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The Identification of Lubricating Oils on Clothing by Column Chromatography, Infrared Spectroscopy, and Refractometry

Occasionally it is necessary in criminal investigations to compare oil stains on clothing with oil from a suspect automobile. The difficulties in identifying oil in such stains are complicated by the small size of sample which is normally available, by contaminants in the stain, and most of all by extraneous materials extracted from the cloth. Sometimes an additional complicating factor is the breakdown of the oil due to prolonged exposure, particularly to sunlight.

This study has been limited to motor and transmission oils. These oils are composed of petroleum stock plus additives. Petroleum stocks are complex mixtures of hydrocarbons which can be characterized on the basis of paraffinic, naphthenic, and aromatic contents [1]. The additives used in oils are numerous: they include polymers and organic compounds containing active sulfur, chlorine, and phosphorus [2,3]. Oils can therefore be characterized by their additives as well as by the petroleum stocks.

The techniques normally used for the identification of fresh lubricating oils are based on physical properties such as density, viscosity, refractive index [4], absorption on paper [5] and on silica gel [6] and infrared absorption [7-12].

Preliminary studies were made of the infrared spectra and refractive indices of fresh and used oils. On the basis of these, a flexible method was developed for the identification of oil stains which varied with the quantity and condition of the oil present. This method involved the use of solvent extraction, either alone or combined with column chromatography, and the determination of two properties of the oil, refractive index and aromatic content.

In simple cases it was possible to readily determine the refractive indices and the aromatic contents of the extracted oils. In more difficult cases where the oil was badly contaminated, these properties could not be measured directly after extraction. It was then necessary to remove the contaminants by fractionating the extracted oil by column chromatography. Where 100 mg or more of oil was extracted, this was accomplished by passing the oil with judiciously chosen eluting solvents through a column of alumina. The chromatographic fractions were then identified by refractometry and infrared spectroscopy.

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Materials and Methods

Equipment

A Beckman model I.R. 4 infrared spectrophotometer equipped with a beam condenser was used throughout this work. The operating conditions were as follows:

Glomer current: 6 mA

Attenuation: 90 percent T at 5.00 μ with sample in beam condenser

Slit program: 3 times standard

Period: 2

Cell thickness: 0.0995 mm

An Abbe-56 refractometer with temperature control was used and the refractive indices were determined at 25°C with a white light source.

Materials

All solvents used for extraction and elution were redistilled from technical grade products.

Paraffinic oil used as a standard for aromaticity was supplied by the Fisher Scientific Co. (0-119).

Alumina powder was used without further treatment, but was kept free of moisture.

A simple chromatographic column was made from a 10 ml pipette (Corning No. 7085-A) packed with 4.4 g of alumina powder (80-200 mesh) to occupy a volume of 5 ml. Both ends of the column were packed with glass wool (about 60 mg at the bottom and 100 mg at the top).

Ninety-five fresh motor and transmission oils of various grades and types were supplied by a number of different companies or their agents.

Twenty-eight used oils were obtained from the Ontario Provincial Police garage in Toronto. These oils were collected after their use in police cruisers for various lengths of time.

Strips of cotton on which drops of oil were deposited were used for exposure and extraction studies. These strips of cotton, 8 × 25 cm in size, were cut from white laboratory coats which had been laundered and were further treated with boiling water, then dried and ironed.

Treatment Prior to Extraction

For extraction studies of fresh and used oils, the oil was dropped on cotton strips and allowed to spread for periods of up to 1 h.

For the study of oxidation of used oils, the oil was used in the condition as removed from the automobile motor without further treatment.

For the study of oxidation by exposure to air and sunlight, the oil was dropped on cotton strips and allowed to stand on a window sill for periods of up to five years.

Extraction

A mixture of chloroform, ethanol, and water (65:30:5) was used as solvent for the recovery of oil from the cloth. The mixed solvent was prepared at least 24 h prior to use. The cloth was cut into small pieces and placed in a 60 ml separatory funnel; to this was added 10 ml of solvent. The funnel was gently shaken and allowed to stand for at least 10 min. The solvent was then filtered through Whatman No. 1 paper and the procedure repeated with a further 5 ml of solvent. The combined filtrates were then placed on a hot

plate and the solvent evaporated at about 75° C. If a relatively contaminant-free extract was not obtained by this procedure, the extract was reextracted with hexane.

