

## Note

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### **Analysis of mechanical lubricant contaminants in aluminum cold rolling oil by reversed-phase liquid chromatography**

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(Received October 29th, 1984)

Cold mill oils for lubrication and cooling during aluminum rolling are composed of a polar additive fraction of C<sub>10</sub>-C<sub>18</sub> fatty alcohols, C<sub>12</sub>-C<sub>18</sub> 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. These oils are specially formulated to be non-staining and, where canstock for beverage cans is being produced, to leave no taste-imparting residues on the metal.

During use, cold mills oils commonly become contaminated with mechanical lubricants, mostly gear and hydraulic fluids, leaking from mill equipment. Because contaminant lubricants have a different chemical composition and viscosity than the mill oil, yet are extremely soluble, they substantially change the mill oil properties. The common practice of stain testing cold mill oils typically detects leaks of mechanical lubricants when staining is already imminent. Because of the high sensitivity of the high-performance liquid chromatography (HPLC) analysis described in this communication, slow leaks can be detected long before problems of metal quality arise.

The primary difficulty in separating the mechanical lubricants from the cold rolling oil is that all of the oils are mixtures of largely nonpolar molecules in similar molecules weight ranges. Consequently, the response to various detectors is not significantly different for any particular oil. Also, it was necessary to detect gear oils in small concentrations (0.1%) in the rolling oil to improve early detection significantly. A further constraint was the desire to develop an analysis not too different from the HPLC method already developed for cold rolling oil additives<sup>1</sup>, *i.e.*, one not requiring significant column changes and equilibration times.

At the time we began the work, no literature citations directly addressing a similar problem were found. However, our literature review suggested that reversed-phase non-aqueous chromatography on a C<sub>18</sub> column using infrared detection<sup>2,3</sup> was a possible method. An alternative, non-aqueous normal-phase HPLC using very long columns of silica or alumina<sup>4,5</sup>, was impractical for use in a rolling mill laboratory because of the long analysis times. Gel permeation chromatography (GPC), using high-efficiency columns for low-molecular-weight materials, was also promising. Riddle *et al.*<sup>6</sup> recently presented (not yet published) a GPC method for this type of analysis. The choice between the HPLC method presented herein and the GPC

method will depend on the mechanical lubricants being analyzed and on the compatibility of either method with other analyses for which the HPLC equipment is being used.

## EXPERIMENTAL

### *Experimental oils*

Five oils (a light and a heavy hydraulic fluid, two gear oils, and a machine oil) were selected as examples of lubricants which might typically contaminate cold rolling oil. A series of reference samples was prepared by dissolving each of these, at concentrations of 0.01–10% (w/w), in a commercial cold rolling oil of 6% (v/v) polar additive in a kerosene basestock.

### *High-performance liquid chromatography procedure*

We tried several of the oil separation techniques discussed in the literature [reversed-phase non-aqueous liquid chromatography using infrared detection, normal-phase chromatography, and GPC on two 100-Å columns (50-Å columns are now available)] before adopting the procedure described below. Results of trying these separation methods indicated that because of the similarities of the oils, we could not achieve adequate separation. However, in gradient elution HPLC, we observed that the rolling oil was generally more soluble than the mechanical lubricants in polar solvents. The gradient elution HPLC method developed relies on this greater solubility.

Table I gives the chromatographic conditions employed. A Waters Assoc. HPLC system with a Model 6000A and M-45 pump, a solvent programmer Model 660 and a UV detector (Model 441), was used for analysis. The used rolling oil being analyzed or the reference sample are dissolved in tetrahydrofuran (THF) at 9% (v/v) and 10  $\mu$ l are removed as the injection sample. In the initial HPLC solvent mix, only the rolling oil and part of the light hydraulic fluid were soluble. Therefore, when the sample is injected, we suspected some precipitation of the contaminant oils (mechanical lubricants) on the head of the column. After eluting the rolling oil for 5 min at 1 ml/min, we began a solvent flow program whereby the percentage of THF in the solvent was rapidly increased (*i.e.*, in 2 min at Waters flow program 10) to 100%. The THF apparently dissolves the precipitated contaminant oils and, as Fig. 1 shows, they eluted in a single peak (retention time  $18 \pm 0.5$  min) that is totally isolated from

TABLE I

#### HPLC CONDITIONS FOR SEPARATION OF MECHANICAL LUBRICANTS FROM COLD ROLLING OIL

Sample	Used cold rolling oil or reference sample at 9% (v/v) in THF, 5–10 $\mu$ l
Column	2 DuPont Zorbax C <sub>8</sub>
Detector	Ultraviolet, 280 nm; typical setting, 0.05 A units
Solvent program	Initial solvent mix [THF–methanol–water (60:20:20)] run for 5 min at 1 ml/min. After 5 min, begin flow program (No. 10 on a Waters Assoc. Model 660 solvent programmer) to increase THF to 100% within 2 min.

