INTRODUCTION

Asphaltene deposition during oil production and processing is a very serious problem in many areas throughout the world, as reported in various papers by researchers and engineers working on the problem (Katz and Beu, 1945; Haskett and Tartera, 1965; Lichaa, 1977; Adialalis, 1982; Tuttle, 1983; Mansoori et al., 1985). To practicing engineers, the importance of knowledge about behavior of asphaltenes in petroleum is similar to the knowledge needed by cardiologists regarding cholesterol in the arteries of patients.

In the Prinos field (Adialalis, 1982) in the north Aegean Sea where one of the authors had personal experience with the asphaltene deposition problem, there were wells that, especially at the start of production, would completely cease flowing in a matter of a few days after an initial production rate of up to 3,000 BPD. The economic implications of this problem were tremendous considering the fact that a problem well workover cost could get as high as a quarter of a million dollars (the presence of H\textsubscript{2}S was a significant cost factor).

In Venezuela the formation of asphaltic sludges after shutting-in a well temporarily and/or after stimulation treatment by acid has resulted in partial or complete plugging of the well (Lichaa, 1977). At the Hassi Messaoud field, Algeria, deposition of asphaltenes in the tubing was a very serious production problem and necessitated frequent tubing washings or scrapings to maintain production (Haskett and Tartera, 1965). Asphaltenes have played a significant...
role in the production history and economics of the deep horizons (zone D-7) of the Ventura Avenue field, California (Tuttle, 1983). Asphaltene problems at the Ventura Avenue field ranged from asphaltene deposition during early oil production to asphaltene flocculation and deposition resulting from well acidizing and CO$_2$ injection (EOR). It was also reported that asphaltene deposits were found in the production tubing in the Little Creek CO$_2$ injection EOR pilot in Mississippi (Tuttle, 1983). Asphaltene deposition has not been reported previously during the primary and secondary recovery of the field.

Asphaltene precipitation, in many instances, carries from the well tubing to the flow lines, the production separator, and other down-stream equipment. This was certainly the experience in Prinos. It has also been reported (Katz and Beu, 1945) that asphaltic bitumen granules occurred in the oil and gas separator while oil was being produced from the Vedder Zone of the Greely field, California.

The downtime, cleaning, and maintenance costs are a sizable factor in the economics of producing a field prone to asphaltene deposition. Considering the trend of the oil industry towards deeper reservoirs, heavier and as a result asphaltic crude oils, and the increased utilization of EOR techniques for recovering oil the role of asphaltene deposition in the economic development of asphaltene-containing oil discoveries may turn out to be important and crucial.

**Field Descriptions and Experiences**

*Prinos field, north Aegean Sea*

The Prinos field (Adialalis, 1982) was discovered in early 1974. Following development drilling and construction of the production facilities the first producing well was opened in July, 1981. The producing formation is the middle Miocene sandstone with shale barriers in between at a depth of 8600 ft and with a pay zone varying from 200 to 300 ft thick covering an area of about 6 km$^2$. The reservoir consists mainly of four different pay zones separated by shale barriers all in a domal configuration. The original reservoir pressure was 5,730 psig. The bubble-point of the crude ranges from 1,100 to 1,250 psig. The GOR ranges from 800 to 900 SCF /BBL depending on the geographical location within the field. The oil is an undersaturated intermediate base crude with a gravity of about 28 °API. It is a sour crude containing approximately 40% by weight H$_2$S. The reservoir temperature is 262 °F. An analysis of the average reservoir effluent is given in Table I.

From the first day of production asphalt deposits were observed in the tubing, separators, pumps, strainers and other locations. Asphaltenes were everywhere. The Prinos asphaltene problem initially was so severe that it was thought it would kill the project economically. The company took a number of steps to alleviate the problem and to a good extent was successful in doing so. The steps that appeared to have the biggest effect in moderating the severity of the problem were the following.

(a) Completing wells with a dual completion with the purpose of: (1) using the second tubing string for solvent injection or circulation; (2) access for lowering
production testing devices; and (3) for circulating around to kill the well. Sometimes the second tubing string was used for production to meet production quotas when the main string was shut-in for maintenance or asphalt cleaning.

