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Study of Paraffin Crystallization Process Under The Influence of Magnetic Fields and Chemicals

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Abstract

Literature data on the influence of magnetic fields on organic deposition process are most oriented to charged species, *e.g.*, calcium carbonate scale. It has also been claimed that the use of magnetic tools can mitigate paraffin deposition in flow lines. If this technique can be applied to subsea flowlines the benefits are potentially high. However, magnetic tool manufacturers do not provide the necessary level of information to make the customer feel comfortable to rely on such devices. Therefore, a research project has been established to shed some light to this yet controversial subject. The paraffin crystallization process under the influence of magnetic fields and paraffin inhibitors (PIs) has been investigated with the aid of Microscopy. The objective of this study was three-folded: - to provide a laboratory evidence to recommend - or not - the use of magnetic tool in the field, - to verify the Microscopy usefulness to study non-isotropic paraffin crystallization process and, - to provide an additional tool to help in selecting PIs. To our best knowledge the technical contributions of this study are- to confirm that magnetic field do alter paraffin crystallization process, - to establish a relationship between PIs and the paraffin crystallization process and, - the development of experimental analytical procedures to investigate paraffin deposition-related processes.

Introduction

Paraffin deposition is a well-known phenomenon that plagues the oil industry all over the world. As a rule paraffin problems can been solved in onshore fields with inexpensive physical and chemical methods. However, as the oil industry is continually moving to deep water scenarios where paraffin deposition takes place in difficult-to-reach subsea flow lines, manifolds and wet Xmas trees, no inexpensive solutions are known. Conversely, operators are concerned to paraffin deposition problems in deepwater production facilities for they are costly, time-consuming and means a serious menace to the economical feasibility of their enterprises.

To cope with operational problems associated to organic deposition in deep waters, Petrobras has been funding an integrated research program - the so-called Petrobras Flow Assurance Program (PROCAP) - aimed at forecasting organic deposition and preventing and/or solving the problem in offshore wells. A set of preventive and remedial solutions were either in-house- or jointly-developed. The major products that arose from this research effort are briefly described as follows:

Pigging A jointly industrial project on pipeline pigging simulation was launched by Petrobras in 1996[1]. More than one hundred successful pigging operations have been conducted in subsea flow lines in Campos Basin so far.

Nitrogen Generating System (SGN) The SGN method comprises the controlled reaction between two nitrogen-containing chemicals which is capable of generating a large amount of nitrogen gas and heat. The method has been successfully used in more than one hundred operations in Campos Basin area[2].

Paraffin Inhibitors The use of paraffin inhibitor (PI) is another approach to solve paraffin deposition problems in offshore fields. The technology which also includes the correct application of these chemicals in the field has been used in a long-term test in the Albacora field, Campos Basin[3]. On-going research on this subject has been oriented toward finding more cost-effective PI´s and understanding how these chemicals prevent paraffin crystals from growing[4].

Magnetic devices

A study to investigate the potential of the so-called magnetic fluid conditioners (MFCs) to inhibit paraffin deposition is being carried out at Petrobras Research Center. The first part of this study comprises a detailed laboratory investigation and some exploratory tests with commercial available MFCs in easy-to-access onshore wells. The objective of this exploratory study is to find a scientific explanation on why/how MFCs works and if such devices are reliable to be recommended to our expensive deep water production projects where they certainly would be a major advantage on traditional paraffin control methods.

As a matter of fact, our curiosity to MFC application has been attracted by the huge number of these devices in operation in People´s Republic of China. According to a recent paper published by Biao and Lijian there are as much as 14 400 MFCs successfully being used in different Chinese onshore fields[5]. Besides, MFCs for different applications are offered by manufacturers, including: inorganic scale inhibition, fuel burning improvement, smoke control, emulsion treatment, among others. Within the scope of this work the controversial theme of MFC application to inhibit either inorganic and organic scale will be discussed on a theoretical basis. Some preliminary laboratory and field results are presented as well.

