

UNDERSTANDING THE POUR POINT DEPRESSION MECHANISM-
I. HPLC AND GPC ANALYSIS OF CRUDE OILS

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SUMMARY

This study offers a preliminary explanation for the high pour point phenomena in waxy crudes, and attempts to differentiate between crude oils that do and do not respond to pour point depressants. Twelve internationally located crude oils were first subjected to a standard wax separation procedure, and the collected waxes were further analyzed by GPC and HPLC methods. The isolated wax fraction was found to be composed of aromatic, polar and hexane insoluble components in addition to the crystallizable saturate components. Based on GPC analysis of the molecular size distribution of the wax components isolated from the crudes, the 12 crudes could be categorized into three types. Regression analysis was successfully used to correlate pour point to the wax content and the saturates in the waxes. The saturates content gave the better correlation. GPC analysis of the saturate cuts was facilitated by the development of a saturates calibration curve to replace the existing polystyrene standard.

INTRODUCTION

Numerous problems occur during the production and transportation of waxy crudes. These crudes have high pour points (often over 100°F) and leave troublesome wax deposits in pipelines and production equipment. When cooled below the temperature for wax precipitation the precipitating waxes tend to form an interacting three-dimensional structure that can effectively tie up the lighter fractions of the crude and cause congealing to occur. A number of previous publications⁽¹⁻¹⁰⁾ have discussed the problems associated with the production and transportation of these crudes, and the methods that have been proposed for minimizing these problems.

Two approaches are commonly taken for handling these crudes. The obvious approach would be to always maintain the crude temperature above its pour point, but this is not always technically or economically feasible. The second approach is to use chemical pour point depressants to modify the interactions between the precipitating waxes, thus reducing the pour point and improving the flow characteristics. The problem arises in that the wax-additive interaction is extremely complex and very poorly understood, so that no prior judgement can be made as to the efficacy of a particular additive for depressing the pour point of a particular crude. The data presented in Table 1 serves to better demonstrate this point by comparing the properties of Cabinda (West Africa) and Handil (Kalimantan) crudes. Both crudes have similar API gravities and wax contents, yet their pour points are quite different. Additionally, Cabinda responds quite well to low concentrations of a

certain additive, yet Handil shows little response to most available additives.

Table 1
Comparison of Two Waxy Crudes

<u>Crude</u>	<u>API Gravity</u>	<u>Wax Content Wt. %</u>	<u>Pour Point °C (°F)</u>	<u>Depressed¹ Pour Point °C (°F)</u>
Cabinda	32.1	16.3	21.1 (70)	-17.8 (0) ²
Handil	32.1	16.5	32.2 (90)	21.1 (70) ³

1. Maximum pour point depression seen with screening 50 pour point depressants.
2. 100 ppmw of Additive A.
3. 1000 ppmw of Additive B.

Based on the performance of these two crudes it was concluded that the wax-additive interaction is complex and poorly understood, and that a detailed analytical evaluation of at least the wax fractions in the crude oil would help in developing a better understanding of the interaction. More Specific questions that the study also attempted to address included: (1) The relationship between precipitated waxes and actual saturates; (2) The relationship between the pour point and the amount and composition of the wax fraction collected; (3) The nature of the waxes collected from different crudes; (4) An understanding of why there appeared to be a specific temperature for many crudes below which the pour point could not be chemically depressed.

Gel Permeation Chromatography (GPC) and High Pressure Liquid Chromatography (HPLC) were the major analytical tools used in this study to try and answer some of the questions raised above.

EXPERIMENTAL

Waxes were first isolated by an in-house procedure frequently used to determine the wax content of crudes and petroleum product. The procedure is a modification of ASTM D-721, and calls for diluting 1 gram of sample with 100 ml of methylethyl ketone. The solution is heated to 65.5°C (150°F) to dissolve the sample, and filtered at this temperature to remove the insoluble components (such as bulk asphaltenes). The solution is cooled to -17.8°C (0°F) and filtered through Whatman No. 50 filter paper to recover the wax precipitate. This fraction is referred to as the TOTAL waxes present in the crude oil.

