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RAPID MONITORING OF VARIATIONS IN LUBRICATING OILS BY GEL PERMEATION CHROMATOGRAPHY*

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SUMMARY

High-speed gel permeation chromatography is a reliable and rapid technique for the examination of both natural and synthetic lubricating oils and their additives. In most instances, a specific fingerprint is obtained on a few microliters of sample, which identifies the oil when dual detectors (RI and UV 254 nm) are utilized. Over fifteen different oils have been examined using this technique. Changes in composition or the results of degradation of the base oil are easily observed. In one instance, the quantitative analysis of a three-component system was reduced from 90 to 25 min. Examples illustrating these results are presented.

INTRODUCTION

The improvement of lubricants for increased resistance to degradation has been of interest for centuries. The additions of antioxidants, viscosity index improvers, synthetic base oils, etc., have all had an impact on the lubricating oil industry. Each new development has made the analytical chemists' search for methods of detection and quantitation more of a challenge. Many methods and techniques have been utilized to identify these components and many references can be found in the literature[1–12].

In about the last 6 years, these materials have been examined by gel permeation chromatography (GPC): crude oils and vacuum cuts by Oelert[13], Coleman *et al.*[14], Oelert *et al.*[15], Done and Reid[16] and Albaugh and Talarico[17]; plasticizers by Alliet and Pacca[18], Hallwachs *et al.*[19] and Howard[20]; antioxidants and stabilizers by Coupek *et al.*[21]; and synthetic oils by the Industrial Laboratory at Kodak Park[22,23], Waters Ass.[24] and DuPont[25]. High-speed GPC is an extension of this type of analysis to include not only the fingerprinting of hydrocarbons, synthetic hydrocarbons and ester base oils, but also to demonstrate that degradation from use can be detected and some additives can be collected, identified and quantitated. In other words, GPC can give a rapid and reliable solution to lubrication problems and also encourages suppliers to maintain specifications.

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For the most part, the oils examined in this work ranged from 300 SUS at 100°F to instrument-type oils of lighter viscosity.

Extensive and detailed literature on GPC is readily available, covering both the theory of molecular size separation (Cazes[26]; Bombaugh[27]) and equipment (Waters Ass.[28]; Cazes[29]; other instrument manufacturers). It will suffice, therefore, to state that all the illustrations of the lubricants presented in this paper were accurately scaled down from curves produced by a Waters Ass. ALC/GPC Model 301 equipped with both a refractive index and an ultraviolet detector (254 nm) which was attached to a Westronics dual-pen strip-chart recorder.

EXPERIMENTAL AND RESULTS

Five microlitres of sample were injected directly into the sample injection port of the chromatograph using a Hamilton 701N 10-μl syringe and an EPR septum (except for cases where an "A" follows the identification number of the oil, *e.g.*, 8A: the exact difference for these few cases is described in the text). No heating or cooling of the apparatus was attempted and the solvent, tetrahydrofuran (Eastman 5308), contained 0.025% of BHT (butylated hydroxytoluene) for stabilization. A flow-rate of 2 ml/min was maintained throughout. Two 4 ft. × 3/8 in. standard columns (Catalogue No. 26900) of 60 Å Poragel, packed by Waters Ass. (Milford, Conn., U.S.A.) with approximately 480 plates/ft., were employed for all of the separations. Polypropylene glycol standards of molecular weight from 3900 to 790 were supplied with the instrument and were complemented by sebacates, adipates, phthalates and toluene purchased from various suppliers. Solvent eluted from the columns was measured in 5-ml increments or counts. The conditions used for the calibration curve were also utilized for the actual sample analysis.

From the calibration curve (Fig. 1), it is evident that the exclusion limit of this set of columns is at about 38.5 ml. Most of the oils which have been considered have

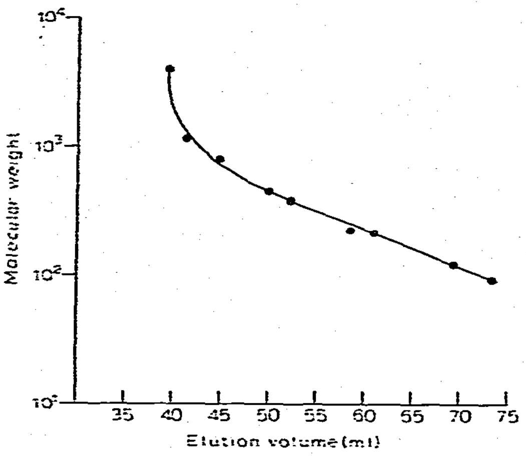


Fig. 1. Calibration curve.

