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COMPOSITION AND OXIDATION OF PETROLEUM FRACTIONS*

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ABSTRACT

A petroleum lubricating oil basestock was separated into fractions by thermal diffusion and silica gel chromatography. Differential scanning calorimetry was used to study the effects of the various aromatic types on the oxidative stability of the saturated fractions. Alkyl benzenes and naphthenobenzenes were found to decrease the stability of the most linear saturated compounds. These one-ring aromatics had either no effect on or increased the stability of saturated fractions containing highly condensed naphthenes. Polynuclear aromatics and sulphur compounds acted as inhibitors for all saturated fractions. This inhibition was least effective with the most linear isoparaffins and substituted cyclohexanes, and was most effective with the condensed naphthenes. Intermediate results were obtained for saturated and aromatic fractions whose composition lay between the extremes. For a given aromatic fraction, stability is always affected by the nature of the saturated compounds.

INTRODUCTION

The work presented here describes the application of thermal analysis techniques in identifying some of the compositional parameters of mineral oil basestocks which influence oxidative stability.

Petroleum basestocks consist of saturated hydrocarbons, isoparaffins and cycloalkanes, as well as aromatic compounds. Usually, paraffins, cyclohexanes and decalins make up the largest part of the saturated fraction which itself accounts for about 75% of a refined petroleum distillate. One-ring compounds make up the greatest proportion of the aromatic fraction, but there are significant amounts of two-ring aromatics as well as a few polynuclear and sulphur compounds.

The relative numbers of these species in the basestock are dependent on both crude source and on subsequent processing conditions. Processing consists of some combination of distillation, solvent extraction, dewaxing and sometimes a finishing step such as hydrofinishing. Processing and crude determine composition, and composition in turn affects oxidative stability. A knowledge of the optimum composi-

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tion for stability thus allows better use of the crude oil and helps to conserve this valuable natural resource.

This paper will describe how thermal diffusion and differential scanning calorimetry (DSC) were combined to provide information on how molecular composition affects oxidative stability.

EXPERIMENTAL

A solvent 150 Neutral from a U.S. mid-continent crude was selected for this study. Viscosity was 32.0 cst at 37.8 °C and 5.32 cst at 98.9 °C. Separation by thermal diffusion was affected by a static column technique which has been described by other workers[1]. Ten fractions of 3 ml volume each were obtained in this way. Each fraction was separated by liquid/solid chromatography through silica gel using hexane, toluene and acetone as elutants. This provided three fractions: saturates containing isoparaffins and naphthenes, aromatics which also contain sulphur compounds including thiophenes, and polar material. Only the first two fractions from gel separation were used in this study.

A mass spectrometry technique similar to that described elsewhere[2] was used to identify the proportions of the different molecular species. This analysis gave the ring distribution of both saturated and aromatic types.

Oxidation stability of the hydrocarbon fractions and their mixtures was measured by differential scanning calorimetry in atmospheric oxygen. The apparatus used was a Perkin-Elmer differential scanning calorimeter Model DSC 1-B. Oxygen was flushed through the system at 30 ml $\min^{-1}$; sample size was 0.5 mg. The resulting exotherms and effect of experimental parameters have been described previously[3]. Experiments were performed at 170 and 190 °C in the present case.

The particular samples studied in this work consisted of either pure saturated or aromatic material or a mixture containing 16 wt % of a particular aromatic fraction in any given saturated fraction.

RESULTS AND DISCUSSION

Thermal diffusion separation

Thermal diffusion of lubricating oils separates according to molecular shape with little selectivity by molecular weight. The most linear compounds tend to move toward the hot wall of the column, the branchier material to the cold. This gives two overlapping tendencies: within one group, such as say isoparaffins, those compounds with fewer branches are separated from the highly branched material; at the same time compounds with high ring numbers tend to be separated from those with low ring numbers. The vertical column technique makes use of convective phenomena to separate the hydrocarbons according to this classification.

