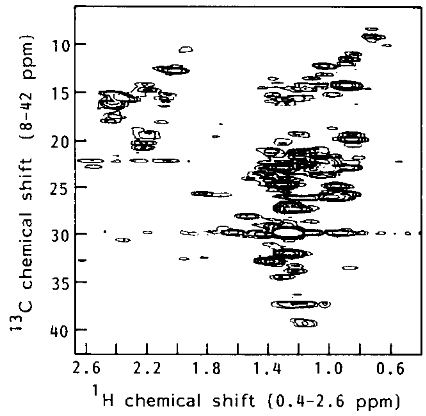

Figure 2 HETCOR n.m.r. plot of twice reduced resid

reduction, the methyl-resid started with 0.9 mmol CD_3—S g^{-1} (which ^{2}D n.m.r. shows to be 100% lost during the second reduction) but only 0.4 mmol S g^{-1} was lost during the second reduction. Thus, 0.5 mmol S g^{-1} was initially present as CD_3—S, and the sulphur portion of this was not lost during the second reduction; this is certainly not behaviour anticipated for aryl, alkyl thioethers, and is, in fact, more the behaviour anticipated, and found, by Sternberg for aryl, alkyl ethers.

This can be explained by assuming that at least 0.5 mmol S g^{-1} (31% of the initial S) is aliphatic carbon bound to sulphur (which is more resistant to C—S bond cleavage[12]) or that the diaryl thioethers found in resids are chemically quite distinct from dibenzothiophene.

In conclusion, it has been shown that the chemistry of reductive alkylation does destroy aromatic stacking interactions in petroleum residua, a result consistent with Sternberg's original hypothesis about the efficacy of reductive alkylation in solubilizing coals. In studying the fate of specific functionality during reductive alkylation, as Sternberg did to infer the relative importance of stacking and polar interactions, a complicated picture is found. The sulphur of the resid behaves in no way like dibenzothiophene, a commonly accepted model for the majority of sulphur in resid. Either the resid has significant quantities of aliphatic carbon bound to sulphur, or the diaryl thioethers in the resid are quite unlike dibenzothiophene in their chemistry.

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Influence of waxes on the flow properties of Bombay high crude

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Waxes present in crude oil are considered to be responsible for its poor flow properties. Bombay high crude is very waxy and has a pour point of +30°C. The influence of nature and concentration of waxes on some of the flow properties, namely pour point, plastic viscosity and yield stress, of dewaxed Bombay high crude have been determined. The hard wax components present in the crude do not appear to significantly influence the low temperature rheology of the crude oil, but do contribute to sludge formation.

(Keywords: crude oil; rheological properties; fluidization)

Waxy crudes present problems in transportation through pipelines, particularly during winter; this arises from adverse flow characteristics influenced by the presence of relatively large amounts of wax. The passage of the pipeline through temperature zones lower than the pour point of the crude oil affects the flow characteristics of the crude. Even before the pour point is reached, wax separation may take place, affecting the flow of crude oil. A thorough understanding of the rheology of crude oil is therefore necessary for tackling the problem of transportation, particularly at lower temperatures. Most of the work[1–5] on the rheology of crude oil is related to use of flow improver additives to modify the rheological properties, making the oil suitable for easy transportation. Little work[6–7] has been done to understand the cause of complex rheological behaviour in relation to composition for waxy crudes.

The rheology of crude oil is believed to be influenced by waxes, resins and asphaltenes present, as well as by the thermal and mechanical history of the crude. However, the nature, type and quantity of the waxes present, as well as their crystallization habits, influence flow properties to a large extent. Bombay high crude is very waxy in nature (wax content

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12–14%) and has a pour point +30°C. The influence of the nature and concentration of waxes on the flow properties of Bombay high crude is studied in this paper.

EXPERIMENTAL

Characterization of Bombay high crude oil

An undoped sample of Bombay high crude oil was characterized for its physicochemical properties using ASTM standard test procedures[8]. The rheological properties of the crude oil, namely plastic viscosity and yield stress, were measured using a Haake rotational viscometer and a NV sensor. Shear stress versus rate of shear curves were drawn at each test temperature. Extrapolation of the straight line portion to ordinate gives the yield stress of the gelled crude oil sample. The slope of the linear portion was taken as plastic viscosity.

Separation and characterization of total waxes (unrefined) from the crude

The crude oil was distilled up to 200°C, then the residue was subjected to multistage solvent dewaxing with an MEK/toluene mixture (1:1 by vol.) at low temperature (−10°C). The unrefined total waxes separated were analysed for their physicochemical properties (using ASTM standard test procedures) and carbon number distribution (by g.c.).

Preparation and characterization of dewaxed 'base' crude

To identify the key components contributing to the high pour point and complex rheology of the crude, a wax free 'base' crude was prepared. The influence of concentration of wax on the physicochemical and rheological properties of this base crude could then be studied systematically. The base crude was prepared by distilling the whole crude up to 200°C, solvent dewaxing the residue, and mixing back the 200°C distillate with the dewaxed oil. The base crude was then analysed for physicochemical and rheological properties.

