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Physico-chemical characterization of base stocks and thermal analysis by differential scanning calorimetry and thermomicroscopy at low temperature

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Abstract

A conventional base stock, solvent refined (SR) and a hydroisomerized base stock (HI) in which differences in behavior of Pour Point Depressant Additive are observed, have been dewaxed and these oils and their fractions have been characterized by analytical methods and thermal analysis.

Differential scanning calorimetry (DSC) is a rapid and valuable technique for characterization of the thermal behavior of lubricating oils, allowing the determination of crystallization temperature and amount of precipitated fractions versus temperature. Differences between these base stocks, more particularly in the amount of crystals which precipitate versus temperature can explain selective effectiveness of pour point Depressant (PPD) additives. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Base stocks; DSC; Thermomicroscopy; Crystallization temperature; Pour point

1. Introduction

Paraffins, or more generally waxes, can cause a lot of trouble for the production, transportation and storage of crude oils and also in the storage and operability of derived products such as diesel fuels, home heating fuels, heavy fuels, asphalt cements or lubricating oils.

A hydrocarbon product does not change from the homogeneous liquid to the solid state at exactly one temperature but in a more or less wide temperature range. As the temperature decreases, the solubility of paraffins or waxes also decreases and precipitation of crystals of the heaviest paraffin or wax appears. This precipitation can occur over a temperature range of 5–15°C until solidification occurs. This limits the use of petroleum products.

In the case of lubricating oils, the freeze resistance properties are defined according to the following parameters:

- Cloud Point (CP) and crystallization temperature (T_c) are the temperatures at which crystals first appear. CP depends on the concentration and the molecular weight of the paraffins or waxes and on the chemical nature of the non-waxy part of the oil that we define as the hydrocarbon matrix. It is well known that the heaviest paraffins or waxes are

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responsible for a cloud point that corresponds to an equilibrium controlled by thermodynamic relationships.

- Pour Point (PP): Due to decreasing temperature, crystal growth continues and simultaneously, the amount of precipitated paraffins or waxes increases. A lattice is obtained leading to freezing at the pour point.

  Glass transition temperature (T_g): Below the pour point, as the temperature continuously decreases, the viscosity of the matrix increases until the solidification occurs. A glass is obtained and T_g is the corresponding temperature.

Generally, addition of flow improvers or pour point depressants (PPD) are needed to reach the requirements of the various product specifications, but as it is shown in this present paper, the pour point additive efficiency is different for conventional base stocks and the new generation of hydrotreated base stocks.

A bibliographic study shows that numerous articles concerning paraffin crystallization in diesel fuels and crude oils have been published in recent years. However, very few of the recent articles dealing with paraffin crystallization in lubricating oils have been written. The recent papers concern the characterization of wax extracted from lubricant base stocks [1]; the efficiency of pour point depressants in lubricating oils [2,3] and the interaction between waxes and methacrylate polymers used as pour point depressant [4,5]; and the studies of low temperature pumpability of diesel engine oils, which is required to avoid premature failure of the engine [6,7,8,9].

The first attempt to characterize lubricating oils by DSC was performed by Noël [10]. Unfortunately, no quantitative determinations have been developed. More recently a Coordination European Council contribution has been published [11] and DSC was recommended as a screening test at low temperature to study wax crystallization in mineral oil. Several mineral oils were selected and tested using an experimental procedure very close to the DSC technique performed for middle distillate [12]. However, the enthalpic law used to calculate the amount of precipitated fractions versus temperature and the correlation between the amount of precipitated wax and pour point have not been done.

In this work, the aim is a characterization of base oils using DSC and thermomicroscopy in order to try to understand the behavior of (PPD) in various base stocks. In fact thermomicroscopic investigations are useful for correlating morphological or structural changes to the thermal effects observed in DSC experiments.

We have developed a thermoanalytical procedure in order to determine waxes with a good accuracy. T_g of the hydrocarbon matrix is determined by DSC by heating from the solid state of the previously cooled hydrocarbon. The homogeneous liquid can be cooled using DSC to obtain T_c and the amount of waxes which precipitates versus temperature. These values will be correlated with the low temperature properties of hydrocarbon matrices.

2. Experimental

2.1. Materials

In this comparative study we have chosen two different base stocks:

1. A conventional base stock of the 150N type, solvent refined (code=SR).
2. The second is a base stock obtained by a paraffin hydroisomerization process (code=HI). Kinematic viscosity is roughly the same at 100°C (5 mm^2/s) for SR and HI, but the viscosity index (VI) are different (SR: VI=97; HI: VI=146).

Likewise, an isoparaffinic base stock not containing any cold crystallizable products was used as a ‘model’ matrix. It was a hydrogenated polyalphaolefin obtained by the polymerization of 1-decene (code=PAO6, for a viscosity of 6 mm^2/s at 100°C.). PPD additive is a commercial product from the polyalkylmethacrylate family (PMA).

2.2. Methods

2.2.1. Dewaxing

Base stocks were dewaxed with methylisobutylketone at −37°C. The obtained waxes were also dewaxed with the same selective solvent at −30°C.

2.2.2. Distillation cuts

Base stocks were fractionated into 8 cuts by preparative distillation according to ASTM D 2892.