The results of thermal diffusion separation and liquid/solid chromatography are outlined in Tables 1 and 2. Saturates content decreases with fraction number

TABLE 1

MOLECULAR COMPOSITION OF THERMAL DIFFUSION FRACTIONS OF SATURATED LUBRICATING OIL HYDROCARBONS

Fraction No.	*1*	*2*	*3*	*4*	*7*
Wt. % saturates in fraction	*94.3*	*92.3*	*89.8*	*87.5*	*74.2*
Analysis of saturates (vol. %)					
Isoparaffins	61.0	51.8	42.1	34.7	3.0
One-ring naphthenes	36.2	42.4	46.3	46.7	33.6
Two-ring naphthenes	1.9	5.0	9.6	14.9	31.8
Three-ring naphthenes	0.5	0.5	1.7	3.4	21.4
Four plus rings	0.4	0.3	0.2	0.3	10.3

TABLE 2

MOLECULAR COMPOSITION OF THERMAL DIFFUSION FRACTIONS OF AROMATIC LUBRICATING OIL HYDROCARBONS

Fraction No.	*1*	*4*	*5*	*6*	*7*
Wt. % aromatics in fraction	*5.0*	*9.8*	*12.7*	*15.2*	*18.6*
Analysis of aromatics (vol. %)					
Alkyl benzenes	86.7	69.2	57.6	47.5	34.1
Naphtheno benzenes	13.1	20.4	23.7	26.3	25.9
Two-ring aromatics	0.0	0.8	9.4	14.5	20.0
Polynuclear aromatics	0.1	0.2	0.3	3.0	7.2
Thiophenes	0.1	5.4	8.3	10.7	12.8

while at the same time composition of the saturated fraction moves to increased content of high ring number material. For example, fraction one which contained some 94% saturates consists of almost all isoparaffins and cyclohexanes. Fraction seven, however, contains only 74% saturates and at the same time has very few isoparaffins but a high proportion of multi-ring compounds. This trend continues for the aromatic fractions shown in Table 2. The aromatic content increases with fraction number while at the same time there is a decrease in alkyl benzenes and an increase in multi-ring aromatics as well as thiophenes.

Oxidative stability

The time for onset of oxidative degradation as measured by DSC decreases with fraction number for pure saturated fractions; Fig. 1 shows results at 170 and 190°C. The trend is most noticeable at 170°C but is weak at 190°C.

Oxidation occurs by a free radical mechanism[4], so the rate of oxidation of these hydrocarbons depends on a rate-controlling step involving abstraction of hydrogen from the hydrocarbon by a hydroperoxide free radical. The ease of abstrac-

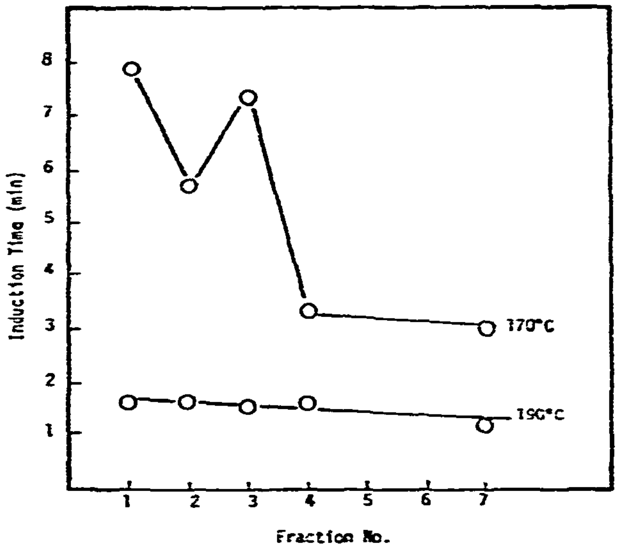

Fig. 1. Peak induction times of saturates fraction oxidation.

tion will depend on the tertiary hydrogen content of the hydrocarbon. Tertiary hydrogen content depends on the branchiness which in this case, as we just saw, increases with fraction number. Indeed, between fractions three and four, there is little change in ring composition, so that a great deal of the decreased oxidative stability between fractions three and four must be accounted for by increased branching.