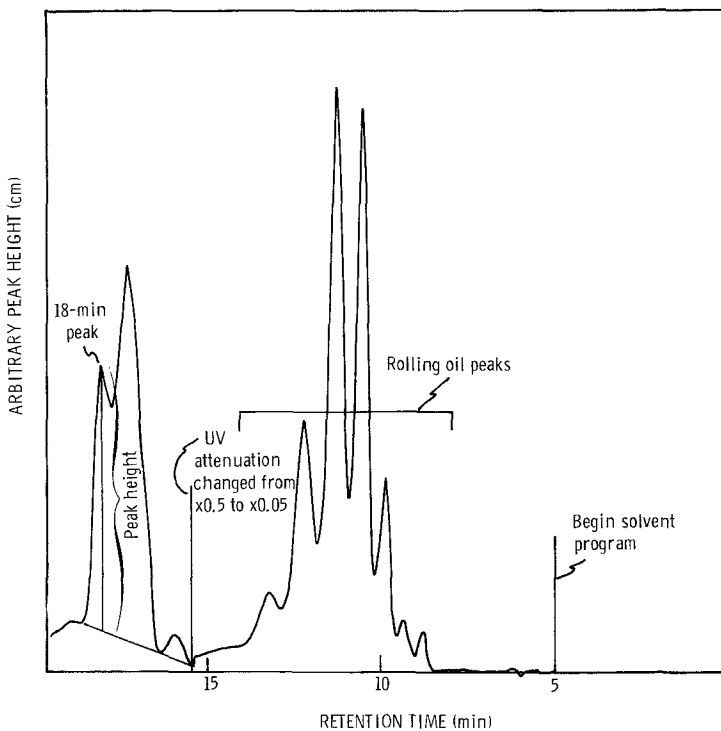


Fig. 1. Separation of contaminant oil from rolling oil (UV chromatogram).

the rolling oil peak. The height of this contaminant peak, measured as in Fig. 1, is almost linearly proportional (at low concentrations) to the concentration of the contaminants. Consequently, contaminants can be rapidly detected at concentrations as low as 0.03%. The peak preceding the contaminant oil peak, at  $\approx 17$  min, is associated with the solvent flow program and can be disregarded.

#### Calibration curves

Each of the five possible contaminants was dissolved in rolling oil and run by the above procedure to check the response to individual oils and to develop calibration curves for the peak height (at 18-min elution time) *versus* the percentage contaminant in the rolling oil. A series of chromatograms for a given oil, at 0–10% concentration in rolling oil (Fig. 2) shows that the 18-min peak grows proportionally to the contaminant oil concentration. Plots of concentration *versus* peak height (Fig. 3) for each oil, provide calibration curves from which the concentration of a given contaminant can be determined from its peak height. Furthermore, we observed that peak height also indicates the tendency of the rolling oil to stain, independent of the particular contaminant or its concentration in the oil. Low staining oils have a small response at 18 min, whereas high staining oils have a high response. For example, as shown in Table II, a low staining, light hydraulic oil and a heavy gear oil at concentrations of 12 and 1%, respectively, in the rolling oil cause staining of aluminum. From the calibration curves at 18 min, 12% light hydraulic fluid gives a peak

