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THERMAL CHARACTERISTICS OF CRUDE OILS TREATED WITH RHEOLOGY MODIFIERS

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Abstract

Thermal characteristics of eight crude oils and their treatment with additives were studied by differential scanning calorimetry (DSC), thermomicroscopy, viscometer and pour point tester. Different additives were found as more effective for different type of crude oils depending on the wax content. Crude oils showed a reduced pour point after treatment with additives. Effects of different additives were also discussed by analysing the DSC curves and thermomicroscopy result.

Keywords: additive, crude oil, pour point, rheology, thermomicroscopy

Introduction

Crude oils contain substantial amounts of waxy materials. When a wax containing crude oil is cooled below its wax appearance temperature (WAT), wax constituents tends to separate from the liquid phase of crude oil and starts to crystallise which causes several problems during production, storage and transportation. The crystallisation behaviour of crude oils are mainly dependent on the wax composition and distribution. This type of crude oils are low viscosity and Newtonian fluids at high temperatures, but during cooling owing to the precipitation of waxes they show non-Newtonian behaviour. In order to decrease the viscosity of crude oil and reduce the congealing temperature and yield strength, chemical additives and pour point depressants should be used. Their structure is mostly polymeric and improve the flow properties of crude oils and decrease the surface deposition of crystals. Among the polymers or copolymers claimed in literature to improve the low temperature behaviour of waxy crude oils, only two types seem to be generally used. These polymers are often polyalkylacrylates or copolymers containing esterified derivatives of maleic anhydride. Efficient additives modifying the wax crystallisation are able to reduce pour point and viscosity at low temperatures. In order to improve the effectiveness and economics of the additives research has been conducted to improve pour point depressant formulations and to study the mechanism of pour point depression [1, 2]. However it is not possible to select adequate addi-

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tive for all types of crude oils due to the complex composition of crude oils. The influence of type and concentration of wax crystal modifiers on the morphology of wax crystals using photo analysis has been evaluated and a correlation between the pour point depression and the extent of wax modification was also detected [3, 4]. It was found that the rheological properties of waxy crude oils are not only relative to their compositions but also dependent on the complicable thermal history, shear action and time effect [5]. Acrylate polymers were also used as flow improvers in waxy crude oils. The majority of the used additives showed good performance in improving the flow properties of the tested crudes [6]. This study was performed in order to see the effect of several additives on the properties of crude oils by viscometer, DSC, thermomicroscopy and pour point tester.

Experimental

Three different additives and eight crude oils which covered a wide range of fluid composition, origin and properties were supplied by ELF Research Centers of Solaize and Boussens (Table 1). Before the experiments, crude oil samples were stored at the desired doping temperature (55°C) for 15 min before they were treated with additives at the desired concentrations. Then treated crude oil samples were stirred for 5 min and allowed to cool at room temperature for subsequent experiments [6]. DSC and thermomicroscopy experiments were performed in the temperature range of +80°C and –20°C at 2°C min^{-1} cooling rate. Viscosity experi-

Table 1a Properties of the crude oils

Oil. No.	Origin	°API Gravity	% Paraffin	Pour point/°C
1	Algeria	36.5	7.5	+06
2	Algeria	38.8	8.8	+06
3	Libya	26.6	10.5	+18
4	Syria	37.5	12.4	+03
5	Angola	36.3	12.9	+12
6	Libya	40.0	16.9	+09
7	Gabon	38.0	17.6	+15
8	Gabon	35.7	18.5	+18

Table 1b Properties of additives

Additive-1: Homopolyacrylate, Mw=130000 (1), Concentration=50%wt (2)
Additive-2: Copolymer acrylate with long chain/vinyl pyridine Mw=35000 (3)
Concentration=55% cut (2)
Additive-3: Mix between EVA and copolymer acrylic acid/alcohol (C_{16} to C_{24})

(1) Mw equivalent polyethylene
(2) In general solvents are aromatic cut, xylene or toluene
(3) Mw equivalent polyethylene glycol