(b) Extensive laboratory work, by different institutions, to develop production methods and special solvents to combat the asphalt problem and in general shed some light on the reasons for asphaltene deposition. Laboratory work at IFP was responsible for the construction of the graph shown in Fig. 1 which indicates the ranges of temperature and pressure where the Prinos crude flocculates asphaltic compounds. From this the company derived the rule of producing the wells at high wellhead flowing pressures (WHFP).

(c) The decision to produce first the A1 zone, the top reservoir, which was less prone to asphalt deposition. Actually most of the producing wells were completed dual comingled A1/A2 zones, but production surveys showed that most of the oil was being produced from the A1 zone. Xylene was the solvent selected, among many tested, to be used in well stimulations, workovers, and asphalt inhibition and cleaning. In one test with well PA-6, xylene injection through the non-producing string actually helped to minimize the asphaltene deposition problem.

Mata-Acema and Boscan fields, Venezuela

These two fields are briefly described by Lichaa (1977). The producing formation in the Mata-Acema field is the Miocene sandstone at a depth of 11,500 ft and a bottom hole temperature of 275 °F. An average composition of the field effluent shows that about 25% by volume is light fractions and the rest consists of C7+ fractions. Other data from the wells studied from this field are shown in Table II. Asphaltene problems in this field were enormous.

The Boscan field is the Eocene sandstone and produces heavy oil with gravities ranging from 9 to 12 °API. The formation is at a depth of about 8,500 ft and a bottom hole temperature of about 180 °F. The importance of this field lies in the fact that it is one of the largest proven heavy oil reservoirs in Venezuela containing about 17.2% asphaltenes and until now no asphaltene deposition problem has been reported. Table III presents data related to the Boscan crude.

So, in Venezuela, it can be observed that the Mata-Acema crudes with asphaltene contents of only 0.4 to 9.8% have asphaltene deposition...
TABLE II

Some properties of the various oils from the Mata-Acema field* 1

<table>
<thead>
<tr>
<th>Crude oil identification</th>
<th>API grav. (60/60 °F)</th>
<th>Asphaltene content (wt.%)</th>
<th>C₁⁺ (vol. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mata-Acema 102</td>
<td>27.1</td>
<td>1.1</td>
<td>68.24</td>
</tr>
<tr>
<td>Mata-Acema 105</td>
<td>28.5</td>
<td>1.2</td>
<td>69.17</td>
</tr>
<tr>
<td>Mata-Acema 202</td>
<td>28.0</td>
<td>1.4</td>
<td>72.04</td>
</tr>
<tr>
<td>Mata-Acema 207</td>
<td>27.1</td>
<td>2.0</td>
<td>—</td>
</tr>
<tr>
<td>Mata-Acema 210</td>
<td>33.4</td>
<td>0.8</td>
<td>—</td>
</tr>
<tr>
<td>Mata-Acema 211</td>
<td>24.1</td>
<td>3.6</td>
<td>74.59</td>
</tr>
<tr>
<td>Mata-Acema 219</td>
<td>16.6</td>
<td>9.8</td>
<td>78.96</td>
</tr>
<tr>
<td>Mata-Acema 221</td>
<td>23.1</td>
<td>9.0</td>
<td>—</td>
</tr>
<tr>
<td>Mata-Acema 223</td>
<td>25.2</td>
<td>3.5</td>
<td>—</td>
</tr>
<tr>
<td>Mata-Acema 224</td>
<td>23.1</td>
<td>1.4</td>
<td>—</td>
</tr>
<tr>
<td>Mata-Acema 225</td>
<td>36.4</td>
<td>0.4</td>
<td>56.72</td>
</tr>
<tr>
<td>Mata-Acema 226</td>
<td>21.5</td>
<td>5.0</td>
<td>77.73</td>
</tr>
<tr>
<td>Mata-Acema 228</td>
<td>21.0</td>
<td>4.0</td>
<td>—</td>
</tr>
<tr>
<td>Mata-Acema 230</td>
<td>20.4</td>
<td>6.2</td>
<td>—</td>
</tr>
<tr>
<td>Mata-Acema 231</td>
<td>26.1</td>
<td>3.4</td>
<td>—</td>
</tr>
<tr>
<td>Mata-Acema 235</td>
<td>19.4</td>
<td>5.4</td>
<td>—</td>
</tr>
<tr>
<td>Mata-Acema 239</td>
<td>26.2</td>
<td>2.0</td>
<td>73.59</td>
</tr>
<tr>
<td>Mata-Acema 245</td>
<td>22.3</td>
<td>4.3</td>
<td>75.61</td>
</tr>
</tbody>
</table>