2.2.3. Physicochemical analysis

Physicochemical analysis of base stocks and derivative fractions were as follows. SAR analysis: Composition in Saturated, Aromatic and Resins (polar fraction) (SAR) was determined by High Performance Liquid Chromatography (HPLC) according to IFP method [13]. Saturated fraction analysis: distribution in paraffinic and napthenic compounds from the saturated fractions was determined by mass spectroscopy (MS) according to ASTM D 2786. Structural analysis was performed by nuclear magnetic resonance of carbon (NMR ^{13}C). Nature and content of *n*-paraffins were determined by gas chromatography (GC) according to ASTM D 5442. Relative molecular weight from viscosity measurements of products were determined according to ASTM D 2502.

2.2.4. DSC measurements

DSC measurements were carried out using a Mettler TA 2000 B apparatus controlled by an Hewlett Packard 85 computer. Calibrations for temperature and enthalpy were performed using the melting point and enthalpy of melting of high purity metals and compounds. Precision of temperature measurements was within ±0.2°C. The apparatus was flushed with argon because of its density and its low thermal conductivity.

The oils (20/30 mg) were transferred into an aluminium crucible which was sealed and weighted.

Studies done on warming to determine DSC profile and wax content were carried out from −130°C up to 25°C at 5°C/min. The cooling rate from 25°C to −130°C was 10°C/min. Additional cooling studies were performed at a rate of 0.5°C/min from −10°C to −40°C to determine T_c and PP. The calorimetric signal was recorded and stored to be used off line.

2.2.5. Thermomicroscopy

The equipment used for observations was composed of: a Zeiss Axioplan microscope using transmitted light (12V, 100 W halogen filament lamp) and equipped with polarized light and contrast phase devices; a hot stage Mettler FP82 which can operate in the range from −70°C to +300°C, controlled by an FP 80 control unit; a video equipment composed of a colour camera (Sony DXC 101 P), two colour video monitors (Sony PVM 1442), a colour video copy processor (Mitsubishi CK 100S) and a video tape recorder (JVC BR 6400).

Polarized light microscopy is most commonly employed to observe anisotropic behavior within substances that exhibit more than one refractive index. These are termed birefringent materials. Small regions within the sample may appear white or coloured under polarized light, and a molecular lattice structure may be apparent. By this method, well crystallized domains corresponding to the precipitated *n*-alkanes in the hydrocarbon matrix were characterized.

The oil (5 mg) was placed into a glass crucible for observation. The same cooling rate for DSC (0.5°C/min) was used for observation.

3. Analytical results

3.1. Base stocks

We have compared the efficiency of the commercial PPD additive in two base stocks. Using 0.5 wt.% of additive, the pour point (PP) is lowered by 26°C for SR (PP from −12 to −38°C) and only by 11°C for HI (PP from −18 to −29°C). The difference in behavior of this additive has thus been verified.

The two base stocks essentially differ by their rheological properties and their overall chemical compositions. HI has (1) very high viscosity index, (2) absence of aromatic compounds, (3) low content of naphthenic compounds and (4) fairly low pour point. SR has (1) high content of aromatic compounds, (2) presence of sulfur, (3) low viscosity index and (4) higher pour point. The principal characteristics determined for the different base stocks are given in Table 1 together with those of the PAO6.

In the first phase, we dewaxed the base stocks SR and HI to isolate the crystallizable fractions responsible for the pour point.

3.2. Dewaxed oils and waxes

3.2.1. Superdewaxing conditions

The SR and HI oils were first dewaxed when they were manufactured. We subjected them to two new dewaxing steps so as to obtain both 'superdewaxed' oils (SR-DW and HI-DW) having PP of around −30 to −35°C and paraffinic extracts containing the species

Table 1
Superdexaxing in two steps — physicochemical characterization[a]

Component	Base stock			SR and HI Dewaxing Step (Dewaxing temp. : -37°C)				W1 Dewaxing Step (Dewaxing temp. : --30°C)	
				Dewaxed oil		Waxes W1		→Waxes W2	
	SR	HI	PAO6	SR-DW	HI-DW	W1-SR	W1-HI	W2-SR	W2-HI
(wt%)	/	/	/	81.8	74.1	17.4	24.1	5.8	2.9
Viscos. at 100°C/(mm^2/s)	5.3	5.0	5.9	5.2	4.8	4.9	5.8	/	/
Viscosity index	97	146	140	94	146	118	147	/	/
Relative molecular weight	400	440	470	394	434	410	470	/	/
Sulfur (wt%)	1.0	0.004	n.d.	1.0	/	0.7	0.007	/	/
Aromatic content (wt%)	33.0	n.d.	none	34.1	/	25.6	/	/	/
Paraffinic content (wt%)	28.6	82.8	92.8	26.1	82	36.5	78	/	90
Naphtenic content (wt%)	37.5	17.2	7.2	38.0	18	35.5	22	/	10
Polar content (wt%)	0.9	none	none	1.6	/	2.4	/	/	/
N-paraffins content (wt%)	(0.3)	(0.16)	none	n.d.	n.d.	1.8	0.65	3.1	1.55
	↑	↑	Balance			↓	↓		
n-C_{17} to n-C_{20}	n.d.	n.d.	/	n.d.	n.d.	0.26	0.0	0.3	0.20
n-C_{21} to n-C_{25}	n.d.	n.d.	/	n.d.	n.d.	0.91	0.23	1.45	0.48
n-C_{26} to n-C_{30}	n.d.	n.d.	/	n.d.	n.d.	0.59	0.42	1.34	0.58
n-$C_{31}$to n-C_{34}	n.d.	n.d.	/	n.d.	n.d.	0.04	0.0	0.04	0.29
Pour Point/°(C)	-12/-15	-18/-21	-68	-33	-33	+3	-6	solid	+3
Cloud Point/°(C)	-11	-16	none	-32	-28	/	-5	/	/

[a] n.d.: non detectable/not measured.

responsible for low temperature crystallization (W1-SR and W1-HI for the first dewaxing step, W2-SR and W2-HI for the second dewaxing step).