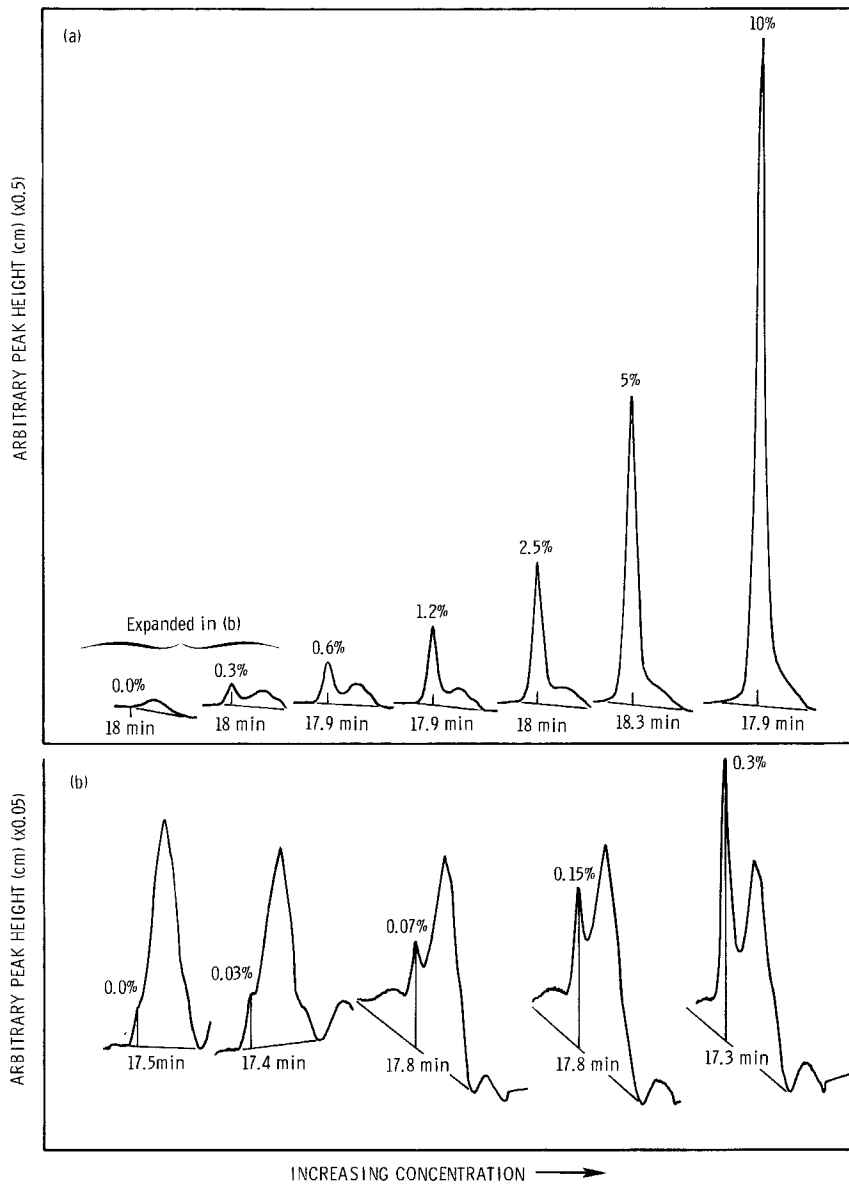


Fig. 2. Side-by-side comparison of contaminant peaks (UV chromatograms). Increasing concentration of gear oil No. 1 in cold rolling oil. (a) High detector attenuation 0.5; (b) expanded view of 0–0.3% region of (a), attenuation, 0.05.

height of 18 cm and 1% of the gear oil gives a peak height of 16 cm, almost the same. Evidently, the UV-absorbing species that elute at 18 min and cause the detector response, are also those that influence staining. Therefore, from a practical viewpoint, a peak height of 2 cm at 18 min in a used rolling-oil analysis constitutes a very early warning that contaminant oils are leaking into the rolling oil and signals the need

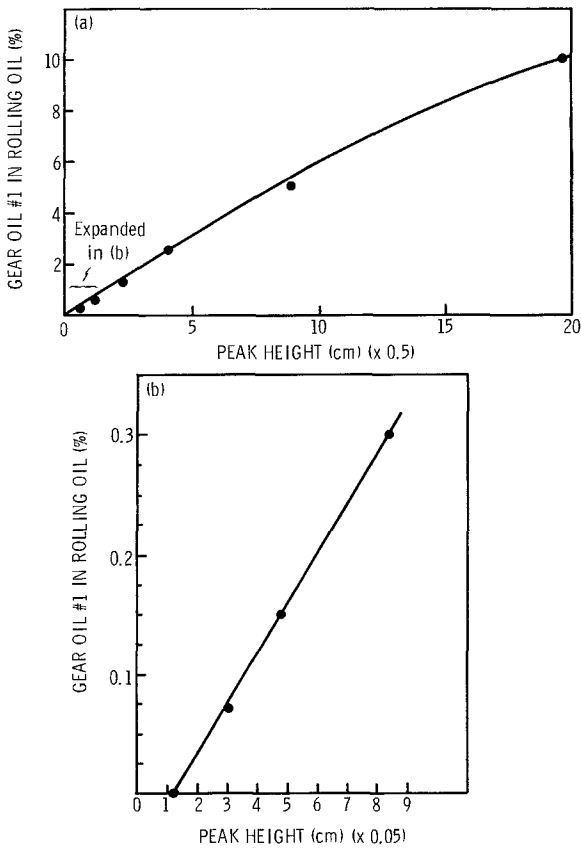


Fig. 3. Concentration of No. 1 gear oil versus peak height. (a) High detector attenuation,  $\times 0.5$ , 0-10%; (b) expanded view of 0-0.3% region of (a).