problems, whereas the Boscan crude with 17.2% asphaltene content does not have asphaltene deposition problems. Boscan crude and Boscan refined oils were found to prevent electrodeposition of asphaltene from Mata-Acema crude, and asphalt precipitation when mixing acid and Mata-Acema crude. So Boscan crude appears to contain something that works against asphaltene flocculation. Also during the same experiments permeability reductions were severe due to acid injection and not so when a slug of Boscan mix was injected into the sand model ahead of the acid.

TABLE III

Properties of Boscan crude* 1

<table>
<thead>
<tr>
<th>API gravity (60 °F)</th>
<th>Viscosity (cp)</th>
<th>Sulfur (wt.%)</th>
<th>Nickel (ppm)</th>
<th>Vanadium (ppm)</th>
<th>Asphaltenes (wt.%)</th>
<th>Resins (wt.%)</th>
<th>Residue at 1 atm and 590 °F (wt.%)</th>
<th>Butane and more volatile components* 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.2</td>
<td>50 000</td>
<td>5.5</td>
<td>1200</td>
<td>150</td>
<td>17.2</td>
<td>29.4</td>
<td>86.7</td>
<td>0.0</td>
</tr>
</tbody>
</table>


* Practically it is all C₁⁺ .

TABLE IV

Average composition of Hassi Messaoud crude* 1

<table>
<thead>
<tr>
<th>Component</th>
<th>Mole percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂</td>
<td>1.80</td>
</tr>
<tr>
<td>CO₂</td>
<td>1.32</td>
</tr>
<tr>
<td>C₁</td>
<td>33.15</td>
</tr>
<tr>
<td>C₂</td>
<td>13.95</td>
</tr>
<tr>
<td>C₃</td>
<td>9.91</td>
</tr>
<tr>
<td>l-C₄</td>
<td>1.29</td>
</tr>
<tr>
<td>n-C₄</td>
<td>4.66</td>
</tr>
<tr>
<td>l-C₅</td>
<td>1.40</td>
</tr>
<tr>
<td>n-C₅</td>
<td>2.48</td>
</tr>
<tr>
<td>C₆</td>
<td>3.59</td>
</tr>
<tr>
<td>C₇</td>
<td>3.30</td>
</tr>
<tr>
<td>C₈</td>
<td>3.25</td>
</tr>
<tr>
<td>C₉</td>
<td>2.89</td>
</tr>
<tr>
<td>C₁₀</td>
<td>2.50</td>
</tr>
<tr>
<td>C₁₁</td>
<td>2.13</td>
</tr>
<tr>
<td>C₁₂ +</td>
<td>12.33</td>
</tr>
</tbody>
</table>


The Hassi Messaoud field (Hasket and Tartera, 1965) is in the Cambrian sandstone and lies at a depth of 11,000 ft with a payzone varying from 100 to 300 ft covering an area of approximately 600 sq. miles. The original reservoir pressure was 6,825 psig and the bubble-point of the crude varied from 2,880 to 2,130 psig on an east-west traverse of the field. The GOR varied from 1,390 to 1,030 SCF / BBL depending on the geographical location within the field. The oil is an intermediate base crude by the standard of the U.S. Bureau of Mines, 42.3 °API, extremely rich in gasoline (40% by weight), and of a light green color. An average effluent analysis is given in Table IV. The asphaltene content of stock tank oil is 0.062 wt.%.

