

Note

Reversed-phase liquid chromatographic separation and quantification of mixtures of fatty alcohols and esters in hydrocarbon bases

F. E. LOCKWOOD, L. J. MATIENZO* and B. SPRISLER

Martin Marietta Laboratories, 1450 South Rolling Road, Baltimore, MD 21227 (U.S.A.)

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In aluminum rolling, the metal is usually deformed in a multistage process, which includes hot and cold rolling. These two types of rolling differ in the type of lubrication packages used; hot rolling lubricants typically are oil in water emulsions, whereas cold rolling lubricants usually are single phase fluids. Because the volume of metal fabricated by rolling is large, these lubricating fluids are subjected to additive depletion, contamination and oxidative degradation. Therefore, it is desirable to monitor their composition and chemistry to ensure adequate additive levels.

Cold rolling oils are typically composed of alcohol and ester additives in a kerosene basestock. A review of the use of liquid-liquid chromatography (LLC) for these materials indicated that reversed-phase LLC was the preferred technique. For example, Vigh and Varga-Puchony¹ used MicroPak CH-10 or Nucleosil C₁₈ octadecyl silica reversed-phase columns to separate C₆-C₁₆ alcohols. Björkqvist and Toivonen² and Scholfield³ used reversed-phase columns similar to Dupont's Zorbax column, for the separation of alcohols and methyl esters, respectively. Hagnauer and Bowse have used reversed-phase LLC with a μ Bondapak C₁₈ column to fingerprint and identify hydraulic fluids. Similarly, Hoffman and Liao⁵ used reversed-phase LLC with a custom-made column of Spherosorb ODS.

For less polar materials, such as mineral oils, silica adsorption columns are preferred. For instance, Frankenfeld and Schulz⁶ used a 1.22-m silica absorption column with isooctane solvent for fingerprinting base oils, and Fodor and Newman⁷ used a 3-m silica gel (Porasil) column and hexane solvent to classify middle-distillate petroleum products. However, although these columns are effective, analysis times are long (≥ 1 h).

Several authors have described techniques to improve the detection sensitivity for alcohols. As an example, Björkqvist and Toivonen² improved their ability to detect aliphatic alcohols by derivation with phenyl isocyanate to form alkylphenylurethanes, which are monitored by their UV absorption. A variety of other derivation methods have also been published^{8,9}, but their use increases the time required for overall analysis.

Recently, Kirk and Ford¹⁰ have described a HPLC approach applicable to some cold rolling fluids. However, the method is limited because the selected solvent, isopropanol, makes high-molecular-weight methyl esters (for example, C₁₈) insoluble, and consequently, mixtures containing these materials cannot be analyzed completely.

We used the Kirk and Ford¹⁰ approach as a starting point for the development of the method described herein. Our method is more broadly applicable to monitoring the composition and additive concentration of cold rolling fluids used in the fabrication of aluminum sheet. The reversed-phase LLC technique allows comparisons of both new commercial samples of cold rolling oils from various suppliers and re-refined lubricating mixtures, and monitoring of key components in the formulation.

EXPERIMENTAL

General separation scheme

The typical cold rolling oil contains a polar additive fraction of C₁₀–C₁₈ fatty alcohols, C₁₂–C₁₈ methyl esters and (in most cases) an oxidation inhibitor such as 2,4,6-tri-*tert.*-butylphenol (BHT), all of which are dissolved at a concentration of 4–6% (v/v) in a light, non-polar, kerosene basestock. Because the chromatographic properties of the polar and non-polar fractions are significantly different, we pre-separated the oil on a disposable silica cartridge (Sep-Pak®; Waters Assoc., Milford, MA, U.S.A.) and chromatographed each of these fractions individually, using different solvent mixtures on a DuPont (Wilmington, DE, U.S.A.) C₈ Zorbax reversed-phase column. A Waters Assoc. HPLC system with a Model 6000A pump, a solvent programmer Model 660, a refractive index detector and UV detector (Model 441) were used for analysis.