HPLC was used to further separate this wax fraction into saturates, aromatic, polar, and hexane insoluble if present. The HPLC equipment and procedure has been discussed elsewhere. (11)

GPC was also used to classify the TOTAL waxes, as well as the saturates isolated from the TOTAL waxes by HPLC. The GPC consists of the following columns: 3- μ styragel, (10^4 , 10^3 , 500 Å), and 2 μ spherogel (50 Å). Tetrahydrofuran solvent was used (20 mg/ml sample dilution). The injection volume was 100 μ l and a 2 ml/min flow rate was maintained. A differential refractometer detector was used. The elution of the sample was automatically monitored by a computer. At the end of the run, the computer integrates the chromatogram, calculates the molecular weight distribution, and prints out the results in digital and graphic form.

A special calibration curve was generated for the GPC analysis of the saturate fractions. For this purpose the saturates present in the wax fraction were separated by elution time in a preparative GPC. A Knauer Vapor Pressure Osmometer was used to determine their actual molecular weights, and their elution times on the analytical GPC were obtained. This molecular weight and elution time data was then combined to develop a calibration curve applicable to the saturate fractions.

RESULTS AND DISCUSSIONS

Twelve waxy crude oils from fields around the world were analyzed in this study. Table 2 identifies the crude oils and presents some of their general properties (API gravity, pour point, wax content, HPLC analysis). Working on the premise that a difference in the composition of the wax fractions amongst these various crudes was responsible for the difference in behavior and response to chemical additives, the wax fractions were isolated and subject to further analysis.

GPC analysis of the wax precipitates provided molecular size distribution data based on which the crudes could be separated into three types. HPLC further indicated that what was being separated as a wax phase was actually a complex mixture of aromatic, polar, asphaltene and crystallizable saturate-type components. By employing a preparative HPLC method, large samples of the saturate fractions were collected and further analysed by GPC in order to identify distinguishing traits in the saturates present in the different crudes. Molecular weight distributions of the saturate components was facilitated by use of an in-house developed calibration curve specifically generated for this application to improve on the results available through the use of the existing polystyrene curve.

Even though the waxy components in a crude are directly responsible for the high pour point, previous attempts to correlate the pour point with the wax content of a crude have not proven very successful. For the 12 crudes used in this study, regression analysis showed a fair fit between the pour point and the wt. % waxes present, and a very good fit with the wt. % saturates present in the collected waxes. Details of this and other results are presented in the following sections.

GPC Calibration Curve

GPC proved a valuable tool for both whole wax and saturates analysis. However, for pure saturates analysis the use of a polystyrene

based calibration curve was felt to give erroneous results. An attempt was made to correct this by developing a calibration curve specifically suited for saturates analysis. Both pure alkanes and saturate fractions isolated from a waxy crude were used to generate the necessary calibration curve. The waxes were first separated from the whole crude using the precipitation method described above, and preparative HPLC then used to isolate the saturates present in the wax cut. The saturates were further cut by preparative GPC into individual fractions, and the retention volume for each fraction established. The molecular weights of each saturate fraction were determined using vapor pressure osmometry. Molecular weight determinations were hampered by the low solubility of the saturates in the solvents used, and special handling procedures had to be used to overcome this problem. The calibration curves obtained are presented in Figure 1, which compares the polystyrene curve to the saturates curve and the pure alkane curve.

The pure alkane curve is limited in scope because pure alkanes were not available above a carbon number of 34, and yet it closely matches the saturates curve which could be taken to higher molecular weights. A substantial discrepancy exists between the saturates curve and the polystyrene curve, so that use of the saturates calibration curve gave a more reasonable molecular weight distribution of the saturates.

Composition of the Wax Fractions

Whereas pure saturates can be expected to be colorless or at most white, the actual wax fractions isolated were highly colored, leading to the conclusion that polar and/or aromatic type components were also present in the collected wax precipitates. Preparative HPLC was used to separate the wax fractions into saturates, aromatics, polars and asphaltenes, with the results shown in Table 2.

