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Analysis for Acyl Components of Neopentyl Polyol Ester Lubricants

J. G. O'REAR AND P. J. SNIEGOSKI

*Surface Chemistry Branch
Chemistry Division*

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U.S. NAVAL RESEARCH LABORATORY
Washington, D.C.

ABSTRACT

Methods of gas chromatography have been applied to the analysis of acyl components in commercial neopentyl esters and in lubricant formulations derived from such esters. Analysis of the free acids produced by hydrolysis of the samples revealed that the ester lubricants were derived from normal acids ranging from C₅ to C₁₀; iso-valeric acid was present in a few samples. Average acid chain length varied from 5.1 to 7.5. From 20 to 83% of the acyl groups found in the lubricant formulations were from n-valeric acid. All results were in good agreement with previous results obtained by nuclear magnetic resonance spectroscopy.

PROBLEM STATUS

This is an interim report; work is continuing on the problem.

AUTHORIZATION

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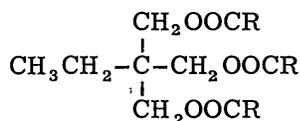
ANALYSIS FOR ACYL COMPONENTS OF NEOPENTYL POLYOL ESTER LUBRICANTS

INTRODUCTION

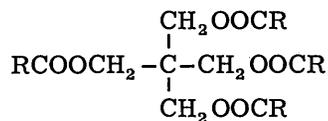
The lubrication requirements of present naval aircraft have led to the specification of a new engine lubricant which is now being used on most naval planes. This oil possesses better oxidative stability, thermal stability, and load-carrying properties, as well as higher viscosity than the previously used oils. It has been found that oils formulated from mono-functional acids with trimethylolpropane, pentaerythritol, and dipentaerythritol can provide the required properties.

Despite the military importance of the neopentyl polyol esters, actual analyses of the commercial products have not been reported. The analysis of the acyl groups and parent polyols present in these commercial lubricants is desirable because the correlation of analytical data with performance data could lead to improved formulations.

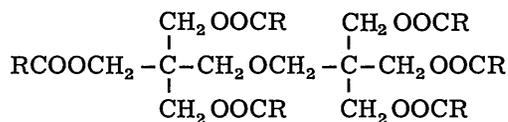
In the general structures of the esters shown below, RCO- represents any acyl group present in a molecule:



Trimethylolpropane Ester



Pentaerythritol Ester



Dipentaerythritol Ester

Many of the esters of the neopentyl alcohols have been prepared and characterized (1-5). Several relationships between structure and properties of these compounds are important in formulating lubricants. The above esters derive their excellent thermal stability from the presence of the neopentyl configuration because the beta carbons of the alcohol portions of these esters contain no hydrogen atoms. Good low-temperature properties can be obtained by preparing the esters from these polyols and a mixture of selected acids.

This report describes a method developed for the analysis of the acyl components of neopentyl polyol esters by gas-liquid chromatography and gives the analytical results obtained on some commercial esters. The results of an analysis of the same samples for polyol type by nuclear magnetic resonance (NMR) (Ref. 6) are also listed as an aid to the interpretation of the data.

EXPERIMENTAL METHOD

Chromatographic Equipment

A Beckman GC-2 gas chromatograph is used with a thermal conductivity detector and a Honeywell Brown Electronik Recorder. The column is a modification of the one described by Metcalfe (7). To a mixture of 6.00 g of diethyleneglycol adipate polyester (HI-EFF 1A, Applied Science Labs, State College, Pa.) and 150 ml of chloroform is added 1.059 g of 85% phosphoric acid. Rapid stirring is continued until the acid is completely dispersed. The solid support, 23.1 g of 60 to 80 mesh, acid-base washed Gas Chrom P (Applied Science Labs), is then stirred into the mixture. After solvent removal by flash evaporation, the packing is tumbled for 2 hours at 200°C and 1 mm and loaded into a 6-ft stainless steel coil of 0.25 in. I.D.