Preparation of standard solutions

All the procedures were optimized using a standard mixture of high purity (> 95%) fatty alcohols (C₁₀–C₁₈) and methyl esters (C₁₂–C₁₈) in a kerosene base oil. We believe the composition and concentration of the standard typified that of commercial oils used for aluminum cold rolling. We prepared a second type of standard in the same way, but dissolved the additives in tetrahydrofuran rather than kerosene. Its polar components could be analyzed by injecting directly into the HPLC, thus avoiding the Sep-Pak procedure.

Separation of polar and non-polar components

The standard mixtures and samples were separated into polar and non-polar fractions by (1) dissolving 1.0-ml aliquots of the sample into 5.0 ml chromatographic-grade *n*-hexane, (2) running the mixture on a Sep-Pak silica cartridge (the eluent contained the non-polar components), (3) washing the column with 5.0 ml of hexane and adding the new eluent to the previous one, (4) eluting polar materials from the silica in 5.0 ml of methanol, (5) evaporating the two fractions under nitrogen and (6) dissolving each of the residues into 1.0 ml of chromatographic grade tetrahydrofuran (THF) for analysis.

Liquid chromatography of the polar fraction

The polar fraction, which contains the fatty alcohols, esters, and oxidation inhibitor (if included by the formulator of the lubricant), was analyzed under the following instrumental conditions: column, DuPont Zorbax C₈ reversed-phase; sample size, 20 μl; mobile phase (solvent), acetonitrile triple distilled water–THF

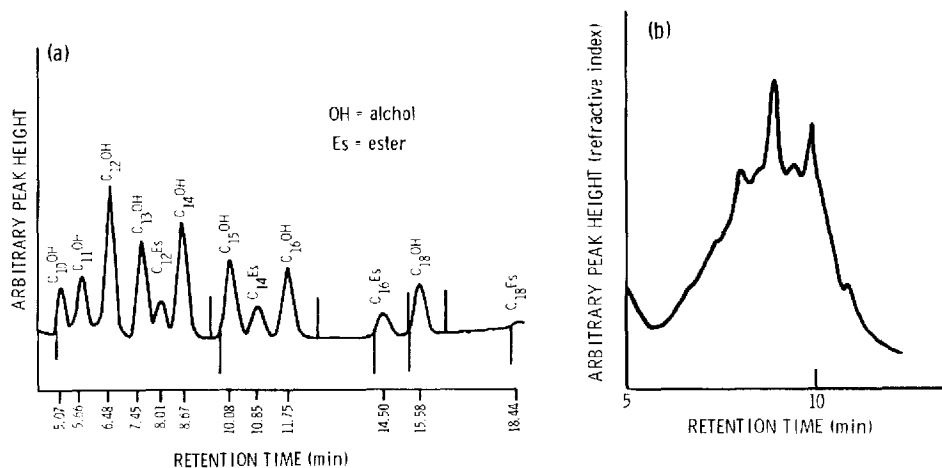


Fig. 1. Refractive index chromatogram of (a) calibration standard for cold rolling oil additives (polar fraction) and (b) kerosene (non-polar fraction).

(78.75:11.25:10) (all solvents of chromatographic grade, and degassed before mixing; THF needed to prevent precipitation of C_{18} ester on the column); refractive index attenuation, $8 \times$; UV setting, 0.05 A units at 214 nm; flow program, 1.0 ml min^{-1} to 3.0 ml min^{-1} on curve 9 of the flow programmer in 20 min.

The refractive index chromatogram of a standard mixture of alcohols and esters is shown in Fig. 1a; retention times of individual components are marked. For unknown mixtures, each component was identified automatically and its concentration (%) in the mixture calculated by a Spectra-Physics SP-4000 processor, using the standard as the calibration fluid. If present, the BHT is detectable in the UV chromatogram. Table I lists the typical results obtained for the analysis of a lubricant standard.

