PARAFFIN WAXES IN THE OIL FIELD

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Background

Crude oil is a complex mixture of organic materials consisting of saturated and unsaturated linear and branched hydrocarbons, organic acids, amines, hetero atomic and polycyclic molecules combined in various proportions. Paraffins waxes are an important component of the saturated linear and branched hydrocarbon portions of these grand mixtures. They are important for several positive reasons; primary among these is their fuel value as a refinery feedstock. However, they are also important because of their tendency to negatively affect the physical properties and behavior of the crude oils in which they reside. Two important physical properties that are affected by the presence of these paraffin waxes are viscosity and deposition tendency. These properties are of significant importance to ability of oil companies transport these crude oils from the reservoir to the consumer. Paraffin waxes form networks of crystals within crude oils as the temperature drops, producing deposits on cold surfaces like pipe walls. These deposited waxes then act to impede the flow of oil fluids through the transporting conduit. But before deposits are formed the Waxes produce large increases in the viscosity of the crude oil fluids that results in higher energy costs as pumping energy requirements are rapidly escalated. Sometimes accumulations of paraffin waxes can have catastrophic consequences such as line plugging and ruptures that can result in severe environmental damage. Thus control measures that act to mitigate the negative physical properties produced by paraffin waxes are of high priority among oil producing and refining companies.

Laboratory distillation methods provide good comparisons to crude oil reservoirs, since gases and fluids are forced from areas of elevated heat and/or pressure to areas of lesser heat and/or pressure within each system. In both cases, gases condense and fluids cool as they migrate from the flask or reservoir. The condensation products may be gas, liquid, or solid at varying temperatures and pressures. In the case of paraffin waxes, these condensation products comprise a spectrum of variable carbon chain lengths ranging from 18 to 100+ carbons. As deeper and hotter reservoirs are put into production higher carbon chain length hydrocarbons become more prevalent, since the lighter gases and fluids have greater mobility through the porous geologic structures above. Thus, with the advent of new technologies enabling greater production depths and increased production in areas of deep water offshore, the crude oils being produced contain increased amounts of paraffin waxes.

Paraffin Waxes in Crude Oil

Problem paraffin waxes found in crude oil systems consist mainly of linear saturated carbon chain molecules (e.g., C_nH_{2n+2}). These molecules tend to form highly ordered multi-molecular aggregates through forces of induction (London forces of attraction). The formation of these multi-molecular aggregates is favored by temperature declines where threshold energies of molecular collisions are of sufficient but not excessive force for inter-molecular combination. Thus, highly ordered crystal structures begin to form as the temperature of the crude oil mixture declines. The process of molecular interaction progresses through several temperature plateaus as paraffin molecules of progressively shorter chain lengths bond to previously formed aggregates. Observations of wax formation in crude oils indicate that the process occurs in four distinct steps, 1.) **Primary aggregation** or nucleation (platelet formation) 2.) **Secondary aggregation** (equivalent chain length platelet interaction) 3.) **Ternary aggregation** (non-equivalent or lower chain length attachment to the higher chain length platelet aggregates) **4.) Quaternary aggregation** (networking between tertiary aggregates by increasingly smaller paraffins). The effects of each stage of aggregation can be observed by different techniques depending upon the physical appearance of the oil under study. Lightly colored and transparent crude oil allows visual observation of the first stage of aggregation, and this stage is usually described as the crude oil cloud point. This stage is reached as the number of nucleates becomes sufficiently great so as to be visible to the naked eye. This stage is also accompanied by minute changes in the viscosity of the crude oil sample, and is described by the first inflection point in the change in viscosity with decreasing temperature. This is fortunate, since opaque oils do not allow direct visual observation of the cloud point. The second and third stages of aggregation are nearly indistinguishable from each other, since both result in increased viscosity. However, as mentioned above, temperature plateaus are observed as decreasing chain length paraffins begin aggregating with the previously formed platelets. Thus, viscosity versus temperature measurements show a smooth but increasingly steep incline in viscosity during the primary and secondary aggregation, while the tertiary phase shows an inflection or increased rate of change in viscosity versus temperature. The quaternary aggregation effect is associated with logarithmic increases in viscosity as temperature decreases, and this phase is normally where the pour point is obtained.