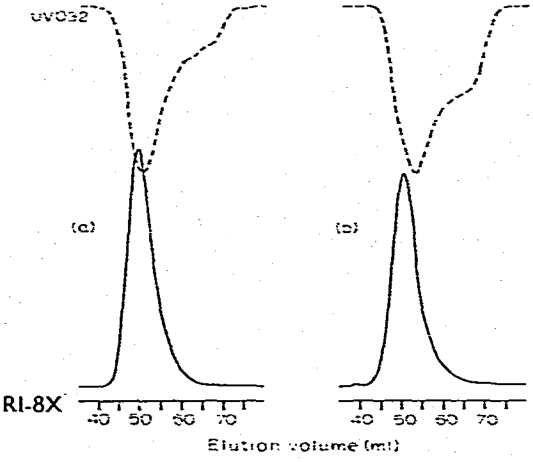


Fig. 2. Hydrocarbon oils: (a) H-1; (b) H-2.

the major peak between an elution volume of 45 and 50 ml, which falls on the slightly curved portion just preceding the straight-line section of the calibration curve. All of the curves of actual samples have been depicted by the refractive index (RI) activity drawn with the base line placed at the bottom of the figure and with the UV response represented by a dotted line with the base at the top of the figure and with the elution of the species of higher molecular weight starting at the left. Changes in sensitivity of either of the detectors has been recorded on the left-hand side of the figure at the base line for the particular detector. All UV sensitivities are expressed as absorbance units full-scale.

Hydrocarbon-type oils

Oil H-1 (Fig. 2a), which is a hydrocarbon type, gives an indication of a cresol additive as part of a shoulder on the right-hand side of the UV curve. Otherwise the main bulk of the UV activity is caused by the hydrocarbon itself due to unsaturation and/or aromatics. Note that the RI indicates the main peak just before an elution volume of 50 ml.

Another hydrocarbon-type oil, H-2 (Fig. 2b), shows that the main RI peak has moved slightly and is now centered directly at an elution volume of 50 ml, indicating a lower molecular size which correlates with lower viscosity, while the UV curve has a sharper shoulder, probably indicating the presence of slightly more additive.

A third hydrocarbon-type oil, H-3 (Fig. 3a), has the RI peak shifted to about 48.0 ml and a slight shoulder at about 58.75 ml, and again the UV trace has a fairly sharp shoulder appearing when 60–70 ml have been eluted. Oil H-3 was obtained from a different supplier than H-1 and H-2.

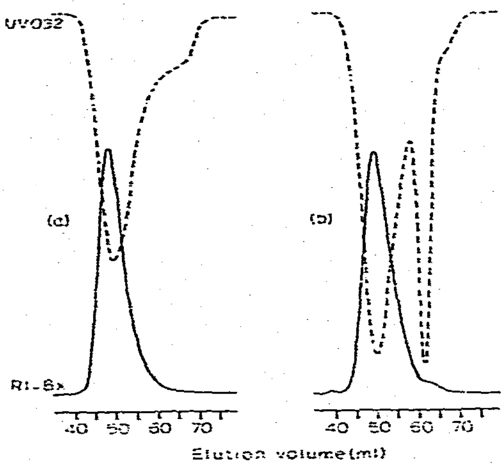
The hydrocarbon-type oil H-4 has several differences which can easily be observed (Fig. 3b). In the RI curve, a small peak is beginning to emerge at about 39.5 ml and another at about 63.5 ml. But the most drastic change is noted in the large UV peak which is evident at 61.5 ml and an increase in UV absorption directly over the main hydrocarbon peak in the RI curve at 50 ml. This could indicate the addition of two additives to the base oil, or an increase in aromaticity and the addition or increase of one additive.

A further hydrocarbon-type oil, H-5 (Fig. 4a), clearly indicates the presence of an oil of lower molecular weight, and one which is composed of several components as indicated by the three shoulders in the RI trace with components between 60 and 70 ml as the major contributors to the large UV absorption. Note that in this case the sensitivity of the UV detector has been halved to 0.64 rather than 0.32 absorbance unit full-scale. Much stronger absorption is apparent.

The last hydrocarbon-type oil, H-6, has a distinctive RI response with a small peak at 40 ml, a peak between 50 and 55 ml and a much broader distribution than the other hydrocarbons, extending to 75 ml before complete return to the base line (Fig. 4b). The UV at reduced sensitivity (0.64) has a small peak at about 40 ml and then an extremely broad absorption band which covers nearly the balance of the total available column volume.