Theoretical Discussion on Magnetic Fluid Conditioners

Fundamentally, every work done on or by the system can be related to a change in its boundary (PdV). Being so, the internal energy of the system (U) can be expressed as a function of the system entropy (S), volume(V) and amount of moles of each of its components ($N_{1,....,}N_n$)[6]. Nonetheless, there are other types of work that may affect the system, for instance, the work to magnetize a specific component of the system. Model and Reid[7] derived an expression for the work done by magnetic field on a given component of a thermodynamic system, as follows:

$$W = V_s \propto_o \int_0^{\mathrm{M}} \mathrm{H}\,d\mathrm{M} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

$$\mathrm{M} = \left(\frac{\propto}{\propto_o} - 1 \right) \mathrm{H} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2).$$

The actual material magnetic permeability (∝) is a function of material, pressure, temperature and magnetic field strength.

Adding Eq. (1) to the fundamental equation of internal energy of the system, the following equation can be derived:

$$U = TdS - PdV + V_S \propto_O \mathrm{H}\,d\mathrm{M} + \sum_J \propto_J dN_J \ldots\ldots (3)$$

According to those authors a minor effect on crystallization temperature can be expected from the application of magnetic field on a given thermodynamic system. Experiments carried out by Rocha with paraffins in organic solvents corroborates such affirmative[8].

For the sake of simplicity the theoretical discussion on the application of MFCs was splitted in two main areas: inorganic and organic scale inhibition

Inorganic Scale. The influence of magnetic fields on the formation of inorganic scale is a proven but dimly understood phenomenon which has been exploited by the industry to mitigate scale formation. It has been reported that different aragonite to calcite ratios can be obtained if adequate magnetic fields are applied to a calcium carbonate-containing system. When aragonite is predominant over calcite crystals a less adhesive scale is formed[9]. Baker and Judd[10] recently published a review on the use of magnetic devices to inhibit inorganic scale in aqueous medium. Those authors mention that MFCs are more effective when operating under orthogonal fluid flow with respect to the magnetic field orientation. The Lorentz forces, which addresses the interaction between polar charged species and magnetic fields, are considered to be the governing mechanism in scale inhibition. The action of these forces in the particle electrical double layer causes a change in its charge at the Helmholtz shear plane. As a result, both particle-to-particle and particle-to-solvating-liquid interactions are affected. thus changing either the crystal habit or the hydration number.

Organic Scale. Under original reservoir conditions different fractions that compose crude oil(crude) are in thermodynamic equilibrium which has been achieved along the geological time. As the production process is started, crude is displaced from its original equilibrium condition. As it is forced to move upwards, crude goes through a continuum of phase equilibria where solid phases might appear. The composition of these solid phases may range from predominantly paraffinic to predominantly asphaltenic. If favorable hydrodynamic conditions are achieved, these solids can agglomerate and migrate to an interface, thus forming the so-called organic deposition (paraffin and/or asphaltene deposition). In general, actual paraffin deposits are a complex mixture of heavy solid alkanes (C_{18}+) crude droplets, small amounts of asphaltenes, sand grains, precipitated salts, rust and water, which are entrapped during the deposition process.

Diffusion process is the key factor controlling paraffin deposition phenomenon under actual field conditions. Independently of its paraffin content should an adequate thermal gradient be applied to a crude a paraffinic deposit will end up being formed. Once the so-called wax (paraffin) appearance temperature (WAT) of crude is reached, paraffin crystallization starts and, below this temperature, a potential to generate a paraffin deposit by the crude is developed[11] .

So far the Lorentz forces are concerned it is difficult to explain the interaction between a magnetic field and a hypothetical crude which only contains non-polar molecules. At first glance, unless the magnetic forces are actually exerted either on the polar molecules or on the brine ionic species commingled with crude it is impossible to explain in the language of physics and chemistry the phenomenon provided by magnetic fields on paraffin deposition.

According to literature data gathered by Rocha[8] when crude is flowed in an adequate magnetic field paraffin molecules tend to align their poles with the ones of the magnetic field as far as thermal agitation is not excessive. Moreover, the action of magnetic field on these molecules changes both electrons rotation and translation patterns thus changing their orbital angular momentum. This leads to a disturbance in the crystal agglomeration processes. As a matter of fact, under a given magnetic field, weak dipoles are actually brought into being in the paraffin molecules. These dipoles generate a repulsion force between these molecules leading to changes in their rheological and morphological properties.

To our understanding the lack of conclusive literature data on the effect of magnetic fields on the phase behavior of paraffins can be assigned to the complex nature of crude, in which innumerable components, having different physical and chemical properties. are found. For instance, the large number of different paraffin molecules in crude prevent the occurrence of a sharp crystallization process and beyond doubt it is a major drawback to study the crystallization of actual crude samples and, consequently, to assess the influence of magnetic fields on this process.