Paraffin Wax Triggers

Temperature changes are among the most important means of triggering the formation of wax aggregates in crude oil systems, however they are not the only triggers. When paraffin waxes are present in crude oils, ***they*** behave so as to create phase separations as the solubility of the paraffin molecules decreases with declining temperatures (e.g., solids appear from the liquid phase). Cold surfaces provide areas within conduits that are conducive to the formation of wax deposits. Additionally, exposure to low environmental temperatures act to cool the transporting lines encouraging wax crystal growth. The presence of solids, such as reservoir fines (fine sand suspended in the oil) can act **to** nucleate wax aggregates by providing a surface from which they can grow. **Rough** surfaces on exposed equipment *can* also serve as a growth site for wax nucleates, tubing, pumps, valves, and sucker rods all encourage wax growth from corrosion pits, scratches, and threaded joints. Additional wax growth sites include asphaltene particles and emulsion interfaces. In fact when both paraffin and asphaltene are present in a crude oil, they tend to co-precipitate as a mixture of solids. The combination of paraffin waxes with emulsions leads to "solids stabilized" emulsions that are extremely stable and hard to resolve by treatment with de-emulsifiers. There are also less common triggers to wax formation such as Joule Thompson cooling effects resulting from large pressure drops within the formation, the near well-bore, through valves, and other constrictions present in the system. With the increasingly prevalent practice of CO_2 flooding, Joule Thompson cooling becomes a much more common cause of wax deposition, asphaltene deposit and scale formation than before its field implementation.

Paraffin Wax Control Methods

I. Remediation

Although there are several methods of **paraffin** control employed by production companies throughout the oilfield, there are only a few truly good methods that should be practiced. Hot oiling, hot Watering, and hot water surfactant treatments performed in the well are examples of archaic and damaging treatments that are practiced all to frequently by the oil producer. By introducing hot fluids to the well, high molecular weight waxes that have accumulated in the near well bore, tubing, and pump are concentrated **by** the selective melting and removal **of** the lower wax fractions. Further, it has been demonstrated by measurements of temperature within the wells undergoing hot fluid treatments that the fluids rapidly lose temperature as they move down the well. Thus, hot fluid treatment causes the accumulation of wax damage rather than alleviating it. However, hot fluid treatment of surface equipment is an acceptable practice since the monitoring of temperatures *can* be conducted with confidence. Solvent treatment of wells constitutes a much superior method for the removal of previously deposited waxes. Because of the high wax carrying capacity of aromatic solvents. the use of these solvents within the well provides a much safer and efficient wax removal procedure. **By** employing these high wax carrier aromatic solvents, the higher fractions of paraffin waxes previously deposited are removed along with the lower waxes present. Frequently, surfactants are included as part of these aromatic solvent packages. These surfactants provide the necessary surface energy reduction that facilitates exposure by increasing the surface areas of deposited waxes to their solvation by the aromatic solvent. The use of these aromatic solvents and solvent surfactant combinations also moderate the extent of the downstream problems **of** interface control when the solvated waxes reach the treatment battery.

II. Deposit and Viscosity Control

Control of wax deposits, and oil viscosity are very important to the successful operation of production, transport, and refining facilities throughout the oil industry. Deposits occurring within wells, pumps, and pipelines obstruct the flow of oil from one location to another. Likewise, increased fluid viscosity restricts the flow of oil and causes dramatic increases in the required pumping energy. Therefore, producers, transporters and refiners frequently implement methods of controlling deposits and fluid viscosity. For several years various chemical companies have introduced solvent and solvent/surfactant combinations into wells and surface equipment in order **to** prevent paraffin wax accumulation. However, large amounts of solvent are necessary for the alteration of **wax** solubility within a given system. This practice has, until recently, been dictated by the physical properties of the much more effective wax crystal modifiers. Wax crystal modifiers are of a class of products that interact with the growing paraffi wax **crystal** by co-crystallization and induced malformation of the normal paraffin crystals. Thus, crystal modifiers exhibit much the same physical characteristics as the paraffin waxes they are intended to modify (e.g., high melting point and freezing point temperatures). High melting points make the use of these modifiers difficult during the colder times of the **year**, since solutions of these products tend to freeze. As implied above, recent developments in the area of winterized paraffin crystal modifiers have provided new products that can be used in very low temperature environments.