Synthetic hydrocarbon-type oils

The first synthetic hydrocarbon oil, SH-1 (Fig. 5a), has a distinctive curve



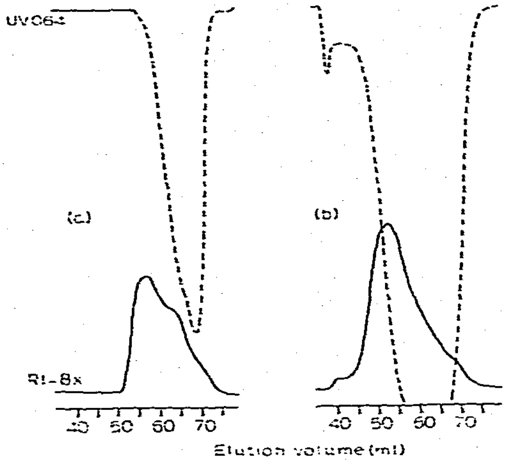


Fig. 3. Hydrocarbon oils: (a) H-3; (b) H-4.

Fig. 4. Hydrocarbon oils: (a) H-5; (b) H-6.

which indicates a high-molecular-weight fraction at 40 ml, a shoulder and peak between 45 and 50 ml and another shoulder between 55 and 60 ml in the RI response. It is interesting to note that nearly all of the UV absorption which begins at about 45 ml centers between 50 and 55 ml, which would tend to indicate that it was an additive, but not the same as in oil H-4 which peaked at about 62 ml.

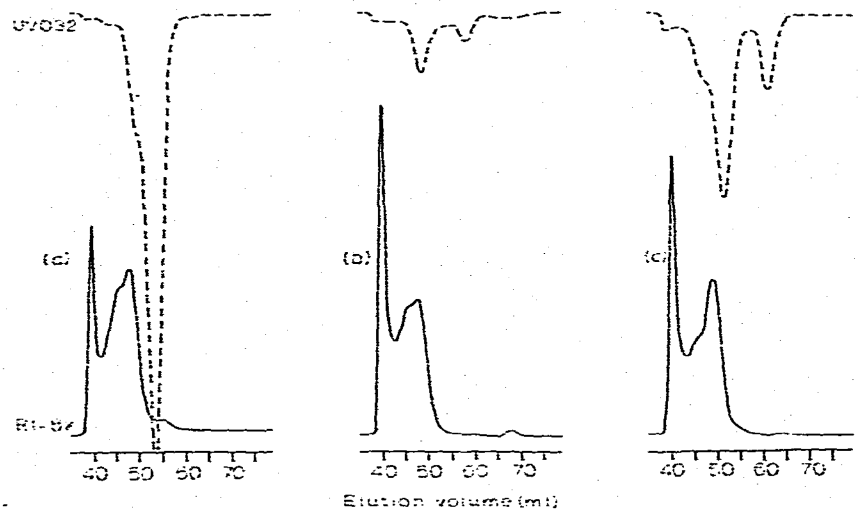


Fig. 5. Synthetic hydrocarbon oils: (a) SH-1; (b) SH-2; (c) SH-3.

Synthetic hydrocarbon oil SH-2 (Fig. 5b) shows a much higher peak in the RI response at 40 ml and a shift in the shoulder to 45 ml with the peak at 47.5 ml. Two very small peaks are evident in the UV curve but much less in total area than the UV absorption shown on the first synthetic hydrocarbon oil.

A different formulation is indicated with synthetic hydrocarbon oil SH-3, with the RI response close to 49.0 ml being much more pronounced (Fig. 5c). In this case, the UV trace indicates four possible UV-absorbing substances which absorb UV radiation more strongly than those in oil SH-2. These differences still remain to be investigated.

Synthetic ester-based oils

Since World War II, ester-based oils, usually adipates or sebacates (Dukek and Popkin[30]) have become increasingly popular. Fig. 6a represents the base ester of an oil stripped of all antioxidants and other performance-improving chemicals. The main peak at about 49.0 ml represents a number-average molecular weight of approximately 500 and only one other small response is noted between 55 and 60 ml. The UV detector shows virtually no response, with only a slight bulge in the base line.

After making certain additions to the ester-base oil S-1, the oil as originally received from the supplier has acquired improved properties (Fig. 6b). A viscosity index improver in the acrylic family has appeared at about 39.0 and a second peak of a substance of a lower molecular weight is apparent at about 64.0 ml on the RI monitor. Not much change has taken place in the UV response until the sharp absorbance which peaks just after 60 ml. This peak actually coincides with that of the compound which causes the slight response in the RI curve between 60 and 65 ml. Note that it was necessary to reduce the sensitivity of the UV detector to 0.64 in order to keep the peak on scale. This demonstrates that the UV detector is much more sensitive than the RI detector with compounds that absorb UV radiation at 254 nm. The compound detected is of the naphthylamine antioxidant family.