K. J. Leontaritis, G.A. Mansoori and T.-S. Jiang
Asphaltene Deposition in Oil Recovery: A Survey of Field Experiences and Field Approaches
ICAT Proced., 11 Pages, DeKalb, IL, USA 1986
From the start of production asphaltene deposits were observed in the tubing strings. Wells often lost 20 to 25% of the wellhead pressure in 15 to 20 days, causing considerable loss in production. Cutting the deposits from the tubing by wireline methods was too time-consuming and sometimes impractical, so a program of washing the tubing with a solvent was established. Some 400 tubing washes were performed in this manner in 1960-1962.

At Hassi Messaoud it is observed that deposition of asphaltenes into the tubing does not occur after the pressure falls below the bubble-point and asphaltenes previously deposited were repolitized by the two-phase crude. If a mechanical choke or an asphaltene deposit choke is available sufficiently deep in the tubing it will cause two-phase flow and thus minimization of asphaltene deposition without the need of tubing wash. This idea was tested in five different wells and an improvement in the productivity of each well was accomplished. So, at the Hassi Messaoud field asphalt deposition was controlled to a reasonable extent by producing wells at low wellhead pressures.

**Ventura Avenue field, California**

In the Ventura Avenue field (Tuttle, 1983) in California asphaltene deposits occurred during primary, secondary, and enhanced oil recovery stages. The asphaltene-prone section of the field is described as the deep horizons, especially zones D-6 and D-7. Zone D-4 was developed in 1944. This zone is at 8,500 ft and is reported to be an unconsolidated sand formation. The bottom-hole temperature (BHT) ranged from 212 to 310°F. The original bottom-hole pressure (BHP) was up to 8,500 psig. The bubble-point of the crude ranged from 3,500 to 4,500 psig. Circulation of oil was used to avoid or reduce the asphaltene deposition problem. The oil was thought to be beneficial because it diluted the crude oil and reduced the tendency of the asphaltenes to precipitate. Solvent treatment and reverse and normal circulation with hot oil were also tried with mixed results. Solvent treatments were not very successful "...largely because the solvents used were limited to aromatic solvents such as toluene."

The problems at Ventura diminished after the BHP fell below the bubble-point of the crude. The wells have produced trouble-free from asphaltenes since the early 1970’s. However, the problems were so drastic because of asphalt deposition at the early history of this field that many wells were redrilled, thus affecting the economics of the project considerably.

It was also suggested that all well stimulation and EOR fluids should be tested for compatibility with the reservoir fluids prior to operations, especially where asphaltenic crudes are present. As mentioned earlier asphaltene deposits were found in the production tubing of the Little Creek CO₂ injection EOR pilot in Mississippi. Asphaltene deposition has not been reported previously during the primary and secondary history of this field. This problem is thought to have been caused by the CO₂ in the produced crude oil, which "...acted in a manner similar to propane in causing deposition of asphaltenes.” Tuttle concludes in his paper that mechanical removal techniques have been the most effective means of combating the asphaltene problems.

**Lake Maracaibo, Venezuela**

In Lake Maracaibo, Venezuela, it is reported (Von Albrecht et al., 1977) that the use of standard well completion techniques has often resulted in costly workovers for asphaltene removal in Cretaceous wells. The Lake Maracaibo offshore operations in western Venezuela accounts for more than half of all the oil produced in Venezuela.

There are three main producing horizons of Miocene, Eocene, and Cretaceous age. The Cretaceous reservoirs contained asphaltenic oils and caused serious asphaltene deposition problems. The Cretaceous production comes from partially dolomitized limestones. The
Cretaceous reservoirs lie from 14,000 to 16,000 ft in depth (underlying the Eocene reservoirs) with initial reservoir pressures as high as 86 MPa (849 atm). These reservoirs, like those of the Eocene age, are highly lenticular with, perhaps, 50 m of net pay distributed over 450 m of gross interval. Rock permeability ranges from 1 to 20 mD and production is by natural flow from cased or open hole completions. Initial production yielded a sweet 40 °API crude from an overpressured reservoir producing by dissolved gas drive.

As exploration proceeded outward from this zone, significant accumulations of a heavier 30 °API crude were found that contained up to 10% by weight asphaltenes and up to 3,000 ppm hydrogen sulfide. Asphalten deposition became so severe that it was threatening the economic production of the reservoir. The problem of asphaltene precipitation was eliminated by "...inexpensive modification of the production practices, rather than by the usual techniques of removal by chemical or mechanical means."