TABLE 2

HPLC ANALYSIS OF WAX FRACTIONS

Crude	API Grav.	Pour Point (°F)	Wax	Wt. % Sats.	Wt. % Arom.	Wt. % Polars	Wt. %* Asph.
			Content* Wt. %				
Bentayan	22.6	110	36.4	55.0	14.2	28.1	2.7
Wasatch	41.8	105	37.1	90.0	8.2	1.7	0.1
Green River	30.3	95	26.8	61.4	16.5	14.9	6.6
Handil	32.3	90	16.5	88.8	6.0	4.0	1.6
Mibale	30.5	85	20.5	62.5	16.9	10.0	0.6
Cabinda	32.1	70	16.3	62.0	11.6	25.4	1.0
Lucina	39.6	60	12.2	73.0	12.5	9.4	5.1
Brega	43.1	50	6.4	73.5	9.7	13.3	3.5
Escravos	36.1	50	6.8	60.9	11.8	27.0	0.3
Mesa	30.4	50	7.3	62.9	15.6	21.0	0.5
Zaire GCO-4	30.4	50	14.2	39.3	11.7	36.0	13.0
Murban	39.7	15	4.8	72.9	17.5	8.6	1.0

*Used in Regression Analysis

Clearly the wax precipitate is actually a very complex mixture of these crude oil components, a fact that compares well with field observations of paraffin deposits. Only in highly paraffinic and low asphaltic crudes do these deposits appear to have characteristics of pure saturates. Generally, depending on the composition of the crude, the deposits range from being high in saturates to almost asphaltic in nature. It is also generally recognized that successful chemical depression of the pour point requires that the additive modify the structure of the precipitating wax as the temperature is lowered. In untreated crude the precipitating waxes are capable of forming a complex, interacting three-dimensional structure which essentially ties up the lighter components of the crude thus reducing its fluidity. Consequently, for a chemical to successfully depress the pour point of a crude oil, it must first successfully destroy the interaction mechanism between these chemically complex species. Because no two crude oils have the same composition, no two wax precipitates can be expected to display a similar chemical interaction. Consequently a large discrepancy in performance between the response of various crudes to the same additive results. This also helps to explain why different crudes with similar saturate distributions show differing response, because the actual interaction is chemically more complex than a simple saturates interaction. For many refined streams, diesel oil for example, the pour point problem is more specific to the saturates present, and additives are capable of showing a much broader response. It is the complexity of the crude oil precipitates that limits the applicability of pour point depressants for their treatment.

Waxy Crude Classification

Review of the molecular size distribution data obtained by GPC for the 12 crudes under study indicated that it might be possible to use this information to classify the crudes. This was attempted, and three types were defined. Even though this classification may be considered loose, and has only been explored for the 12 crudes, the results are sufficiently encouraging to warrant extending this study to a larger number of crudes.

Type-1 crudes, as defined by the molecular size distribution of the total waxes, is shown in Figure 2. Many of the West African crudes fall in this category, which is characterized by a bimodal molecular size distribution. However, even though the C-25 and lower carbon numbers are well represented, the bulk of the wax components are in the higher molecular weight range. Extrapolation of this observation implies that the higher pour point crudes could perhaps fall in this type.

Type-2 crudes are presented in Figure 3. A bimodal distribution persists but there is a reversal in the relative contributions by the low and high carbon number fractions. The C-25 species are now more dominant, with the C-25+ species providing a hump at the tail end of the distribution. The remaining four crudes are classed together as Type-3 (Figure 4), but this is a weaker correlation. The primary trend for Type 3 crudes is towards a narrower distribution range as shown in Figure 4. Two of the crudes, Brega and Murban, show a continuation of this trend, with the two distinct peaks of the Type 2 crudes replaced by a single

peak in the C-25-30 range, and a declining contribution by the C-30+ fractions. Handil crude is an extreme example, in which almost the entire contribution is from the C-25-30 range material and only a limited contribution is from the C-30+ material. The one exception appears to be Escravos crude for which a distinct C-25-30 peak is present, but a very substantial contribution by components of very high carbon number is also observed.

Based on these noted differences in crude types it is now feasible to attempt to explain differences in crude responses to chemical additives. For example, the difference in behavior of Cabinda and Handil crudes can be attributed to the differences in the nature and distribution of the wax components in the two crudes, wherein a much narrower distribution of waxes is present in Handil relative to Cabinda. The response of these two crudes to additives would also be substantially different. Any additive in Handil crude would be swamped by a large amount of wax precipitating over a very narrow temperature range, whereas with Cabinda the effect would be much more gradual, with the additive capable of modifying the initial wax precipitate, which in turn could serve to modify the interaction between successive wax precipitates.