Presentation of Data and Discussion.

Magnetic Fluid Conditioning Back in 1995 a scoping trial was conducted by Vieira[12] using an in-house-built single-pass MFC lab unit and crude samples. Neodymium-Iron-Boron magnets (up to 0.66 T), permanent magnetic field geometry and different exposition times were used in this experimental work. After being magnetized some viscosity reduction could be observed in some of the tested samples but no influence could be observed on their WAT and pour point. A relationship between temperature at which the magnetic field was applied to the sample and viscosity reduction could be observed. However, it was not possible to get a good correlation between magnetic field, exposition time and viscosity reduction.

More recently a series of experiments was carried out using a revamped MFC lab unit (magnetic loop) (Fig.1). On this series the following fluid systems were tested:

#1-.an industrial paraffin blend (C_{16}-C_{38}), containing 95% n- paraffins and 5% iso- and cyclic-paraffins, in n-icosane (33 % wt)

#2-.octacosane ($C_{28}H_{56}$) in n-heptane (33 % wt)

#3-.n-tricosane ($C_{23}H_{48}$) in n-heptane (33 % wt)

#4- crude

This experimental study was performed as follows:

-the rheological memory of the samples was eliminated by a thermal treatment[13], prior to allowing them to flow through the magnetic loop;.

.-orthogonal fluid flow with respect to the magnetic field orientation was adopted;.

.-by setting the distance of the magnets around the tubing different magnetic fields - 0,23, 0,60 and 0,83 T (+/- 2%) - were applied to the flowing fluids,

.-by setting the flow rate different exposition times to the magnetic field were obtained and;

-temperature-controlled conditions

The parameters that were investigated in both untreated and magnetically-treated samples are presented in Tab.1. The three synthetic paraffin solutions (#1, 2 and 3) were magnetically treated as a yardstick to measure whether magnetic fields interact with paraffin crystals or not and, if positive results were obtained, to verify how long this interaction lasts. In the same way one paraffinic crude sample (25 % by wt paraffins) was also magnetically-treated. Data obtained from these different samples after they were magnetically-treated in the magnetic loop are grouped as follows: Viscosity reversibility as a function of the elapsed time are depicted in Figs. 2 and 3. Viscosity - temperature profiles for different magnetic fields are depicted in Figs. 4 and 5. SEM microphotographs of untreated and magnetically-treated n-octacosane and tricosane solutions are depicted in Fig. 6**.** Electronic paramagnetic ressonance(EPR) analysis results are depicted in Fig.7**.**

Some authors claim the interaction between crude and a magnetic field is not actually dependent on paraffin crystals but on other polar compounds present in crude (asphaltenes molecules) or commingled with it (brine's ions, rust, inorganic debris). A traditional MFC manufacturer states that the tool creates nucleation sites in the "surrounding fluids' where paraffin crystals will deposit in the flow rather than on pipe walls[14]. However, to our best knowledge, our lab results have proven that pure paraffin in hydrocarbon solutions do show susceptibility to magnetic treatments. A time-dependent viscosity reduction in both synthetic paraffin solutions that undergone the magnetic treatment was observed. It was as well possible to observe by SEM analysis that paraffin crystallization habit was changed by magnetic treatment. Regard to the magnetically-treated crude sample one can observe a viscosity decrease but no sensitive changes in the pour point or WAT. Neither SEM nor CPLM methods were useful to detect any crystalline modifications by virtue of the magnetic treatment of crude. EPR analysis was performed to confirm that paraffin solutions - in spite of being less paramagnetic than crude - are able to interact with magnetic fields.

Field Test. Stimulating results, obtained by this experimental investigation have encouraged us to conduct a field test with commercial MFCs. Therefore, two easy-to-access rod-pumping onshore wells (Wells A and B) were screened to be magnetically-treated. Two MFC manufacturers (Alpha and Beta) have decided to join this research program and have designed and provided an MFC for the field test according to their standard procedures for selecting this kind of tool. Crude parameters that were investigated are presented in Tab.2.