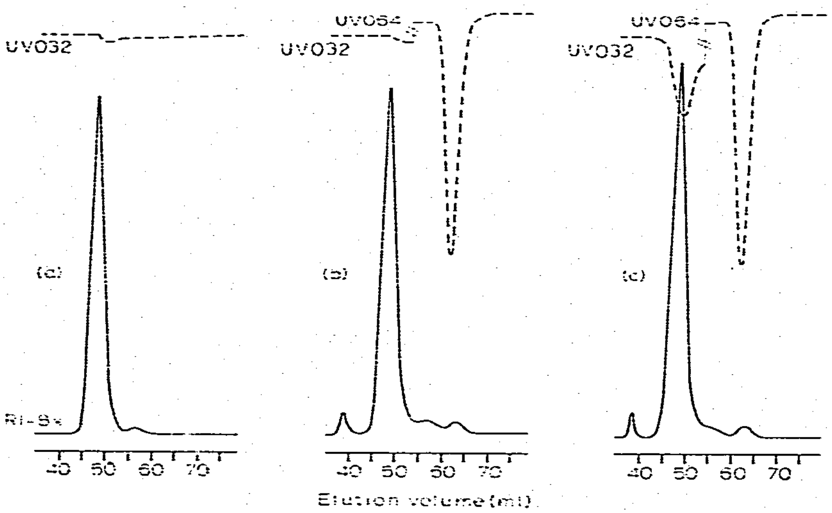


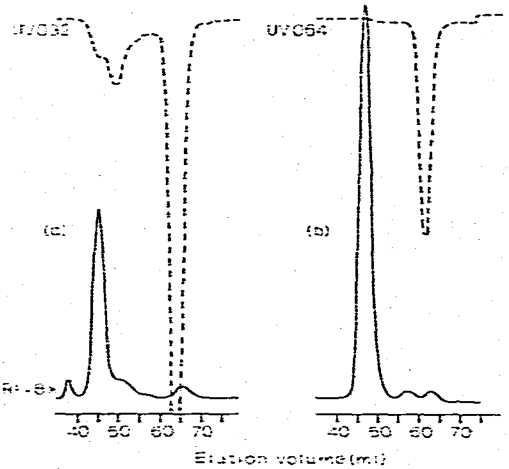
Fig. 6. Ester-base oils: (a) S-1; (b) S-2; (c) S-3.

Fig. 6c represents an improved version of oil S-2 with a slight increase in the amount of viscosity index improver, reduction of the lower-boiling ester peak between 55 and 60 ml and the introduction of a cresol-type antioxidant of higher molecular weight which appears on the UV curve directly over the main ester peak at 49.0 ml.

This oil has been used as a standard and more will be said about it later.

This sample of ester-base oil S-3A (Fig. 7a) was run in chloroform rather than tetrahydrofuran and it is apparent that changes have occurred in the retaining capacity of the Poragel which makes the main ester elute at 45 ml and the antioxidant between 65 and 70 ml with the appearance of a shoulder between 50 and 55 ml. The UV trace has developed a shoulder over the peak at 45 ml and maintained the peak between 45 and 50 ml. Adsorption effects, the hydrodynamic volume of the material and/or shrinkage of the gel could contribute to this effect. Variations such as this could prove very valuable if fraction collection was to be undertaken.

Ester-base oil S-4 (Fig. 7b) is another synthetic base oil with an ester of slightly higher molecular weight with the main RI peak eluting at 47 ml and with the amine antioxidant peaking slightly past 60 ml in UV absorbance.



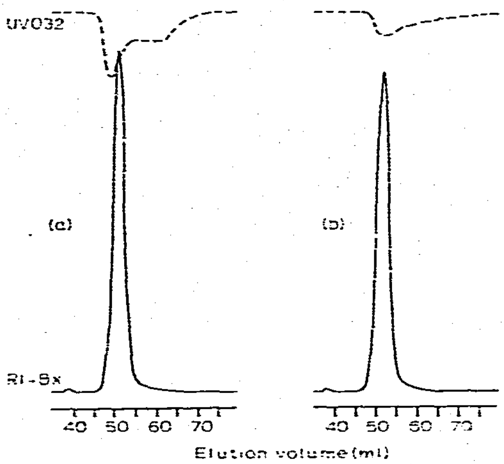


Fig. 7. Ester-base oils: (a) S-3A; (b) S-4.

Fig. 8. Ester-base oils: (a) S-5; (b) S-6.

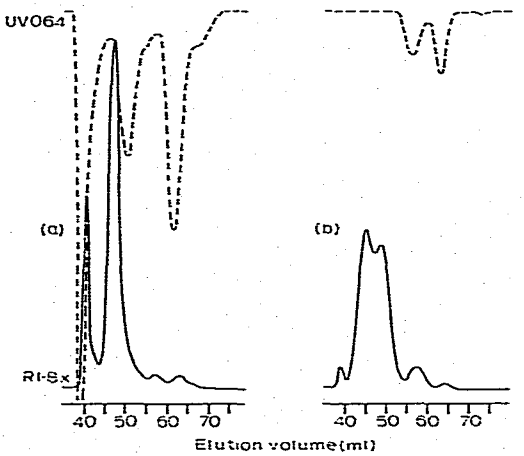
The trace of ester-base oil S-5 (Fig. 8a) indicates that the oil is of lower viscosity, peaking at 51 ml and with a great reduction in antioxidant activity. Ester-base oils S-3 and S-5 pass the oxidation stability test of MIL-L-6085A (ref. 2).