TABLE I

TYPICAL REVERSED-PHASE HPLC ANALYSIS OF A LUBRICANT STANDARD

Peak no.	Alcohol (OH) or methyl ester (Es)	Amount ($\times 10^2 \text{ g/2 l}$)	Retention time (min)	Percentage by weight
1	$C_{10}\text{OH}$	147.7	5.0	5.7
2	$C_{11}\text{OH}$	158.2	5.6	6.1
3	$C_{12}\text{OH}$	380.5	6.4	14.7
4	$C_{13}\text{OH}$	259.4	7.4	10.0
5	$C_{12}\text{Es}$	119.7	8.0	4.6
6	$C_{14}\text{OH}$	367.5	8.6	14.2
7	$C_{15}\text{OH}$	268.2	10.0	10.3
8	$C_{14}\text{Es}$	134.8	10.8	5.2
9	$C_{16}\text{OH}$	261.5	11.7	10.1
10	$C_{16}\text{Es}$	120.8	14.5	4.7
11	$C_{18}\text{OH}$	249.4	15.5	9.6
12	$C_{18}\text{Es}$	120.9	18.4	4.7
Total		2588.6		99.9

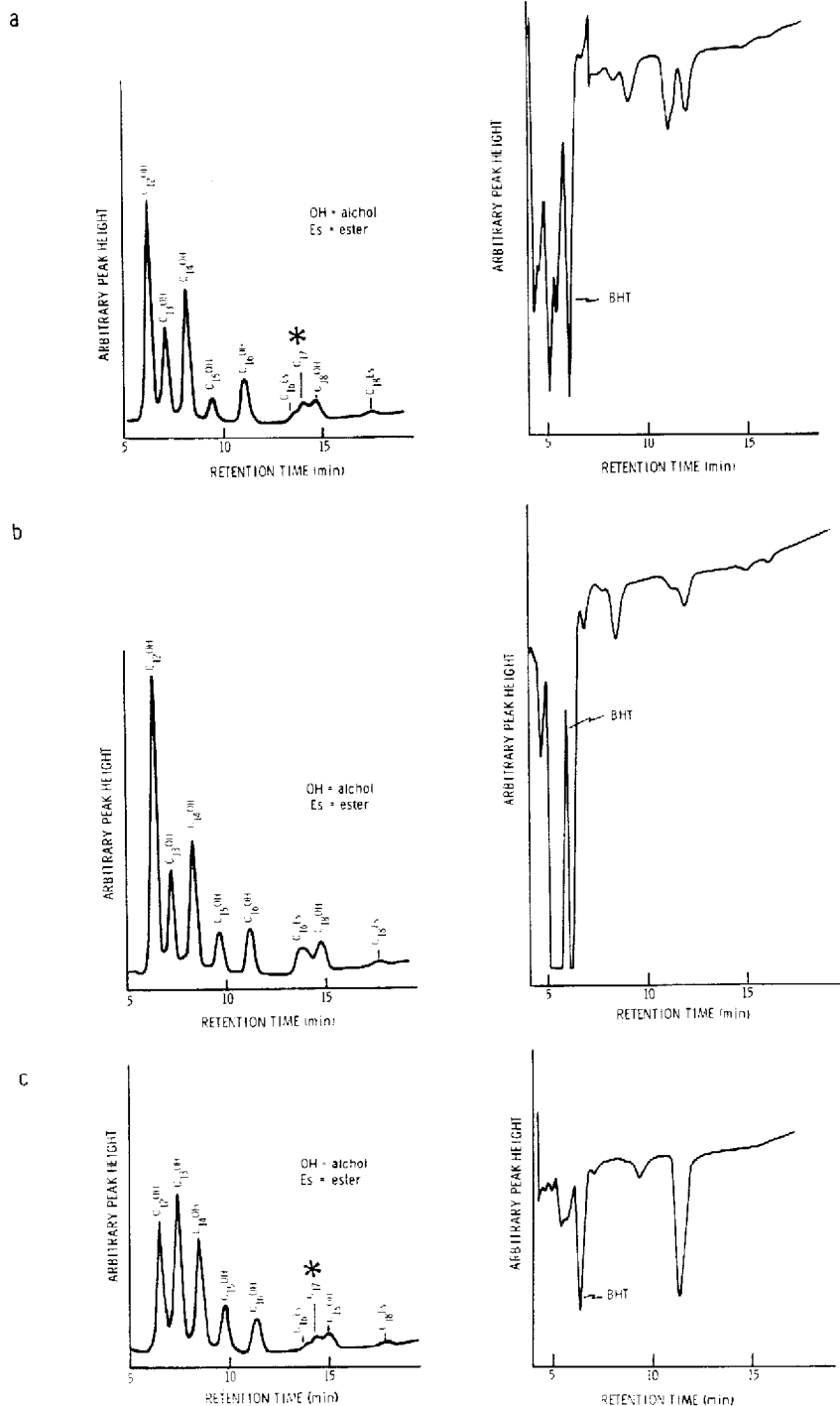


Fig. 2. Refractive index (left series) and UV (right series, 254 nm, 0.01 Å) chromatograms of commercial formulations (a) A, (b) B and (c) C. An unidentified 17-carbon component, not a critical component in the mixture, appears in formulations A and C (marked *).

Liquid chromatography of the non-polar fraction

Kerosene, the non-polar fraction of the cold rolling oil, is also chromatographed on the Zorbax C₈ reversed-phase column, but to prevent column plugging the solvent used is acetonitrile-carbon tetrachloride (85:15). The non-polar fraction (the Sep-Pak hexane filtrate) prepared in THF is injected in either 10.0- or 20.0- μ l samples at a flow-rate of 1.0 ml min⁻¹. The characteristic refractive index pattern of the kerosene under these chromatographic conditions is shown in Fig. 1b. Used rolling oil may also contain some non-polar contaminants from gear, machine and hydraulic oils. Because the contaminants have much higher molecular weights than the kerosene and fairly complex compositions, they do not elute well under this procedure and must be flushed from the column periodically with THF. These compounds will be the subject of a future publication.