Well A produces a highly paraffinic crude. Production records shows the need of a paraffin-rig every 51 days to remove organic deposits. After "Alpha"MFC was installed in the well a 110 day continuous production period was observed. After this test period the MFC ended up being pulled out of well because it was plugged by inorganic scale. As a consequence of "Alpha" installation, workover job (US$ 12,000) was avoided and an additional volume of crude was produced. As per our estimate the MFC generated a net gain of US$ 32,000 for Petrobras. It is important to mention that the hard scale formed (100% inorganic) on the MFC entrance slot was characterized by X-rays Fluorescence Analysis as being a mixture of Barium Sulfate (predominant), Calcium Carbonate and Magnetite. A slight increase of the water cut was observed along the MFC test period.

Well B produces a mild paraffinic crude. Production records shows the need of a paraffin-rig every six months. Prior to running "Beta" MFC in the well a retrievable reel (deposition probe) was installed in the surface flow line to monitor organic deposition. Magnetically-treated crude´s viscosity and pour point were measured at the wellsite. Crude viscosity was slightly reduced (Fig. 8) but no significant pour point change was observed. Initial dynamometric analysis data also indicates a 30 % torque reduction on pumping unit´s gear box axis. No major flow rate changes have been observed so far. The reel that has been installed in the surface flow line is scheduled to be removed for inspection and quantification of organic deposition in the near future. This information is one of those that were negotiated with the MFC manufacturer to evaluate MFC performance. Well B is still under appraisal

Paraffin Inhibitors. Fig.9 shows SEM microphotographs of pure n-octacosane (Sol. #2) crystals(20 kV, 250 X). Figs. 10 and 11 show the same n-octacosane samples doped with an ineffective and an effective PI inhibitor, respectively. It can be observed that needle-shaped crystals are present in both untreated n-octacosane sample (Fig. 9) and the one doped with the ineffective PI (Fig. 10). Those needle-shaped paraffin crystals are able to form a tridimensional netting that leads to the stop-flowing material that may deposit in the formation or stick to the pipe wall[4].

As a matter of fact, paraffin crystallization in presence of PIs was initially investigated using both CPLM and SEM. Nevertheless, due to the sharper images obtained with the late technique we have chosen SEM to run our experiments. Also a decision was also taken to use the n-octacosane- and n-tricosane- solutions (#2 and 3), instead of the industrial paraffin blend solution (#1) , to investigate the effect of PIs on paraffin crystallization process. Sharp crystallization images were not obtained with the late solution.

Conclusions

1.The influence of magnetic fields on paraffin crystallization process is still dimly understood Lack of precise scientific explanation on the whole process is definitely a drawback to get the most from MFCs

2.In our laboratory experiments a fair relationship between magnetic field intensity, exposition time and viscosity reduction was obtained for a crude sample.

3.The two field results with MFCs have provided encouraging results so far. Further tests in other onshore wells. are on schedule.

4.In a broadest sense this initial series of experiments with the magnetic loop was worthy to confirm that magnetic fields do alter pure paraffin crystallization process and that this phenomenon is time-dependent. However, future experimental work must address the influence of other parameters on the efficiency of magnetic treatments, *e.g.*: microcomponents of crude, formation water salinity, fluid velocity across magnetic field and magnetic field geometry. After going on these further experiments we will be able to properly considering MFCs for offshore applications.

5.SEM is a suitable analytical tool to study non-isotropic paraffin crystallization process. This technique has allowed us to prove the influence of magnetic field and PIs on paraffin crystallization process.

Nomenclature

W = work, ML^2T^{-1}, J.
V_s = volume of system, L^3, m^3.
H = magnetic field strength, AL^{-1}, A/m
M = magnetization, AL^{-1}, A/m.
$\propto_o$ = free space magnetic permeability, $VtA^{-1}m^{-1}$, $VsA^{-1}m^{-1}$,
$\propto$ = actual substance magnetic permeability, , $VtA^{-1}m^{-1}$, $VsA^{-1}m^{-1}$.