Table 1 shows the main physicochemical characteristics of the different fractions obtained and in particular the PP and composition by chemical family. It can thus be seen that the fractionations performed reached their goal of obtaining both a matrix with a low PP (−33°C) and a fraction that was crystallizable at a higher temperature (PP=+3°C for W1-SR and −6°C for W1-HI).

3.2.2. *n-paraffin content*

The *n*-paraffins were present in very small amounts and cannot be determined in the base stocks or in the dewaxed matrices SR-DW and HI-DW. Only the determination and distribution of the *n*-paraffins contained in the extracts W1-SR, W2-SR, W1-HI and W2-HI were obtained by gas chromatography. The results are given in Table 1. From the amounts of *n*-paraffins contained in fractions W1-SR and W1-HI, we can calculate their contents in the base stocks and thus obtain the overall chemical composition (Table 1).

The results clearly show that the oils examined contain only very small amounts of residual *n*-paraffins. Consequently, the species that cold crystallize and are responsible for the PP are probably of a different nature, which also leads us to study the physicochemical properties of the dewaxed oils (SR-DW and HI-DW) and of the paraffinic extracts (W1-SR and W1-HI).

3.2.3. Characterization of solvent refined oil fractions

The physicochemical characteristics and elemental analysis of the fractions obtained from the mineral oil are given in Table 1.

These results show that fractionation by dewaxing was effective. The PP of the SR-DW (−33°C) and W1-SR (+3°C) fractions show that these cold crystallizable species are mainly concentrated in the W1-SR fraction. This fraction contains only 1.8% *n*-paraffins. The overall compositions of fractions SR and SR-DW are very close. Compared to SR and SR-DW, the W1-SR fraction is richer in saturated compounds especially isoparaffins, to the detriment of aromatic content.

For the hydroisomerized oil fractions the results in Table 1 show that the overall compositions of HI, HI-DW and W1-HI are similar. The difference in the PPs of the HI-DW (−33°C) and W1-HI (−6°C) fractions shows that the cold crystallizable species are effectively concentrated in the W1-HI fraction and that the superdewaxing operation was effective. However, the W1-HI fraction contains only 0.65% of *n*-paraffins.

The second dewaxing step concentrates the *n*-paraffins (1.55%) and the low temperature crystallizable fractions in W2-HI (PP=+3°C).

3.2.4. Analysis of 'paraffinic' fractions

The results given in Table 1 and the structural analysis by NMR ^{13}C (Table 2) show that the W1-HI fractions are more paraffinic than the W1-SR fractions, but less branched.

3.3. Base stocks distillation cuts

At 450°C, only 13% of SR oil remains that is not distilled compared to 45% for oil HI, which effectively confirms the difference between these two products (Table 5). Oil HI contains more long-chain saturated hydrocarbons than SR oil (C36 average=45% mass for oil HI compared to 13% maximum for SR oil).

4. DSC results

4.1. Base stocks

4.1.1. Evaluation of the paraffin or wax content

Typical DSC curve of a base stock SR is shown in Fig. 1 for heating from −130 to +25°C. Several thermal effects occur similarly to those observed with diesel fuels or crude oils.

- An increase of the heat capacity (ΔC_p) causes an endothermic shift and corresponds to the transition glass T_g (1 in Fig. 1). The T_g value depends on the molecular weight of the matrix and takes place in the temperature range −100 to −80°C. T_g is assumed to be the temperature when half of the heat capacity increase is reached. To evaluate T_g, two parallel baselines are used as shown in Fig. 1: one before T_g rises the calorimetric signal, the other is a tangent line at the top of the signal.
- After T_g a small exothermal effect (2 in Fig. 1)due to the crystallization of species that does not crystallize on cooling.
- A broad endothermal effect (3 in Fig. 1) corresponding to the dissolution of the wax into the liquid matrix.

Determination of wax content requires the computation of the base line and the knowledge of the experimental relation of the enthalpy of dissolution (ΔH_{diss}) versus temperature (T) which allows to transform the measured heat into a mass of waxes.

Table 2
Structural analysis of SR and HI waxes (1st and 2nd steps) by NMR ^{13}C

Characteristics	Mineral oil		Hydroisomerized oil	
	W1-SR	W2-SR	W1-HI	W2-HI
Structural analysis % (NMR^{13}C)				
C	0	/[a]	0	0
CH	13.4	/	10.4	9.1
CH2	73.2	/	75.6	76.1
CH3	13.4	/	14.0	14.8

[a] /: not measured.