Influence of concentration of total wax on flow properties of dewaxed base crude

The dewaxed base crude was blended with the separated total wax at various concentrations (1–5 wt%). The pour point and rheological properties (plastic viscosity and yield stress at various temperatures) were measured for these blends.

Isolation of high melting waxes

The concentration of high melting waxes (m.p. > 90°C) in Bombay high crude is very small (< 0.5%), so they were isolated from tank bottom sludges. The sludge was distilled up to 500°C to remove the volatiles; oil and soft waxes were removed by solvent dewaxing. The high melting crude waxes obtained were purified by bauxite percolation. Details of isolation of high melting waxes from tank sludges have been reported previously[9]. The properties of refined waxes obtained were determined, to understand their effect on the flow properties of the crude oil.

Influence of hard high melting waxes on properties of dewaxed base crude

The dewaxed base crude was blended at various concentrations (0.1–5 wt%) with the refined high melting waxes. The pour point, yield stress and plastic viscosity at various temperatures were determined for these blends.

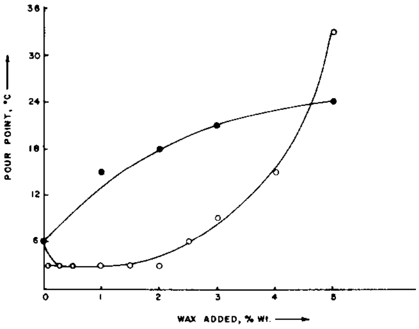

Figure 1 Influence of waxes on pour point of dewaxed oil: —●—, total wax; —○—, hard wax

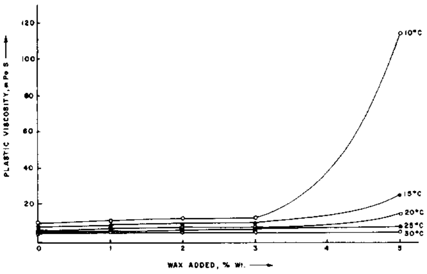

Figure 2 Influence of total wax on plastic viscosity of dewaxed oil

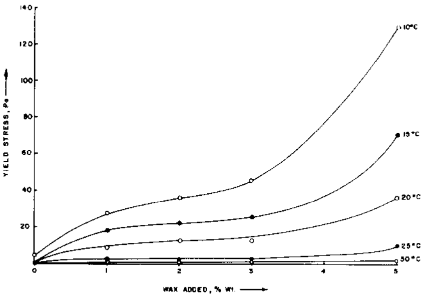

Figure 3 Influence of total wax on yield stress of dewaxed oil

Table 1 Properties of crude oil

Properties	Bombay high crude oil	Dewaxed crude oil
Density (D_4^{15})	0.8302	0.8441
API gravity	38.0	36.1
Pour point (°C) (ASTM D-97)	+30	+6
Kinematic viscosity (cSt)		
40°C	2.93	4.06
50°C	2.43	3.34
Wax content (wt%) (Engler-Holde method)	11.8	1.5
Plastic viscosity (mPas)		
40°C	2.70	3.84
30°C	7.40	4.80
20°C	35.20	6.30
15°C	52.00	8.20
10°C	—	10.56
5°C	—	14.40
Yield stress (Pa)		
40°C	0	0
30°C	5.0	0
20°C	52.0	0
15°C	150.0	0
10°C	—	5.34
5°C	—	25.81

Table 2 Physical properties of waxes

Properties	Total wax	Hard wax
Melting point (°C)	60	95.4
Oil content (wt%)	0.9	1.3
Kinematic viscosity (cSt) at 100°C	6.46	18.3
Needle penetration (dmm)		
10°C	19	2
15°C	27	3
Saturates (wt%)	90.0	96.0
General nature	Soft plastic	Hard and brittle
Yield on basis of crude (wt%)	13.8	—

RESULTS AND DISCUSSION

Changes in rheological properties on solvent dewaxing

Wax is an ill-defined term in the context of rheology of crude oils. The solid hydrocarbons that separate out from a petroleum fluid at given conditions constitute the 'wax'. There is no standard test method for wax estimation, and the values differ significantly depending on the estimation procedures and experimental conditions. The Bombay high crude sample used in this study has a wax content of 11.8 wt% (refined wax yield) estimated by the Engler-Holde method[10] (*Table 1*). The preparative MEK-toluene solvent dewaxing method gave yields of 13.8% unrefined wax. This unrefined wax contained 90% saturated hydrocarbons, plus small quantities of asphaltenes and resins. The wax had a drop melting point of 60°C and consisted of C_{21}–C_{38} hydrocarbons (n-alkanes), as shown in *Table 2*. Traces of higher alkanes (above C_{38}) were also detected.

