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High Pressure Liquid Chromatography: A Brief Introduction, and Its Application in Analyzing the Degradation of a C-ether (Thio-ether) Liquid Lubricant

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ABS: The general principles of classical liquid chromatography and high pressure liquid chromatography (HPLC) are reviewed, and their advantages and disadvantages are compared. Several chromatographic techniques are reviewed, and the analytical separation of a C-ether liquid lubricant by each technique is illustrated. A practical application of HPLC is then demonstrated by analyzing a degraded C-ether liquid lubricant from full scale, high temperature bearing tests.

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HIGH-PRESSURE LIQUID CHROMATOGRAPHY: A BRIEF INTRODUCTION, AND ITS APPLICATION IN ANALYZING THE DEGRADATION OF A C-ETHER (THIO-ETHER) LIQUID LUBRICANT

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SUMMARY

The general principles of classical liquid chromatography and high-pressure liquid chromatography (HPLC) are reviewed, and their advantages and disadvantages are compared. Several chromatographic techniques are reviewed, and the analytical separation of a C-ether liquid lubricant by each technique is illustrated. A practical application of HPLC is then demonstrated by analyzing a degraded C-ether liquid lubricant from full scale, high temperature bearing tests.

INTRODUCTION

High-pressure (or performance) liquid chromatography (HPLC) is a relatively new separation method (the major developments occurring during the years 1965 through 1969) based on the classical separation technique, liquid column chromatography (ref. 1). Chromatography, in general, is a method of physically separating a mixture of substances due to the equilibrium distribution of the substances between a stationary phase (or bed) and a mobile phase which percolates through the stationary phase. The mixture of substances (to be separated) are solutes in a solvent mobile phase.

In liquid column chromatography (classical or HPLC) the mobile phase is a liquid, where a gas mobile phase is employed in gas chromatography. Although HPLC is not used as extensively as gas chromatography, its advantage lies in the fact, that while only about 20 percent of all organic material is volatile enough to be examined by gas chromatography (ref. 2), a higher percentage of organic material can be dissolved in an appropriate solvent for examination by HPLC.

HPLC has been utilized at Pennsylvania State University to study the high temperature oxidation of ester-based lubricants (refs. 3 and 4) and has also been used in the analysis of space-qualified lubricants (ref. 5). At NASA Lewis Research Center, HPLC is one of several laboratory instruments used to study the compositions, oxidative mechanisms, and kinetics of candidate high temperature lubricants. Understanding oxidation mechanisms is essential in facilitating a logical approach to the synthesis and formulation of new lubricants with improved high temperature stability in air.

The C-ethers (thio-ethers) are a promising class of fluids for high temperature liquid lubricant applications (ref. 6). They have excellent thermal stability (390° C), very good oxidation stability (260° C), and adequate pour

points (-29° C). The main deficiencies of the C-ethers have been their poor boundary-lubricating ability and poor wetting characteristics (ref. 7).

Another drawback of the C-ethers is the high wear obtained and the excessive formation (under boundary lubricating conditions) of an insoluble deposit. This deposit may degrade the boundary-lubricating properties and certainly reduces the useful life of the fluid. The high wear and deposit formation is especially prevalent when lubricating conditions are taking place in a low oxygen, low moisture environment (ref. 8).

The objective of this paper in this Symposium is to introduce high-pressure liquid chromatography to those not familiar with the subject, and to show how HPLC can be applied in the analysis of a degraded C-ether lubricant.

HPLC, A BRIEF SURVEY

Classical liquid column chromatography. - Figure 1 represents the separation of a mixture of three substances (solutes) by classical liquid column chromatography. The column is an open tube which is commonly packed with alumina or silica. The mixture is separated by adsorbing the solute substances from a small volume of solvent onto the packed bed and then leaching the column with a sequence of solvents (the mobile phase) of increasing polarity. The eluant is then collected in fractions for examination (ref. 9).

Classical liquid column chromatography, although a valuable analytical tool, has several drawbacks: (1) It is a time consuming method of separation, (2) examination of the collected fractions is difficult because of poor resolution, and (3) the manual operation of the column is greatly dependent on the operator's skill. HPLC, on the other hand, has several advantages: (1) Separation times are generally fast, (2) resolution is excellent, and (3) there is less dependence on the operator's skill as a result of automation.

Modern high-pressure liquid chromatography. - A modern HPLC system consists of four major components (fig. 2):

(1) A solvent delivery pump
(2) A sample injection port
(3) A separatory column (or columns)
(4) A detector.

The solvent delivery pump must provide a continuous, controlled flow of solvent (the mobile phase) through the separatory column and to the detector, and the sample injection port must provide the means of introducing the sample under study into the HPLC system without interruption of the solvent flow rate. The detector must be capable of detecting the separated solute substances that elute from the column.

The first step in separating a mixture of substances by HPLC is to dissolve a small quantity of the mixture into an appropriate solvent (the mobile phase). A small volume of the resultant solution is then injected into the HPLC system where it merges into the mobile phase (from the solvent delivery pump to the separatory column). Due to the packing of a column (the stationary phase generally consists of very fine particles), the HPLC system must operate at high-column inlet pressures to overcome the column resistance to the mobile

phase flow. The mobile phase flow rate is controlled by adjustments to the solvent delivery pump; flow rates of 1-ml/min are common. The mixture of substances in the sample is separated because of their different rate of passage through the column. Their presence is sensed by detectors at the downstream segment of the column. A refractive index detector and a fixed wavelength ultraviolet light detector are two popular optical instruments used to detect the separated substances which elude from the separatory column.

A refractive index detector is adjusted to the refractive index of the mobile phase solvent and responds to any eluted substance (in the mobile phase) that has a different refractive index from that of the mobile phase. A fixed wavelength ultraviolet light (UV) detector will respond to any eluted substance that is UV sensitive at that particular wavelength. The UV detector wavelength may be adjusted.

A modern HPLC system, because it overcomes the inherent difficulties of classical liquid column chromatography, has gained widespread use in the laboratory as a routine analytical instrument. In many instances its versatility has allowed it to be used as an on-line analyzer in industrial process plants (ref. 10). It is also a valuable research tool in the study of chemical reaction mechanisms and kinetics and has been used extensively in our laboratory for the separation of the components of synthetic lubricants and for the separation of their oxidation degradation products.

Modes of Separation

Different types of separatory columns can be used in an HPLC system depending on the type of separation best suited for the particular mixture of substances being studied. The two main classes of separation are those separations affected by the physical characteristics (size exclusion) of the substances and those affected by the chemical nature (adsorption, partition) of the substances (ref. 11).

