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Determination of the Ester Composition of Neopentyl Polyol Ester Lubricants

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ABSTRACT

Methods of gas-liquid chromatography and thin-layer chromatography have been applied to the analysis of neopentyl polyol ester lubricants. By direct programmed-temperature gas chromatography of the lubricants, the components were separated according to volatility; in most cases resolution was adequate for semiquantitative analysis. Gas-liquid chromatographic analysis of the free acids produced by hydrolysis of the sample revealed the acyl composition. The parent polyols were determined by programmed-temperature gas chromatography of their valerate esters. A semipreparative thin-layer chromatographic method permitted the isolation of the three main ester types—trimethylolpropane, pentaerythritol, and dipentaerythritol for further analysis. By a combination of these analytical methods the actual ester composition of the lubricant may be determined. Such detailed information had not previously been accessible by analytical procedures.

PROBLEM STATUS

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

AUTHORIZATION

NRL Problem C02-01
Project A33-536-501/6521/F012-03-05

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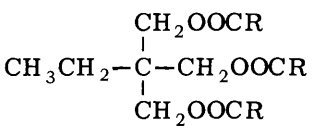
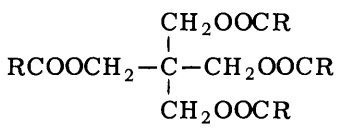
DETERMINATION OF THE ESTER COMPOSITION OF NEOPENTYL POLYOL ESTER LUBRICANTS

INTRODUCTION

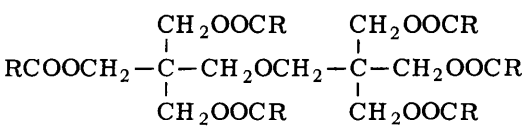
At present, Navy jet-engine lubricants meeting Specification MIL-L-23699 are formulated from esters of the saturated aliphatic monocarboxylic acids (C_4 to C_{10}) and the neopentyl polyols trimethylolpropane (TMP), pentaerythritol (PE), and dipentaerythritol (DPE). The structural formulas of these esters are as follows, where RCO- represents any of the acyl groups.



trimethylolpropane ester



pentaerythritol ester



dipentaerythritol ester

An ester lubricant may be a complicated mixture of many ester species in order to secure a low freezing point. Table 1 illustrates the rapid increase in ester species possible when the polyols are esterified with more than one acid. The calculations are based on the solution to the algebraic problem of determining the number of r combinations of n things when each thing may be repeated any number of times up to r (1):

$$N = \frac{(n + r - 1)!}{r!\,(n - 1)!},$$

where N represents the possible number of ester species when a polyol containing r hydroxyl groups is esterified with n different acids.

Two NRL reports (2,3) have been published that were concerned with the analysis of the acyl groups and the parent polyols of these neopentyl polyol esters. The analytical methods that were developed are suitable for identification, for monitoring base stocks, and for checking blend compositions. By means of these analytical methods it was possible to identify the parent polyols and acids present in a formulation. Since the finished lubricant can be formulated from base stocks prepared separately, it is quite likely that the acyl composition for each polyol type is different. If this is true, the information furnished by these two methods of analysis is not sufficient to establish the ester species actually present. It is possible to conceive of two or more samples having identical acyl and parent polyol analyses but entirely different esters. To be able to show the ester composition of a sample would not only be advantageous for identification purposes but would also allow studies concerning the relative stabilities,

Table 1
The Number of Possible Species of Polyol Esters According to the Number of Acids in the Esterification Mixture

Number of Acids	Possible Number of Species		
	TMP	PE	DPE
1	1	1	1
2	4	5	7
3	10	15	28
4	20	35	84
5	35	70	210
6	56	126	462
7	84	210	924

volatilities, etc., of the different ester species during use. The object of this study was to develop a method of determining the actual ester species present in lubricants formulated from commercially available raw materials.

The decision to use programmed-temperature gas chromatography (PTGC) where the temperature of the chromatographic column is raised systematically during the operation, as an analytical tool for this problem was based on the success of this method in the separation and analysis of mixtures of components or homologs covering a large boiling-point range (4). This report describes the PTGC method and shows how it can be used with other analytical information to determine the ester composition of neopentyl polyol ester lubricants.