Pour point of the dewaxed crude is 6°C, compared with 30°C for the whole crude. The plastic viscosity of the dewaxed crude at 40°C is a little higher than that of the whole crude (3.84 and 2.7 MPas respectively). On cooling, the flow behaviour of the crude oil changes from essentially Newtonian (coefficient of viscosity independent of shear rate) to non-Newtonian. At $\approx$30°C and below, an initial shear stress (yield stress) has to be applied before flow of crude oil occurs; this is characteristic of Bingham plastic behaviour. The dewaxed crude starts exhibiting Bingham behaviour at temperatures below 15°C (the yield stress at 10°C for dewaxed crude is 5.34 Pa), and on cooling the plastic viscosity increases by only a limited extent, from 3.84 mPas at 40°C to 14.40 mPas at 5°C.

The whole crude, in contrast, shows a sharp increase in plastic viscosity as the temperature is reduced, from 2.7 mPas at 40°C to 52 mPas at 15°C. The yield stress for the whole crude also increases sharply as the temperature is lowered (5 Pa at 30°C to 150 Pa at 15°C). From these results it is obvious that the wax present in the crude is responsible for the high pour point and complex rheology (non-Newtonian flow) of the crude oil.

Effect of concentration of total wax on flow properties of dewaxed base crude

Influence of total wax, at various concentrations, on pour point, plastic viscosity and yield stress of dewaxed crude oil is shown in *Figures 1, 2* and *3* respectively. The addition of 1% total wax increases the pour point of the dewaxed crude from 6 to 15°C. Even at a concentration of 5% total wax, the pour point increases to 24°C, close to the pour point of the original crude oil. Increase of total wax concentration from 5 to 13.8% (for original crude) thus increases the pour point by only 6°C. Plastic viscosity of the dewaxed crude oil rises gradually at 1% wax concentration, then remains steady up to 3% wax concentration. Yield stress increase shows a trend similar to that of plastic viscosity in relation to wax for dewaxed crude oil. By increasing the wax concentration from 3 to 5 wt%, a sharp change in plastic viscosity and yield stress is observed, although pour point changes by only 3°C.

The crude oil is visualized as a complex multicomponent colloidal suspension, with the disperse phase consisting of a conglomerate of hard waxes (carbon number >40), asphaltenes, resins, and mineral matter in association with high molecular weight liquid hydrocarbons. The entire crude oil thus functions as a near Newtonian liquid. The bulk of the waxes are in solution in the liquid medium (dispersant) above the pour point of the crude oil. On cooling, this liquid becomes saturated with respect to hydrocarbons which form the bulk of the wax. As the wax crystals separate out, they interlock to form a three dimensional structure. This structure is associated with parameters such as yield stress and high plastic viscosity of the crude oil near and below its pour point.

Influence of hard high melting waxes on flow properties of dewaxed base crude

The hard waxes separated from the tank sludges melted at 95°C (*Table 2*). Study of the effect of hard, high melting waxes on the pour point of dewaxed crude (*Figure 1*), shows that up to the 2% level, the pour point actually decreases, suggesting that the hard waxes are possibly acting as pour point depressants. Above the 2% level, the pour point starts increasing, reaching a value of 33°C at a 5% concentration of hard wax. At higher concentrations of hard wax, gel formation takes place and is responsible for the sharp increase in pour point.

The effect of hard wax addition on plastic viscosity and yield stress of dewaxed crude is shown in *Figures 4* and *5* respectively. Below the 1% level, the pour point, plastic viscosity and yield stress are all depressed. Plastic viscosity and yield stress start increasing sharply at 3% wax concentration, apparently due to gel formation in the crude. However, above this concentration the hard wax does not remain in solution due to its poor solubility in the crude oil, and starts separating out. The viscometer thus measures the viscosity of the oil portion only. Since the concentration of hard waxes in whole crude is quite small (<0.5%) and because they have limited solubility in the crude, they do not appear to contribute to the low temperature rheology of the crude. They do, however, contribute to sludge formation.

Thus the hard waxes that separate out with the sludge depress the pour point,

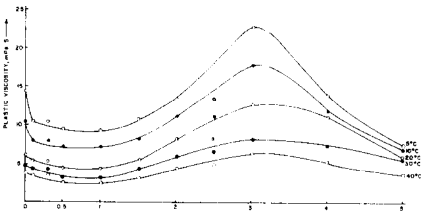

Figure 4 Influence of hard wax on plastic viscosity of dewaxed oil

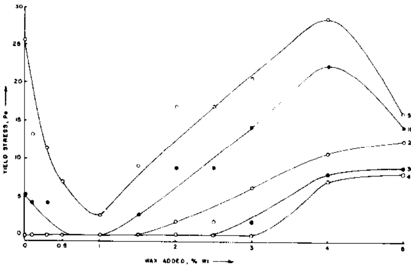

Figure 5 Influence of hard wax on yield stress of dewaxed oil

and lower the plastic viscosity and yield stress of the dewaxed crude oil, when added to it at low concentration. The bulk of the waxes in Bombay high crude are in the dissolved state above the natural pour point (30°C) of the crude. They seem to be largely responsible for high pour points as well as for adverse rheological properties on cooling.

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