However, an intriguing question that remained unanswered was whether the differences in behavior of the two crudes could be attributed more to the differences in the saturate fractions present in the crudes, or to the more complex combination of material that represented the precipitated wax fraction. To this end preparative HPLC was used to isolate the pure saturate fractions from a number of crudes, and these saturate fractions analysed by GPC. The results, presented in Figure 5, indicated that the pure saturates are remarkably similar in size distribution, and consequently differences in behavior must be dependent on the chemical nature of the complexes formed between the saturates and aromatic, polar and asphaltene type components also present in the crudes.

Correlating Wax Content to the Pour Point

Numerous previous attempts to correlate the pour point to the wax content of a crude oil have not been very successful. Our studies have shown that the complex chemistry of the interactions involved would preclude any general correlation. Regression analysis was used to explore possible correlations between the pour point and the wax content of the crudes or the saturates present in the waxes. Table 3 presents the several variables ($x_1 - x_2$) explicitly defined as functions of wax content and saturates in wax respectively.

TABLE 3

Variables for Multiple Regression analysis

$x_1 = x$	$x_5 = x^2$	$x_9 = 1/e^x$
$x_2 = 1/x$	$x_6 = 1/x^2$	$x_{10} = \ln x/x$
$x_3 = \ln x$	$x_7 = 1/e^{x^2}$	$x_{11} = (1-x)^2$
$x_4 = e^x$	$x_8 = e^{1/\ln x}$	$x_{12} = x(\ln x)$

x = Wt. % Wax or Wt. % of Saturates in Wax

Functions x_4 , x_7 and x_9 were not used as they did not correlate well with the available data. Even though the remaining nine functions were used in multiple regression analysis, not all appear in the final regression equations, since the occurrence of singularities in the coefficient matrix indicated that the regression coefficient could not be solved simultaneously.

Equation 1 presents the relationship between the wax content and pour point.

$$\text{Pour Point } (^\circ\text{F}) = -44522.14 - 1333.95x_1 + 15754.08x_3 + 41954.46x_6 + 69462.51x_{10} + 226.71x_{12} \quad 1)$$

The correlation coefficient for this equation is .9423. A much higher correlation coefficient (0.9978) was obtained for the correlation between the pour point and the amount of saturates present in the wax fraction. Equation 2 is the necessary equation for this case.

$$\text{Pour Point } (^\circ\text{F}) = 49395.11 - 416.66x_1 + 50834.54x_2 - 14439.62x_3 - 2.78x_6 - 125575.07x_6 - 103337.73x_{10} \quad 2)$$

CONCLUSIONS

The pour point phenomena in waxy crudes is a complex chemical event which is influenced both by the amount of the saturates present in the crude and the chemical composition of the crude. GPC characterization of the wax precipitates allowed classifying the 12 crudes into three distinct types. HPLC analysis of the wax precipitates indicated that they are comprised of a complex mixture of saturate, aromatic, polar and asphaltic material. Differences in the behavior of the crudes and in their response to additives can be attributed to the differences in the distribution and composition of the wax fractions.

ACKNOWLEDGEMENTS

The assistance of the following Gulf personnel was greatly appreciated: J. Suatoni, R. Ruberto, and G. Chao for the GPC and HPLC analysis, and M. Greco for the VPO studies.

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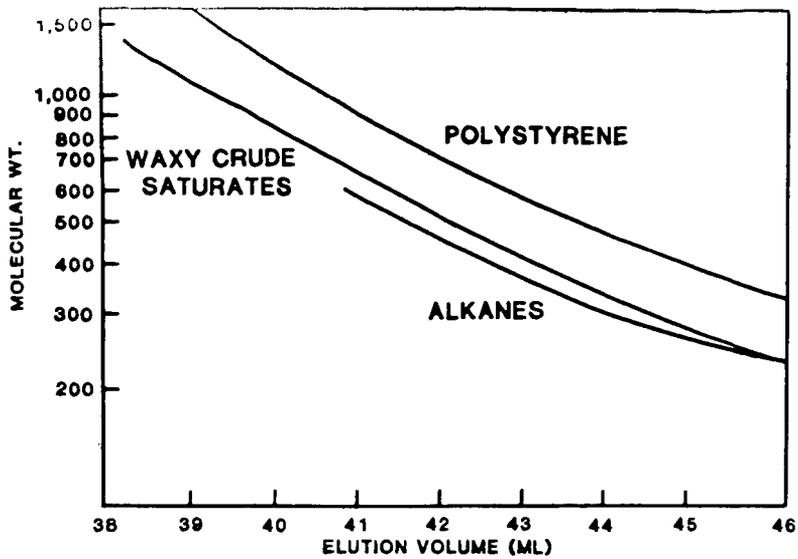