Ester-base oil S-6 (Fig. 8b) shows very little character, but it is apparent that it is an oil of lower molecular weight due to the shift of the main peak to an elution volume of about 51.5 ml.

The high-temperature oil S-7 (Fig. 9a) is characterized by a large peak at 40 ml together with peaks at 55–60 and 60–65 ml. In the UV response there are three distinct and well separated peaks which should lend themselves to easy fraction collection for identification purposes.

Ester-base oil S-8 (Fig. 9b) has a very distinctive curve with five components indicated by the RI detector, with two very weak UV-absorbing substances.

The ester-base oil S-9 shown in Fig. 10a is a blend of two esters and also contains a viscosity index improver and includes a shoulder between 55 and 60 ml. Not much activity was recorded by the UV detector.



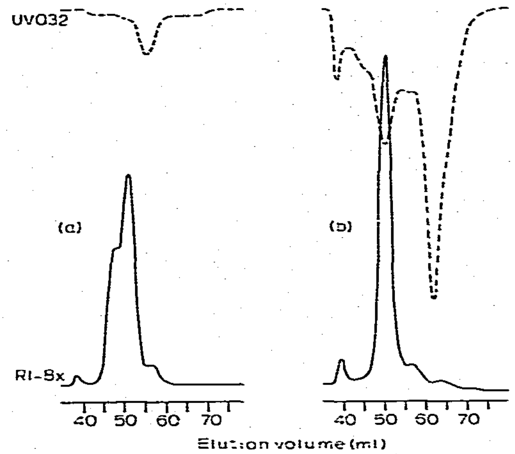


Fig. 9. Ester-base oils: (a) S-7: (b) S-8.

Fig. 10. Ester-base oils: (a) S-9: (b) S-10.

Oil S-10 is the new version of S-9 (Fig. 10b) substituted by the supplier without notification or designation change, and was originally detected by the disappearance of one ester peak using a gas chromatographic method. It is obvious that GPC gives a much more detailed description of what the oil actually contains. Besides the disappearance of one shoulder at 47.5 ml there has been an increase in the higher molecular weight peak at 40 ml and the appearance of a peak between 60 and 65 ml which matches the largest of the UV peaks. In addition, the UV response shows a peak above 40 ml, a shoulder and then another peak at 50 ml. Obviously, the supplier had changed the components of the oil more drastically than it had been realized when the change was made.

In oil S-11 (Fig. 11a), the RI sensitivity was reduced to 16 × and a larger peak appears in both the RI and UV responses between 60 and 65 ml. Because of the width

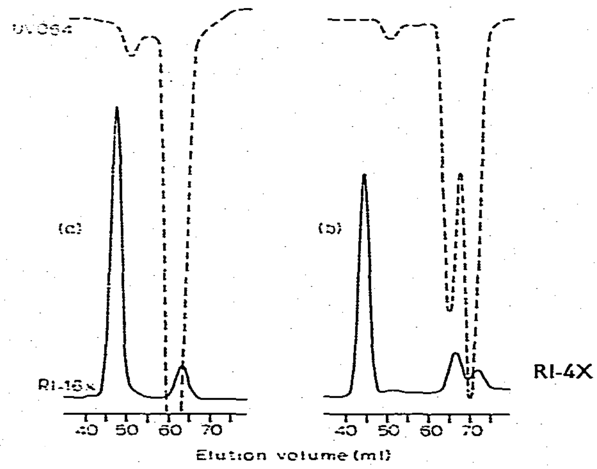


Fig. 11. Ester-base oils: (a) S-11: (b) S-11A.

of this peak, is was suspected that there might be two additives involved at this point.

After changing the eluting solvent to chloroform, a better separation was achieved (Fig. 11b) and the peaks at 65 and 70 ml were collected and identified by IR spectroscopy as a naphthylamine and a thiazine antioxidant. It should be noted that only 2.5 μl were used for this curve with an increase in sensitivity to 4× on the RI detector. The smaller UV-absorbing peak at 50 ml has not yet been identified but could possibly be an antigumming agent. Again, the chloroform eluent provided a better separation and eased the problem of fraction collection. This emphasises the fact that even though a satisfactory separation is being achieved with one solvent system, it can be useful to try another.