Size exclusion chromatography. - This mode separates a mixture of substances according to their molecular size (geometry) differences by permeation into a solvent-filled matrix in the column (fig. 3). This matrix can be either an inorganic (i.e., silica gel) or organic (i.e., styrene, divinyl benzene) stationary phase. The substances having the greater molecular size will tend not to permeate into the matrix pores as much as the smaller molecular size substances. Thus the order of elution from a size exclusion column is from the larger to the smaller molecular size substances.

The ideal size exclusion process is illustrated in figure 4. There are three regions of importance: The total exclusion region, the selective permeation region, and the total permeation region. In the total exclusion region, all substances above a certain molecular size (M_t) will be excluded from permeation into the stationary phase matrix; these substances will elute at the same time, T_t (the total exclusion time). In the selective permeation region, substances having a molecular size smaller than M_t will permeate into the stationary phase matrix and elute at increasing times greater than T_t. In the total permeation region, all substances below a certain molecular size (M_p) will be small enough to travel throughout the stationary phase matrix with the

mobile phase molecules; these substances will elute at the same time, T_p (the total permeation time).

A calibration curve can be constructed for a size exclusion column by plotting the log of the molecular weights of known substances (molecular weight is proportional to molecular size) versus their retention times. Figure 5 is a calibration curve constructed from known standards. By measuring the retention time of an unknown substance, its approximate molecular weight can be calculated.

Adsorption chromatography. - In adsorption chromatography, chemical interactions (hydrogen-bonding, dipole interactions) between the solute substances and the stationary phase affect separation of a mixture of substances. The solutes are reversibly adsorbed from a nonpolar mobile phase (i.e., heptane) onto the surface of a polar stationary phase. Silica gel, which has a high concentration of hydroxyl groups, is widely used as a stationary phase in adsorption chromatography (fig. 6).

Figure 7 illustrates the mechanism of separation on a silica gel stationary phase. The phenol solute, because of its greater polarity, will interact more strongly with the stationary phase than will the hindered phenol solute. The phenol solute will be retained for a longer period of time, and thus will elute from the column after the hindered phenol solute has eluted.

Partition chromatography. - In this mode, the solute substances partition themselves between the mobile phase and a stationary organic phase which can be either coated or chemically bonded to a solid bed support (silica is commonly used). Separation of the substances is achieved because of the different equilibrium distributions (solubilities) of the substances between the mobile phase and the stationary phase. Partition chromatography can be classified as either liquid-liquid chromatography or bonded phase chromatography. In liquid-liquid chromatography, an organic liquid (the stationary phase) is coated onto the surface of a solid bed support (fig. 8). The liquid stationary phase is normally a very polar substance such as $B_1 B^1$-oxydiproprionitrile, and the mobile phase a nonpolar substance such as heptane.

In bonded phase chromatography, an organic phase is chemically bonded to a solid bed support. Bonded phase chromatography can be further classified as either normal phase or reversed phase chromatography.

Normal phase chromatography results from chemically bonding a polar functional group, such as -CN, $-NH_2$ to a solid bed support (fig. 9). The substances to be separated are dissolved in a nonpolar mobile phase (hexane, chloroform). Figure 10 illustrates a normal phase separation using a cyano (-CN) bonded phase column, with the result that the less polar substance elutes first.

Reverse phase chromatography is just the opposite of normal phase chromatography. A nonpolar functional group such as $-C_8$, $-C_{18}$ is chemically bonded to a solid bed support (fig. 11), and the substances to be separated are dissolved in a polar mobile phase (methanol, water). Figure 12 illustrates a reversed phase separation using a C_{18}-bonded phase column, with the result that the more polar substance elutes first.

Gradient elution. - When a sample is a mixture of substances having a very wide variation of polarity, the separation of the sample becomes more difficult; figure 13 illustrates the problem. A sample containing six substances (of different polarity) is separated by adsorption chromatography. If a weak mobile phase is used (heptane), then all six substances may not be eluted (fig. 13(a)). If a strong mobile phase is used (chloroform), then all six substances may not be completely separated (fig. 13(b)). A blend of the weak and strong mobile phases may optimize the separation of the intermediate polar substances (the center), but the separation of the nonpolar and polar substances will be unsatisfactory (fig. 13(c)).

If, however, the separation of the sample mixture is started with the weak mobile phase and then the strong mobile phase is gradually fed in, optimum separation of all six substances will be achieved (fig. 13(d)). This separation method is called gradient elution chromatography as opposed to an isocratic chromatographic separation where the mobile phase composition is constant with time. Figure 14 depicts one way of obtaining a polarity gradient of the mobile phase. The most important variable in gradient elution is the mobile phase program, which varies the mobile phase composition with time.

Gradient elution is a powerful chromatographic technique generally used for the more difficult separations.

HPLC Analytical Separation of a C-Ether Lubricant

Figure 15 is the schematic of the HPLC system used to separate a C-ether lubricant, which is a blend of four chemical components (ref. 12). Figure 16 depicts the chemical composition of the lubricant. Four modes of chromatography were used to separate the C-ether lubricant to illustrate and compare the more common chromatographic techniques.

Size exclusion separation. - A set of size exclusion columns (fig. 17) consisting of a 500-Å μ-styragel column and two 100-Å μ-styragel columns was used to separate the C-ether lubricant. This combination of columns allowed for the separation of substances to molecular weights of 10 000. Chloroform was used as the mobile phase at a flow rate of 1 ml/min. Twenty microliters (μl) of the lubricant were dissolved in 3 ml of chloroform, and 50 μl of this solution were injected into the HPLC system. Figure 18 is the chromatogram (the recorded separation) of this sample. Peak A was identified as the mixture of the four-ring phenyl components (components A1, A2, and A3 of figure 16) and peak B as the three-ring phenyl component (component B of fig. 16). All peaks were identified by concentrating the sample with the four pure components of the C-ether lubricant (one component at a time), injecting the sample into the HPLC and noting which peak on the chromatogram increased relative to the other peaks.

Normal phase separation. - A -CN bonded phase column was then used to separate the C-ether lubricant. Heptane was used as the mobile phase at a flow rate of 1 ml/min. Twenty μl of the lubricant were dissolved into 3 ml of n-heptane and 50 μl of the resulting solution were injected into the HPLC system. Figure 19 is the chromatogram of the injected sample. Peaks A1, A2, and A3 were indentified as the four-ring phenyl components and peak B as the three-ring phenyl component.