EXPERIMENTAL PROCEDURE

Materials

For the preparation of various test mixtures of esters, high-purity (greater than 99%) preparations of TMP (Celanese), PE (Trojan Powder Co.), and DPE (Heyden Chemical) were purchased. The numerous samples for qualitative analysis were prepared by heating a mixture of 0.1g of the polyols, 1g of the acids, and 0.01g of p-toluenesulfonic acid monohydrate on a hot plate for 30 min, just below the reflux temperature. The known lubricant ester mixture was prepared by blending together three materials that had been prepared separately by conventional esterification techniques. Table 2 shows the weight-percent, mole-percent, and acyl composition of each of the blending stocks in the mixture. Also used in this investigation were the commercial esters studied previously at NRL for acyl analysis (2).

Gas-Liquid Chromatography (GLC) of the Esters

Samples of the commercial neopentyl polyol esters, 1 μl of a 10% solution in ether, were chromatographed in a Beckman GC 4 equipped with a thermal conductivity detector and a temperature programmer.

Table 2
Results of the Analysis of the Known Lubricant Mixture

Method of Analysis	Ester Type	Content		Mole-Percent of Acyl Groups According to No. of Carbons			
		Wt-%	Mole-%	5	7	8	10
Calculated	TMP	7.1	10.0	0	100	0	0
TLC-GLC	TMP	9	—	0	100	0	0
Direct PTGC	TMP	—	12* 10†	0	100	0	0
Calculated	PE	40.3	50.0	50	50	0	0
TLC-GLC	PE	41	—	46	53	1	0
Direct PTGC	PE	—	50* 53†	49	51	0	0
Calculated	DPE	52.6	40.0	65	0	25	10
TLC-GLC	DPE	50	—	68	0	22	10
Direct PTGC	DPE	—	38* 37†	66‡	0‡	24‡	10‡

*From peak areas corrected with calibration factors for valerate devrivatives.
†From parent polyol analysis.
‡Found by difference (method given in text).

The stainless-steel GLC columns were 1 ft in length with a 1/8-in. O. D. They contained 3% JXR on 60/80 mesh Gas Chrom Q. The GLC conditions were as follows: an initial temperature of 150°C, a program rate of 9°C per minute, a maximum temperature of 360°C, a vaporization inlet temperature of 370°C, and a helium flow rate of 20 ml per minute.

The columns were previously conditioned by heating them at 360°C for 3 hr with a helium flow rate of 40 ml per minute. The high temperature of the vaporization inlet is necessary for resolution of the DPE components.

Acyl Analysis

A 1-g sample of the ester mixture was refluxed for 16 hr in a mixture of 1 g of potassium hydroxide, 1 g of water, and 20 ml of ethyl alcohol. A portion of the material was evaporated to dryness in a watch glass on a steam bath. The residue was placed in a 3-ml vial, 1 ml of water was added, and the mixture was acidified with concentrated hydrochloric acid. The material was extracted with three 1-ml portions of ether.

Samples of the ether extract were chromatographed using a Beckman GC 4 chromatograph with a thermal conductivity detector. The stainless-steel columns of 1/8-in. O. D. and 6-ft length were packed with 20% diethylene glycol adipate polyester (HI-EFF

1A, Applied Science Laboratories, State College, Pa.) and 3% phosphoric acid on 60/80 mesh Gas Chrom P (Applied Science Laboratories). The column temperature was 180°C, and the helium flow rate was 20 ml per minute. The temperature of the vaporization inlet was 230°C. The quantitative analysis was accomplished by normalization of the peak heights of the chromatogram (2). Calibration factors were determined from known mixtures of the acids.

Parent Polyol Analysis

A mixture of 1 g of the ester sample, 50 ml of methyl alcohol, and 5 ml of concentrated hydrochloric acid was allowed to stand for 16 hr (overnight), and the volatiles were removed by flash evaporation (5). The residue was then heated just below reflux temperature for 20 min with 2 g of valeric acid and 0.1 g of p-toluenesulfonic acid catalyst. The alcoholysis and esterification procedures were then repeated. Samples of the final esterification mixture were chromatographed under the same conditions as the original ester mixture. Calibration factors were determined from known materials. The relative mole-to-peak-area ratios for the valerates of TMP, PE, and DPE were 1.19, 1.00, and 1.36, respectively.