Heat-treated oils

We can now consider the changes that can be brought about by heating some of the oils which have been fingerprinted and note the changes which can be detected. Comparison of the original curves of the various oils with the curves for those which have been heated will be most advantageous in assessing the true value of the GPC technique and, therefore, the original identification numbers have been maintained for ease of reference. After heating oil H-3 for 330 h at 250°F, a weight loss of 3.26% was noted (Fig. 12a). A slight change was evident in the RI response, a shoulder developed on the high-molecular-weight side and the antioxidant shoulder disappeared using UV (compare Fig. 12a with Fig. 3a).

Oil H-4, after the same heat treatment, suffered a 3.58% loss in weight and a more pronounced increase in UV absorption in the high-molecular-weight region. Again, the antioxidant to the right of the curve has disappeared and this is most apparent when Fig. 3b is examined.

After heating oil H-1 at 500°F for 4 h (Fig. 13a), much more drastic results were noted, with the build-up of a peak in the RI curve at 40 ml and a shift of the main peak towards a slightly higher molecular weight. The UV detector followed suit, with a large increase in the UV absorption just before 40 ml.

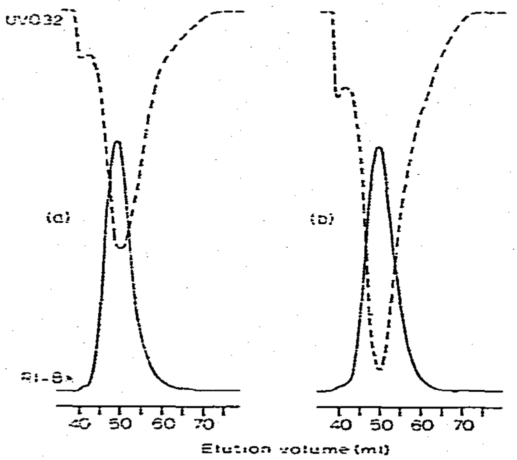


Fig. 12. Hydrocarbon oils: (a) H-3; (b) H-4. Each heated for 330 h at 250°F.

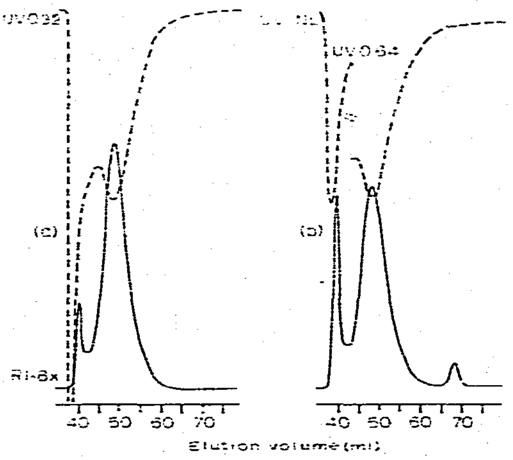


Fig. 13. Hydrocarbon oils: (a) H-1 heated for 4 h at 500°F; (b) H-1 after product life test for 2000 h.

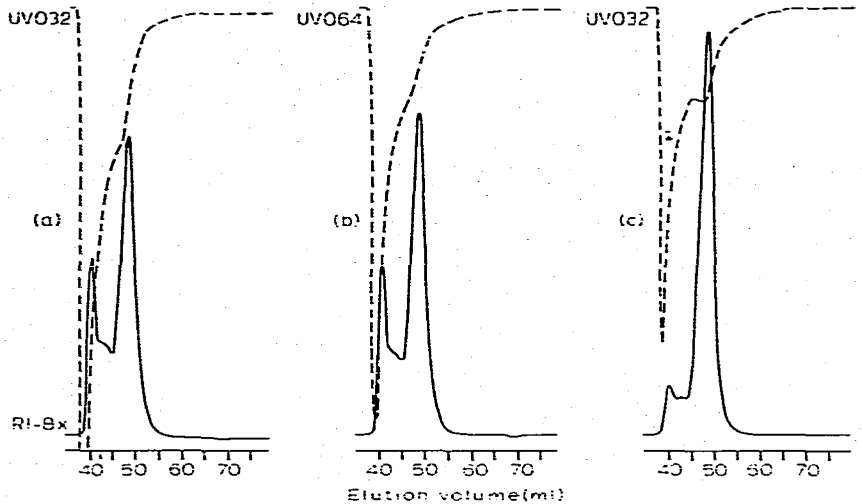


Fig. 14. Ester-base oils: (a) S-1; (b) S-2; (c) S-3 each heated for 4 h at 500°F.

After running a product using oil H-1 for over 2000 h to failure (Fig. 13b), the oil showed the typical heat-induced pattern except that it was more pronounced. The small peak between 65 and 70 ml was due to chloroform.