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SI Metric Conversion Factors

cp x 1.0 E-03 = Pa.s
T x 1.0 E-04 = G
^{o}C +273.15 = K

TABLE 1 - CRUDE PARAMETERS

Investigated Parameter	**Method(s)**
Viscosity Profile/ Viscosity Reversibility	Rheology
Pour point	ASTM D-97 modified
Density	ASTM D-4052
WAT	Differential Scanning Calorimetry (DSC), CPLM
Paraffin crystalline habit	SEM, CPLM
Electronic Paramagnetic Ressonance (EPR)	EPR Analysis System

TABLE 2 - CRUDE PARAMETERS

Investigated Parameter	**Method(s)**
Viscosity Profile/ Viscosity Reversibility	Rheology
Pour point	ASTM D-97 modified
WAT	DSC, CPLM
Flow rate profile	Production test
Organic deposition over time	Probe installed in the surface flowline

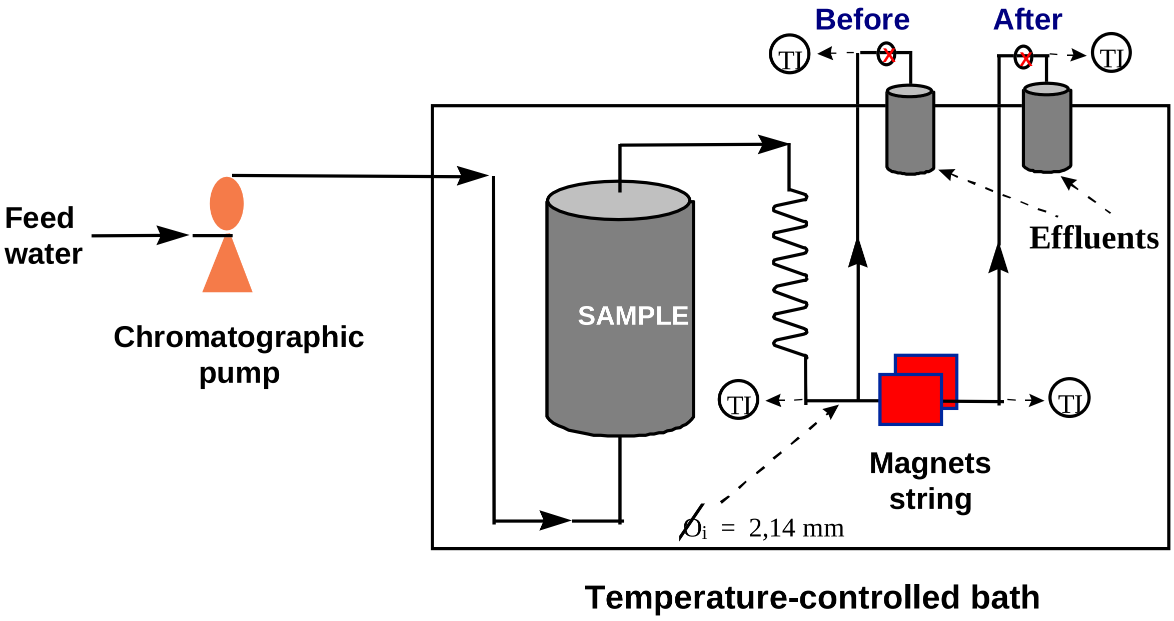

Fig. 1- Schematic View of the Revamped MFC Lab Unit (Magnetic Loop).

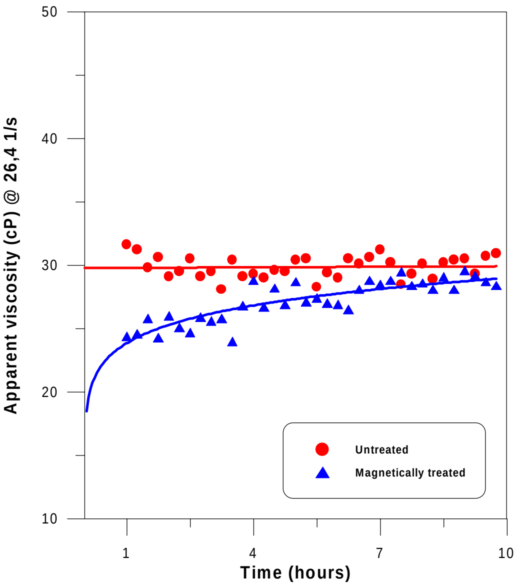

Fig. 2- Apparent Viscosity of Syntetic Paraffin Solution Versus Elapsed Time.(Sample: Untreated and Magnetically -Treated at 0.83 T @40°C).

