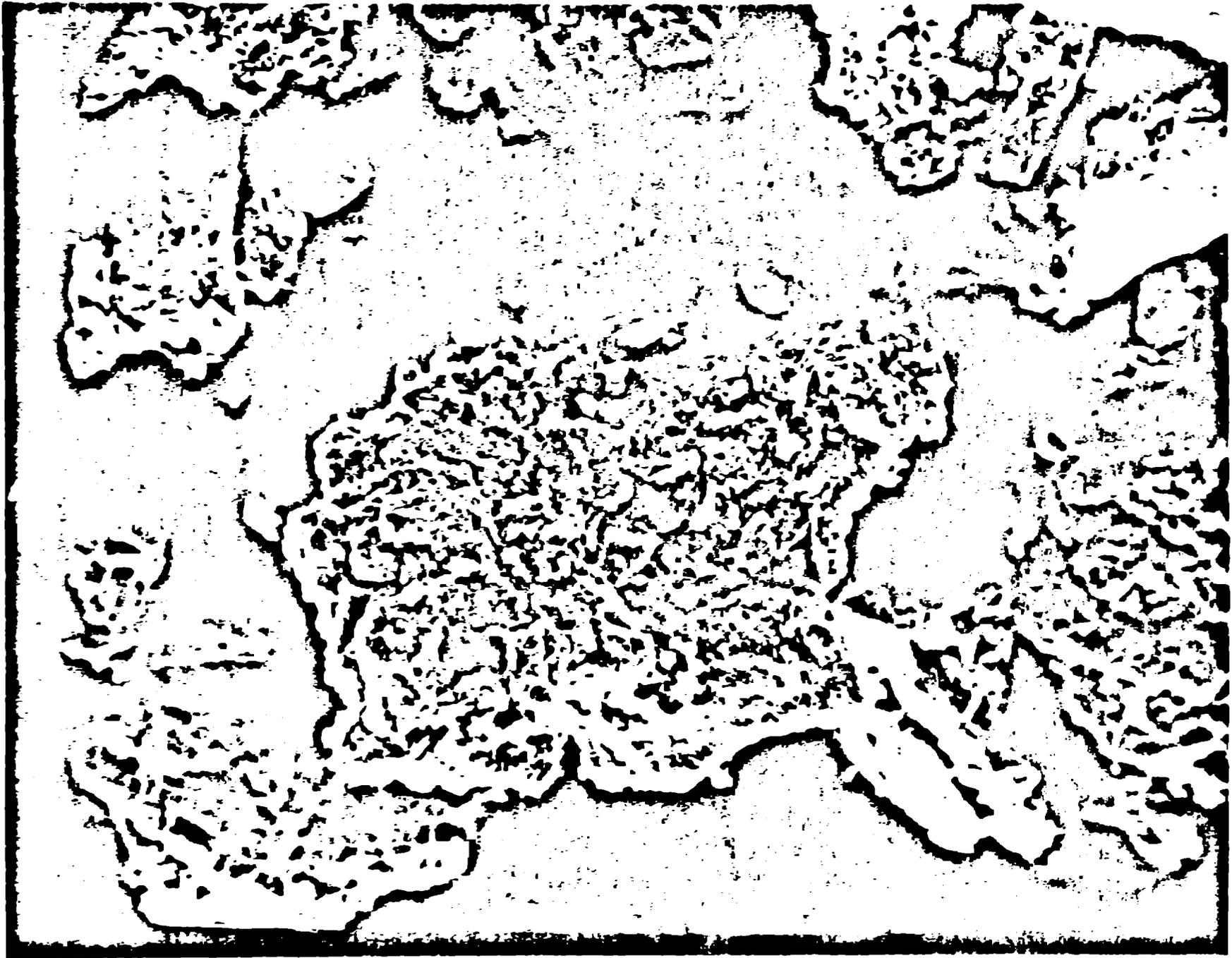


Figure 1
Original material



*Original artist's
Figure 2.*



Original
Fig 3 mate:

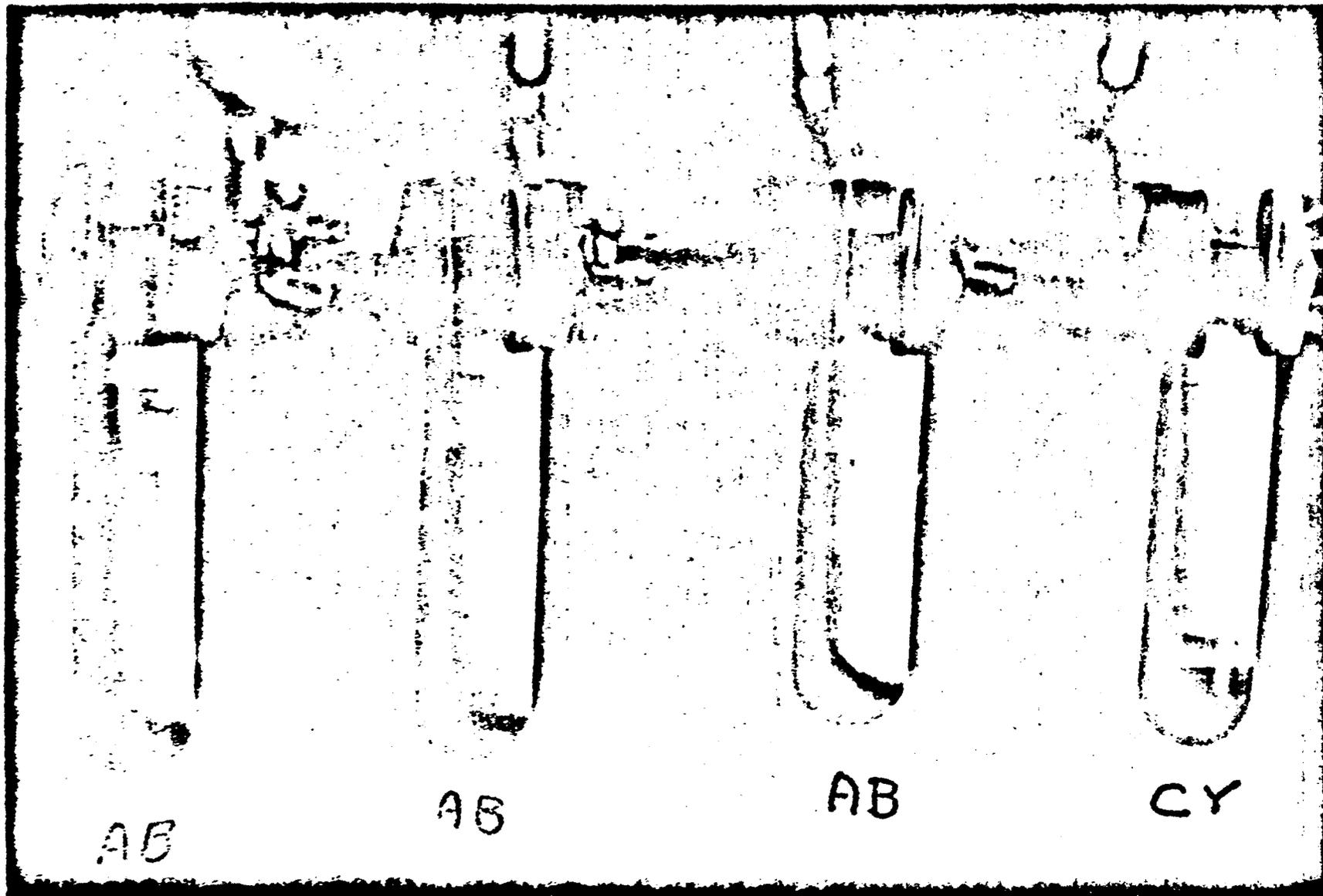


Figure 4
O.D. material