RESULTS AND DISCUSSION

Lubricant suppliers claim to produce outstanding products, but often provide little information on their formulation. Such information is important to the user, who sometimes must make product substitutions. The suitability of two new products, A and B, being recommended as substitutes for an existing one, C, were tested. The UV and refractive index chromatographic traces (Fig. 2) showed that qualitatively the materials were similar and quantitatively they also had similar compositions (see Table II). Therefore, they can safely be substituted for each other without affecting plant productivity. The UV traces obtained at 254.0 nm indicate that all three commercial materials contain BHT.

Use of the method to detect changes in lubricant composition during passage through a fabrication line is illustrated in Fig. 3. In this case, a lubricant sample from a cold rolling mill, which contained an unusually large fraction of metal fines, was analyzed after filtration to remove the solid particles. At least two additional peaks are detected; they are believed to be decomposition products of the additive package. The UV chromatogram also indicated that the concentration of the BHT additive had decreased.

In recent years, with the increasing price of petroleum derivatives, re-refining of oils and lubricants has become very attractive because of the potential savings if

TABLE II
COMPOSITIONS OF SEVERAL COMMERCIAL OILS

<i>Alcohol (OH) or methyl ester (Es)</i>	<i>Formulation A (%, w/w)</i>	<i>Formulation B (%, w/w)</i>	<i>Formulation C (%, w/w)</i>
C ₁₂ OH	29	32	20
C ₁₃ OH	17	15	30
C ₁₄ OH	24	20	20
C ₁₅ OH	4	7	8
C ₁₆ OH	8	7	6
C ₁₆ Es	7	7	5
C ₁₈ OH	6	7	6
C ₁₈ Es	7	6	5
BHT	yes	yes	yes