Isolation of the Acids

A 25-g sample of the commercial ester is refluxed for 22 hours in a mixture of 20 g of potassium hydroxide, 40 ml of water, and 150 ml of ethyl alcohol. After water and alcohol have been removed by flash evaporation, a mixture of 28 ml of concentrated hydrochloric acid and 75 ml of water is added. The fatty acids are extracted with two 100-ml portions of ether, and the extract is washed with three 50-ml portions of cold water. The wash water is then extracted with 50 ml of ether. This second ether extract is washed with two 25-ml portions of cold water and added to the main extract. The combined ether solution is dried over anhydrous magnesium sulfate, and solvent is flash evaporated at room temperature. The ether extraction of the water washings is necessary because of the appreciable water solubility of the lower-molecular-weight acids. Experiments with appropriate acid mixtures show that less than one percent of the most water-soluble component present is lost to the water. It was also experimentally determined that the flash evaporation of the ether does not change the relative amounts of acid present.

Analysis of the Acids

Acids obtained from hydrolysis of the commercial samples are identified from their relative retention times, the retention time for valeric acid being taken as unity. Valeric acid is chromatographed prior to each unknown mixture in order to establish this standard time. The values obtained from pure acid samples are listed in Table 1.

The quantitative analysis of the acids is accomplished by normalization of the peak heights of the chromatogram. By the use of chromatograms of synthetic mixtures a correction factor, the peak height per mole of valeric acid divided by the peak height per mole of the component, is determined for each acid. Correction factors are listed in Table 1. By multiplying the peak height of each component in the chromatogram of an unknown sample by the appropriate correction factor, the relative number of moles of the components is found. The mole-percent of a component is equal to 100 times the corrected height of the component divided by the sum of the corrected heights.

Chromatograms were obtained from 1- μ l samples of the acid mixtures. The column temperature was 221°C and the inlet pressure of the helium was 20 psi. The time required to chromatograph a sample was approximately 15 minutes. Table 2 illustrates the calculations and presents the results for one chromatogram.

Table 1
Relative Retention Times and Mole-Height Correction
Factors for Fatty Acids at 221°C on a Diethyleneglycol
Adipate Polyester-Phosphoric Acid Column

Acid	Relative Retention Time	Mole-Ht. Correction Factor
Propionic	0.55	
2,2-Dimethylpropionic	0.59	
Butyric	0.73	
DL-2-Methylbutyric	0.78	0.96
Isovaleric	0.80	0.91
Valeric	1.00	1.00
2-Ethylbutyric	1.04	0.99
2-Methylvaleric	1.05	
4-Methylvaleric	1.20	1.23
Caproic	1.38	1.15
Isoheptanoic	1.64	1.46
2-Ethylhexanoic	1.82	1.32
Heptanoic	1.88	1.38
Octanoic	2.57	1.78
Nonanoic	3.48	2.25
Decanoic	4.74	2.92
Undecanoic	6.40	4.30
Dodecanoic	8.69	5.74

Table 2
Data and Calculations for NRL-S-302

Identified Acid	Observed Relative Retention Time	Peak Height	Corrected Height	Mole %
Valeric	1.00	484.0	484.0	63.9
Caproic	1.36	7.0	8.0	1.1
Heptanoic	1.88	2.9	4.0	0.5
Octanoic	2.57	103.0	183.3	24.2
Nonanoic	3.6	1.4	3.2	0.4
Decanoic	4.74	24.2	70.7	9.3
Undecanoic	6.47	1.0	4.3	0.6