Separation by Thin-Layer Chromatography

The semipreparative thin-layer chromatography (TLC) was carried out on six Merck, 20-by-20-cm precoated TLC plates of 0.25-mm silica-gel layers. In a straight line 2cm from the side of a plate, the ester was applied from a 10-μl syringe as small, closely spaced spots (1.5 μl) of a 25% solution in heptane. The plates were developed in a tank containing a solution of heptane-acetone (95:5) until the liquid front had risen approximately 10 cm (in approximately 1/2 hr). After they had been dried, the plates were lightly sprayed with a 0.2% solution of dibromofluorescein in ethyl alcohol and viewed under long-wave ultraviolet light. The R_f values (the ratios of the distances traveled by the substances to the distance traveled by the solvent front) for the TMP, PE, and DMP esters were approximately 0.50, 0.35, and 0.15, respectively. The areas of the respective components were scraped off of the plates and combined. The combined samples of each individual component were extracted with acetone, evaporated to dryness, and weighed. For further analysis the residues were saponified, and the acyl content was determined as described previously.

RESULTS AND DISCUSSION

By means of the PTGC procedure described, TMP, PE, and DPE esters of monofunctional acids from C_4 to C_{10} were eluted within 25 min. The three homologous ester series of the three polyols were prepared and chromatographed. The chromatogram of the consecutive members of each of the series showed that the spacing of the peaks is an approximate arithmetic series with the same temperature increase between each succeeding member (4). The members of each series are referred to by their acyl carbon number, which is the number of acyl carbons in the ester molecule. The acyl carbon number, therefore, does not identify specific acyl groups on the ester. In Table 3 a partial tabulation of the observed retention temperatures of known samples shows that there is some overlapping in the three series of esters. The resolution of the TMP and PE components was adequate for semiquantitative analysis. However, because of the poorer resolution of the DPE components, the relative amounts of such components differing by one carbon number can only be approximated.

Table 3
Retention Temperatures for the
Neopentyl Polyol Esters

Acyl Carbon Number	Retention Temperature (°C)		
	TMP	PE	DPE
15	182	—	—
20	220	212	—
25	246	247	—
30	270	272	282
35	—	289	300
40	—	306	318
45	—	—	332
50	—	—	347

By combining information concerning the acyl groups and the parent polyols, much of the ambiguity of the chromatogram can be removed. Analysis of acyl groups was carried out by the method previously developed at NRL (2) with slight modifications. Instead of analyzing for the parent polyols by the NMR method (3) also developed at NRL, the valerate derivatives were analyzed by GLC under the same conditions as for the original esters. Other polyol derivatives, such as the acetates (6) and the trimethylsilyl ethers (7), could be used but with different GLC conditions. Parent polyol content can also be estimated by comparing the corrected areas under the chromatogram associated with each polyol type. The correction factors derived for the valerate esters were adequate for this purpose. The separation of the ester mixtures into the three polyol types by TLC, based on the method of Green and Ravner (8), followed by acyl analysis, led to the determination of the kinds and relative numbers of acyl groups in each ester family but did not show, in general, the presence of any specific ester. The method is extremely helpful for analyzing mixtures in which the overlapping of chromatographic peaks is extensive. A weighing of the components separated by TLC also furnishes a method of determining the amount of each polyol type present.

It is found that on esterification of a neopentyl polyol with a mixture of normal acids from C_4 to C_{10} the distribution of the acyl groups is approximately a random one. This has been determined by a comparison of the percent peak areas or percent peak heights of the chromatographic peaks of known materials with the calculated random probabilities of forming the different ester combinations. Calculations are based on the multinomial distribution formula (9)

$$P = 100 \left[\frac{n!\, p_1^{k_1}\, p_2^{k_2} \ldots p_r^{k_r}}{k_1!\, k_2! \ldots k_r!} \right],$$

where P is the mole-percent of the ester species, n is the number of acyl groups in one molecule of the polyol ester, the p's are the acyl-group fractions (the number of acyl groups of a given kind divided by the total number of acyl groups in the ester mixture), and the k's are the numbers of times the specified acyl groups are present in a molecule of the ester.