Fig. 1 WAXY CRUDE SATURATES CALIBRATION CURVES

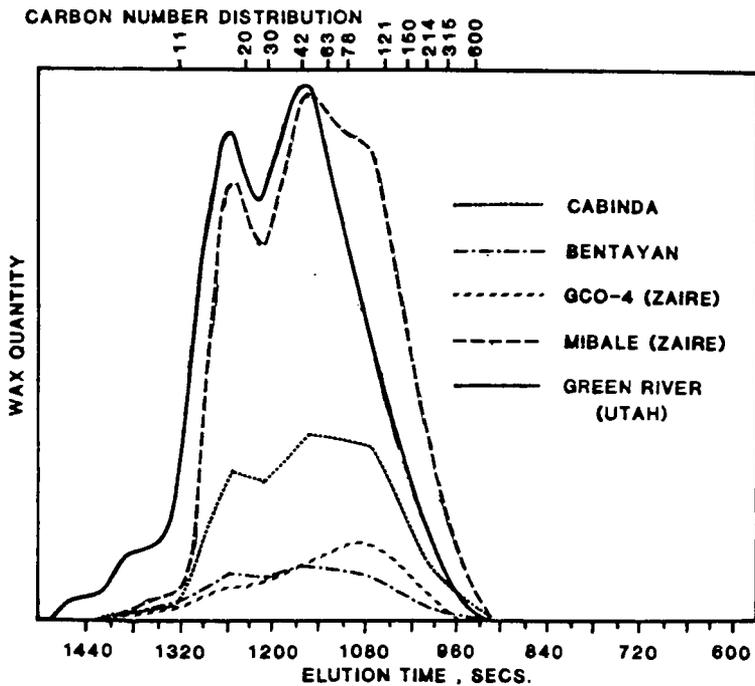


Fig. 2 TYPE - I CRUDES

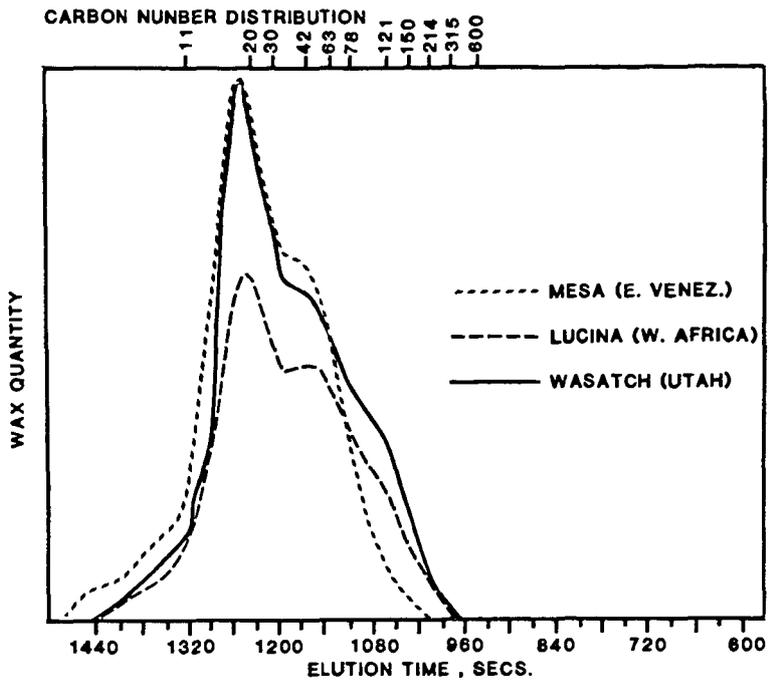