Table 3
Parent Acids and Polyols of Commercial Neopentyl Polyol Ester Lubricants

Sample Designation	Parent Acids (mole-%) According to Number of Carbons							Av. Acid Chain Length*		Parent Polyols† (mole-%)		
	iso-C ₅	C ₅	C ₆	C ₇	C ₈	C ₉	C ₁₀	GLC	NE	PE	DPE	TMP
NRL-S-300		53	14	18	6	9		6.1	6.1	99	1	
NRL-S-301†		49	13	20	7	11		6.2	6.2	100		
NRL-S-302		63	1	1	25		10	6.3	6.2	10	90	
NRL-S-303**	2	58	2		29		9	6.4	6.3		100	
NRL-S-304		98			2			5.1	5.1	96	4	
NRL-S-305		57	10	12	12	6	3	6.1	6.3	82	18	
NRL-S-306		20	2	23	35	1	19	7.5	8.0	3	23	74
NRL-S-307	16	28	1	25	19	1	10	6.6	7.2	83	8	9
NRL-S-308		83	1	1	11		4	5.5	5.6	73	27	
NRL-S-309	20	46			2	31	1	6.4	6.9	87	13	

*As determined by gas-liquid chromatography (GLC) and neutralization equivalent (NE) methods.

†Ref. 6. PE = pentaerythritol, DPE = dipentaerythritol, TMP = trimethylolpropane.

‡Another lot of NRL-S-300.

**Another lot of NRL-S-302.

RESULTS

The results of the acid analysis of the hydrolyzate together with the polyol analysis by NMR (6) are reported in Table 3. Values are averages of two runs rounded off to the nearest percent. The analyses reveal the relative amounts of the acid and polyol parts of the esters, but not the actual ester species present.

The products analyzed are seen to consist of esters of acids from C₅ to C₁₀. Esters of valeric acid are present in substantial amounts for all the products. The only branched acid found was tentatively identified as isovaleric acid. (This branched acid might possibly be DL-2-methylbutyric, which has a similar retention time, but the commercial unavailability of the latter makes its presence unlikely.) The amount of branched acyl groups present in the lubricants is verified by the results of the NMR analysis (6). It should be noted that the inclusion of certain other branched acids would lead to mixtures beyond the resolving power of the chromatographic column used.

NMR data show that the commercial esters examined (NRL-S-300 through -304) are essentially pentaerythritol or dipentaerythritol esters. Each of these polyol esters is derived from a mixture of acids except NRL-S-304, which is mainly pentaerythritol tetra-valerate. The pure compound in this case has a melting point of 6° F (Ref. 3). Experimentally it was difficult to induce crystallization in NRL-S-304, but once frozen, melting did not start until -4° F. No freezing could be induced in NRL-S-300 through -303.

All the lubricant formulations of Table 3 are esters of two or three parent polyols, namely, pentaerythritol, dipentaerythritol, and trimethylolpropane. For the lubricants containing mainly pentaerythritol and dipentaerythritol esters, the average parent acid chain length lies in the rather narrow range of 5.1 to 6.6. Where trimethylolpropane esters predominate, the length is 7.5.