At 170°C the trends observed for induction time are supported by measurements of exotherm peak areas—which we will call heats of oxidation (Fig. 2). If peak area is a measure of the amount of oxidation, then oxidation stability is greatest for iso-

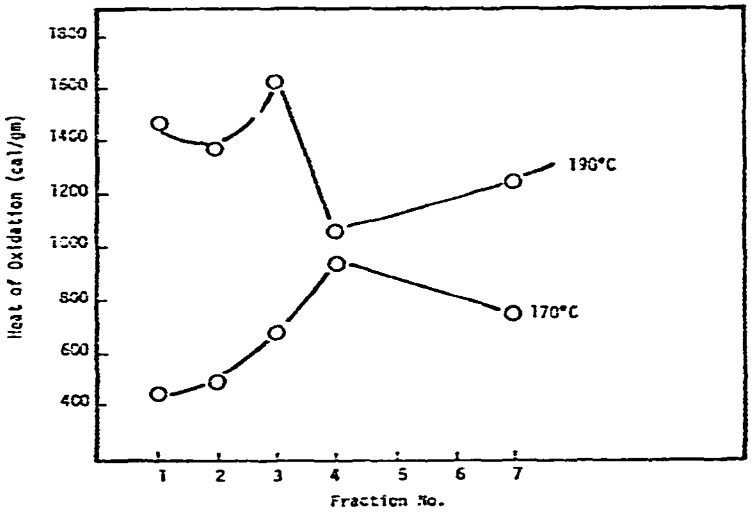

Fig. 2. Heats of oxidation of saturates fractions.

paraffins and cyclohexanes as represented by fraction one, and this stability decreases with increasing ring number and branching of the saturated hydrocarbons.

The situation is not clear at 190°C, however. The broad trend is to decreased heats of oxidation with higher fraction number, in opposition to the admittedly weak trend in induction times. In any case, since these heats represent the sum of a set of complex steps in a free radical mechanism, analysis of the relation between heats and molecular structure is obviously more complicated than the simple relation between branching and reactivity that we have suggested.

When aromatic fractions were oxidized at 170 and 190°C no heat effects were observed in the thermographs; oxidation had obviously taken place after 30 min as was apparent on visual examination. The rate of aromatic oxidation is slow and produces little heat evolution under the present conditions.

Addition of fraction 1 aromatics, which are alkyl benzenes and naphthenobenzenes, decreased the induction time for oxidation of the first saturates fraction. With no aromatics added, this saturated fraction had an induction time of 8 min. With the addition of 16 wt. % of fraction 1 aromatics, this is reduced to 5 min (Fig. 3). On the other hand, pure fraction 7 saturates gave a 3-min induction time and addition of the same fraction 1 aromatics increased the induction time slightly to 4 min.

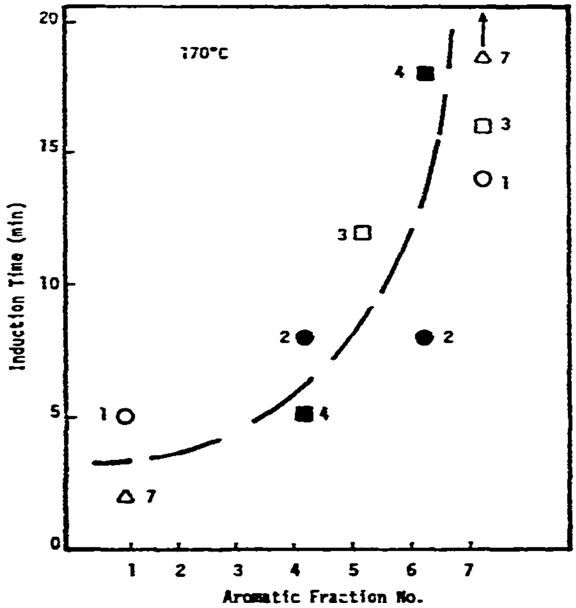

Fig. 3. Induction time and aromatic fraction number. Numbers refer to saturates fraction no. 16 wt. % aromatics in saturates.

The relative stability of the saturated fractions also changes with the aromatic fraction. In contrast to the trend we have just noted using fraction 1 aromatics, the addition of fraction 7 aromatics causes the isoparaffinic fraction 1 to be the least stable while the multi-ring compounds in saturates fraction 7 are stabilized to the greatest extent.

The nature of the saturates fraction has as much influence on oxidation stability as does the composition of the aromatic portion.