TABLE II  
RELATIONSHIP BETWEEN 18-min PEAK HEIGHT AND STAINING

<i>Oil contaminant</i>	<i>Peak height of 1% contamination (cm)*</i>	<i>Contamination causing staining (<math>\approx</math>%)</i>	<i>Peak height (approximate) causing staining (cm)</i>
Light hydraulic fluid	1.5	12	18
Hydraulic fluid	2	12	24
Gear oil No. 1	16	2	32
Gear oil No. 2	16	1	16
Machine oil	2.4	8	19

\* 1% peak height, measured by the method indicated on Figs. 1 and 2, from limited data for 0.5% contamination of these oils and corrected by subtracting the baseline height at 0%.

TABLE III  
HPLC CONDITIONS FOR IDENTIFICATION OF MECHANICAL LUBRICANTS

Sample	From HPLC analysis of Table I, 18-min peak is collected and condensed by evaporation of THF under N <sub>2</sub> to ≈4% (v/v) oil in THF, 10 μl
Column	DuPont Zorbax C <sub>18</sub>
Detector	Ultraviolet, 280 nm; typical setting, 0.5 A units
Solvent program	Pump 1, water-THF (60:40), flow program pump 2, 0%-100% THF, No. 6 on a Waters Assoc. Model 660 solvent programmer, in 7 min, flow-rate 1.8 ml/min

for preventive maintenance. Similarly, a peak height of 16 cm at 18 min would indicate that staining is imminent and that a partial dump of the rolling oil should be considered.

#### Identification of contaminant oils

A particular oil is often known to leak into the rolling oil on a given mill. In this case, the purpose of HPLC monitoring of the rolling oil is to determine the

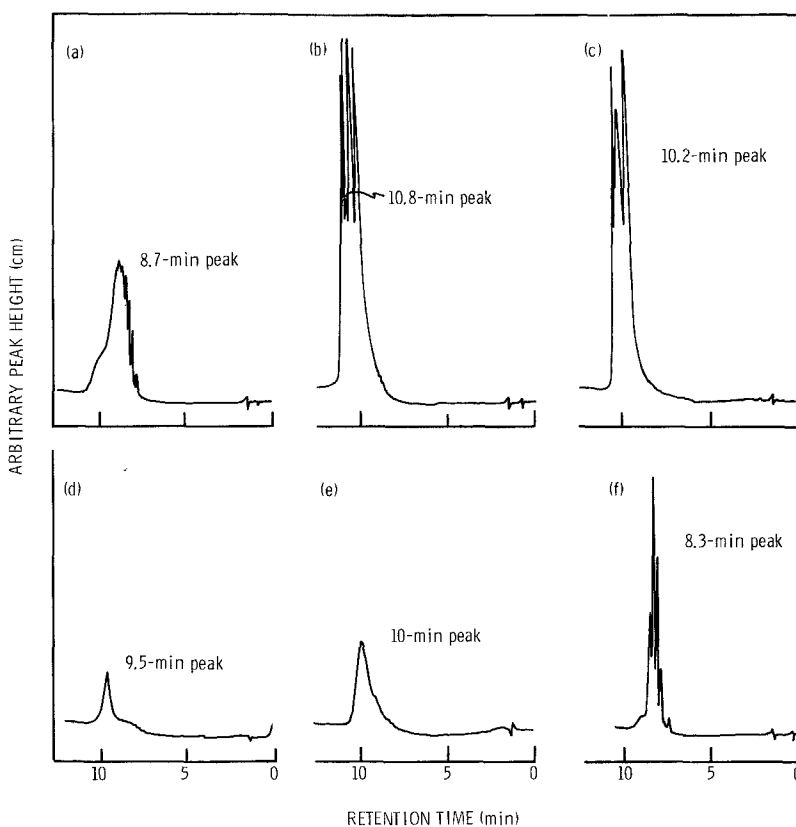


Fig. 4. UV chromatogram (fingerprints).. (a) Light hydraulic fluid; (b) gear oil No. 2; (c) gear oil No. 1; (d) Machine oil; (e) hydraulic fluid; (f) cold rolling oil.

amount of the contaminant oil present and to look for sudden increases that would signal the need for maintenance. However, in cases where more than one oil can significantly contaminate the rolling oil, and in cases where it is necessary to identify the specific contaminant, an additional step is required, whereby the contaminant oil is collected and rechromatographed.