DISCUSSION

Differing views and experiences on asphalt deposition

By reading through the field experiences and practical approaches related to the asphaltene deposition problem or when reviewing the research and experimental work performed or in progress one may develop the impression that insofar as finding a rigorous universal solution to the problem is concerned there is still a long way to go. Only five years ago (Tuttle, 1983) it was reported that mechanical removal techniques were the most effective means of combating the asphaltene problems. Provided that Tuttle's statement is fairly broadbased, it underscores the fact that until 1983 the state of the art with respect to the asphaltene deposition problem, in the field, was acceptance that asphaltene will precipitate and then it must be cleaned out (in this case mechanically) periodically to permit production operations. Tuttle's statement clearly applies to the operating phi-losophy in the Prinos project, even though the company was actively engaged in research and experimental work to solve the asphaltene problem entirely.

As it is demonstrated, the current state of the art is not geared towards preventing asphalt deposition but only towards remeding the problem. It has been reported (Lichaa, 1977) that "...there is no information in the literature on any successful inhibitor being used with asphaltenes. The development of the more desirable alternative of preventing these deposits has lagged, currently, because of a lack of understanding on the mechanism involved in the deposition process." Elaborate experimental work has been performed (Lichaa and Herrera, 1975; Lichaa, 1977) and three of the most important findings are the following:

(1) Resins serve as peptizing agents for the asphaltenes. Resins are easily oxidized to asphaltenes.

(2) Effective inhibition of asphaltene deposits in the formation (and surface equipment) appears possible by injecting to the formation additives containing sufficient amounts of peptizing agents.

(3) Electrical effects play an important role in the asphaltene deposition problem, thus controlling the electrodeposition of the asphaltene particles can lead to the development of preventive techniques.

It is observed (Lichaa, 1977) that in certain cases the asphaltene content of the crude may play a lesser role in the flocculation process than the amount of peptizing agents, i.e. resins. In other words, it is possible to find a crude with high asphaltene content and no deposition problem if the required amount of peptizing agents is present. For instance, the Boscan crude contains 17.2% by weight asphaltenes and yet it does not cause an asphaltene problem.

In the Hassi Messaoud field (Haskett and Tartera, 1965) it was reported that the asphaltene problem was largely controlled by producing
the wells at low wellhead pressures. In the Prinos project, however, the rule was to produce above 100 atm wellhead flowing pressures (WHFP). At the start of production in Prinos the wells were produced at the separator WHFP of 17-20 atm and the results were disastrous. Some of the wells were plugging up in a matter of days. It was the rule of production above 100 atm, as suggested by the IFP Laboratory, that alleviated somewhat the problem.

The experience at Lake Maracaibo (Von Albrecht et al., 1977), however, resembles that in Hassi Messaoud with respect to WHFP. Asphaltene deposition was prevented in certain Lake Maracaibo wells by minimizing WHFP with large surface chokes. The experiences at Hassi Messaoud and Lake Maracaibo are in line with the refinery propane deasphalting process, where propane is mixed with the crude to reduce the asphalt solubility in the crude and flocculate it out. It is apparent that in these fields producing at low WHFP meant that a large portion of the gas in the reservoir fluid was forced out of solution thus altering the composition of the crude to a point that asphaltenes were peptized.

The experience at the Greeley field in California (Katz and Beu, 1945) gives another insight into the problem of asphaltene deposition. At the Greeley field asphaltene granules were found all the way into the production separator. Of course, in the production separator the crude is flashed out and most of the gas leaves the crude oil. So the fact that most of the gas is separated from the oil in the separator suggests that (in line with the Lake Maracaibo and Hassi-Messaoud experiences) asphaltenes should not flocculate out and some or all of those that flocculated earlier must be repptized. This certainly was not the case at the Greeley field. Similar was the experience in Prinos where asphaltene deposition was taking place every-where during processing of the oil. In fact, in Prinos asphaltene deposition continued to take place even in the finished oil storage tanks, where the crude goes after it has been stabilized (when nearly all of the gas is stripped out).