Identification

Extracted oils which were relatively free from contamination were differentiated by their refractive indices (N_D^{25}) and aromatic content (percent aromatic). To evaluate the aromaticity of an oil, $A_{6.27\mu/\text{mm}}$ (the infrared absorbance at 6.27 μ per mm of oil film) was measured by the base line method. This included scanning a paraffin oil from 6.0 to 6.5 μ to provide the base line. With the aid of published data [9] a plot of absorbance versus aromaticity was made as shown in Fig. 1. If the extracted oil contained appreciable amounts of contaminating materials and was insufficient in amount for chromatographic purification, the absorption band at 12.3 μ was used. A calibration curve for the absorbance at 12.3 μ per mm ($A_{12.3\mu/\text{mm}}$) versus aromaticity is shown in Fig. 2. The base line region scanned was 12–12.5 μ .

If the extracted oil contained an appreciable amount of contaminants and weighed 100 mg or more, 5 or 6 drops (approximately 100 mg) were dissolved in 5 ml of hexane in a 10 ml beaker. This solution was introduced onto the chromatographic column which had previously been wetted with 10 ml of hexane. The average flow rate was about 1 to 1.5 ml per minute. Immediately after the last drop of effluent was collected, a further 2 ml of hexane was added to dissolve the remaining oil in the beaker, and this was also passed through the column. A total of approximately 7 ml of effluent was collected, evaporated, and the residue designated as F_1 . Additional 10 ml samples of the solvents listed below were passed through the column, collected, and evaporated. The residues were designated as follows: F_2 for hexane, F_3 for acetone, F_4 for chloroform, F_5 for methanol, and F_6 for 80 percent ethanol in water.

Since F_1 and F_2 were of relatively large quantity, the infrared spectra were obtained using a fixed path micro cell (0.0995 mm). Refractive indices of these fractions were also measured. The infrared spectra of the remaining four fractions were obtained by inserting the samples (chloroform soluble) between a pair of rock salt plates.

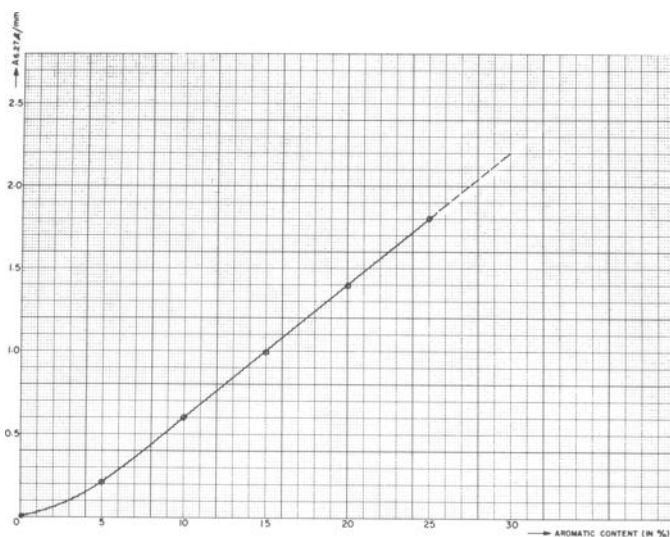


FIG. 1—Absorbance versus aromaticity at 6.27 μ .

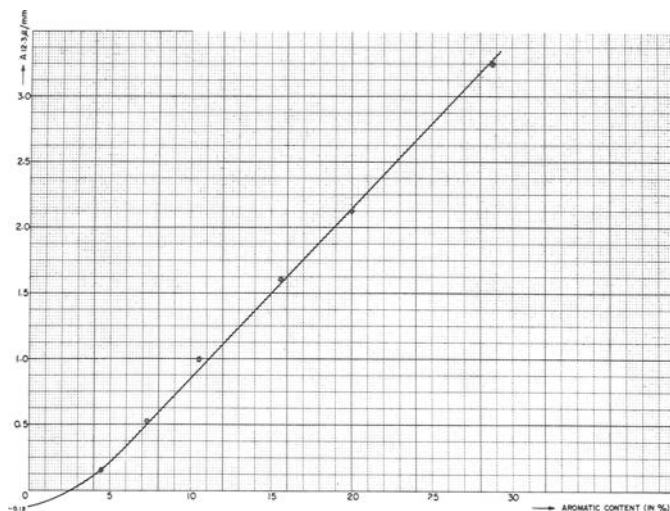


FIG. 2.—Absorbance versus aromaticity at 12.3 μ .