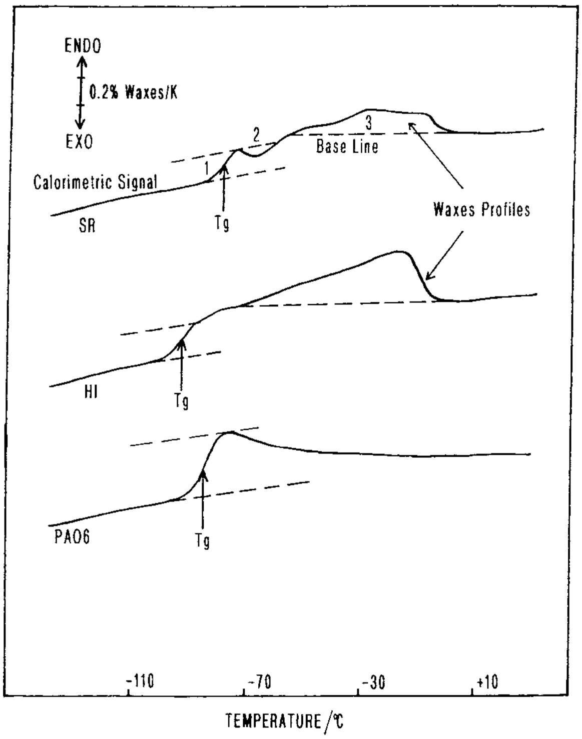


Fig. 1. DSC curves on heating of SR (mineral oil), HI (hydro-isomerized oil) and PAO6 Polyalphaolefin).

For this last point, the relation used in this work is the same used for Diesel fuels [14].

$$\Delta H_{\mathrm{diss}} = -8.111 \times 10^5 T^3 - 1.605 \times 10^{-2} T^2 + 4.489 \times 10^{-1} T + 197\ \mathrm{J g^{-1}} \quad (\text{with } T \text{ in } ^\circ\mathrm{C})$$

The base line is assumed to be a straight line (dashed line in Fig. 1) between the end of the exothermal effect after T_g and the end of the dissolution of waxes (return to baseline). This straight line corresponds to a linear variation of the thermal capacity of the hydrocarbon matrix.

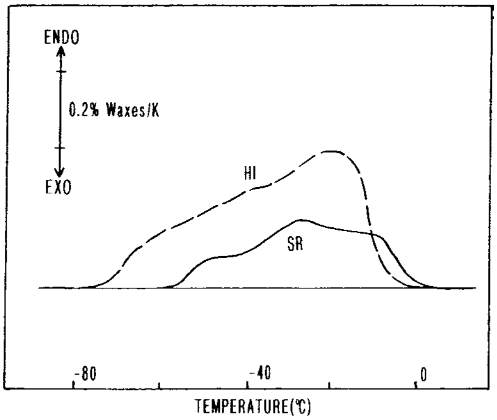


Fig. 2. Comparison of DSC profiles of waxes of SR and HI (on heating).

Results are given in Table 3. DSC curves of HI and PAO6 are also shown in Fig. 1. Owing to the difference between the production processes of both base stocks, the values of T_g of HI and SR in Fig. 1 and the wax content are very different. T_g of PAO6 is included between the values of T_g of both basestocks. This fact justifies the use of PAO6 as the hydrocarbon matrix for future studies.

Differences between DSC profiles on heating HI and SR are observed. As above-mentioned, the endothermal effect corresponds to the dissolution of CF which have crystallized during the cooling (Fig. 2). The shape of the thermal effect depends on the *amount and the chemical structure of CF* (length of hydrocarbon chains for example). This fact explains the differences between DSC profiles of both the base stocks.

Table 3
Thermal parameters of base stocks and dewaxed oils

Oils	Glass transition temperature (°C)	Crystallizablle fractions (% mass)	Crystallization temperature (°C)	Pour Point ASTM D 97 (°C)
SR	−80	6.1	−13.9	−15
SR-DW	−81	4.2	−33.6	
HI	−91	14.8	−19.4	−21
HI-DW	−93	11.6	−30.8	
PAO6	−87	none	none	−68

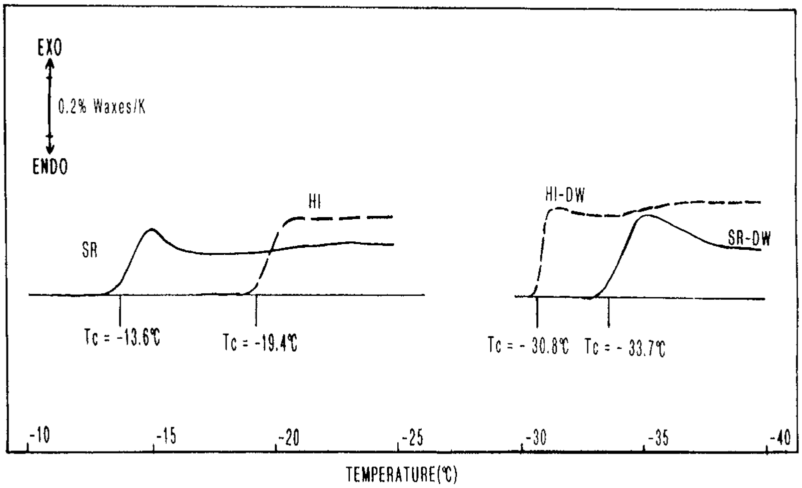


Fig. 3. Comparison of crystallization peak of dewaxed oils (on cooling).

4.1.2. Determination of thermal properties on cooling

DSC experiments on cooling were used to determine precisely the temperature T_c at which the first crystal appears in oil and to quantify the amount of waxes which precipitates versus temperature. In a previous work we have shown that a good correlation is obtained between Cloud Point (ASTM D 2500) and T_c for diesel fuel [12].