Testing and monitoring

I. Cold Finger Testing

Specialty chemical companies employ a variety of methods for the testing of oilfield fluid properties. The problems associated with paraffin waxes provide a good example of the ingenuity required for the development of such testing capabilities. Cold **finger testing** (See Figure I) is one of the most widely used methods employed for the determination of wax deposit tendencies within a given field environment. Generally, this method consists of temperature controlled metal probes immersed in a stirred oil sample that is maintained at a temperature slightly above the oil samples cloud point **by** an external heating bath. The cold surface, provided by the probe or cold finger, initiates the formation of solidifying waxes contained by the oil. Testing times and temperatures are carefully controlled to allow a sufficiently large collection of wax for weighing to deposit on the probe surface. Attention to the field conditions is also critical to the effectiveness of these measurements; thus probe temperature and fluid temperatures are adjusted to provide as close an approximation to field conditions as possible.

11. ASTM D-97 Pour Point Testing

Pour point testing (See Figure 2) is among the most reliable and important methods for the monitoring of oil field fluid behavior. This method consists of placing a sample of oil in a specially designed pour point tube, attaching a cork fitted with a thermometer, immersion in an air cooled sub-ambient refrigerated chamber, and observing for fluid movement for *5* seconds after tilting the tube thermometer combination 90" to the upright. This method serves as a very quick screening technique for chemical effectiveness on the physical behavior of the oil under study. It is a very qualitative test since no actual measurement of viscosity or crystal formation is performed.

III. Gas Chromatographic Testing

Gas chromatography *(See* Figures 3 and 4) has become an increasingly important tool for the measurement of the characteristics of oils and waxes present in crude oil. This device is often employed to determine the boiling point fractions possessed by crude oil samples. The gas chromatograph is a device that contains a coiled tubular column filled with various adsorbing solid materials that act as condensation sites for fluids moving through it. The test fluids are introduced to this column and swept by **inert** gas through the column to a detection device located at the exit port of the column. *As* the fluid progresses through the column, heat is applied to it to boil the various components of the sample. Each component of the sample moves with variable velocity and exits the column at variable elapsed times from the initial injection time. Upon exit from the column the detector **sends** a signal to a recording device which records the elution time, and the magnitude of the signal which is related to the quantity of sample being eluted. By the use of this instrument, it is possible to examine the nature of deposits formed in systems and boiling point distributions various organic species present in oils.

IV. Sonic Testing

A relatively recent development employing the use of sound as a means of characterizing the behavior of fluids containing crystallizing species is represented by the "sonic *portable* testing laboratory (See Figures *5* and 6). This device consists of an immersion probe containing several signal sources and sensing transducers that measure temperature, sound, and light transmissions. Temperature differences between the external cooling bath and the oil sample are monitored by separate thermistors, while the temperature of the oil is measured by themistors in the immersion probe. The immersion probe possesses a calibrated geometric cavity that accommodates the sample fluid, and a sound source and receiver are located at opposing ends of the cavity. Since sound travels at variable velocities through media of different physical form (e.g., gas, liquid, and solid), an interference pattern can be obtained between the two waveforms of the emitted and fluid transmitted signals. Further, the sonic portable testing laboratory utilizes the principle of "molal freezing point depression" to develop melting point behavior over a range of cooling rate measurements. By differentiating the integral form of the cooling rate curve and comparing the results to empirically derived measurements of pure solvent wax mixtures, melting point fractions contained in the sample are ascribed carbon chain indices. All of the signals generated and measured by the probe are logged by an analog to digital data-logger and further processed by algorithms programmed to a computer. The algorithms process the signals and present graphical data that represents carbon number distribution, crystal energy absorption, and viscosity versus cooling curves.

V. Viscosity Measurements

Dynamic viscosity measurements of crude oil liquids are made by highly sensitive devices that measure variable spindle speeds as a function of their immersion in the oil sample (See Figures 7 and 8). Responses to the oil samples resistance to the spin of the spindle are measured by torque transducers that measure the difference between imparted and actual rotational force. The control of external physical variables such as shear rate, and temperature are varied to observe the behavior of the fluids under study. Thus, inflections in the shear stress versus cooling rate can be related to certain physical changes taking place within an oil sample (e.g., cloud point). Examinations of the temperature versus shear stress curves reveal various landmarks within the sample of fluid. These landmarks are usually indicated by inflections from smooth curve behavior as solid waxes appear from the liquid phase (e.g., aggregation of multiple wax molecules).