These observations hold for the most part when the temperature is increased to 190°C (Fig. 4). At this temperature, however, addition of the one-ring aromatics in fraction 1 improved the stability of the saturates from fraction 1 while addition of the one-ring aromatics to fraction 7 saturates caused the induction time to remain constant. The first fraction saturates, the most linear hydrocarbons, give the longest induction time on addition of one-ring aromatics but give the shortest induction time on addition of the polynuclear and sulphur compounds of fraction 7. Indeed, beyond the addition of fraction 1 aromatics, these data at 190°C show that the multi-ring condensed naphthenes provide the greatest stability. The more complex the saturated compounds, the better they respond to improvement in stability by addition of multi-ring aromatic and sulphur compounds.

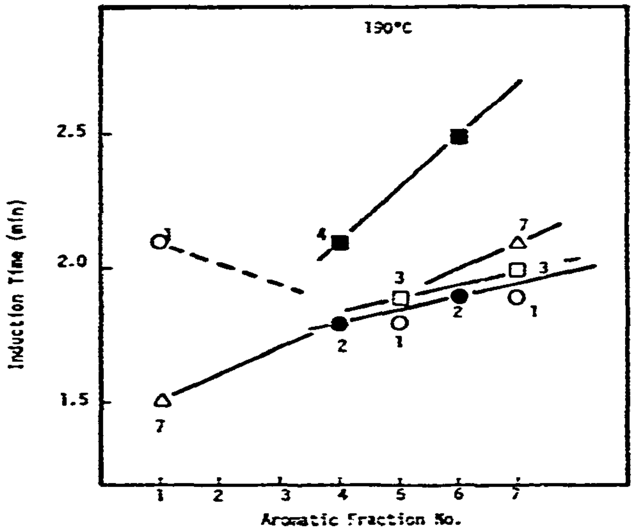

Fig. 4. Induction time and aromatic fraction number. Numbers refer to saturates fraction no. 16 wt. % aromatics in saturates.

Heats of oxidation reflect many of the same effects observed for induction periods. Figure 5 shows that the heat of oxidation decreases with increasing aromatic fraction number at 170°C. The heat effect shown for addition of fraction 1 aromatics to fraction 1 saturates again reflects a decrease in stability over the pure saturated fraction. Fraction 1 aromatics added to fraction 7 saturates has little effect on the heat of oxidation.

At 190°C, Fig. 6 shows the familiar effect of increasing complexity in the nature of the aromatics. As with pure saturated compounds, the tendency that is suggested by these data is to greater heats of oxidation (lower stability) as the saturated fraction

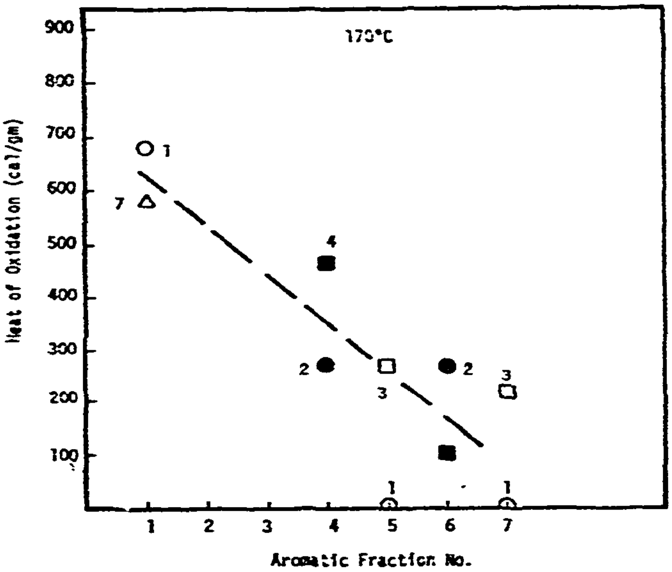

Fig. 5. Heats of oxidation and aromatic fraction number. Numbers refer to saturates fraction no. 16 wt. % aromatics in saturates.