Fig.3 TYPE II CRUDES

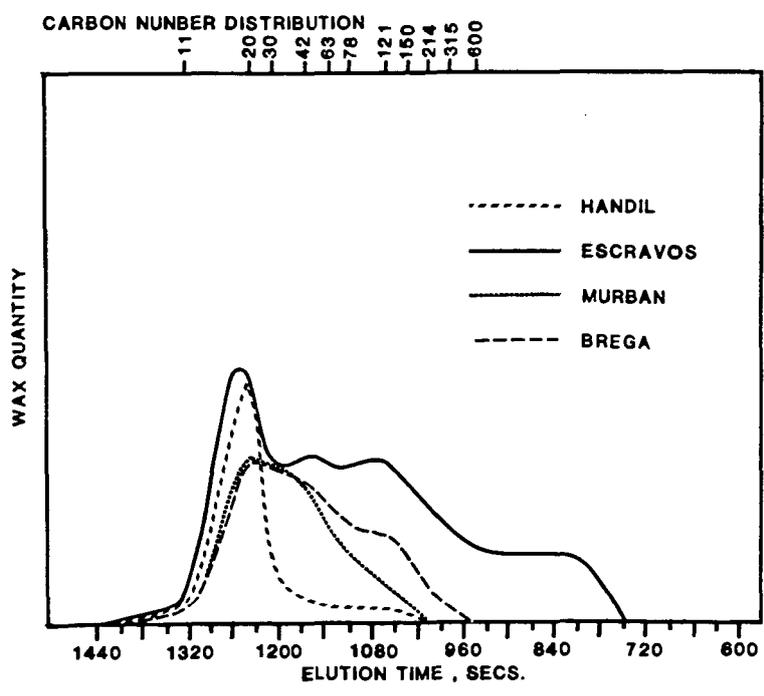


Fig.4 TYPE III CRUDES

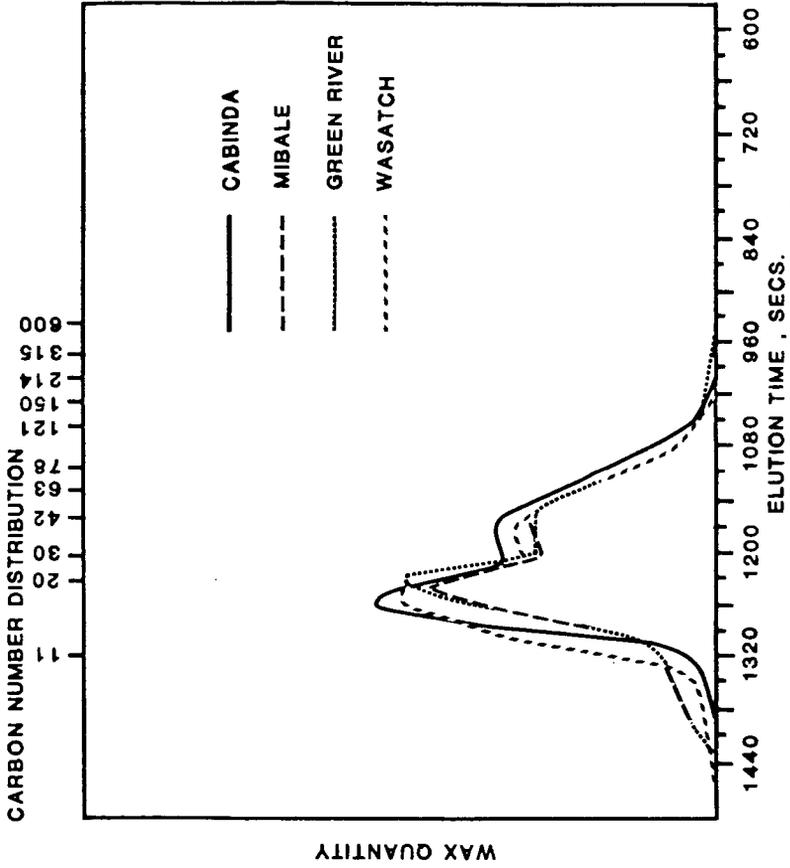


Fig.5 COMPARISON OF SATURATES FRACTIONS