For these experiments, a cooling rate as low as possible is used in order to attain a better approach to the equilibrium solid↔liquid. This cooling rate must be close to the average cooling rate used in the ASTM Cloud Point test.

Detection of the exothermal effect of crystallization of the paraffins or waxes must be both sensitive and accurate. The thermal noise of the DSC apparatus being 7 mW, the crystallization temperature T_c is defined as the temperature at which the thermal power developed by the heat of crystallization in the lubricating oil is 15 mW during cooling at 0.5°C/min.

As discussed earlier, the amount of crystallized paraffins or waxes can be determined by DSC. Base line computation was carried out as follows: least square fitting was achieved with the values of the calorimetric signal included in a temperature range of 3°C before the value of T_c. Determination of the amount of crystals CF required knowledge of the relationship between the enthalpy of crystallization (ΔH_{cryst}) and temperature. The same linear relation obtained for diesel fuels has been used for lubricating oils [12].

$$\Delta H_{\text{cryst}} = 1.5167T + 211.7\,\text{J}\,\text{g}^{-1} \quad (\text{with } T \text{ in } ^\circ\text{C})$$

The results are given in Table 3.

Comparison between crystallization peaks of SR and HI is shown in Fig. 3. The slope of each peak which depends on the precipitation rate (nucleation-growth process) are the same. After T_c, the amount of precipitated CF which corresponds to the area below the calorimetric signal are more important for HI than SR.

4.2. Dewaxed oils and waxes

Dewaxed oils and their waxes have been studied using only DSC experiments. Comparisons between

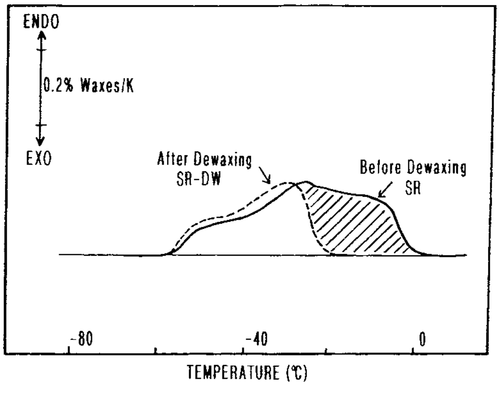


Fig. 4. Comparison of DSC curves of SR and SR-DW (on heating).

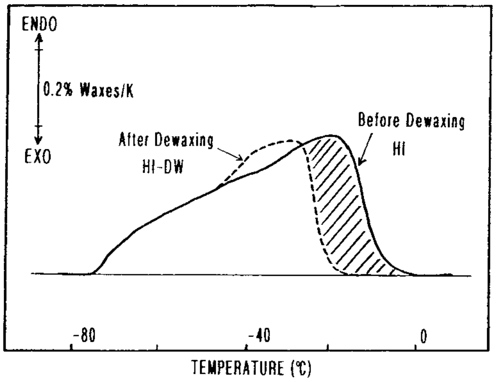


Fig. 5. Comparison of DSC curves of HI and HI-DW (on heating).

Table 4
Crystallizable fractions (*n*-alkanes and isoalkanes) in PAO6[a]

Component (mass%)	Crystallization temperature (T_c/°C)
PAO6+*n*−C18 (2%)	−28.5
PAO6+*n*−C20 (2%)	−16.3
PAO6+*n*−C22 (2%)	−4.9
PAO6+*n*−C24 (2%)	+4.6
PAO6+MOD (2%)	−50.2
PAO6+MOD (5%)	−42.0
PAO6+MHD (5%)	−50.2
PAO6+MHD (10%)	−40.2
PAO6+MHD (15%)	−33.9

[a] MOD: methyloctadecane; MHD: methylheptadecane.

oils and dewaxed oils are shown in Fig. 4 (SR-DW) and Fig. 5 (HI-DW).

Precipitation of waxes by selective solvent does not modify the value of T_g of the hydrocarbon matrix as shown in Table 3. For dewaxed oil, the decrease of the amount of paraffins corresponds to the lowering of T_c (Fig. 3). A value of −33.6 and −30.8°C, respectively is reached for SR-DW and HI-DW. It seems that the efficiency of the dewaxing process is better with SR (T_c lowered by 19.7°C) than HI (T_c lowered by 11.7°C).

4.3. Identification of crystallized fractions CF

Attempts to identify the chemical species which crystallize in the temperature range T_c−30°C for SR