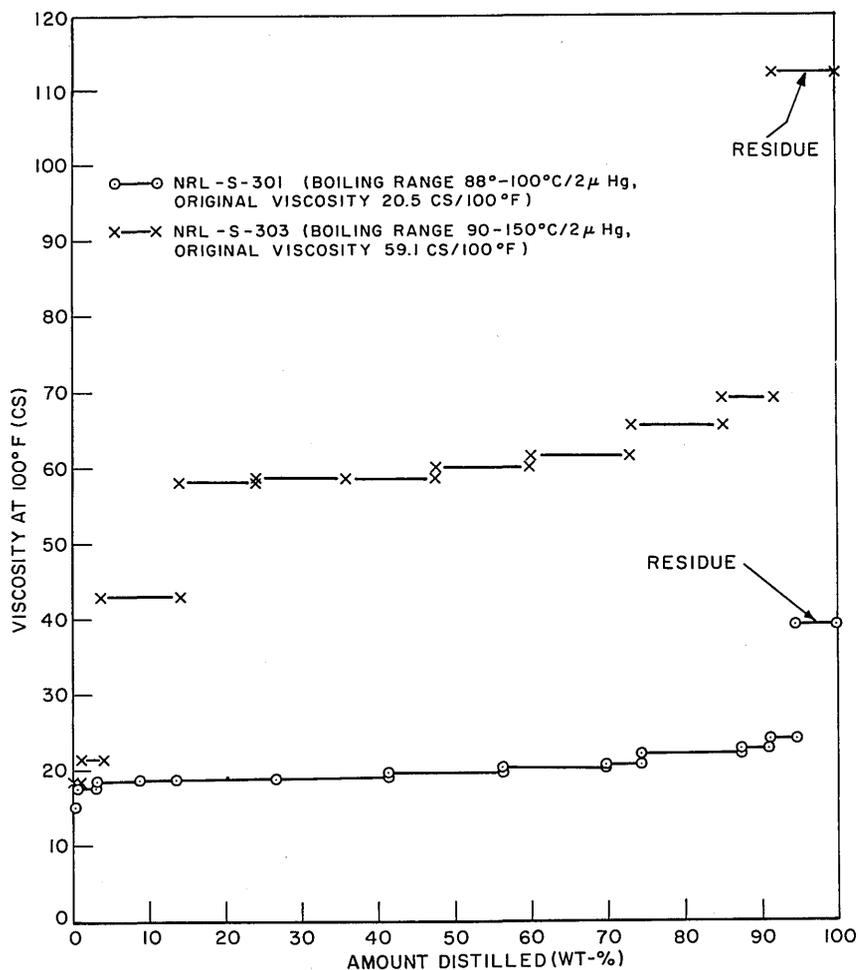


Fig. 1 - Viscosity of distillate fractions

The average chain lengths of the parent acids (Table 3) are calculated from both chromatographic analyses and neutralization equivalents. Almost identical values are obtained for the commercial esters by either method. Deviations are greater for the lubricant formulations, since some contain additives that interfere with the determination of the neutralization equivalent. In the presence of additives, the chromatographic method is considered more reliable. In all cases, the average chain lengths found by gas chromatography closely match those obtained independently by NMR (6).

Samples of NRL-S-301 and NRL-S-303 were fractionated through a CMS-5 molecular still. Analytical data in Table 3 show that the former consists of monopentaerythritol esters and the latter of dipentaerythritol esters. Viscosities of the fractions collected are given in Fig. 1. The center fractions from the monopentaerythritol esters amounting to about 70 wt-% have viscosities ranging from 18.5 to 20.6 cs at 100° F. This viscosity range approximates the viscosity of pentaerythritol tetracaproate, 18.8 cs. The last three fractions (20 wt-%) have viscosities of 22.0 to 23.9 cs reflecting an increasing average acid chain length. The residue with a viscosity of 39.2 cs consists of even higher-molecular-weight esters.

The first two fractions from NRL-S-303 amount to 3.7 wt-%. Their viscosity and boiling range correspond approximately to those of monopentaerythritol caproate. NMR

examination shows these fractions to be 95% monopentaerythritol esters. The third fraction with a viscosity of 43 cs is somewhat less viscous than dipentaerythritol hexacaproate, 53 cs at 100°C. Viscosities of the other fractions correspond to dipentaerythritol esters of acids having an average chain length of 7 and above. The data from Table 3 and Fig. 1 indicate that both the mono- and dipentaerythritol esters were derived from a mixture of acids. The resulting products are mixtures of mixed esters having a statistical distribution of acyl groups.

SUMMARY AND CONCLUSIONS

Acyl components in commercial neopentyl esters and in lubricant formulations derived from such esters were determined by gas-liquid chromatography of the free acids isolated from hydrolysis of the sample. Parent polyol components, determined by NMR and described in Ref. 6, are trimethylolpropane, pentaerythritol, and dipentaerythritol. Acyl components ranged from C₅ to C₁₀ with an average chain length of 5.1 to 7.5. Isovaleric acid was the only branched-chain acid identified. In general, the lubricant formulations were esters derived from several acids and at least two of these polyols.

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