Results and Discussion

Many automotive lubricating oils have bands in their infrared spectra which are characteristic of the types of additives and/or hydrocarbons present. The infrared spectra of 95 fresh lubricating oils fell into ten general classes. Typical examples of these classes are shown in Fig. 3. The first three spectra in Fig. 3 are of the three basic petroleum stocks from which lubricating oils are formulated. In these three oils, the content of additives is so low that there is little indication of them in any of the three spectra. In contrast to these, a class 10 oil containing appreciable amounts of many additives is also shown in Fig. 3.

In the remaining six classes, bands occur which are characteristic of the additives contained in the oil although bands characteristic of the petroleum stock may also be present. The differences between the spectra of two different classes are sometimes quite minor, as in the case of class 4 and class 5. Polyisobutylene has a band at 8.1 μ and polymethacrylates have a band at 8.05 μ . These are the main distinguishing features in these two classes of oils and care must be taken to identify these bands accurately.

The spectra of classes 8 and 9 illustrate oils containing two different thiophosphate additives. Since some organic phosphate additives have absorption bands in the 9.8–10.4 μ region [7], oils containing these additives will also have spectra similar to that of the class 8 oil. The naphthenic oils have a strong symmetrical peak in the 10.3–10.4 μ region, which should not be confused with the asymmetrical band of the oil containing the organic phosphates and thiophosphates. The remaining classes shown in Fig. 3 have spectra more clearly characteristic of their additives.

Fresh oils, after 1 h on pieces of clean cloth exposed to the atmosphere were recovered by extraction and showed no changes from the original oil samples in their infrared spectra, their aromatic content, or in their refractive indices. After a longer period of exposure to the atmosphere, oxidation products developed. In general, the major problem in identifying oil stains on clothing was not caused by oxidation products but by extraneous materials (for example, waxes) which were extracted from most items of clothing along with the oil stains.

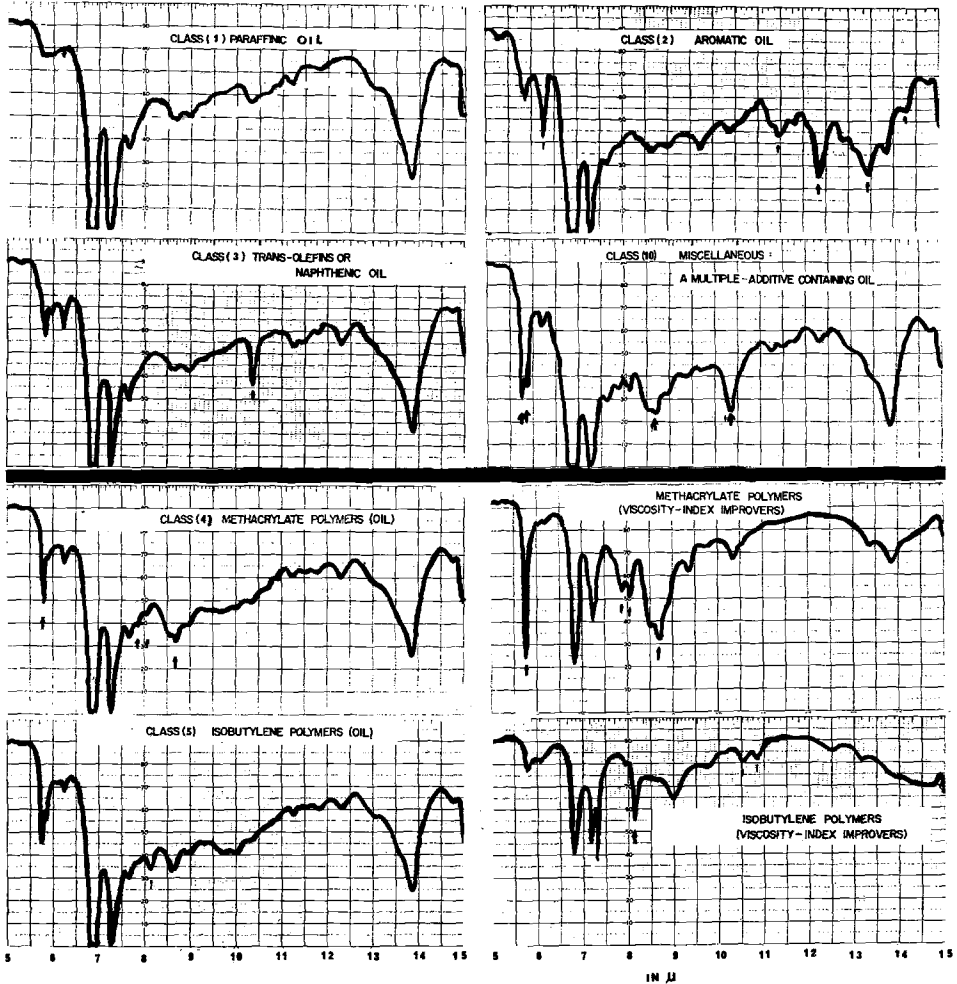


FIG. 3—Spectra of 10 classes of lubricating oils and their additives.