Table 4 illustrates this random distribution of the acyl groups for the PE portion of a commercial raw material. The random probabilities of all 70 possible combinations were calculated and tabulated under the 17 possible acyl carbon numbers. As a sample calculation, the probability of forming the acyl carbon number 22 is the sum of the probabilities of forming the two acyl combinations 5557 and 5566. Therefore,

$$P_{PE22} = 100 \left[\frac{4!\,(0.53)^3\,(0.18)}{3!} + \frac{4!\,(0.53)^2\,(0.14)^2}{2!\quad 2!} \right],$$

$$= 10.7 + 3.3 = 14.0 .$$

These values, when compared with the mole-percents as estimated from the percent peak heights of the chromatogram, are seen to agree closely. Similar comparisons for TMP and DMP mixed esters also showed such a random distribution. Computer programs have been set up for calculating the probabilities of the random distribution. The programs are included in Appendix A.

Table 4
Analysis of the Penthaerythritol Esters of a Commercial Base Stock

Method of Analysis	Distribution of Esters (Mole-%) According to Acyl Carbon Numbers																
	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36
Found	10.8	9.9	14.0	12.8	14.4	11.3	10.3	6.4	5.4	2.5	1.3	0.5	0.3	0.1	–	–	–
Random (calc.)*	7.89	8.34	12.02	12.65	15.93	11.72	10.80	6.94	5.45	2.87	1.85	0.83	0.46	0.15	0.07	0.02	0.01

*The parent acid analysis in mole-% was 53 for C_5, 14 for C_6, 18 for C_7, 6 for C_8, and 9 for C_9.

Several of the ester mixtures examined contained a branched C_5 acyl group which gave chromatographic behavior corresponding to a carbon number increment of about 4.5 under the conditions of the PTGC. Ester mixtures containing this branched C_5 group along with normal C_5 groups were so poorly resolved that little information concerning the distribution of this branched group could be obtained.

A number of neopentyl polyol ester mixtures has been successfully analyzed by the methods described. In general, the acyl makeup was found to be different for each parent polyol in a blended lubricant, as would be expected if the polyols had not been esterified together. Complexity of the lubricants analyzed ranged from a mixture with five species to one with more than a hundred.

To illustrate the analysis, a sample of known composition was blended as described in the experimental section. The composition of this mixture is given in Table 2; it does not correspond to Specification MIL-L-23699 lubricants except in types of esters and complexity.

All of the analytical procedures described in the experimental section were carried out on this ester mixture. Results of the acyl analysis and parent polyol analysis given in Table 5 illustrate the degree of accuracy that can be expected. Results of the TLC procedure shown in Table 2 indicate that the three polyol components were not completely separated by this procedure. In the separated PE component the extra C_7 acyl groups must have come from the TMP ester and the C_8 groups from the DPE esters. The work of Green and Ravner (8) indicated that as the average acyl chain length increases within each polyol type the compound moves further up the chromatogram during the