Another point of interest is that in the Prinos project the IFP Laboratory findings pointed to the need of maintaining the reservoir pressure above 3,000 psi to avoid asphaltene deposition and reservoir damage. Even though this is laboratory experience and does not necessarily reflect what would happen in the field, it behooves us to compare this with the experience at the Ventura field, California, where it is reported that the asphaltene deposition problems diminished after the BHP fell below the bubble-point of the crude. This is exactly the opposite of the IFP recommendation for Prinos.

Of interest is also the controversy as to whether or not the asphaltene deposition process is irreversible. The IFP Laboratory during its work for Prinos found that the asphaltene deposition process is irreversible and that "...it could not reconstitute the reservoir fluid from its constituents after asphaltene deposition and oil and gas separation." However, Hirschberg and coworkers (1984) report that in view of their experience, it seemed reasonable to assume that asphaltene deposition was reversible. Incidentally, reversibility of the asphaltene flocculation process is considered necessary for the development of a thermodynamic model that treats the phase transition of asphaltenes from liquid to solid and vice versa. So it is apparent that pressure, temperature, and composition are not the only factors affecting asphaltene deposition. Nonetheless, it has been reported that in Lake Maracaibo the asphaltene problem was controlled by simple temperature and pressure manipulations of the reservoir fluid.

Hence, it seems as though what one does to solve the asphaltene problem another tries to avoid. The natural question that arises is (Leontaritis et al., to be published): why has the asphaltene problem been so elusive? or can one formulate an analytical model that would predict all of these seemingly contrasting phenomena? Before one can try answering this question one must first see what are, if any, the common de-
nominators of all of these apparently contrasting experiences.

General trends in industry and research

Despite the apparent mix of ideas and opinions and practical approaches with regards to the asphaltene problem certain general trends can already be distinguished. With respect to the oil industry the solution to the problem, wherever it occurs, seems to take the form of applying whatever means are available to remedy the asphaltene problem to the point that an oil discovery can be economically produced. To date, this involves techniques that are suitable and applicable to a particular project which may be: (a) mechanical cleaning of the wells and surface equipment, i.e., wireline methods, opening of vessels, etc.; (b) chemical cleaning of the wells and surface equipment, i.e., circulation of solvents; (c) temperature and pressure manipulation of the produced fluids in order to minimize the occurrence of conditions that have been determined to promote asphaltene deposition and thus extend the on-stream efficiency of wells and equipment, i.e., bottom hole chokes, etc.; (d) some cases where solvents are used to effect peptization of asphaltenes during production and thus act as preventive means have been reported.

In the research community there appear to be two different trends or directions in the quest for finding a solution to the asphaltene problem. One school of researchers is pursuing the asphaltene problem by considering the asphaltenes as "molecules" in liquid phase (the oil phase) which may or may not form a solid phase depending on the thermodynamic conditions of temperature, pressure, and composition. The formation of the solid phase is manifested by asphaltene deposition. This idea, of course, requires that the phase change which the asphaltene molecules undergo must be reversible. However, mixed experimental results have been reported on this matter. Some say that the process is not reversible (Adialalis, 1982), and others say that the process is reversible (Hirschberg et al., 1984). So the matter seems to be in limbo for the moment.

Another school of researchers is pursuing the asphaltene problem by considering the asphaltenes as solid particles of different sizes that are suspended colloidal in the crude oil and are stabilized by large polymeric molecules (resins) adsorbed on their surface. This idea requires that the asphaltene problem be irreversible as, by definition, colloidal suspensions are. Colloidal science techniques such as electrokinetics and adsorption are in this case utilized to describe the precipitation of asphaltenes. Works that have been done by Nellesteyn (1938), Preckshot et al. (1943), Moore et al. (1965), Lichaa and Herrera (1975) are in support of colloidal suspension of asphaltenes. The ultracentrifuge studies of Witherspoon (Witherspoon et al., 1957) have also played a significant role in establishing the existence of the colloidal asphaltene particles in petroleum.