Reversed phase separation. - Next, a C-18 bonded phase column was used to separate the C-ether lubricant. A mixture of tetrahydrofuran (THF) and water (50 percent THF and 50 percent water by volume) was used as the mobile phase at a flow rate of 1 ml/min. Ten μl of the lubricant were dissolved into 3 ml of the solvent, and 20 μl of this solution were injected into the HPLC system. Figure 20 is the chromatogram of the injected sample. Peaks A1, A2, and A3 were identified as the four-ring phenyl components, and peak B as the three-ring phenyl component.

Adsorption separation. - Finally, a silica adsorption column was used to separate the C-ether lubricant. A mixture of n-heptane and chloroform (98 percent n-heptane and 2 percent chloroform by volume) was used as the mobile phase at a flow rate of 0.1 ml/min. Five μl of the lubricant were dissolved into 2 ml of the solvent, and 10 μl of this solution were injected into the HPLC system. Figure 21 is the chromatogram of the injected sample. Peaks A1, A2, and A3 were identified as the four-ring phenyl components, and peak B as the three-ring phenyl component.

Comparison of results. - The size exclusion separation (fig. 18) of the C-ether lubricant (a blend of four components) indicated the presence of only two components. The μ-styragel columns were able to separate the three-ring phenyl component from the four-ring components but were unable to separate the four-ring components from each other.

The normal phase separation (fig. 19) of the lubricant indicated the presence of all four components. However, the -CN-bonded phase column was able to completely separate the three-ring phenyl component from the four-ring components but unable to completely separate the four-ring components from each other.

The reversed phase separation of the lubricant also indicated the presence of all four components. The C-18 bonded phase column, like the -CN-bonded phase column, was able to completely separate the three-ring phenyl component from the four-ring components but unable to completely separate the four-ring components.

The optimum separation was obtained with the silica gel column used in the adsorption mode. It completely separated all four components.

HPLC, ITS USE IN THE ANALYSIS OF A DEGRADED C-ETHER LIQUID LUBRICANT

Bearing tests. - The C-ether liquid lubricant was tested in full scale, high temperature bearing tests; test details and results are reported in reference 6. All bearing tests were marred by excessive deposit formations and repeated filter pluggings. Lubricant samples were collected after each bearing run and these samples were analyzed by HPLC. The lubricant sample from a 111-hr bearing test had the appearance of a black viscous sludge. This sample was prepared for HPLC analysis by dissolving 40 μl of the sample into 3 ml of chloroform. The resulting mixture were then filtered in order to separate out the insoluble deposits. 25 μl of the filtered solution was then injected into the HPLC system which was set up in the size exclusion mode. Figure 22 is the chromatogram comparing the unused C-ether lubricant with the used C-ether lubricant from the 111-hr bearing test. There has been an obvious loss in the

amount of the three-ring phenyl component and an apparent increase in the amount of the four-ring phenyl components. This is probably caused by preferential volatilization of the three-ring phenyl component. In addition, there is the appearance of some higher molecular weight material in the 400 to 1000 molecular weight range.

Micro-oxidation tests. - In order to study the C-ether liquid lubricant degradation process under controlled laboratory conditions, the Penn State University micro-oxidation test was employed (refs. 3 and 4). This micro-oxidation test is a simple, quick bench test and will hopefully correlate laboratory lubricant oxidation and thermal degradation results to actual field data.

The micro-oxidation apparatus is shown in figure 23. It consists of a glass tube fitted with an air (or nitrogen) entry tube. A catalyst specimen is placed at the bottom of the tube. The apparatus is located in a temperature controlled oven. A test is conducted by injecting 40 μl of a lubricant sample into the catalyst surface and letting the sample degrade for a known period of time after which the test is stopped and the sample prepared for HPLC analysis.

A M-50 steel catalyst was chosen for the micro-oxidation tests (the high temperature bearing tests used bearings made of M-50 steel). Both the temperature and the length of time for the micro-oxidation tests, conducted under an air atmosphere, were varied in order to reproduce the bearing test chromatogram result. It was found that a test run of 60 min at 350° C gave the best reproduction (fig. 24). The preferential volatilization of the three-ring phenyl component occurred and the slight appearance of a higher molecular weight product is detected at the 450 molecular weight calibration point. Examination of the catalyst surface and the sample lubricant at the end of the run revealed no deposit formation.

The micro-oxidation test was then repeated using a nitrogen atmosphere. Figure 25 is the size exclusion chromatogram of the C-ether sample tested under the nitrogen atmosphere. The preferential volatilization of the three-ring phenyl component again occurred, and the appearance of at least three higher molecular weight products was detected. Deposit formation did not occur.

Micro-Oxidation Test and Bearing Test; Any Correlation

The HPLC analysis of the 111-hr bearing test sample revealed some degradation of the C-ether lubricant but not the extreme amount of degradation that was expected from visual inspection of the bearing oil sample. This pointed out a limitation of HPLC in that analysis is limited to samples that are soluble in the mobile phase solvent, in this case chloroform; the deposit also proved insoluble in other solvents which included tetrahydrofuran, acetonitrile, and methanol.

Unlike the bearing oil sample, the HPLC analysis of the micro-oxidation test samples was not complicated by the presence of insoluble deposits.

The size exclusion analysis (fig. 24) of the micro-oxidation test C-ether sample, conducted under an air atmosphere, revealed the excellent oxidative

stability of the C-ethers under the severe static conditions of extreme temperature and time in the presence of a catalyst. It was the size exclusion analysis of the micro-oxidation test sample, conducted under a nitrogen atmosphere, which revealed a surprising result, the detection of at least three higher molecular weight products. A quick calculation using the molecular weight calibration curve indicates that the molecular weights of the three degradation products correspond to five-, six-, and seven-ring phenyl products. One is tempted to speculate that the C-ether, under certain conditions, may slowly polymerize, and that the presence of oxygen tends to inhibit this process.

The Question of C-Ether Polymerization

A controlled experiment was conducted to investigate the possible polymerization of the C-ethers using a free radical initiator. One weight percent of the initiator, diphenyl disulfide, was added to the C-ethers. Ten ml of this solution were heated in glassware at 350° C for 4 hours under a nitrogen atmosphere, after which a sample was withdrawn and prepared for size exclusion analysis. Figure 26 is the chromatrogram of the sample. In addition to the C-ether peaks, there are four other peaks. Based on the calibration curve, these peaks correspond to two, five, six, and possibly seven phenyl-ring products. At 350° C, the diphenyl disulfide initiator will cleave to free radicals (fig. 27). These free radicals may attack the C-ethers causing a slow polymerization process to occur. This test, coupled with the micro-oxidation tests, substantiates the polymer forming properties of the C-ethers.