Figure 4 shows that 81 out of 95 fresh oils were differentiated by a combination of their refractive indices and aromatic contents. It will be seen, however, that 80 percent of the fresh oils examined had an aromatic content within the range of 7–14 percent and refractive indices within the range of 1.4775–1.4875. Chromatography of an oil and analysis of the separated components provide a more satisfactory and complete identification than can be obtained by analysis of the unfractionated oil. The first two fractions, F_1 and F_2 , contained petroleum stock without additives. The first fraction had a lower and the second fraction had a higher aromatic content than the original oil. In the third fraction, F_3 , additional aromatic hydrocarbons appeared together with methacrylate polymers when these additives were present in the oil. Isobutylene and methacrylate eluted in the fourth fraction, F_4 . The organic phosphates and thiophosphates eluted mainly in fraction five, F_5 , while

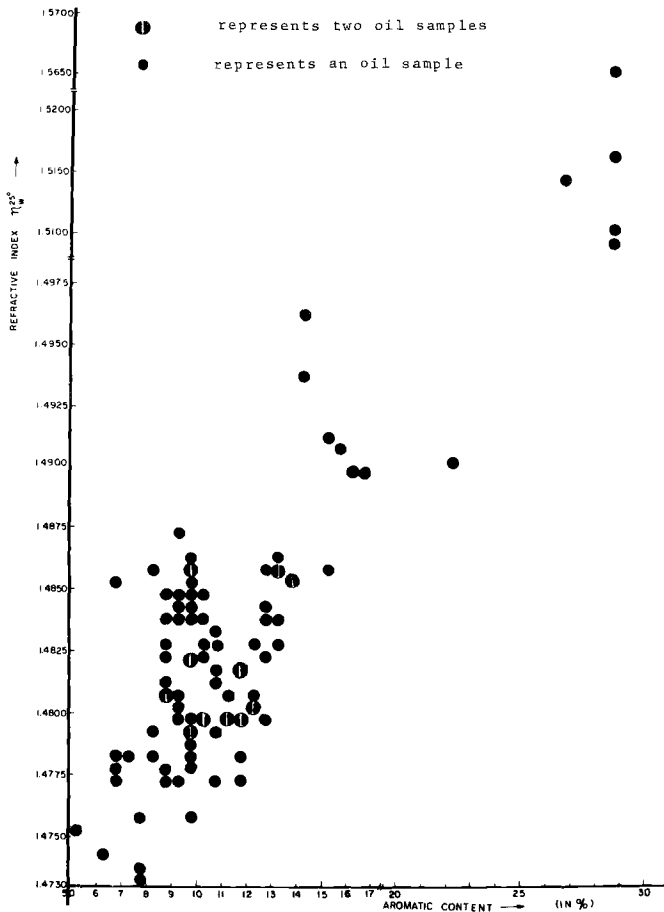


FIG. 4—Differentiation of oils by refractive index and absorption.

the salts of sulphonates, naphthenates, and fatty acids eluted mainly in the sixth fraction, F_6 . The same additive eluted into two or three successive fractions, if present in large amounts.

Figure 5 shows the spectra of six fractions separated from a class 10 multi-grade additive oil. Some of the components can be readily identified by comparing these spectra with the known spectra of Fig. 3.

In most instances where used oil was extracted from clothing, it was too dark prior to purification for refractive index determinations; and the infrared band at 5.8μ was so broad and intense that it seriously distorted the infrared spectrum in the short wavelength region. Where 100 mg or more of oil was extracted, it was purified by the use of column chromatography. The infrared spectra and refractive indices of the fractions could then be compared with those of corresponding fractions of a control sample.