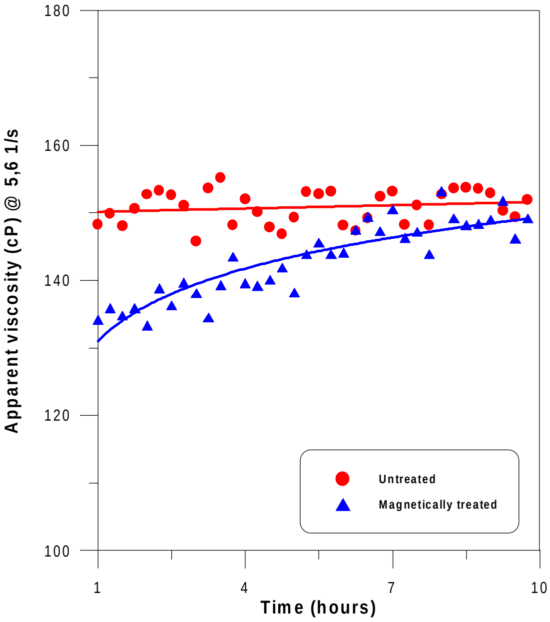

Fig. 3- Apparent Viscosity of Crude Oil Versus Elapsed Time.(Sample: Untreated and Magnetically-Treated at 0.83 T @ 40°C).

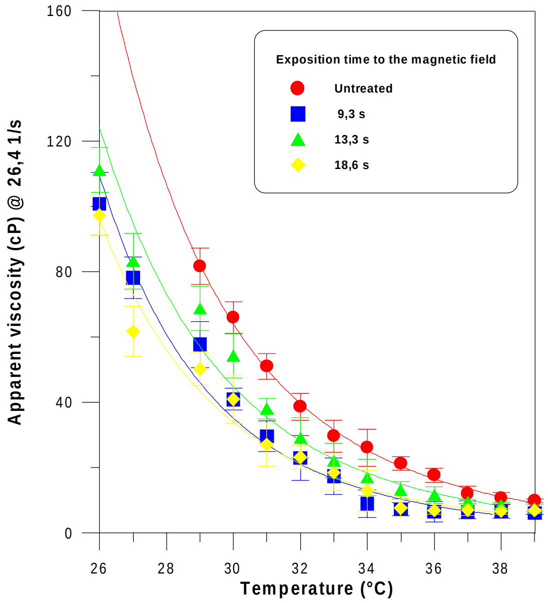

Fig.4-Apparent Viscosity of Synthetic Paraffin Solutions versus Temperature for Different Exposition Times (Magnetic Field of 0.60 T @ 40°C).

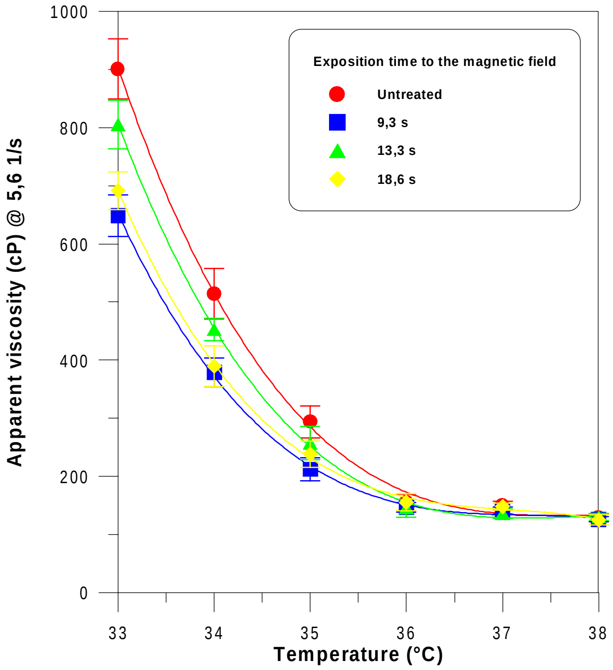

Fig.5- Apparent Viscosity of Paraffinic Crude versus Temperature for Different Exposition Times (Magnetic Field of 0.60 T @ 40°C).