Still no Explanation for Formation of Insoluble Deposit

Several things become apparent at this point; the problem associated with the C-ethers is not due to oxidative degradation; and the static mirco-oxidation test, while providing valuable information, did not duplicate the insoluble deposits found in the bearing test samples. One can speculate that in the bearing test the C-ethers polymerized to form a high molecular weight insoluble product; however, two pieces of information obtained from the micro-oxidation test and the bulk free radical test challenge this speculation. Polymerization seems to occur at a very high temperature, ~ 350° C, which is much higher than the temperatures measured in the bearing tests (the test oil inlet temperature: 260° C, the bearing outer race temperature, 316° C), and the size exclusion chromatogram (fig. 22) of the bearing test sample fails to indicate polymerization products (other than the product detected at the 450 molecular weight point).

The formation of the insoluble deposit appears to be the result of a dynamic condition, something that the micro-oxidation test cannot simulate. Chemical analysis shows the deposit to be very high in iron, indicating the deposit is probably the debris of corrosive wear where the debris is likely to be a mixture of insoluble organo metallics, and inorganic iron compounds such as iron sulfides and oxides.

Dynamic test. - A pin-on-disk rig was used to conduct boundary lubrication experiments using the C-ethers, hoping to duplicate the bearing test results. A stationary M-50 steel pin was loaded against a rotating M-50 disk, which was mounted horizontally on the rig. A 1 kg normal load was applied to the pin,

and the disk allowed to rotate at 12.5 rpm. The rotating disk was lubricated with 2 ml of C-ether. A series of runs were to be conducted under both a nitrogen and air atmosphere at increasing temperatures from 25° to 260° C. As soon as the initial test began (25° C and a nitrogen atmosphere) a black deposit was noticed forming around the contact area. The test ran 24 hours. At the end of this period, the C-ether lubricant had the appearance of a black sludge. A sample was collected and prepared for HPLC analysis. Figure 28 is the size exclusion chromatogram of the soluble portion (chloroform soluble) of the sample, which reveals only the two peaks of the C-ether. No soluble degradation products were detected.

The black insoluble portion of the sample (like the bearing sample) proved to be insoluble in all organic solvents.

The pin on disk test indicates that the C-ethers are easily broken down during the boundary lubrication of M-50 steel with the resultant formation of a black insoluble deposit. Several models can be proposed to explain the C-ether behavior:

(1) Even though the bulk temperature of the C-ether lubricant and the M-50 steel disk and pin is 25° C, the temperature and pressure at the frictional contact could be sufficiently high to break down the C-ethers and cause a rapid polymerization reaction leading to a black deposit. This model, however, does not explain the high iron content in the deposit.

(2) The breakdown of the C-ethers, during boundary lubrication, could be triggered by the presence of iron leading to the formation of iron sulfides, possible insoluble organo metallics, iron oxides, and hydrates. These compounds are continuously worn away from the surface and may be considered the debris of corrosive wear.

Future work on developing a procedure to analyze the deposit will hopefully clarify the breakdown process.

CONCLUDING REMARKS

A short introduction to the field of high-pressure liquid chromatography was presented to acquaint those not familiar with the subject. The analytical separation of a C-ether liquid lubricant demonstrated the various separation techniques.

The use of HPLC in analyzing a degraded C-ether lubricant, from full scale, high temperature bearing tests demonstrated the value of this technique in obtaining information relating to the C-ether breakdown process; however, the analysis also pointed out the shortcomings of HPLC, that analysis of a sample is limited by the solubility of the sample in an appropriate mobile phase solvent.

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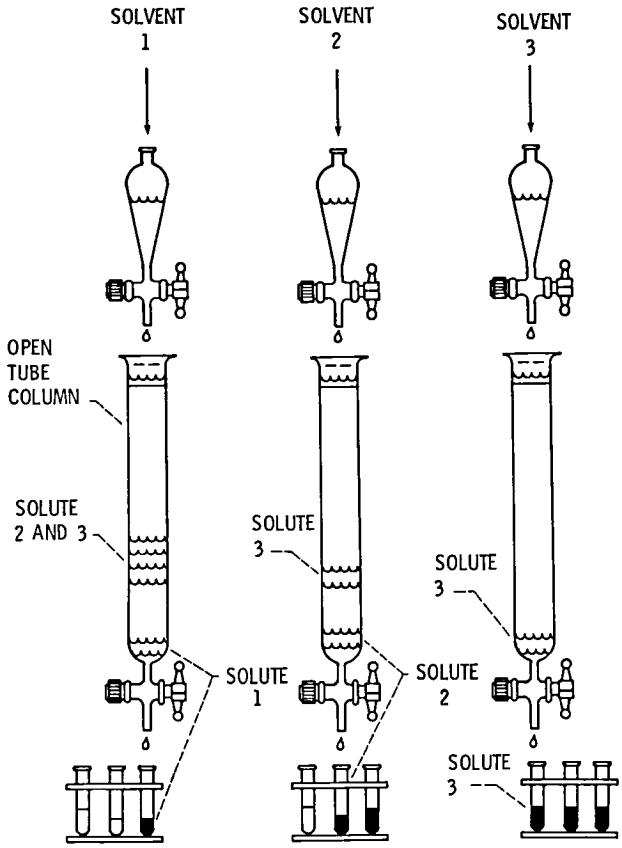


Figure 1. - Classical liquid column chromatography.

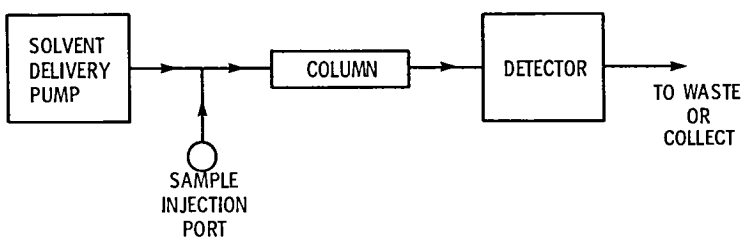


Figure 2. - Modern HPLC system.

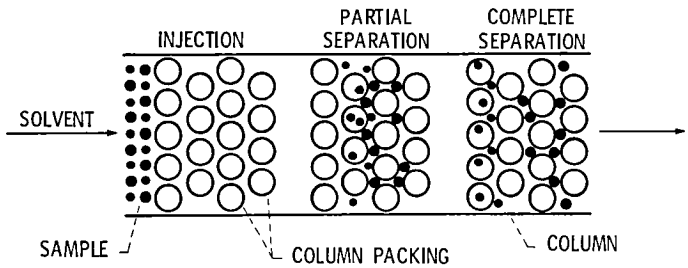


Figure 3. - Schematic diagram of size exclusion chromatography.