DONCLUSIONS

The mere fact that there are different schools of thought with regards to the asphaltene de-position problem points out that we are still far from formulating a universally accepted model for describing the behavior of asphaltenes in crude oil. Basically, there does not appear to be a consensus as to the mechanism of asphaltene flocculation and deposition. Because the asphaltene problem is so elusive, it seems that before one can formulate an accurate analytical model describing the problem the true asphaltene deposition mechanism(s) must be clearly understood and backed by field and experimental data.

It has been shown experimentally that the electrical charge of asphaltenes is a very important property and, regardless of the charge
sign, it seems possible to devise asphaltene de-
position preventive measures by controlling the
electrical effects attributed to the charge of as-
phaltenes. The primary electrokinetic
phenomenon in effect is the "streaming potential"
generated by the movement of the electrically
charged asphaltene particles due to the flow of oil.
This streaming potential seems to neutralize the
similar charge of the asphaltene particles and cause
them to flocculate. The electric charge of
asphaltenes has not yet been explained, primarily
because of the complexity of the composition of
asphaltic materials. The difference in charge (+ or
-) displayed by asphaltenes derived from
different crudes has not been explained either. One
suggestion has been that the large quantities of
nickel and vanadium found in asphaltenes may hold the key to these charges. This idea may
be investigated by analyzing metal contents of
asphaltene deposits that contain asphaltene particles with different electric charge.

One thing that appears to have universal
acceptance is that resins in the crude act as
peptizing agents of the asphaltene particles. A
number of experiments have been performed that
point out the peptizing role of resins. However,
because of the significance of the resins as peptizing
agents of the asphaltene particles and the fact that
based on current experimental information they
appear to be utilizable for combating the
asphaltene problem in the field, more experiments
must be performed to establish clearly and
beyond any doubt the resin role in the asphaltene
deposition problem and generate enough
thermodynamic properties of the resins to be
utilized in modeling efforts to the problem.

Experimental evidence (Swanson, 1942; Lichaa,
1977) suggests that for an oil mixture there is a
critical concentration of resins below which the
asphaltene particles may flocculate and above
which they cannot flocculate regardless of how
much the oil mixture is agitated or refluxed. The
authors believe that there should be certain unique
geological conditions which favor the
formation of an oil whose actual resin
concentration is less than its critical resin con-
centration. Such conditions are responsible for the
transformations the hydrocarbon deposits
undergo. These geological conditions could conceivably be identified and established after
sufficient experimental data on actual resin
concentration and critical resin concentration are
generated for different crude oils around the world.
As a result, geological conditions alone may
provide clues for predicting potential asphaltene
problems even for oils that have not yet been
produced.

The postulated and sufficiently proven notion
that asphaltenes are oxidation products of resins
and that resins are oxidation products of oil
(Sachanen, 1945) sort of makes the probability of
finding oils whose actual resin concentration is
less than their critical resin concentration small.
In other words, an oil deposit needs to contain a
substantial amount of resins before starting to
form asphaltenes during the natural geological
transformation process. Table V seems to
corroborate this statement where in most cases
the resin content is larger than the asphaltene
content. In some oils the asphaltene content is
zero while the resin content is sizable. Thus, it
would be interesting to find out what kind of
geological conditions are suitable for generating
oils whose actual resin concentration is less than
their critical resin concentration. A model which
is based on the notion of the resin critical
concentration described above and attempts to
predict the phase behavior of asphaltenes in oil
mixtures will be published by the authors.

Since asphaltene deposition takes place during
primary, secondary, and tertiary oil recovery,
injection of peptizing agents (i.e., resins) in
proper amounts and places may prevent or at
least control the asphaltene deposition problem.
Furthermore, experiments could be performed
(i.e., of the coreflood type) where peptizing
agents are injected to study their effect on
TABLE V