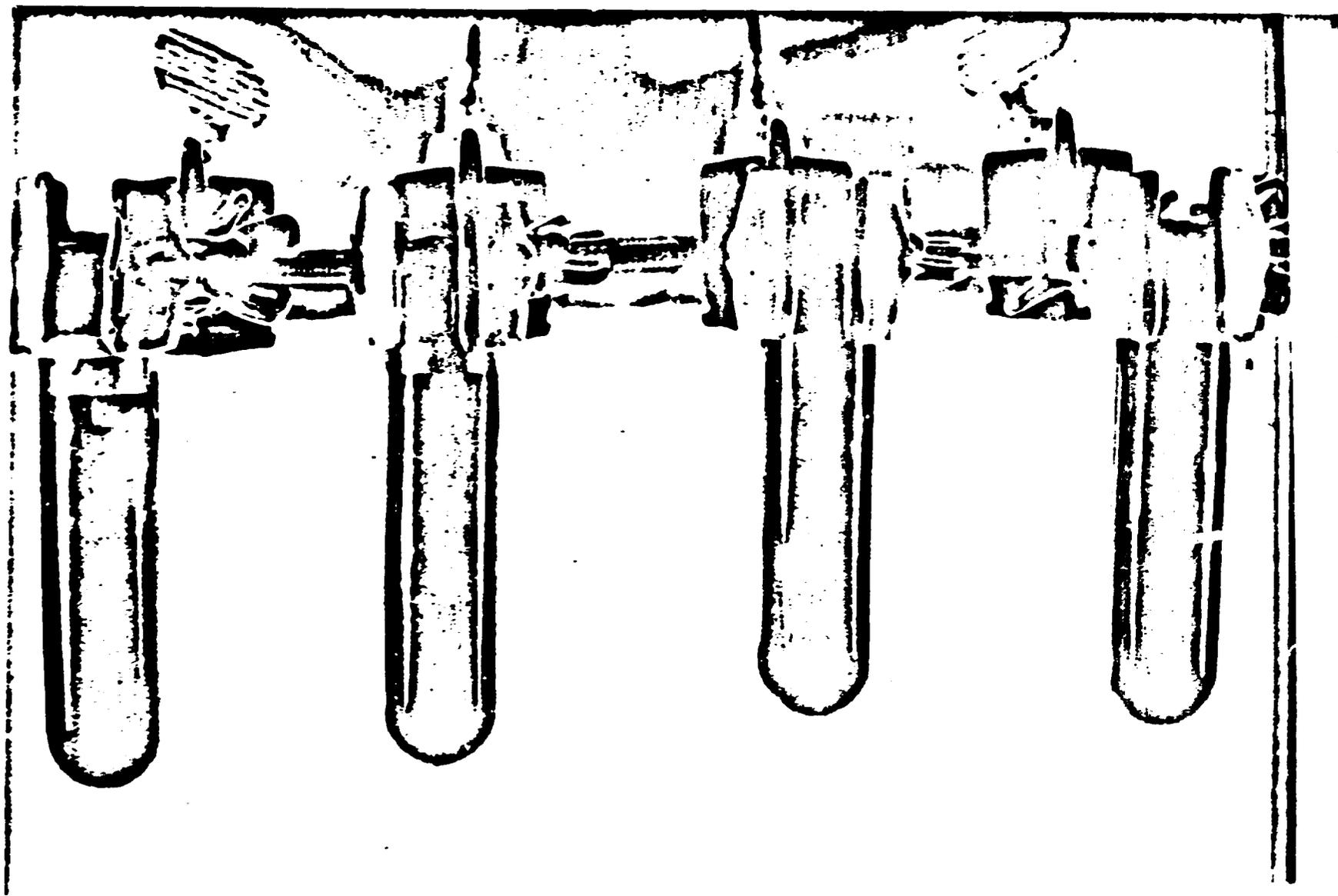


Figure 5
Diagram of the mechanism