VI. Dynamic testing Loops

Many production companies have begun to request data obtained from specially constructed pipeline simulation devices. This requires the construction of highly specialized and expensive devices that measure fluid behavior of crude oils as they are subjected to different conditions of temperature, pressure, and flow velocity. The design of these devices is highly subjective, and variables such as pressure, temperature, and flow velocity are strongly dependent upon the configuration of these devices. One design consists of a fluid transport conduit with a pump, inlet pressure transducer, outlet port thermistor, and an exit port thermistor. The conduit temperature is controlled by a constant temperature bath, and the inlet fluid temperature is controlled by a variable heat *source.* Fluid displacement is measured by monitoring the speed of a positive displacement pump. These devices can be extremely complex and costly, but there appears to be no standard agreed upon by industry. Because there is no agreed upon standard, the company that requested these tests considers much of this data spurious.

VII. Bottle Tests

Simple tests are also conducted by the specialty chemical company, among which bottle tests perhaps represent the most simple. These tests involve the placement of deposited waxes of a given quantity in bottles containing water, water/surfactant, organic solvent, and/or organic solvent/surfactant combinations and observing the action of the solvent on the sample. These tests are conducted with and without heat and with and without agitation. The solvent and/or solvent/surfactant combination that most rapidly and most completely disperses or solvates the test sample is chosen as the most effective.

Product Field Applications

Case History I

A large West Texas production area had been experiencing accumulations of wax in a number of wells as primary production methods were being replaced by secondary water-flood recovery. This wax accumulation resulted in frequent well failures and a significant reduction in production volume. As had been the practice over the years, hot oiling was employed to remove the accumulated wax damage. This method requires the use of specially constructed tank trucks equipped with high-pressure pumps and boilers capable of heating stock tank oil to high temperature and pumping it through the constricted areas. Over several years these treatments concentrated the high molecular weight fractions of the accumulated waxes present in the wells worsening the extent of the damage. As hot oiling down hole began to receive attention as a negative method of paraffin wax removal, several specialty chemical companies began to employ the use of hot water and hot water/surfactant combinations in place of stock tank oil. This method soon replaced the hot oiling throughout this production area. Hot oil trucks were still employed to heat and pump the hot water and hot water/surfactant combinations down hole to remove the wax damage. New problems associated with this practice began to appear as interface pads in dehydration units began to increase and emulsion resolution was greatly diminished. It was at this point that this laboratory became involved in attempting to remedy some of these problems.

Although wax crystal modifiers had been successfully applied to remedy wax problems for several decades by highly visible and costly production operations such as those offshore, the widespread use of these products had rarely been employed in marginally productive fields. Several factors such as physical properties, high cost, and availability of these products prevented their implementation as a means of controlling wax related problems. A major problem with the use of crystal modifiers involved their tendency to become solid as the environmental temperature declined thereby necessitating special handling for their delivery to the problem areas. However, in this particular area well spacing and surface equipment configurations allowed for the placement of a special heat traced chemical storage facility. Thus, it was possible to store the crystal modifier chemical at a central location and conduct truck treating from this site. The program began by conducting a thorough well clean-up utilizing aromatic solvent and aromatic solvent/surfactant combinations. The solvent was placed in the wells in sufficient quantity to cover the perforations, allowed to soak for twelve hours and, where possible, circulated an additional twelve hours to remove the accumulated wax damage. After the solvent cleaning of the well was complete and the wax damage removed, it was placed on a periodic backside injection of crystal modifier via a truck treatment program. Since these wells were on a pump-off schedule (e.g., well casing annular fluids are periodically reduced by automated methods) it was questionable that the crystal modifier would remain at an effective treatment level within the well. Pour point monitoring of these wells was conducted to determine whether a depression of the pour point from the untreated oils produced was being realized. This testing indicated that indeed the chemical was reaching the problem areas, and that significant pour point reduction was being achieved. Prior to the implementation of this program many of the wells in this area were on a hot water/surfactant clean-up schedule averaging once every thirty days. After the implementation of the crystal modifier program, it is not uncommon to find the frequencies decreased to once every one hundred and eighty to three hundred and sixty plus days. Additionally, interface problems experienced by down stream dehydration treatment have virtually disappeared.