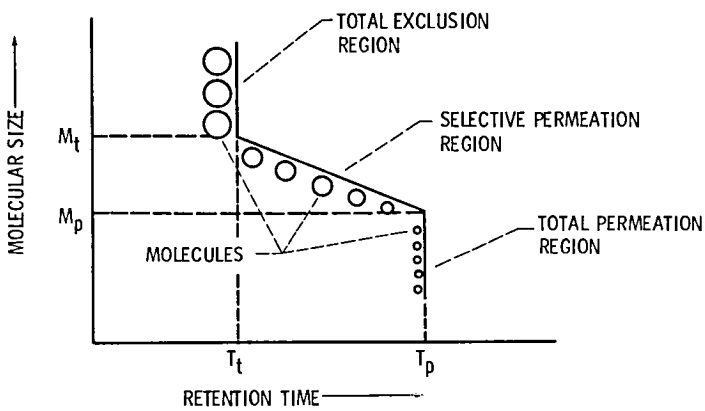


Figure 4. - The ideal size exclusion process.

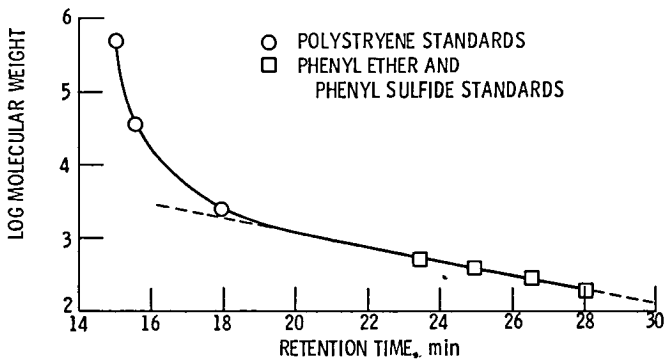


Figure 5. - Calibration curve for a size exclusion column set (one 500 Å and two 100 Å u-styragel columns). Flow rate, 1 milliliter/min; mobile phase, tetrahydrofuran.

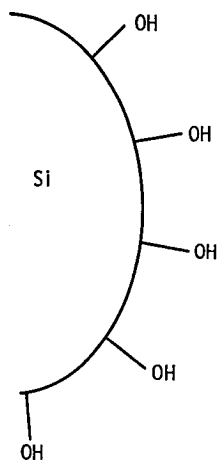


Figure 6. - Silica gel stationary phase.

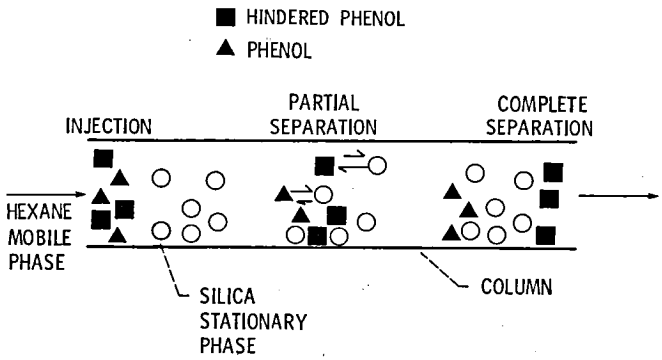


Figure 7. - Typical adsorption chromatographic separation.

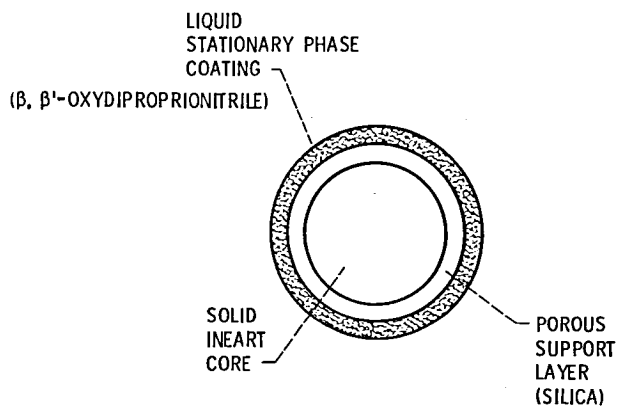


Figure 8. - Liquid-liquid chromatographic stationary phase.

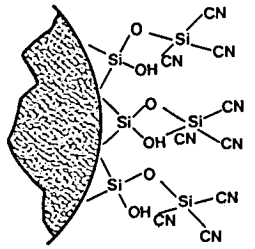


Figure 9. - Normal phase stationary phase.

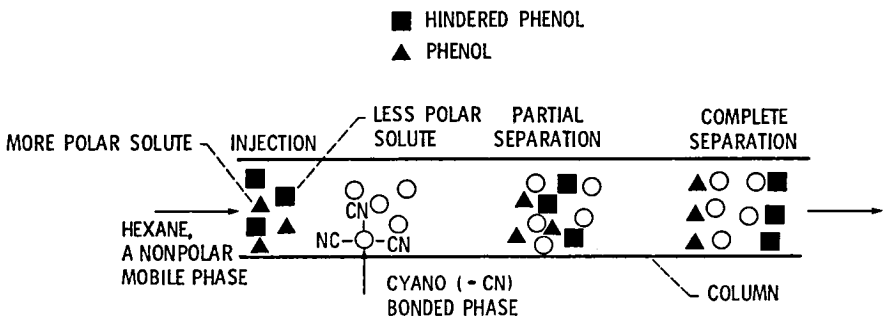


Figure 10. - Normal phase chromatography.

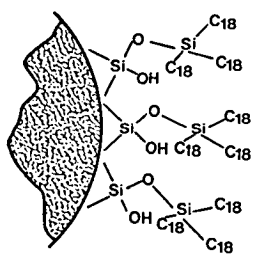


Figure 11. - Reverse phase stationary phase.

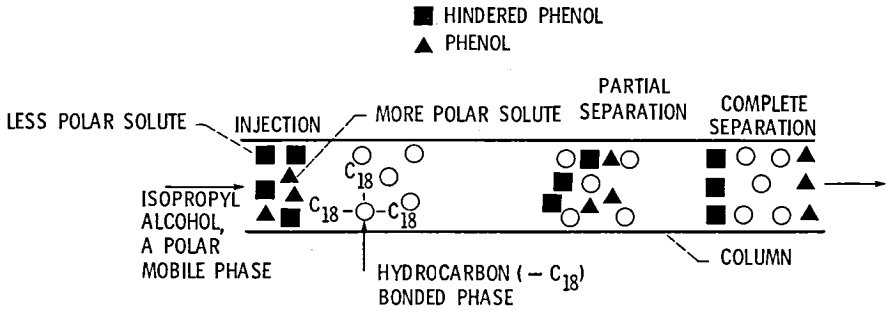


Figure 12. - Reverse phase chromatography.