Table 5
Thermal parameters of mineral and hydroisomerized oil distillation cuts

Cut	Preparative distillation (ASTM D 2887)				Thermal analysis by DSC		
	Temp. range (°C)	Balance (wt.%)	Relative molecular weight(ASTM D 2502)	Average carbon	Glass transition temperature (°C)	Crystallizable fractions CF (% mass)	Crystallization temperature (°C)
SR	/	/	400	C_{28}	−79.7	6.1	−14.3
SR1	IP-400	12.9	327	C_{23}	−93.6	9.0	−13.9
SR2	400–410	11.4	353	C_{25}	−86.5	9.7	−14.4
SR3	410–420	21.1	390	C_{27}	−83.1	8.6	−15.2
SR4	420–430	11.5	401	C_{28}	−80.6	7.6	−15.7
SR5	430–440	17.0	425	C_{30}	−78.1	7.0	−15.0
SR6	440–450	11.4	427	C_{30}	−76.0	7.1	−16.1
SR7	450–453	1.7	not determined	/	−75.6	6.4	−16.1
SR8	>453	12.8	497	C_{35}	−72.2	5.9	−16.0
HI	/[a]	/	440	C_{31}	−94.4	14.8	−20.1
HI1	IP–400	11.9	328	C_{23}	−104.0	15.7	−23.2
HI2	400–410	4.4	355	C_{25}	−101.0	16.6	−21.0
HI3	410–420	6.3	377	C_{27}	−99.8	16.7	−20.2
HI4	420–430	9.6	387	C_{27}	−97.2	16.8	−19.7
HI5	430–440	0.8	378	C_{27}	−96.9	16.1	−19.4
HI6	440–450	8.3	431	C_{30}	−95.6	15.9	−19.3
HI7	450–456	3.1	410	C_{29}	−95.6	15.5	−18.9
HI8	>456	45.3	514	C_{36}	−86.3	13.5	−18.7

[a] /: not measured.

and HI have been performed to support the addition of *n*-alkanes and isoalkanes into the PAO6 matrix. Determinations have been carried out on heating and cooling following the same procedure used for the base stocks.

4.3.1. *n-alkanes*

Previous analysis of *n*-alkanes performed by chromatography formed only small amount of *n*-alkane in the waxes obtained by dewaxing of base stocks. Therefore, *n*-alkanes (C_{18}, C_{20}, C_{22}, C_{24}) in low percentage (2%) were added to PA06. Results are given in Table 4.

As expected the solubility of the alkanes decreases and T_c rapidly increases when the carbon number increases.

So we can conclude, according to the results of chromatography and owing to the low temperature of T_c that:

- *n*-alkanes are present in low percentage ; in the waxes and in the base stocks
- the length of hydrocarbon chain is in the range C_{18}–C_{24} for the majority of *n*-alkanes.

4.3.2. *Isoalkanes*

Methylheptadecane (MHD) and methyloctadecane (MOD) have been used for simulations. They do not crystallize easily (exothermal effect before melting). For the same number of carbon in the chain, one grafted methyl decreases the temperature of melting