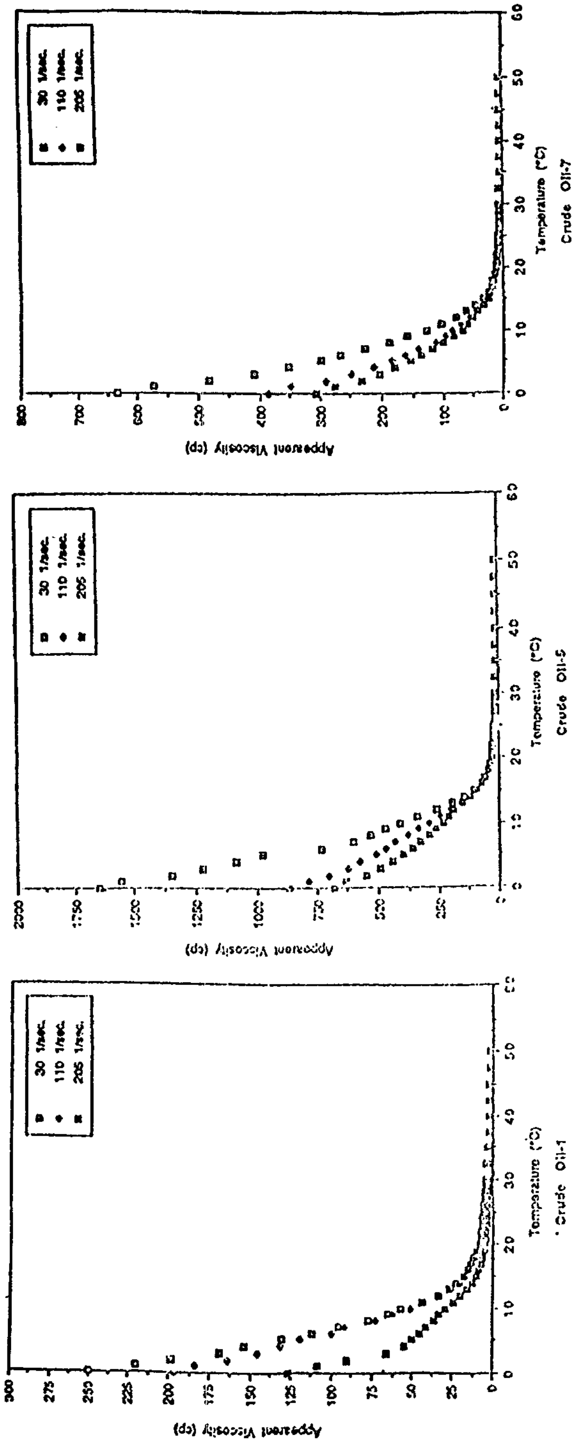


Fig. 1 Apparent viscosity *vs.* T curve of crude oils (30, 110 and 205 s^{-1})