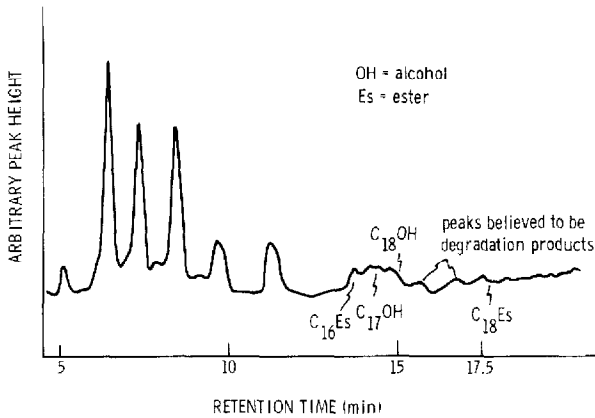


Fig. 3. Refractive index chromatogram (additive package) of used cold rolling oil from a fabrication mill.

the integrity of the product can be maintained during purification. Fig. 4 shows a refractive index chromatogram of (a) the polar fraction of new oil and (b) that of re-refined oil. Based on these chromatograms and the compositions determined from them, we concluded that there was no significant difference between the two, and that surprisingly little additive was lost during re-refining. However, there were small differences in the UV spectra (not shown). The re-refined oil generally absorbed less in the UV, which was considered desirable. A similar analysis of the non-polar kerosene fraction of the two oils demonstrated that the kerosene fractions also had comparable compositions.

Results of analysis of four samples of re-refined oil, successive samples of which had been distilled one additional time, showed that the distillation did not cause any component of the oil to be oxidized or depleted nor any significant amount of degra-

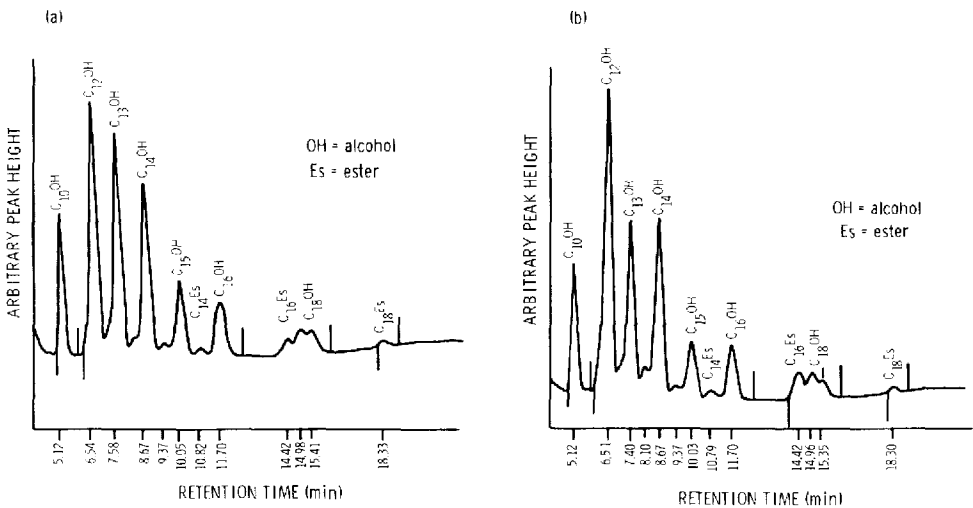


Fig. 4. Refractive index chromatograms of (a) cold rolling oil additive (new oil mill), and (b) cold rolling oil additive re-refined after use in a fabrication line.

dation products to be accumulated in the re-refined oil. The results also showed that there was no advantage to successive distillations. Overall, the chromatographic data indicated that re-refining of cold rolling oil can be safely recommended as a way of increasing operating savings without damaging product quality.

CONCLUSIONS

Our results demonstrate that additives used as lubricating fluids in aluminium cold rolling, mainly alcohols and esters dissolved in hydrocarbon bases, can be satisfactorily separated and quantitatively analyzed by reversed-phase high-performance liquid chromatography. The method described here is simple and can be applied to the analysis of plant samples to detect changes in composition, compare commercial products or show that the lubricating fluids can be recycled by distillation without altering the key additives in a particular formulation.

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