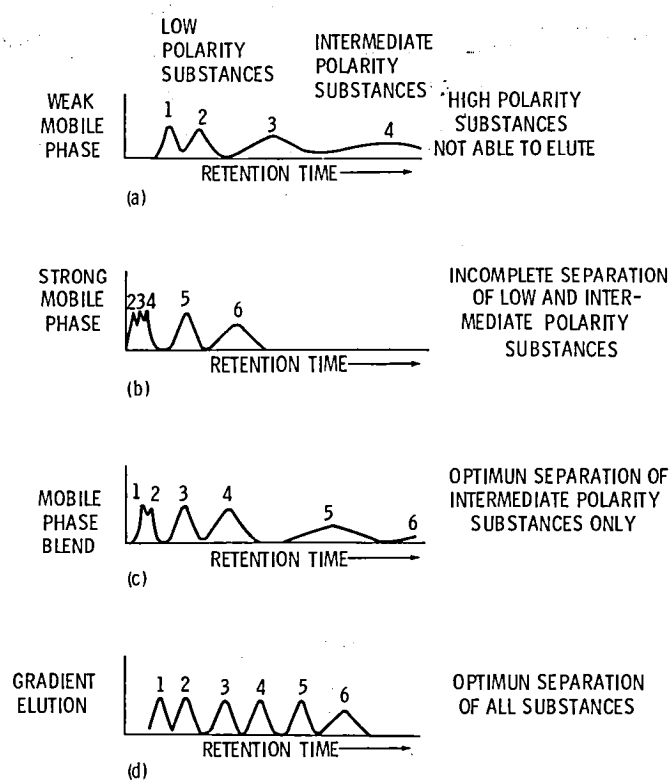


Figure 13. - Sample separation optimization.

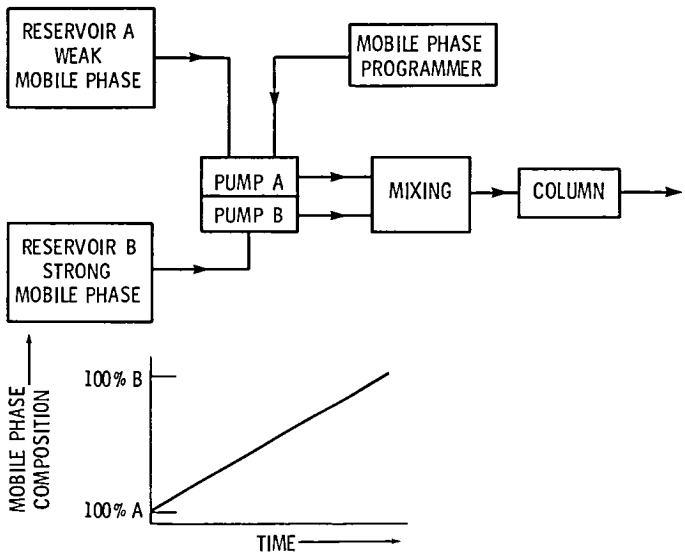


Figure 14. - Gradient elution chromatography.

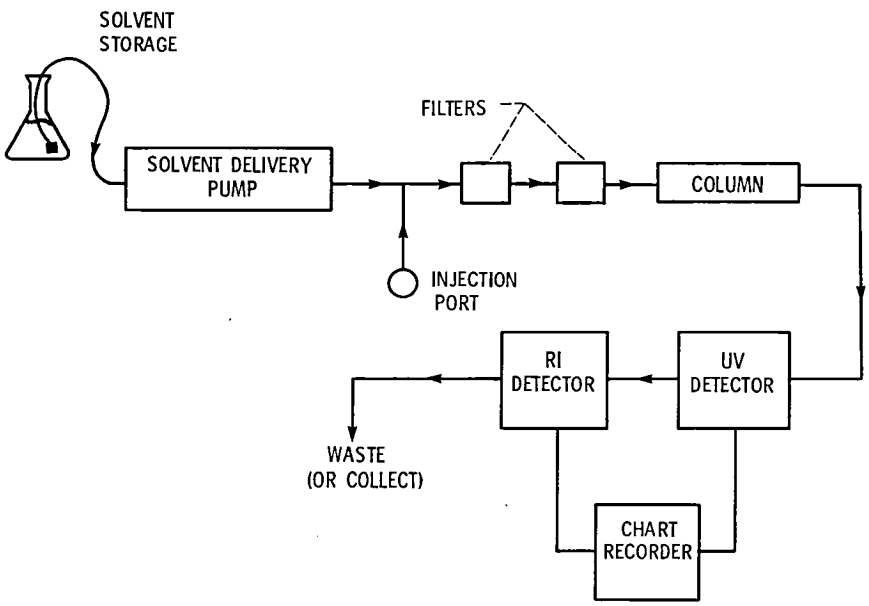
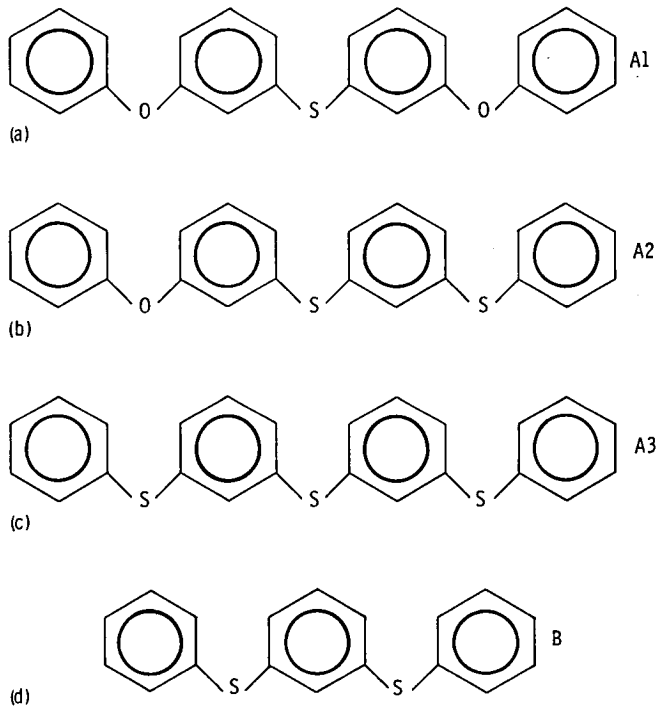


Figure 15. - HPLC system used in the analysis of the Thio-ether lubricant.