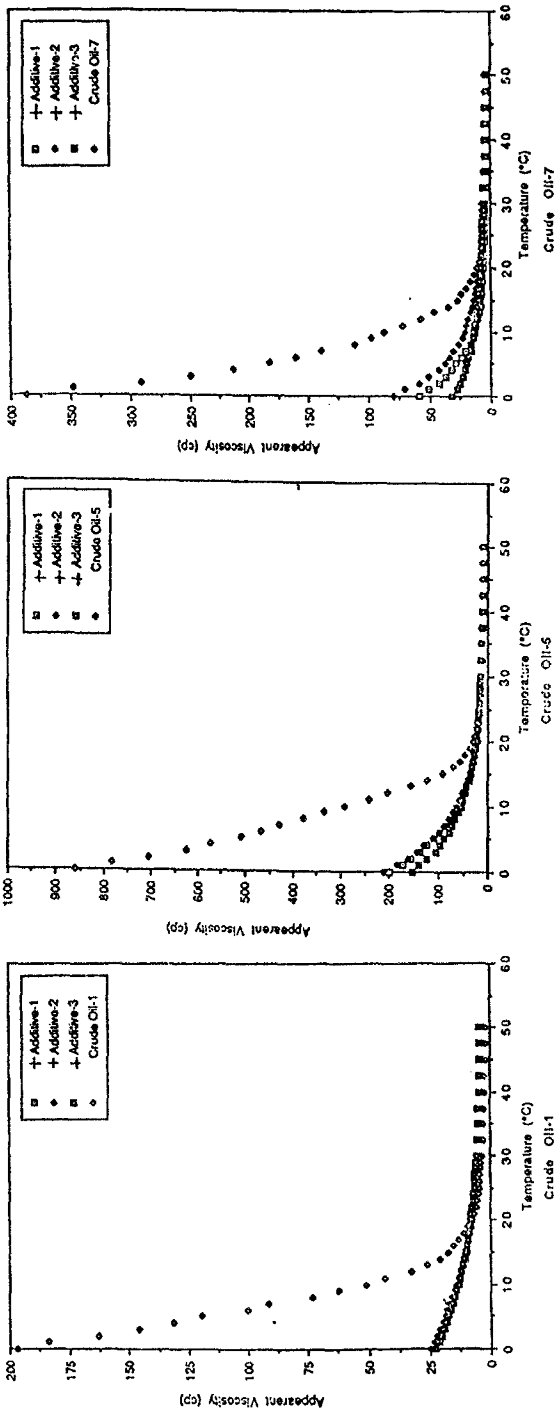


Fig. 2 Apparent viscosity *vs.* T curve of crude oils+additives

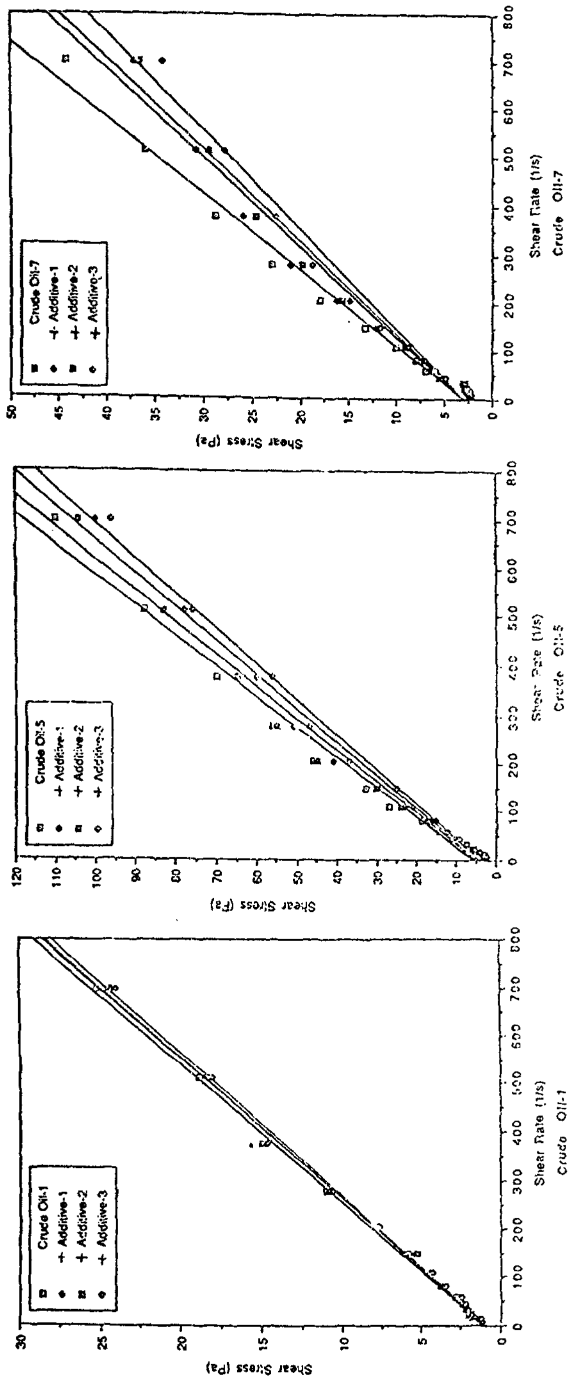


Fig. 3 Shear stress *vs.* shear rate curves of crude oils+additives

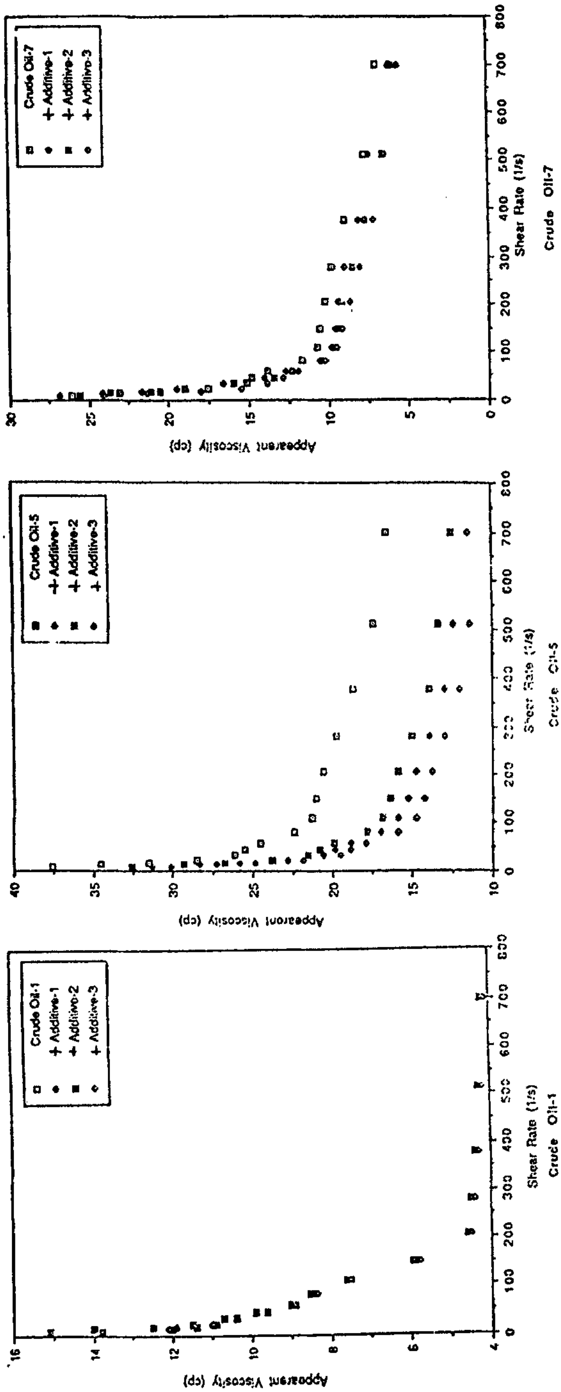


Fig. 4 Apparent viscosity *vs.* shear rate curves of crude oils + additives

ments were done at 0.5°C min^{-1} cooling rate in the temperature range of +50°C and –10°C with rotational viscometer. Pour points of the samples were determined following ASTM standard. Details of the experimental procedure is given elsewhere [7].