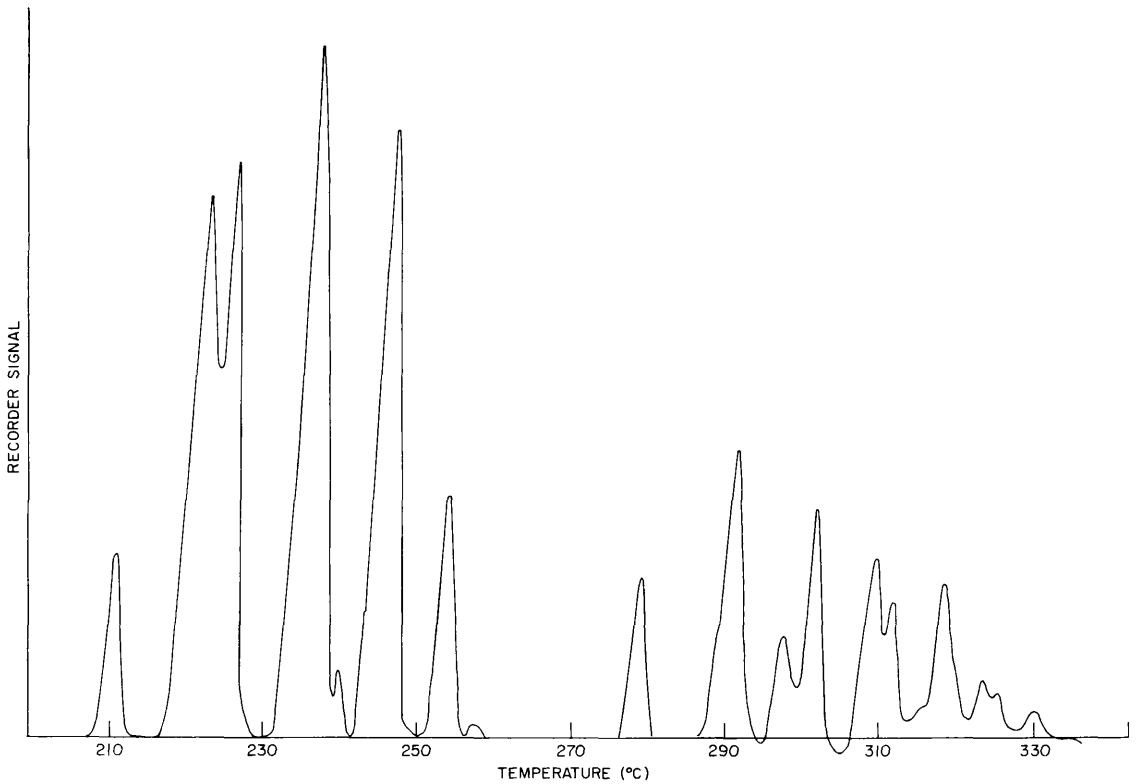


Fig. 1 - Chromatogram of known lubricant mixture

development time. Therefore, for certain compositions, resolution of the three components will be incomplete. In the example the overlap was not excessive; observation of the visualized chromatogram will indicate to a large extent the effectiveness of the separation.

From Fig. 1, the chromatogram of the known lubricant mixture, the retention times of the first six peaks together with the results of the acyl and parent polyol analysis (Table 5), indicate PE ester components of C_5 and C_7 acyl groups and a TMP C_7 ester. The peak areas assigned to the PE components agree better (as indicated by average deviation calculations) with a random distribution of 49 mole-% of C_5 acyl groups and 51 mole-% of C_7 acyl groups than with that of a 50-50 mixture (Table 6). The composition of the DPE esters can be estimated by a subtraction process. From the acyl contents found for the blend (Table 5) are subtracted the corresponding acyl contents for 10 mole-% of a TMP C_7 ester and for 53 mole-% of a PE ester with a composition of 49 mole-% C_5 and 51 mole-% C_7 acyl groups. The remaining acyl groups are contained in the 37 mole-% of DPE esters, as shown in Table 2. Agreement is good between the calculated random distribution of acyl groups using the values obtained from the subtraction method and those estimated from the chromatogram (Table 7). Acyl composition for each polyol type by two independent methods agrees quite well with the calculated values (Table 2).

In some cases, the actual breakdown of the lubricant mixture into ester species may not be required. The procedure for the direct GLC of the esters finds use in determining whether two samples are identical. In this method the peaks of the two chromatograms

are compared without the actual identification of the components. The preferential loss of components during engine lubricant service has been clearly revealed in several cases where a sample of the original unused material could be obtained for comparison with the used oil. If information concerning the distribution of the ester components is not necessary, only the TLC procedure of determining the weight-percents and acyl makeup of the polyol need be used.

Table 5
Parent Acid and Polyol Analyses of Synthetic Lubricant Mixture

Mole-Percent of Acid	Parent Acid According to No. of Carbons			
	5	7	8	10
True	54.5	27.6	12.8	5.1
Found	56	27	12	5

Mole-Percent of Polyols	Parent Polyols		
	TMP	PE	DPE
True	10.0	50.0	40.0
Found	10	53	37

Table 6
Distribution of PE Ester Species in the Synthetic Mixture

Method of Analysis	Distribution of PE Ester Species (Mole-%) According to Acyl Carbon Numbers				
	20	22	24	26	28
Found	6.1	25.5	34.2	26.4	7.8
Random*	5.76	24.00	37.47	26.00	6.77
Random†	6.25	25.00	37.50	25.00	6.25
Acyl combination	5555	5557	5577	5777	7777

*Calculated for acyl composition 49% C_5 and 51% C_7.
† Calculated for "True" acyl composition 50% C_5 and 50% C_7.