Resin and asphaltene content of crude oils*

<table>
<thead>
<tr>
<th>Crude oil</th>
<th>Sp. grav. (60°/60°F)</th>
<th>Resins (% by wt.)</th>
<th>Asphaltenes (% by wt.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pennsylvania</td>
<td>0.805</td>
<td>1.5</td>
<td>0.0</td>
</tr>
<tr>
<td>Oklahoma, Tonkawa</td>
<td>0.821</td>
<td>2.5</td>
<td>0.2</td>
</tr>
<tr>
<td>Oklahoma, Okla. City</td>
<td>0.835</td>
<td>5.0</td>
<td>0.1</td>
</tr>
<tr>
<td>Oklahoma, Davenport</td>
<td>0.796</td>
<td>1.3</td>
<td>0.0</td>
</tr>
<tr>
<td>Texas, Hould</td>
<td>0.936</td>
<td>12.0</td>
<td>0.5</td>
</tr>
<tr>
<td>Texas, Mexia</td>
<td>0.845</td>
<td>5.0</td>
<td>1.3</td>
</tr>
<tr>
<td>Louisiana, Rodessa</td>
<td>0.807</td>
<td>3.5</td>
<td>0.0</td>
</tr>
<tr>
<td>Calif., Huntington Beach</td>
<td>0.897</td>
<td>19.0</td>
<td>4.0</td>
</tr>
<tr>
<td>Mexico, Panuco</td>
<td>0.988</td>
<td>26.0</td>
<td>12.5</td>
</tr>
<tr>
<td>Russia, Surachany</td>
<td>0.850</td>
<td>4.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Russia, Balachany</td>
<td>0.867</td>
<td>6.0</td>
<td>0.5</td>
</tr>
<tr>
<td>Russia, Bibi-Eibat</td>
<td>0.865</td>
<td>9.0</td>
<td>0.3</td>
</tr>
<tr>
<td>Russia, Dossor</td>
<td>0.862</td>
<td>2.5</td>
<td>0.0</td>
</tr>
<tr>
<td>Russia, Kaluga</td>
<td>0.955</td>
<td>20.0</td>
<td>0.5</td>
</tr>
<tr>
<td>Asia, Iraq (Kirkuk)</td>
<td>0.844</td>
<td>15.5</td>
<td>1.3</td>
</tr>
<tr>
<td>Mississippi, Baxterville*</td>
<td>0.959</td>
<td>8.9</td>
<td>17.2</td>
</tr>
</tbody>
</table>

* Reproduced from Sachanen, 1945.
* Reproduced from Lichaa, 1977.

inhibition of asphaltene deposition or permeability reductions.

One interesting question posed by previous researchers (Katz and Beu, 1945; Adialalis, 1982) is why there was asphalitic bitumen deposited at the bottom of the well considering that no phase change or any substantial temperature or pressure changes had taken place. The conclusion was that the question could only be answered after considerable light was thrown upon the nature of the asphalitic bitumen prior to its separation from the crude oil in the well. There were a few efforts to try to determine the size and nature of asphaltene particles while they still are in the original oil (Katz and Beu, 1945; Witherspoon et al., 1957). Katz and Beu did not see any asphaltene particles in the original oil of size 65 Å or larger, but they did see these particles after mixing the crude with solvents. They concluded that the particles, if they do exist, must be smaller than 65 Ångstron. Witherspoon et al., using ultracentrifuge techniques, found that the particles that eluded Katz and Beu do exist and are of the 35-40 Ångstron range, for the oils they studied.

Establishing the state of the asphaltene particles in the original crude oil seems to be a basic building block in the scientific quest to find a solution to the asphaltene deposition problem. Experimental work towards this end has been performed (Yen, 1972; Speight, 1981), but more is needed. More experiments need to be done to duplicate the ultracentrifuge work of Witherspoon et al. for different oils and possibly utilize other contemporary experimental techniques to establish the state of asphaltenes in crude oils. Meanwhile, it appears, that any modeling effort that describes the phase behavior of asphaltenes in oil should take into account the lack of positive information on the structure of asphaltenes in the original oil and their molecular characteristics. This was the philosophy followed in our model (Leontaritis and Mansoori, To be Published) mentioned earlier, proposed for predicting the phase behavior of colloidal asphaltenes in crude oil.
Acknowledgement

This research is supported by the National Science Foundation Grant CBT-8706655.

BIBLIOGRAPHY


Leontaritis, K.J., Kawanaka, S. and Mansoori, G.A., Descriptive accounts of thermodynamic and colloidal models of asphaltene flocculation (to be published).