Case History II

Another West Texas production facility that had gone through the same evolution of wax treating methods as those utilized by the producer in the previous case history was complaining about the ineffectiveness of these methods. This producer was on the verge of replacing the chemical company then treating the field with a competitor. Field engineers had heard about the effectiveness of crystal modifiers in preventing wax accumulation problems and were keen to attempt such a program. Chemical sales representatives were concerned about the potential loss of this account, and called this laboratory in to consult on and recommend a solution to the problem. It was decided that this facility should implement a program similar to that implemented in case history I above, but that treatment would be required on a continuous basis. The requirement for continuous treatment meant that a crystal modifier product had to be developed which would not freeze during colder periods of the year since the logistics of providing continuous treatment to widely dispersed production sites precluded the centralized heated storage required. Thus, a product was developed which would withstand temperatures from above **140"F** to below **– 20 ° F.** Testing had been performed on a large sampling of the oils produced from this area and this product had shown a significant reduction in the pour point and deposit tendency of these oils.

Prior to the implementation of this program the hot water/surfactant treatment frequencies for these wells averaged approximately every **20-60** days. After performing the solvent/surfactant clean-up as described in case history I, and continuous injection streams installed, this frequency has declined to once every two hundred seventy to three hundred *sixty* plus days. Since the initial placement of this program began on a five well sampling (see Tables land 2) approximately one plus years ago, the program has expanded to over *one* hundred wells. Implementation of a truck-treating program for wax control such as that described in case history I is under consideration.

Summary

Paraffi waxes contained in crude oil present significant problems for petroleum companies and they challenge the ingenuity of specialty chemical companies contracted to solve them. The problems of deposition and crude oil viscosity alteration associated with the presence of paraffin waxes must be carefully diagnosed and treated. Many of the methods historically employed for control of wax associated problems have been found to exaggerate the severity of the problems rather than adequately address them. Thus, the approaches to solving these problems have evolved to include specifically designed chemicals (e.g., winterized crystal modifiers) possessing properties that allow for their use under even the harshest environmental conditions. As deeper and hotter production zones are brought into production the extent and severity of paraffin wax problems have and are expected to increase, and in the future as in the past specialty chemical companies will be challenged to provide solutions.

References

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2. Becker, H.L. ***(JR)***, "Kinetic Model of Pour Point Phenomena", SPE **22830,** 66th Annual Technical Conference **and** Exihibition of the Society of Petroleum Engineers, Dallas, **TX** (October **6-9, 1991).**
3. Becker, JR, "Crude Oil Emulsions, Waxes and Asphaltenes", PennWell Publishing Company, **1997,** Tulsa Oklahoma.
4. Mansure, **A.J.,** Barker, **K.M.,** "Insights Into *Good* Hot Oiling Practices", SPE **25484,** Production Operations **Symposium,** (March **1993) 689-694.**

Table 1 - Four-month Savings due to the Implementaion of a Crystal Modifier Program

Well Number	Days on Modifier	$/day Modifier	Treatment Cost to Date	Hot Water Treatment Frequency	Hot Water Treatments Skipped	Hot Water $/Treatment	Cost to Hot Water	Savings
1	132	$ 5.43	$716.76	20	7	$543	$3,584	$2,867
2	118	$ 5.43	$640.74	20	6	$543	$3,204	$2,562
3	118	$ 5.43	$640.74	30	4	$543	$2,136	$1,495
4	117	$ 5.43	$635.31	30	4	$543	$2,118	$1,482
5	119	$ 5.43	$646.17	60	2	$543	$1,077	$430

Work-over rig and clean-up cost	$15,175
Chemical cost savings	$8,836
Installation cost	($10,188)
Total cost savings	**$13,823**

Table 2 - Twelve-month Savings due to the Implementation of a Crystal Modifier Program

Well Number	Days on Modifier	$/day Modifier	Treatment Cost to Date	Hot Water Treatment Frequency	Hot Water Treatments Skipped	Hot Water $/Treatment	Cost to Hot Water	Savings
1	380	$5.43	$2,063	20	19	$543	$10,317	$8,254
2	366	$5.43	$1,987	20	18	$543	$ 9,774	$7,787
3	366	$5.43	$1,987	30	18	$543	$ 9,774	$7,787
4	365	$5.43	$1,982	30	12	$543	$ 6,516	$4,534
5	367	$5.43	$1,992	60	6	$543	$ 3,258	$1,265

Work-over rig and *clean-up cost*	$45,524
Chemical cost savings	$29,625
Installation cost	($10,188)
Total cost savings	**$64,961**