Table 7
Distribution of DPE Ester Species in the Synthetic Mixture

Method of Analysis	Distribution of DPE Ester Species (Mole-%) According to Acyl Carbon Numbers*				
	30	33	35	36	38
Found	11	25	7	17	12
Random †	8.26	18.03	7.51	16.39	13.66
Random ‡	7.54	17.40	6.96	16.74	13.39
Acyl combination	555555	555558	5555510	555588	5555810

*Only the first five carbon numbers are considered.
†Calculated for an acyl composition 66% C_5, 24% C_8, and 10% C_{10}.
‡Calculated for the "true" acyl composition 65% C_5, 25% C_8, and 10% C_{10}.

SUMMARY AND CONCLUSIONS

By means of the procedures of GLC and TLC described in this report, neopentyl polyol ester lubricants may be analyzed for acyl and parent polyol content, distribution of components according to volatility, and the acyl content of each of the polyol type esters. From this information the ester composition of the mixture may be determined. These analytical methods should be of use not only for problems of identification, of monitoring base stocks, and of checking composition but also in detecting changes that occur during performance. Studies of changes in lubricant composition due to pyrolysis, oxidation, or evaporation could lead to the formulation of better products.

ACKNOWLEDGMENT

The author thanks Mr. Robert N. Bolster of the Surface Chemistry Branch, Chemistry Division, NRL, for writing the Fortran programs for the calculation of the probabilities of ester formation.

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Appendix A

COMPUTER PROGRAMS FOR THE CALCULATION OF ESTER FORMATION PROBABILITIES ACCORDING TO ACYL CARBON NUMBER

These programs are written in Fortran for use with the CDC 3800 computer at NRL. Esterifications of TMP, PE, or DPE with any mixture of acids from C_4 to C_{10} are considered. The random probabilities of the formation of esters according to their acyl carbon number are calculated and expressed as mole fractions. The amounts of the acids found in the esterification mixture are entered on the data cards as decimal fractions. For illustration, the acid mixture found by the acyl analysis of Table 4 is entered in each program as the last line.