The 12.3μ band which is due to absorption by para-disubstituted aromatics hydrocarbons [13] was found to have an intensity approximately proportional to the total aromatics band at 6.27μ . Since extraneous materials which absorb strongly at the shorter

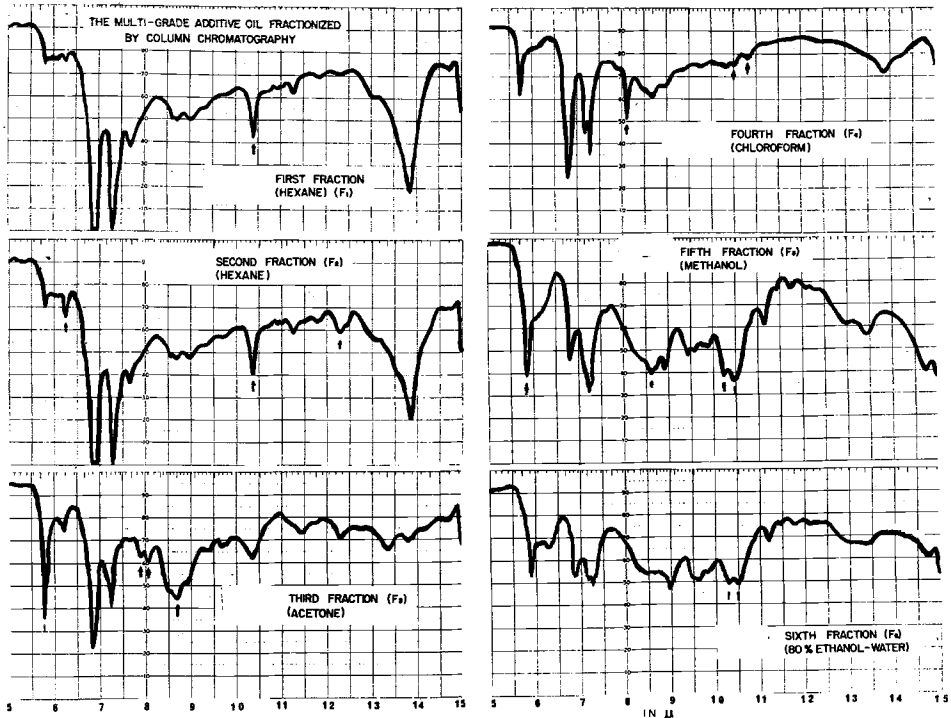


FIG. 5—Spectra of chromatographic fractions of a multi-grade additive oil (class 10).

wavelengths did not affect the 12.3μ band, this band was found to be extremely useful in the identification of small contaminated oil stains where there is insufficient material for chromatographic purification. Although the analysis is not as complete in these cases, extracts containing as little as 20 mg of oil have provided useful information.

The 12.3μ band was also used to determine the rate of oxidation and breakdown of motor oil during service. A different type of oil was placed in each of two police cruisers. Samples of oil were periodically withdrawn from the motors for analysis. The decrease in absorption at 12.3μ was found to be about 0.5 percent and the decrease in refractive index was about 0.004 units per 1000 miles of service. These changes due to service are small compared to the changes brought about 1) by materials extracted from the cloth and 2) through long exposure to air and sunlight and introduce no significant interference in the identification of an oil.

Oil was added to clean strips of cotton and exposed for several years to air and sunlight. Samples were periodically taken and examined to determine the extent of oxidation and degradation. The total aromatic content, as measured at 6.27μ , and the p-disubstituted aromatic content as measured at 12.3μ decreased at a rapid rate. After one month, most of the additives were so changed that they could not be recovered in their original forms. In this case, only the petroleum stock was left for the identification.

Most transmission oils examined in this study fell into classes 4 and 9. However, differences between transmission oils and other lubricating oils lie mainly in the quantity of additives rather than the kind of the additives used in oils [2].

Summary

Fresh oils can be identified from their infrared spectra and refractive indices. The identification is more definite when the oil is fractionated and the petroleum and additive fractions are individually compared with corresponding fractions of a control sample. Used oils can be identified as definitely as fresh oils if the oil has not been exposed for extended periods of time to oxidizing conditions.

Most clothing contains materials which are extracted with the oil and distort the absorption bands in the 5.8 to 6.3 μ region in the infrared spectrum. The band at 12.3 μ is unaffected by these extracts and can, therefore, be used to determine the aromatic content of oil in stains extracted from clothing. Impurities, oxidation, and breakdown products are readily fractionated by column chromatography permitting identification with a control sample.

Identification of an oil which has been exposed to the air and sunlight for more than a month is very difficult due to the significant loss of aromatics and decomposition of the additives.

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