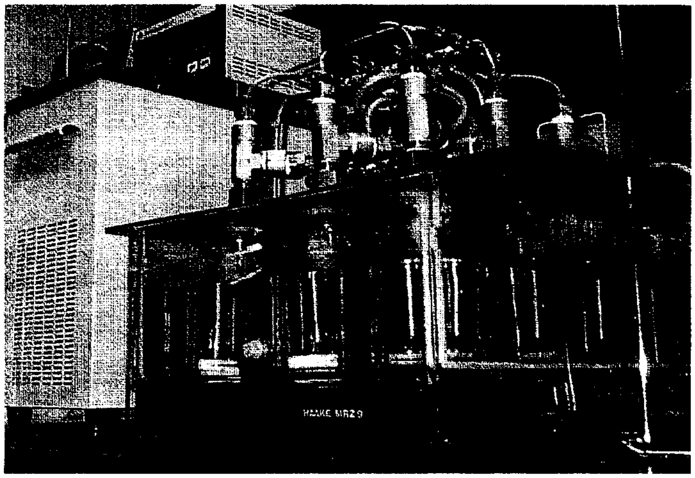
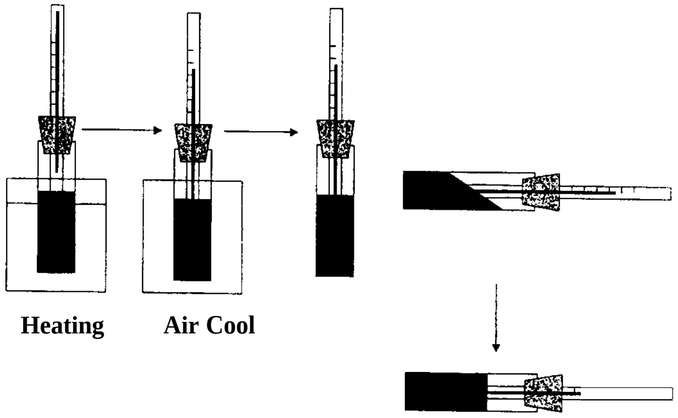