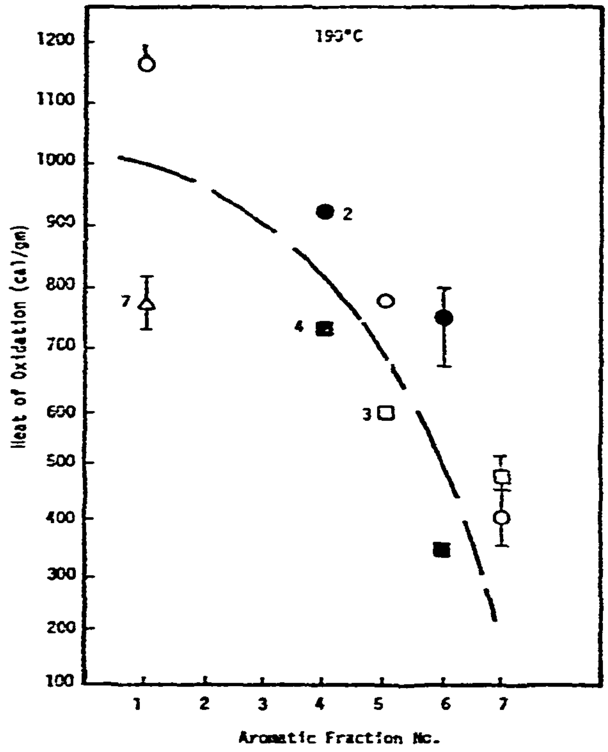

Fig. 6. Heats of oxidation and aromatic fraction number. Numbers refer to saturates fraction no. 16 wt. % aromatics in saturates.

becomes more linear. With addition of fraction 1 aromatics, fraction 1 saturates are less stable than fraction 7 saturates; with addition of fraction 4 aromatics, fraction 2 saturates give a greater heat of oxidation than fraction 4 saturates, etc.

CONCLUDING REMARKS

A number of workers have observed that polynuclear material provides the most effective inhibiting power for lubricating oil saturates$^{5-7}$. We have shown in this study that the more detailed nature of these saturates also has a marked influence on oxidative stability not only for pure saturated fractions but also for those containing specific aromatic compounds.

The induction time prior to oxidation is probably a more effective measure of stability than heats of oxidation. If this is the case, then addition of one-ring aromatics, which include both alkyl benzenes and naphthenobenzenes, tends to decrease the stability of mixtures of the most linear saturated compounds. These aromatics have little effect, however, on the oxidative stability of the complex multi-ring naphthenes.

Polynuclear aromatic fractions which also contain sulphur compounds inhibit all saturated fractions. Their effect, however, is greatest for the multi-ring saturates. The most effective combination at any temperature is polynuclear aromatics and multi-ring naphthenes.

To return to our original statement, lubricating oil distillates have different molecular compositions depending on their crude origin and on the way in which they are manufactured. Physical requirements actually favour the combination of saturates and aromatics similar to fraction 1 since these have the highest viscosity index, a desirable physical property. As can be seen from our results, this trend leads to a sacrifice in stability. Conversion processes which affect the saturates distribution also increase the relative amount of the more linear saturated hydrocarbons which again leads to a decrease in resistance to oxidation.

These remarks, of course, are limited to trends for oils which contain no added antioxidant. It is interesting to note that oils which provide the best service under such conditions are the so-called naphthenic basestocks. These are typically rich in both multi-ring naphthenes and polynuclear aromatics, a combination which should be the most oxidation stable according to the present study.

REFERENCES

1 J. Denis and G. Parc, *J. Inst. Petrol. (London)*, 59 (1972) 70.
2 H. E. Lumpkin, *Anal. Chem.*, 28 (1956) 1946; and *1974 Annual Book of ASTM Standards*, Part 25, D 3239-73T, ASTM, Philadelphia, 1974.
3 F. Noel, *J. Inst. Petrol.* (London), 57 (1971) 357.
4 L. Reich and S. S. Stivala, *Autoxidation of Hydrocarbons and Polyolefins*, Marcel Dekker, New York, 1969.
5 A. J. Burn and G. Greig, *J. Inst. Petrol.* (London), 58 (1972) 346.
6 V. Vesely, *Ropa Uhlie*, 11 (1969) 297.
7 J. L. Jezl, A. P. Stewart and A. Schneider, *Div. Petrol. Chem. Preprints, ACS Meeting, April 1957*, p. 27.