(a) 1, 1-thiobis [3-phenoxybenzene]; molecular weight, 370.
(b) 1-phenoxy-3-[[3-(phenylthio) phenyl] thio] benzene; molecular weight, 386.
(c) 1, 1-thiobis [3-(phenylthio) benzene]; molecular weight, 402.
(d) 1, 3-bis (phenylthio) benzene; molecular weight, 294.

Figure 16. - Chemical components of MCS 524 C-ether base fluid.

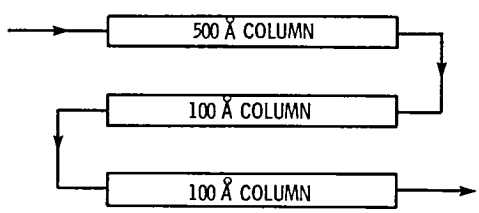


Figure 17. - Set of μ-Styragel size exclusion columns.

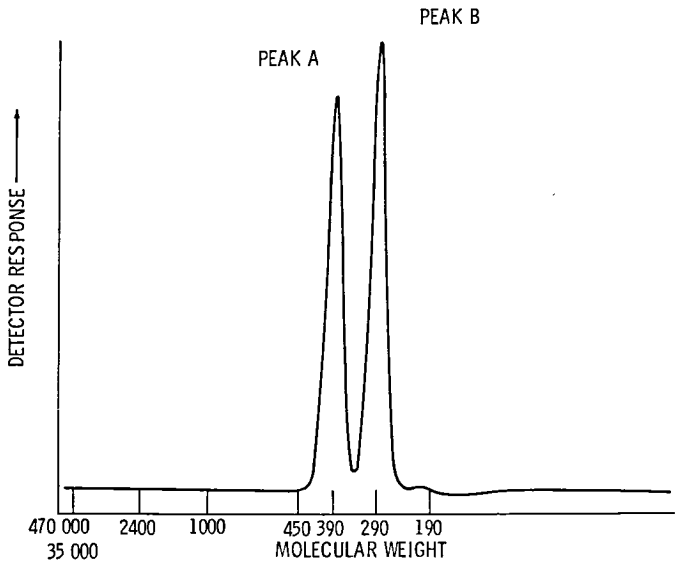


Figure 18. - Size exclusion chromatogram of C-ether lubricant using μ-styragel columns. Flow rate, 1.0 milliliter/min; mobile phase, chloroform; RI detector (8X).

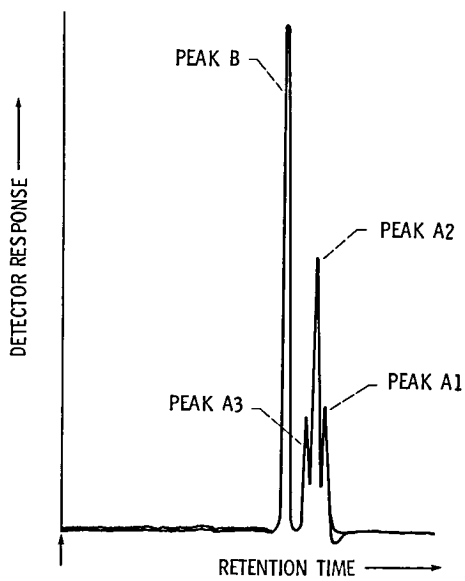


Figure 19. - Normal phase chromatogram of C-ether lubricant using a CN column. Flow rate, 0.50 milliliter/min; mobile phase, heptane; RI detector (8 X).

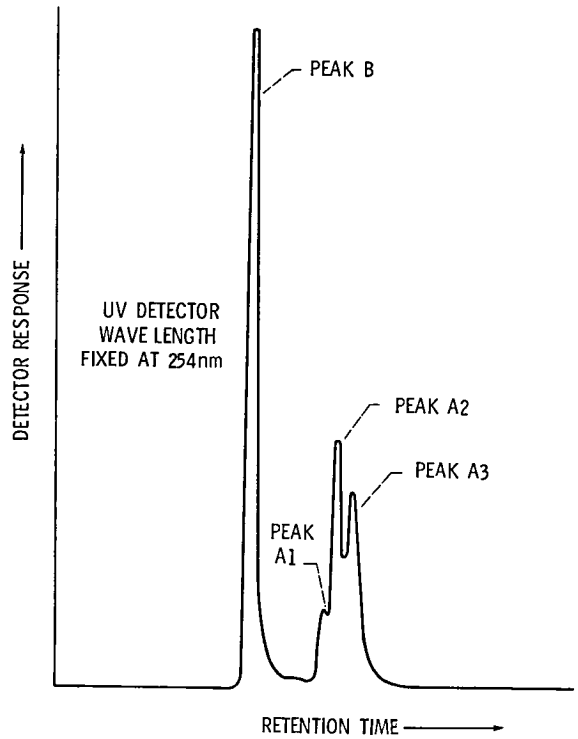


Figure 20. - Reverse phase chromatogram of C-ether lubricant using a C_{18} column. Flow rate, 0.5 milliliter/min mobile phase, water/tetrahydrofuran (50/50); UV detector (2.0 AUFS) set at 254 nm.

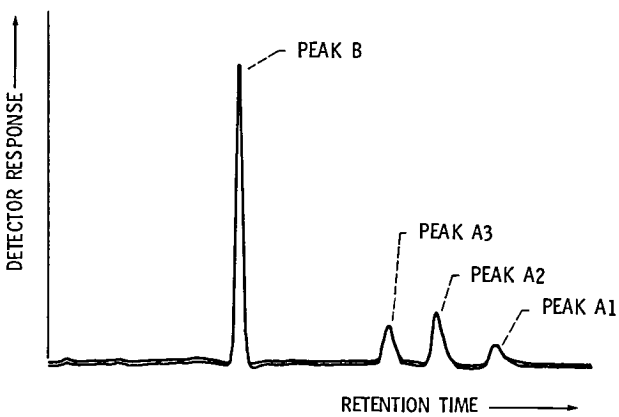


Figure 21. - Adsorption chromatogram of C-ether lubricant using a silica column. Flow rate, 0.1 milliliter/min; mobile phase, heptane/chloroform (98/2); RI detector (8X).

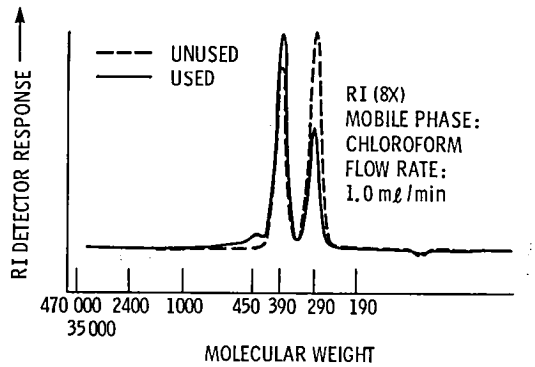


Figure 22. - Size exclusion chromatogram for unused C-ether lubricant and for the tested (111-hr bearing test) C-ether lubricant.