After exposing ester-base oil S-1 to a temperature of 500°F for 4 h (Fig. 14a), a pattern of degradation similar to that of the hydrocarbon-type oils was produced. Note the changes at 35, 40, 45 ml in both the RI and UV traces.

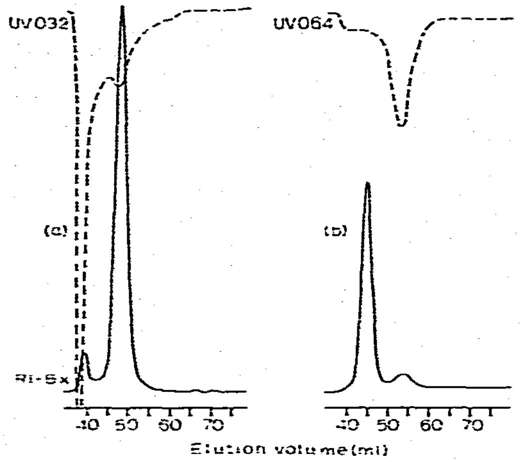
Ester-base oil S-2, when heated for 4 h at 500°F (Fig. 14b), showed a loss of the amine antioxidant and the build-up of higher molecular weight components between 40 and 47.5 ml. The temperature of 500°F was chosen as a rapidly acting temperature to show the degradation which could take place and MIL-L-9236A (ref. 2) called for a corrosion oxidation stability test at this temperature.

After exposing ester-base oil S-3 (Fig. 14c) to a temperature of 500°F for 4 h, the amine antioxidant had been consumed and some high-molecular-weight build-up was noted, with some loss of the acrylic additive. Comparison of oil S-3 with S-2 indicates that the addition of the cresol additive made the oil more stable at elevated temperatures. When considering the original curve of oil S-3 earlier, it was stated that it would be used as a standard, so several references to it will be made from this point.

Heating oil S-3 in the presence of copper (Fig. 15a) increased the degradation slightly, as indicated by the elongation of the UV peak at an elution volume of 39.5 ml.

When ester-base oil 11-A was heated for 4 h at 500°F (Fig. 15b) there was a lack of build-up of high-molecular-weight substances in the UV trace which was so evident with ester-base oil S-3 (see Fig. 11b, which was also run with chloroform as the eluent).

In Fig. 16a, the amine antioxidant has disappeared but a high-molecular-weight UV-absorbing peak did not appear after heating at 212°F for 158 h and at 320°F for 24 h. The higher temperature cresol-type antioxidant still remains effective. After the MIL-L-6085A (ref. 2) oxidation stability test, the amine antioxidant was only slightly affected.



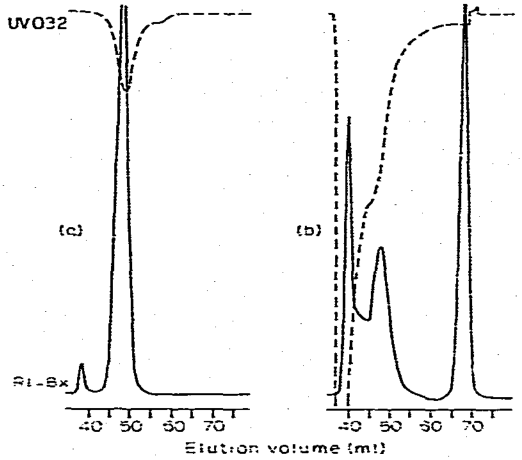


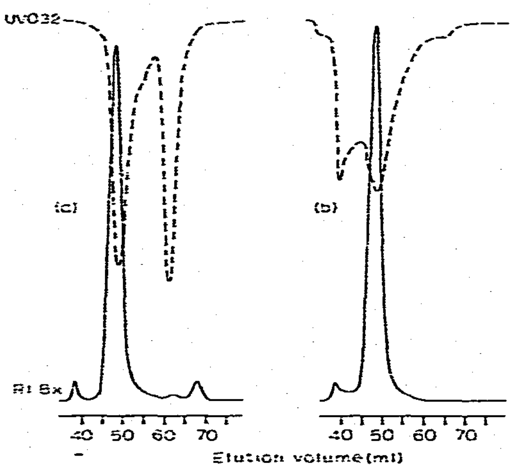
Fig. 15. Ester-base oils: (a) S-3 heated for 4 h at 500°F with Cu; (b) S-11A heated 4 h at 500°F.

Fig. 16. Ester-base oils: (a) S-3 heated for 158 h at 212°F and for 24 h at 300°F; (b) S-3 thin film heated for 20 min at 400°F.

After heating a thin film of oil S-3 at 400°F for 20 min (Fig. 16b), degradation was so advanced that chloroform had to be used in order to dilute the viscous residue so as to allow it to be drawn into the syringe. The large RI response between 65 and 70 ml is due to chloroform. The volume of the oil exposed to degradation conditions is an important consideration in overall performance.