Figure 1 - Eight Probe Cold Finger



Pour Point when held 90° to upright for 5 seconds

Figure 2 - Pour Point Test

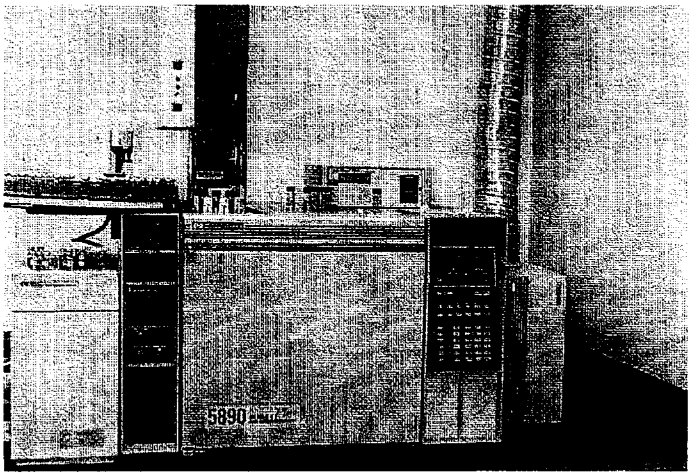


Figure 3 - Gas Chromatograph

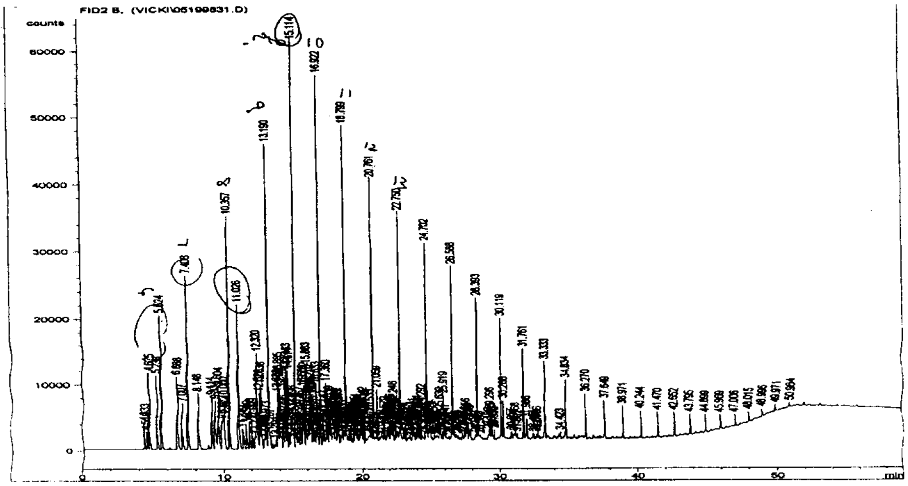


Figure 4 - Gas Chromatogram of a Crude Oil Sample

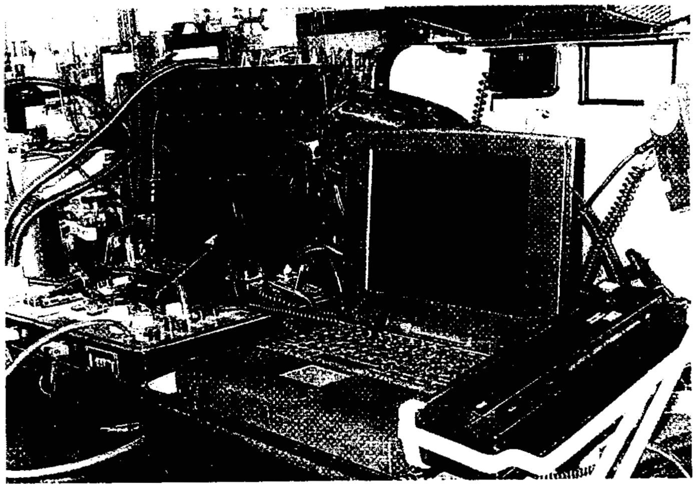


Figure 5 - Sonic Portable Laboratory

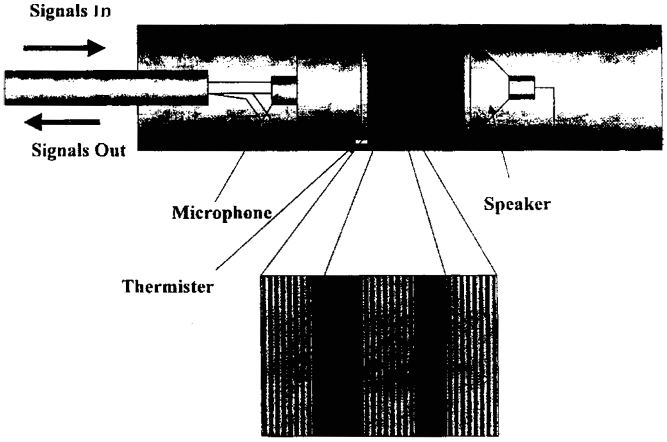


Figure 6 - Sonic Portable Laboratory Test Probe

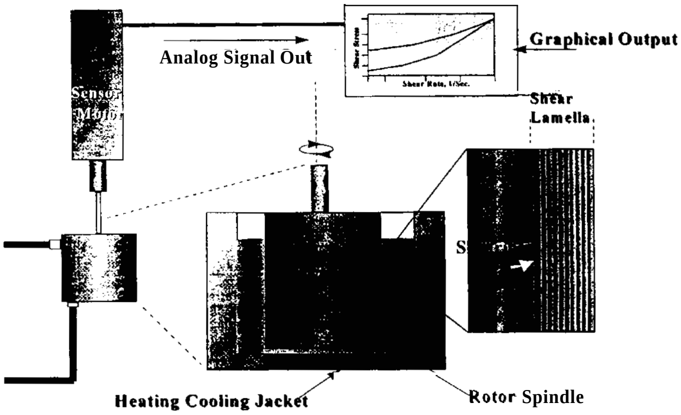


Figure 7 - Dynamic Viscometer

Wax In Crude Oil

- **Viscosity versus temperature profiles show the results of aggregation.**
- **These aggregates can be correlated to the species responsible using cooling rate data.**

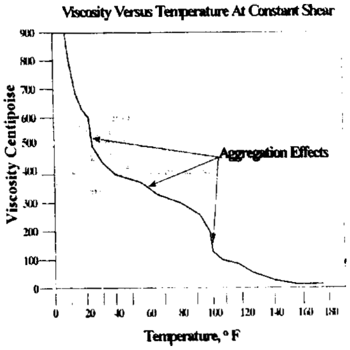


Figure 8 - Viscosity Curve of **Wax** Containg Oil