Results and discussion

In the first part of this research, eight crude oils were characterised rheologically with emphasis on properties related to the content of wax. In order to test the accuracy of the viscometer, apparent viscosity of several viscosity standards were measured at four different temperatures before the experiments. It was observed that the original and measured results were in good order. In order to see the reproducibility, viscosity experiments of three crude oils were performed under the same experimental conditions. Repeatability of the experiments was in the order of 2%. In all the crude oils studied, apparent viscosity's are increased as the temperature is decreased. As a result of this experiments it was observed that crude oil-3 (26 °API) has the highest and crude oils 2 and 6 (38 and 40°API) have the lowest viscosity's in the temperature interval studied. Apparent viscosity's of the crude oils were also determined at three different shear rates (30, 110 and 205 s^{-1}). As mentioned in the literature, apparent viscosity's of the crude oils decreased as the shear rate is increased (Fig. 1). Depending on the wax content and properties of crude oils, different additives were found as more effective for different type of crude oils. But in general viscosity of all crude oils are decreased considerably with the treatment of additives (Fig. 2). For crude oil 1 and 8 the most effective additive was additive-1, on the other hand additive-3 was found as more effective for crude oils 5 and 7. Shear stress-shear rate measurements was performed at constant temperature (20°C). Experimental data were fitted to Bingham plastic model using a linear regression program (Fig. 3). At 20°C, apparent viscosity's of the crude oils are decreased significantly at low shear rates (Fig. 4). Pour points of the samples were also examined with the treatment of 500 (crude oils 1, 3, 6 and 7) and 1000 ppm additives. In order to see the reproducibility, experiments were performed twice. When differences were observed between two results, a third experiment was performed and the average is assumed to be the pour point of the sample. It was observed that all the crude oils were responsive to all the additives tested except crude oil-5. As expected, when the amount of treatment is increased from 500 ppm to 1000 ppm pour points of the samples were decreased more. Pour points of the crude oils with three different additives are given in Table 2. As it was mentioned before [7], in DSC experiments when 2% wt of waxes have precipitated into the crude oil matrix, the best correlation was obtained with the pour points of the crude oils. When crude oils were treated with three additives it was observed that except crude oil-5 average of 6–7% wt of waxes have precipitated into the crude oil matrix at their pour points (Table 3). From the DSC experiments it was also observed that the crude oils show very little or no decrease in the heats of crystallisation when treated with additives. Table 4 represents the heat of crystallisation of three crude oil and their treatments with additives.Thermomicroscopy is a fast and simple screening tool for conforming the low temperature flow properties of additives treated with

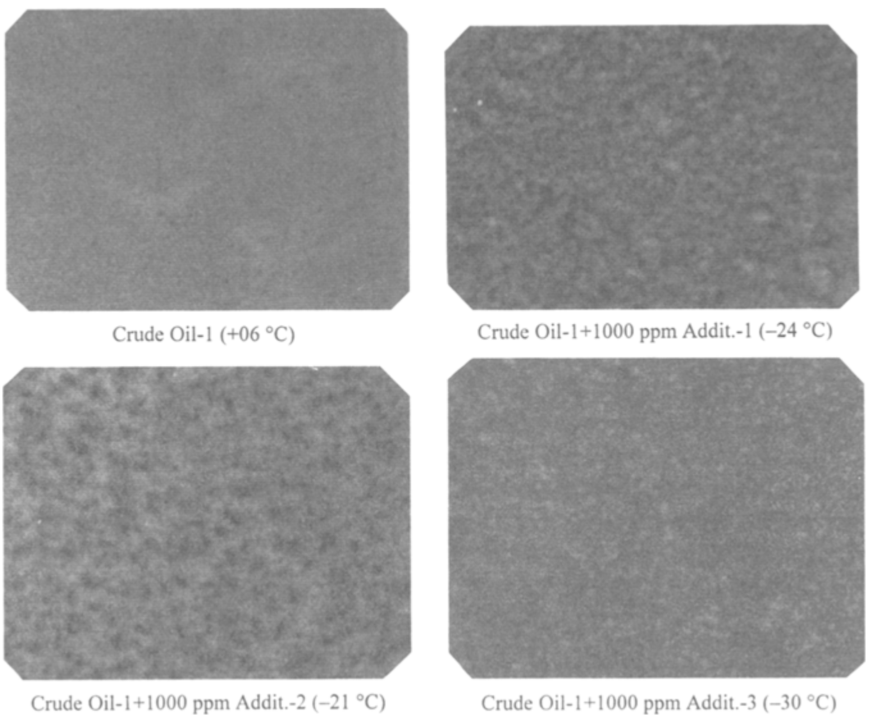
Table 2 Pour points (°C) of the crude oils+additives