Printouts for the three examples are included.

```
C     ESTER COMBINATION PROBABILITIES FOR TRIMETHYLOLPROPANE
        PROGRAM TMOP 7
        DIMENSION G(10)
        DIMENSION PROB(40)
        READ 29,G(4),G(5),G(6),G(7),G(8),G(9),G(10)
     29 FORMAT(7F5.3)
        PRINT 40,G(4),G(5),G(6),G(7),G(8),G(9),G(10)
     40 FORMAT(7F7.3)
        KA=KB=KC=4
        KWT=0
        PRT=0
        DO 1 I=12,30
      1 PROB(I)=0
      2 IF((KA.EQ.KB).AND.(KA.EQ.KC))3,4
      3 P=(G(KA))**3*100
        GO TO 20
      4 IF(KA.EQ.KB)5,6
      5 P=300*(G(KA))**2*G(KC)
        GO TO 20
      6 IF(KB.EQ.KC)7,8
      7 P=300*(G(KA))*(G(KB))**2
        GO TO 20
      8 P=600*G(KA)*G(KB)*G(KC)
     20 KWT=KA+KB+KC
        PROB(KWT)=PROB(KWT)+P
        KC=KC+1
        IF(KC.EQ.11)18,2
     18 KC=KB=KB+1
        IF(KB.EQ.11)9,2
      9 KC=KB=KA=KA+1
        IF(KA.EQ.11)10,2
     10 PRINT 11
        PRINT 27
     27 FORMAT(33H ACCUMULATED TOTAL PROBABILITIES   )
        PRINT 11
     11 FORMAT(X)
        PRINT 12
```

```
   12 FORMAT(10X,27H    WT     P PCT       PT PCT    )
      DO 13 I=12,30
      PRINT 25,I,PROB(I)
   25 FORMAT(10X,I5,F11.6)
   13 PRT=PRT+PROB(I)
      PRINT 26,PRT
   26 FORMAT(26X,F11.6)
      END
0.00 0.53 0.14 0.18 0.06 0.09 0.00

C    ESTER COMBINATION PROBABILITIES FOR PENTAERYTHRITOL
      PROGRAM PE 7
      DIMENSION G(10)
      DIMENSION PROB(70)
      INTEGER AR(10),COUNT(10)
      L=4
      PT=0
      DO 28 I=1,L
   28 AR(I)=4
      READ 29,G(4),G(5),G(6),G(7),G(8),G(9),G(10)
   29 FORMAT(7F5.3)
      PRINT 40,G(4),G(5),G(6),G(7),G(8),G(9),G(10)
   40 FORMAT(7F7.3)
      DO 2 I=16,40
    2 PROB(I)=0
   16 KA=AR(1)$ KB=AR(2)$ KC=AR(3)$ KD=AR(4)
      DO 3 K=1,8
    3 COUNT(K)=1
      J=0
    4 J=J+1
      IF(J.EQ.L)12,5
    5 IF(AR(J).EQ.0)4,6
    6 K=J
    7 K=K+1
      IF(K.GT.L)4,8
    8 IF(AR(K).EQ.0)7,9
    9 IF(AR(K).EQ.AR(J))10,11
   10 COUNT(J)=COUNT(J)+1
      AR(K)=0
   11 GO TO 7
   12 ITOT=1
      DO 13 I=1,L
      KDUM=COUNT(I)
      ITOT=JFACT(KDUM)*ITOT
   13 CONTINUE
      P=2400*G(KA)*G(KB)*G(KC)*G(KD)/ITOT
      KWT=KA+KB+KC+KD
      PROB(KWT)=PROB(KWT)+P
      AR(1)=KA$ AR(2)=KB$ AR(3)=KC$ AR(4)=KD
      AR(4)=AR(4)+1
      IF(AR(4).EQ.11)15,16
   15 AR(4)=AR(3)=AR(3)+1
      IF(AR(3).EQ.11)17,16
   17 AR(4)=AR(3)=AR(2)=AR(2)+1
      IF(AR(2).EQ.11)18,16
   18 AR(4)=AR(3)=AR(2)=AR(1)=AR(1)+1
      IF(AR(1).EQ.11)19,16
   19 PRINT 20
   20 FORMAT(X)
      PRINT 21
   21 FORMAT(33H ACCUMULATED TOTAL PROBABILITIES   )
      PRINT 25
```

```
   25 FORMAT(35X,27HWT          P PCT     PT PCT     )
      PRT=0
      DO 23 I=16,40
      PRINT 22,I,PROB(I)
   22 FORMAT(31X,I6,4X,F11.6)
   23 PRT=PRT+PROB(I)
      PRINT 24,PRT
   24 FORMAT(52X,F11.6)
      END
      FUNCTION JFACT(JARG)
      KFACT=1
      LF=1
   25 LF=LF+1
      IF(LF.GT.JARG)27,26
   26 KFACT=KFACT*LF
      GO TO 25
   27 JFACT=KFACT
      RETURN
      END
0.00 0.53 0.14 0.18 0.06 0.09 0.00

C    ESTER COMBINATION PROBABILITIES FOR DIPENTAERYTHRITOL
      PROGRAM DPE 7
      DIMENSION G(10)
      DIMENSION PROB(70)
      INTEGER AR(10),COUNT(10)
      L=6
      PT=0
      DO 28 I=1,L
   28 AR(I)=4
      READ 29,G(4),G(5),G(6),G(7),G(8),G(9),G(10)
   29 FORMAT(7F5.3)
      PRINT 40,G(4),G(5),G(6),G(7),G(8),G(9),G(10)
   40 FORMAT(7F7.3)
      DO 2 I=24,62
    2 PROB(I)=0
   16 KA=AR(1)$ KB=AR(2)$ KC=AR(3)$ KD=AR(4)$ KE=AR(5)$ KF=AR(6)
      DO 3 K=1,8
    3 COUNT(K)=1
      J=0
    4 J=J+1
      IF(J.EQ.L)12,5
    5 IF(AR(J).EQ.0)4,6
    6 K=J
    7 K=K+1
      IF(K.GT.L)4,8
    8 IF(AR(K).EQ.0)7,9
    9 IF(AR(K).EQ.AR(J))10,11
   10 COUNT(J)=COUNT(J)+1
      AR(K)=0
   11 GO TO 7
   12 ITOT=1
      DO 13 I=1,L
      KDUM=COUNT(I)
      ITOT=JFACT(KDUM)*ITOT
   13 CONTINUE
      P=72000*G(KA)*G(KB)*G(KC)*G(KD)*G(KE)*G(KF)/ITOT
      KWT=KA+KB+KC+KD+KE+KF
      PROB(KWT)=PROB(KWT)+P
      AR(1)=KA$ AR(2)=KB$ AR(3)=KC$ AR(4)=KD$ AR(5)=KE$ AR(6)=KF
      AR(6)=AR(6)+1
      IF(AR(6).EQ.11)141,16
```

```
  141 AR(6)=AR(5)=AR(5)+1
      IF(AR(5).EQ.11)142,16
  142 AR(6)=AR(5)=AR(4)=AR(4)+1
      IF(AR(4).EQ.11)15,16
   15 AR(6)=AR(5)=AR(4)=AR(3)=AR(3)+1
      IF(AR(3).EQ.11)17,16
   17 AR(6)=AR(5)=AR(4)=AR(3)=AR(2)=AR(2)+1
      IF(AR(2).EQ.11)18,16
   18 AR(6)=AR(5)=AR(4)=AR(3)=AR(2)=AR(1)=AR(1)+1
      IF(AR(1).EQ.11)19,16
   19 PRINT 20
   20 FORMAT(X)
      PRINT 21
   21 FORMAT(33H ACCUMULATED TOTAL PROBABILITIES   )
      PRINT 25
   25 FORMAT(35X,27HWT          P PCT     PT PCT     )
      PRT=0
      DO 23 I=24,60
      PRINT 22,I,PROB(I)
   22 FORMAT(31X,I6,4X,F11.6)
   23 PRT=PRT+PROB(I)
      PRINT 24,PRT
   24 FORMAT(52X,F11.6)
      END
      FUNCTION JFACT(JARG)
      KFACT=1
      LF=1
   25 LF=LF+1
      IF(LF.GT.JARG)27,26
   26 KFACT=KFACT*LF
      GO TO 25
   27 JFACT=KFACT
      RETURN
      END
0.00 0.53 0.14 0.18 0.06 0.09 0.00
```