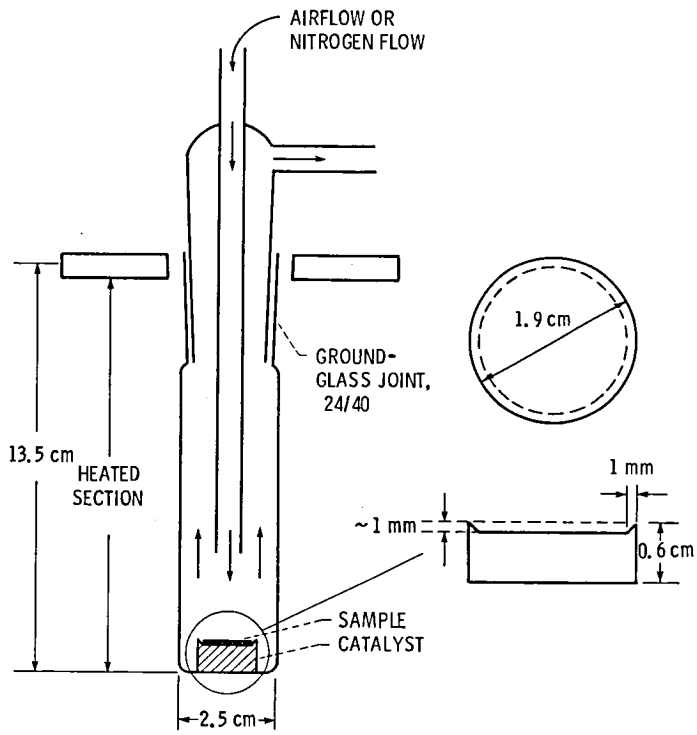


Figure 23. - Micro-oxidation apparatus.

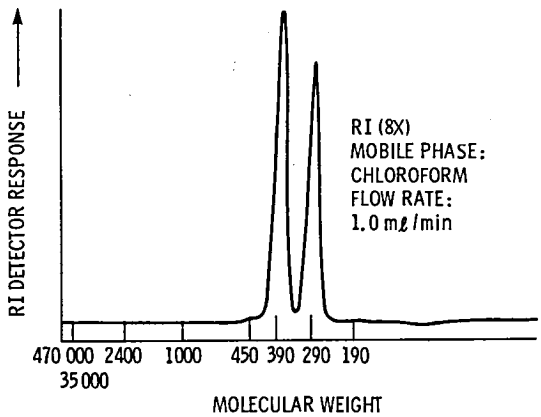


Figure 24. - Size exclusion chromatogram of C-ether lubricant from micro-oxidation test (350° C, 60 min) catalyst, M-50 steel, test atmosphere, dry air.

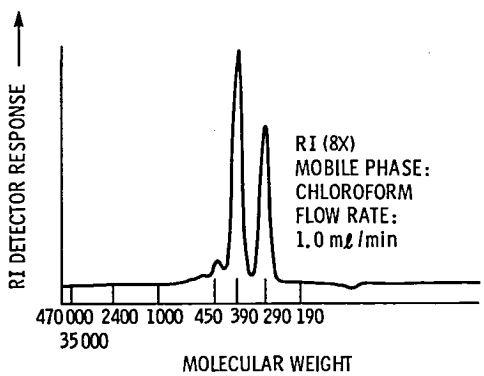


Figure 25. - Size exclusion chromatogram of C-ether lubricant from micro-oxidation test (350° C, 60 min) - catalyst, M-50 steel, test atmosphere, dry nitrogen.

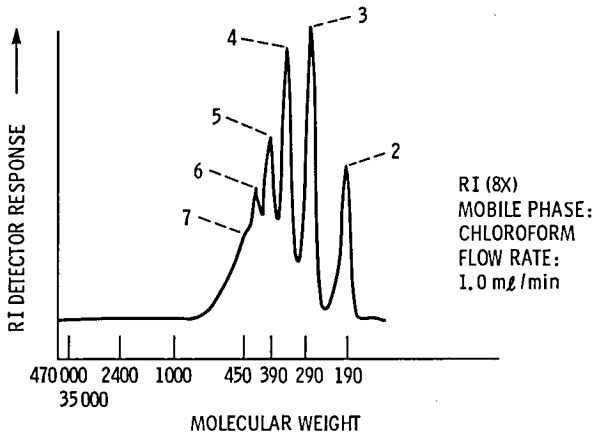


Figure 26. - Size exclusion chromatogram of C-ether lubricant containing 1% wt diphenyl disulfide (350° C, 4 hr) - test atmosphere, dry nitrogen.

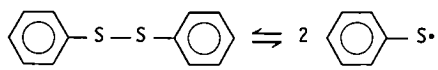


Figure 27. - Free radical formation from diphenyl disulfide.

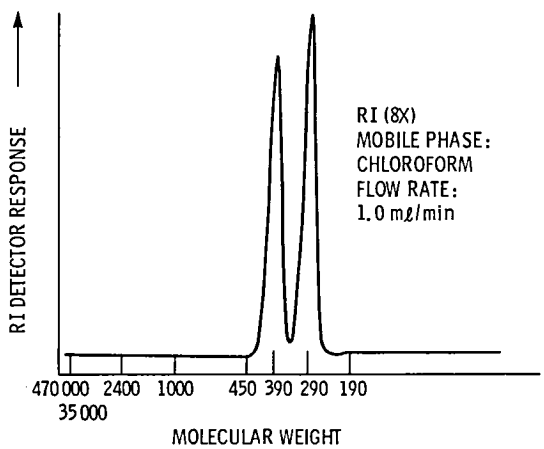


Figure 28. - Size exclusion chromatogram of C-ether lubricant from pin-on-disk test (25° C, 24 hr) - test atmosphere, dry nitrogen.

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15. Supplementary Notes

16. Abstract

The general principles of classical liquid chromatography and high-pressure liquid chromatography (HPLC) are reviewed, and their advantages and disadvantages are compared. Several chromatographic techniques are reviewed, and the analytical separation of a C-ether liquid lubricant by each technique is illustrated. A practical application of HPLC is then demonstrated by analyzing a degraded C-ether liquid lubricant from full scale, high temperature bearing tests.

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