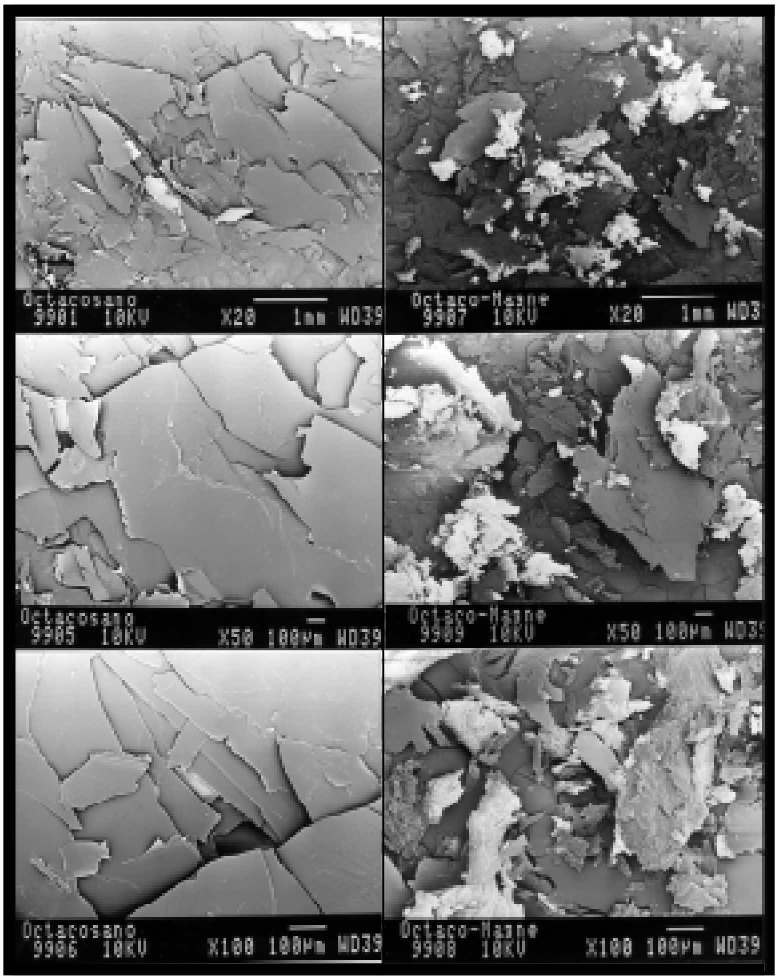

Fig. 6 - SEM Microphotographies of Untreated and Magnetically Treated n-Octacosane.

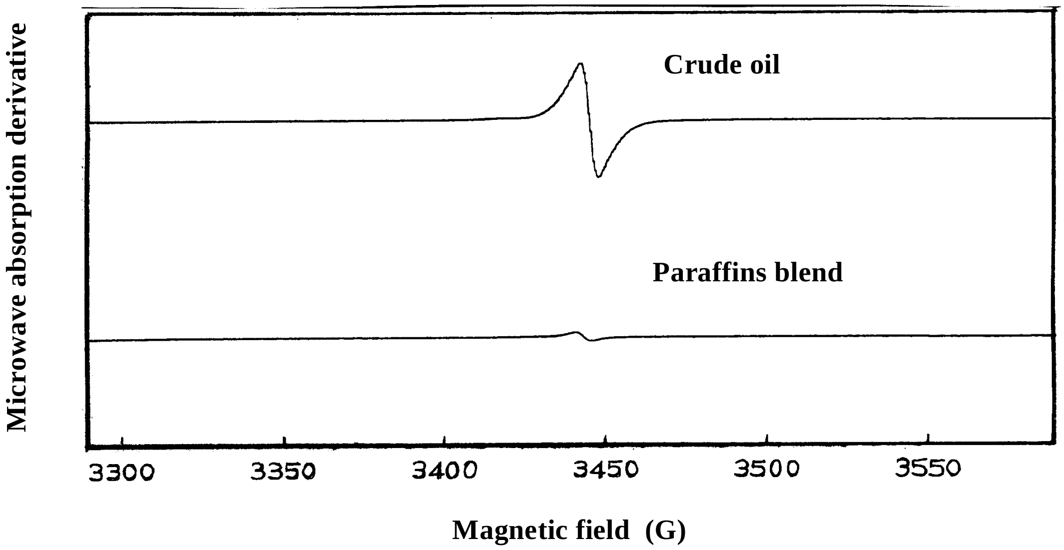

Fig. 7- EPR Analysis