The computed distributions resulting from the acid mixture given are as follows for the three polyols considered:

Trimethylolpropane

WT	P PCT
12	0.000000
13	0.000000
14	0.000000
15	14.887700
16	11.797800
17	18.285000
18	13.344200
19	16.465500
20	9.154800
21	7.743600
22	3.812400
23	2.810700
24	0.945000
25	0.534600
26	0.145800
27	0.072900
28	0.000000
29	0.000000
30	0.000000

Pentaerythritol

WT	P PCT
16	0.000000
17	0.000000
18	0.000000
19	0.000000
20	7.890481
21	8.337112
22	14.022528
23	12.649192
24	15.933964
25	11.718072
26	10.795872
27	6.941448
28	5.448438
29	2.869128
30	1.847232
31	0.833976
32	0.464940
33	0.153576
34	0.069984
35	0.017496
36	0.006561
37	0.000000
38	0.000000
39	0.000000
40	0.000000

Dipentaerythritol

WT	P PCT
24	0.000000
25	0.000000
26	0.000000
27	0.000000
28	0.000000
29	0.000000
30	2.216436
31	3.512842
32	6.836313
33	8.287744
34	11.394725
35	11.490986
36	12.267928
37	10.704595
38	9.722687
39	7.420184
40	5.815648
41	3.938556
42	2.727077
43	1.629456
44	0.995289
45	0.526017
46	0.284551
47	0.129812
48	0.061389
49	0.023858
50	0.009712
51	0.002937
52	0.000992
53	0.000213
54	0.000053
55	0.000000
56	0.000000
57	0.000000
58	0.000000
59	0.000000
60	0.000000

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13. ABSTRACT

Methods of gas-liquid chromatography and thin-layer chromatography have been applied to the analysis of neopentyl polyol ester lubricants. By direct programmed-temperature gas chromatography of the lubricants, the components were separated according to volatility; in most cases resolution was adequate for semiquantitative analysis. Gas-liquid chromatographic analysis of the free acids produced by hydrolysis of the sample revealed the acyl composition. The parent polyols were determined by programmed-temperature gas chromatography of their valerate esters. A semipreparative thin-layer chromatographic method permitted the isolation of the three main ester types—trimethylol propane, pentaerythritol, and dipentaerythritol for further analysis. By a combination of these analytical methods the actual ester composition of the lubricant may be determined. Such detailed information had not previously been accessible by analytical procedures.

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Pentaerythritol						
Dipentaerythritol						

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