Crude oil	Pour point/°C	Treatment	Treated pour p./°C
Crude oil-1	+06	500 ppm additive-1	–21
		1000 ppm additive-1	–24
		500 ppm additive-2	–18
		1000 ppm additive-2	–21
		500 ppm additive-3	–21
		1000 ppm additive-3	–30
Crude oil-2	+06	1000 ppm additive-1	–27
		1000 ppm additive-2	–24
		1000 ppm additive-3	–33
Crude oil-3	+18	500 ppm additive-1	+09
		1000 ppm additive-1	+06
		500 ppm additive-2	+09
		1000 ppm additive-2	+06
		500 ppm additive-3	+03
		1000 ppm additive-3	–06
Crude oil-4	+03	1000 ppm additive-1	–18
		1000 ppm additive-2	–21
		1000 ppm additive-3	–21
Crude oil-5	+12	1000 ppm additive-1	+09
		1000 ppm additive-2	+09
		1000 ppm additive-3	+09
Crude oil-6	+09	500 ppm additive-1	–03
		1000 ppm additive-1	–24
		500 ppm additive-2	–21
		1000 ppm additive-2	–27
		500 ppm additive-3	00
		1000 ppm additive-3	–21
Crude oil-7	+15	500 ppm additive-1	+06
		1000 ppm additive-1	+03
		500 ppm additive-2	00
		1000 ppm additive-2	–03
		500 ppm additive-1	–03
		1000 ppm additive-2	–06
Crude oil-8	+18	1000 ppm additive-1	–09
		1000 ppm additive-2	–21
		1000 ppm additive-3	–21

Table 3 % of wax precipitation at the pour points of the samples

Crude oil+additives	% of waxes precipitated (average)
Crude oil-1+(additive 1, 2, 3)	5.5
Crude oil-2+(additive 1, 2, 3)	8.7
Crude oil-3+(additive 1, 2, 3)	6.3
Crude oil-4+(additive 1, 2, 3)	5.8
Crude oil-5+(additive 1, 2, 3)	3.6
Crude oil-6+(additive 1, 2, 3)	8.2
Crude oil-7+(additive 1, 2, 3)	5.9
Crude oil-8+(additive 1, 2, 3)	7.3

crude oils. Regarding the wax modification effects of additives in crude oils, thermomicroscopy experiments were performed for evaluation the dependence of the crystallisation behaviour on type of additives. Figure 5 represents the thermomicroscopy of crude oil and its treatments with 1000 ppm additives. All photos were taken at precise temperatures corresponding to the pour points of the samples. Very small crys-



Crude Oil-1 (+06 °C)

Crude Oil-1+1000 ppm Addit.-1 (–24 °C)

Crude Oil-1+1000 ppm Addit.-2 (–21 °C)

Crude Oil-1+1000 ppm Addit.-3 (–30 °C)

Fig. 5 Thermomicroscopy of crude oil-1 +additives

Table 4 Heat of crystallisation (J g^{-1}) of the samples

Samples	Crude oil-1	Crude oil-2	Crude oil-3
Original	+26.0	+23.4	+26.0
1000 ppm addit.-1	+26.3	+22.8	+22.5
1000 ppm addit.-2	+26.0	+23.8	+22.6
1000 ppm addit.-3	+26.0	+22.8	+22.2

tal sizes and fine orientations were observed at the pour points of the crude oils. On treatment with additives, well-defined fine dispersed crystals were seen in all crude oils. Comparing wax morphology lead to the conclusion that wax modification caused by additives is more significant in crude oil-7 than their effect in other crude oils at the same concentration.

Conclusions

Depending on the wax content and properties of crude oils, different additives were found as more effective for different type of crude oils. But in general viscosity of all crude oil decreased considerably with the treatment of additives.At constant temperature apparent viscosity's of the crude oils decreased significantly at low shear rates. As expected, when the amount of treatment is increased from 500 ppm to 1000 ppm pour points of the samples were decreased considerably.

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