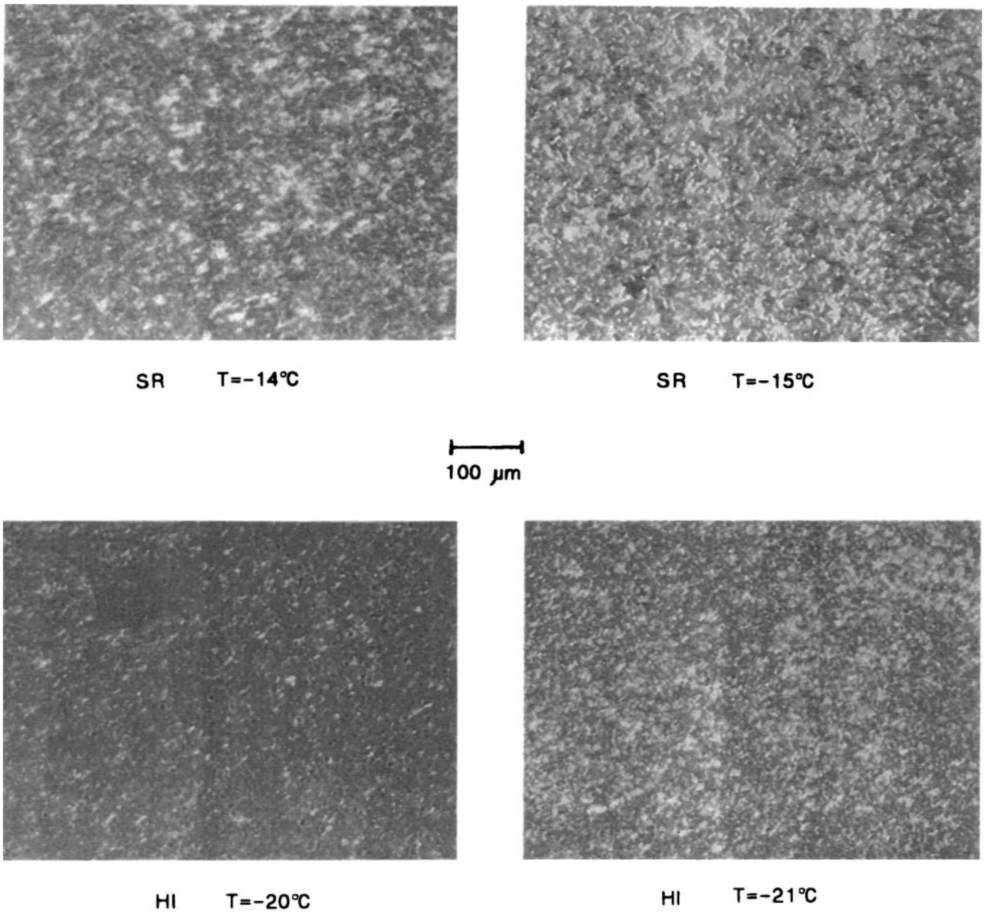
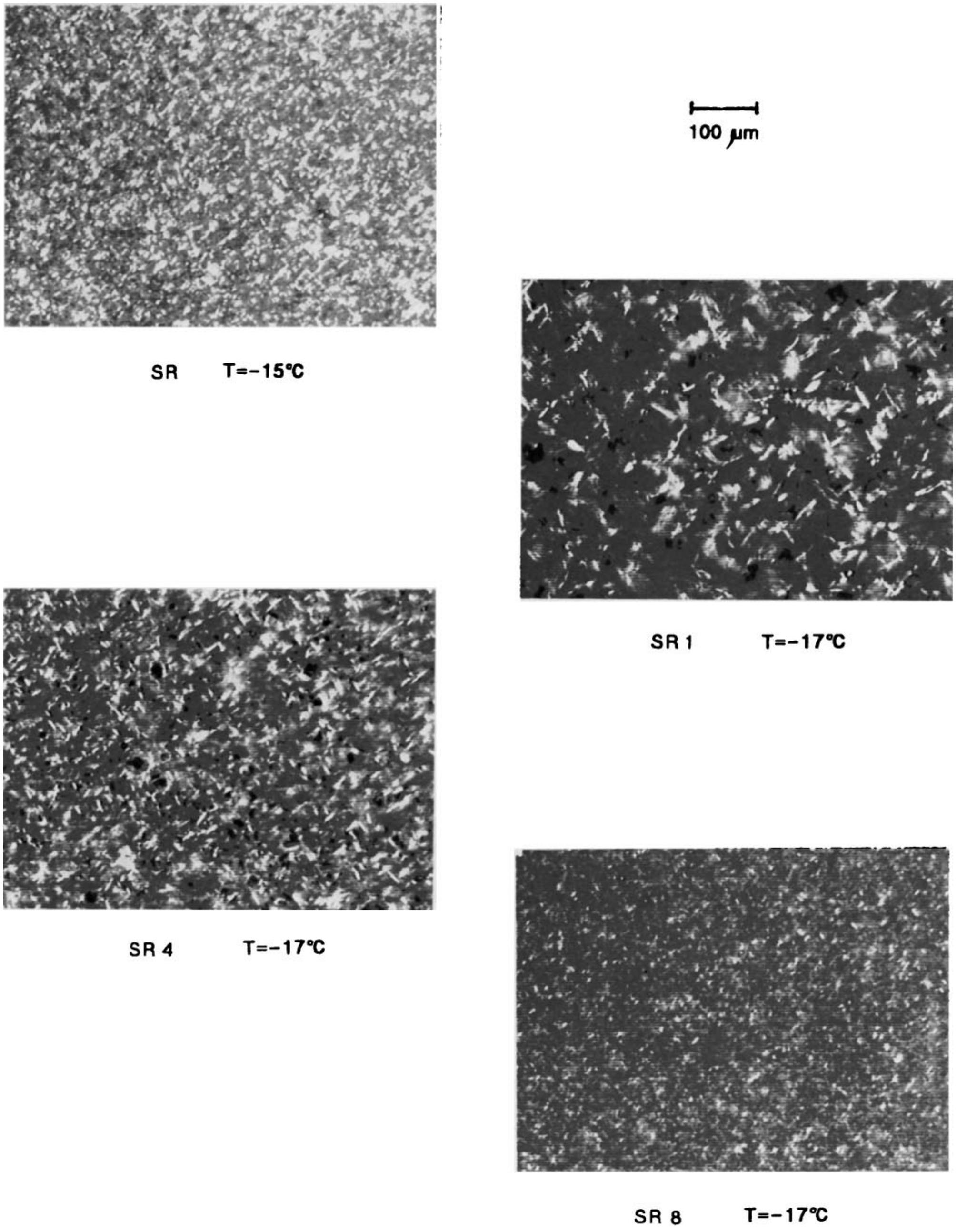


Fig. 6. Thermomicroscopy of base oils.

(40–50°C). Even in the case where an important amount of MHD was added, the value of T_c is very low: -33.9°C. Results are shown in Table 4.

Even in the case where an important amount of MHD was added, the value of T_c is very low also: -33.9°C.