Ester-base oil S-3, after a product test for 100 h (Fig. 17a), showed some loss of amine antioxidant and an increase in UV absorption at 50 ml. Residual chloroform from extraction was also evident in the RI response.

Changes that occurred with product test oil S-3 after 1500 h (Fig. 17b) show some indication of UV build-up of a high-molecular-weight fraction and also loss



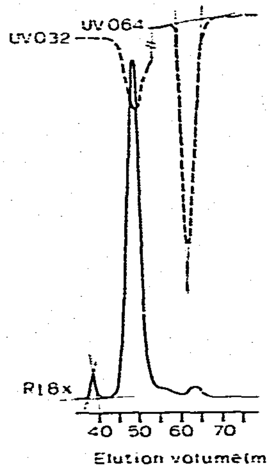
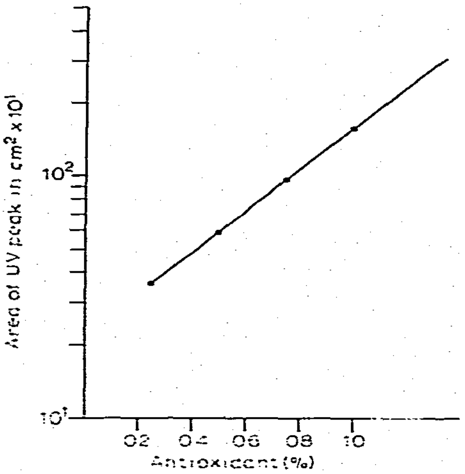


Fig. 17. Ester-base oils: (a) S-3 after product test for 100 h; (b) S-3 after product test for 1500 h.

Fig. 18. Ester-base oils: S-3 triangulation method for area of amine and acrylic additives.



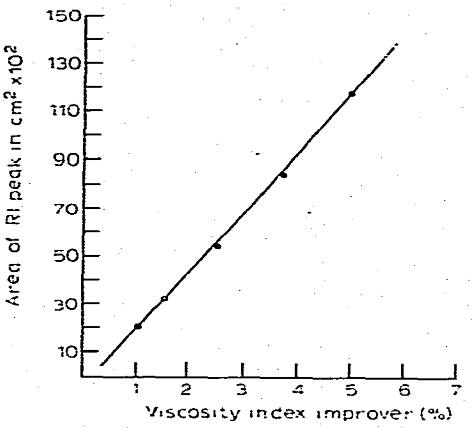


Fig. 19. Calibration curve for the amine antioxidant in oil S-3.

Fig. 20. Calibration curve for the acrylic viscosity index improver in oil S-3.

of the amine antioxidant. Comparison should be made with Fig. 6c to appreciate the changes.

Fig. 18 shows the triangulation method used for the area of the acrylic and amine peaks for quantitation in oil S-3. This quantitative analysis, run by older methods (IR spectroscopy, gas chromatography and methods in refs. 3 and 4), required 90 min while GPC required 25 min.

The calibration curve for the amine antioxidant is represented in Fig. 19 and indicates the linear response of the UV detector in the range of interest. An area of 94.2 cm^2 is equal to 0.74% of amine.

Fig. 20 is the calibration curve for the acrylic; an area of 45 cm^2 equals 2.1% of acrylic.

CONCLUSION

It has been found that slight changes in the response of RI and UV detectors occur and that the calibration curves have to be run occasionally in order to maintain accuracy in quantitation. This can easily be checked by retaining a standard of an oil with known values and checking the peak areas from time to time.

The following advantages have been noted:

(1) Various oils can be rapidly fingerprinted, identified and changes detected.

(2) Small samples (5 μl or less) are required.

(3) No prior sample preparation is necessary.

(4) More information, such as number-average molecular weight, as well as the presence or depletion of additives in fresh or used oils, is available from this technique than from thin-layer or gas chromatography or other methods.

(5) Fractions can be collected since the detectors are non-destructive and IR spectroscopy, mass spectrometry, etc., can be used for identification. This is especially helpful with ester-base oils because their additives are difficult to separate from the base oil by other methods.

(6) Quantitative results can be obtained after calibration.

On the other hand, the following disadvantages are apparent:

(1) All additives do not appear as separate entities, and materials with the same molecular weight could overlap.

(2) Some changes in columns after a long period of use are to be expected.

At this stage in our investigation of oils, many peaks remain unidentified, but we have found that mixtures or contaminants can be detected. Correlation of exposure values based on the loss of amine and build-up of high-molecular-weight compounds at high temperature (500°F) and in actual production testing of the ester-base oils is feasible. From our experience to date, GPC has permitted a much deeper understanding of lubrication possibilities and is considered to be a most valuable addition to our analytical problem-solving capability.

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