The 18-min peak is collected at the HPLC outlet over a time period predetermined by timing the injection and release of an oil-soluble blue dye. The collected peak is concentrated by approximately ten times by evaporating off the THF solvent under nitrogen, and is then rechromatographed on a C<sub>18</sub> column under the conditions given in Table III. A distinctive chromatographic pattern or a different peak retention time, shown in Fig. 4, is produced for each contaminant oil. The identity of the contaminant, therefore, can be confirmed by comparison with the chromatographic patterns of reference oils. The chromatographic conditions of Table III can also be used to identify mechanical lubricants for other purposes, *e.g.*, verifying drum labels, checking contents of sumps, etc.

The above method for detecting and identifying contaminant oils has proven in the laboratory to be fairly simple and repeatable, providing that the C<sub>8</sub> and C<sub>18</sub> columns are periodically flushed with THF to remove any residual precipitates.

## RESULTS

### *Contamination in used mill oils*

Several used cold rolling oils from an aluminum rolling mill, a used cold rolling oil that had been re-refined, and a new cold rolling oil basestock were analyzed by the above method. The HPLC results were compared with the results of a qualitative stain test. In the qualitative test, 0.8 ml of oil was spread on a standardized aluminum plate and heated in a pre-heated oven at 343°C for 30 min. As indicated in Table IV, the 18-min peak heights of the three oils known to cause staining in the plant were high (19–25 cm). The lower staining oil had a low peak height, and the non-staining re-refined oil had almost a baseline peak. The latter finding indicates that re-refined oils are as good as new oils as far as staining is concerned.

### *Contaminant oil identification*

A used oil was chromatographed under the conditions noted in Table I, then

TABLE IV

CONTAMINATION IN USED MILL OILS AND REFERENCE SAMPLES

<i>Sample</i>	<i>18-min peak height</i>	<i>Stain plate number*</i>
Mill No. 1, A	4.8	2
Mill No. 1, B**	24.6	3
Mill No. 2, A**	18.8	4
Mill No. 2, B**	19.6	4
Re-refined oil	1.7	—
Kerosene base oil, new	1.0 (average, 2 samples)	—

\* High number indicates the tendency to stain on a scale of 1 to 5.

\*\* High contaminant levels in these samples caused staining.

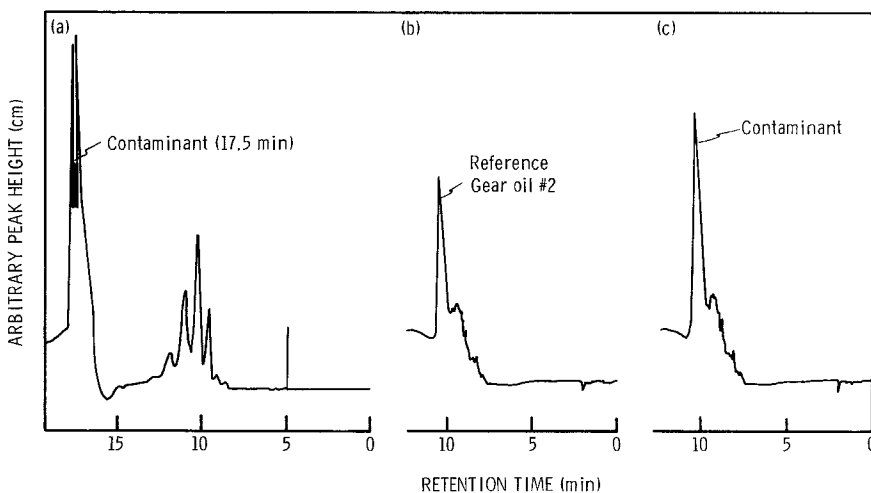


Fig. 5. Fingerprint of contaminant gear oil in used mill oil, B. (a) First run-conditions from Table I; (b) and (c) confirming runs, conditions from Table III.

collected, concentrated  $10\times$ , and rechromatographed under the conditions noted in Table III. The shape of the peak (Fig. 5c) shows that the contaminant is the gear oil No. 2. Referring to the first chromatograph (Fig. 5a), its concentration is approximately 1.5%. This finding is consistent with the plant observation of staining with the rolling oil tested.

#### CONCLUSIONS

Small amounts (as low as 0.03%, w/w) of mechanical lubricants present as contaminants in a cold rolling oil can be detected by reversed-phase HPLC. The individual lubricants can be identified by a second HPLC procedure if necessary. The second procedure is also generally useful for identification of mechanical lubricants.

#### ACKNOWLEDGEMENTS

We thank the management of the Aluminum Division of Martin Marietta Corporation for allowing the publication of this communication. The advice of J. Lewelling of Martin Marietta Aluminum, Lewisport, KY, U.S.A., and the help of J. J. Mills of this laboratory, are also gratefully acknowledged.

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