SR T=−15°C

SR 1 T=−17°C

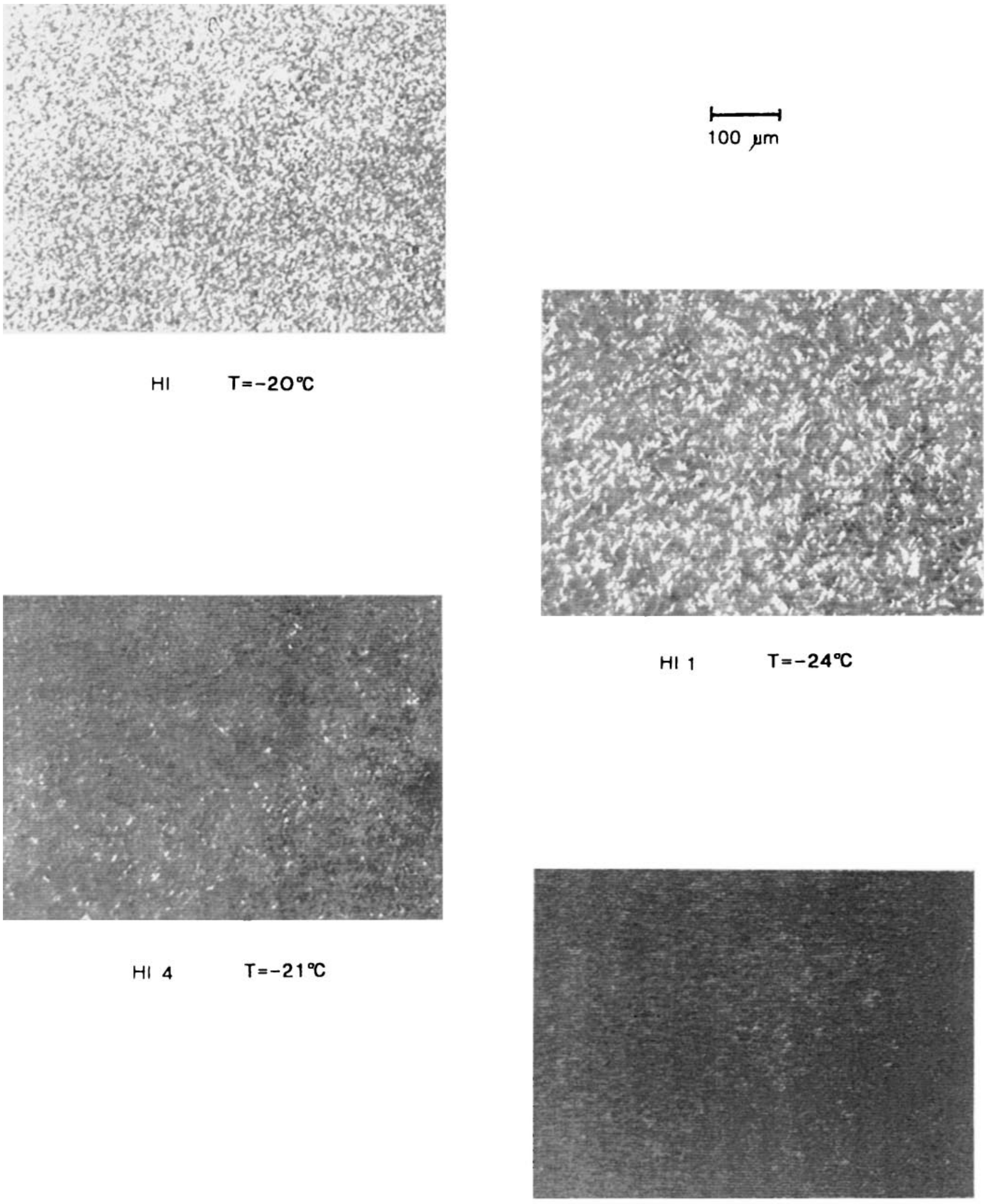
SR 4 T=−17°C

SR 8 T=−17°C

Fig. 7. Thermomicroscopy of SR distillation cuts.

We have tested other heavy grafted isoalkanes : phenylbutadecane, 4-methylpentadecane (pristane), hexamethyltetracosane (squalane), but crystallization did not occur for these compounds.

So we may conclude that CF consists mainly of isoalkanes having one or two methyl groups and a linear carbon chain in the range $C_{16}-C_{20}$ or more.



HI T=-20°C

HI 1 T=-24°C

HI 4 T=-21°C

HI 8 T=-20°C

Fig. 8. Thermomicroscopy of HI distillation cuts.

4.4. Base stocks distillation cuts

Determination have been performed with the same procedure used previously. Results are given in Table 5 for SR and HI.

The evolution from light up to heavy distillates is characterized by :

- an increase of transition glass T_g;
- a decrease of the amount of CF;
- an increase of T_c for HI and a decrease of T_c for SR.

5. Thermomicroscopy results

5.1. Base stocks

The microphotographs are shown in Fig. 6 (1°C/min). No difference has been found if different cooling rates of 0.5–2°C/min were used.

Different to diesel fuels where large plater white crystals (100–200 µm) are observed for both base stocks small white crystals (1–5 µm) were obtained. The red orange color is due to the hydrocarbon matrix and the difference in color depends on the thickness of each sample. As expected, the number of crystals increases since continuous precipitation occurs in the sample during cooling. These differences are due to the chemical structure of CF. In diesel fuel CF consists mainly of *n*-alkanes and the crystalline network can easily grow with molecules having the same linear structure. At the contrary, in base stocks *n*-alkanes content are very low and the various structures of iso-alkanes hinder the crystals growth. Therefore for base stocks, small crystals are always obtained.

5.2. Distillation cuts

Thermomicrophotographs are given in Figs. 7 and 8. The size of crystals is decreasing from light up to heavy distillates, base oils having crystals of intermediate size. As observed with the base stocks in Fig. 4, the red color is also due to the hydrocarbon matrix, the difference in color depending on the thickness of each sample.

6. Conclusions

Physicochemical and thermal characterization of base stocks and derivative fractions (distillation cuts and waxes) allows to put in evidence differences between base stocks SR and HI which can explain the selective effectiveness of PPD additives. The main differences concern the chemical species which crystallize and the amount of crystals which precipitate versus temperature.

The value of cloud point of both oils are different −13°C for SR and −19°C for HI. Assuming that the solvent power of each matrix is the same, crystals of SR are developed showing heavier molecules than HI. More precisely, the carbon chains of alkanes or iso-alkanes which precipitate are longer in SR than those obtained in HI. This difference could be correlated to the selectivity and the efficiency of pour point depressants.

For example, the evaluation of precipitated crystals has been performed at the temperature of −36°C. We found 3.7% for SR and 6.2% for HI. It is obvious that for a same concentration in pour point depressant, it should be difficult to reach a same value of pour point for both base stocks.

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