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ULTRASYSTEMS, INC.

USBM CONTRACT ANNUAL REPORT
CONTRACT No. H0133004

September 1976

DEPARTMENT OF THE INTERIOR
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# FOREWORD

This report was prepared by Ultrasystems, Inc., Chemicals and Materials Research Department, Irvine, California, under USBM Contract No. HO133004. The investigations were performed by K. L. Paciorek, program manager, R. H. Kratzer, J. Kaufman, and J. H. Nakahara with assistance from A. C. Jones. The contract was initiated under the Coal Mine Health and Safety Research Program. It was administered under the technical direction of the Pittsburgh Mining and Safety Research Center with Mr. T. Christos acting as the technical project officer. Mr. Larry L. Rock was the contract administrator for the Bureau of Mines.

This report is a summary of the work recently completed as part of this contract during the period 14 October 1975 to 15 September 1976.

In view of the analytical nature of the work performed no subject inventions were made under this program.

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# I. ABSTRACT AND SUMMARY

The aim of this program was to develop a reliable and meaningful basis for assessing certain safety aspects, namely fire and, in particular, toxicity hazards of articles employed in underground coal mining operations. The present investigation was concentrated on the thermal oxidative degradation of representative hydraulic fluids.

To achieve this goal all products formed on thermal oxidative degradation of the fluids studied were analyzed, identified, and the amount of each individual species present was determined quantitatively on a weight of product per weight of material basis. The weight/weight data thus obtained can then be factorized to reflect the relative toxicity of each individual species present, using for example the Threshold Limit Values adopted by the American Conference of Governmental and Industrial Hygienists, whereby an overall "toxicity index" can be arrived at which makes it possible to compare the different fluids and/or classes of fluids in a quantitative manner insofar as their toxicity is concerned.

For these studies a quiescent system was employed and all the materials were treated for 30 min in air at 370°C. Selected fluids, which failed to be affected significantly at 370°C were also subjected to thermal oxidative degradation at 400-420°C. Differential thermal analyses were performed to supplement and extend the sealed system investigations and to provide information regarding thermal oxidative behavior under dynamic conditions.

The selection of materials was based on the list of fire resistant hydraulic fluids approved by the Bureau of Mines under Schedule 30 for underground use. The listed fluids comprise five broad groups or classes: (i) glycol-water solutions, (ii) mineral

oil-water emulsions, (iii) synthetics other than phosphate esters, (iv) synthetic phosphate esters, (v) mixtures of phosphate esters with mineral oils and chlorinated solvents. At least one representative composition of each class was investigated.

Three glycol-water based hydraulic fluids, Ucon Hydrolube 275 CP, Citgo Glycol FR-20XD and SNFH fluid were subjected to thermal oxidative degradation. None of these, under the test conditions employed, afforded large quantities of toxic products. Although for Ucon Hydrolube 41 components were identified in the volatiles only traces of toxic species were found, these were: carbon monoxide (TLV, 55 mg/m$^3$), formic acid (TLV, 9 mg/m$^3$), acetic acid (TLV, 25 mg/m$^3$), acetonitrile (TLV, 70 mg/m$^3$) and ethylene oxide (TLV, 90 mg/m$^3$). Similarly, in the case of Citgo Glycol FR-20XD a total of 36 degradation products was identified and quantitated, yet only traces of toxic compounds such as carbon monoxide, acetonitrile and ethylene oxide were found. In the case of SNFH fluid the most toxic component found among the 31 compounds formed was acrolein (TLV, 0.25 mg/m$^3$). The latter is most likely derived from propylene glycol which is, together with ethylene glycol, the glycol constituent of this fluid. No acrolein was detected in the other two fluids which were composed essentially of ethylene glycol and water. Thus it can be speculated that the presence of propylene glycol provides the inherent potential for acrolein production. It can be furthermore speculated that substantial quantities of acrolein may have been formed to allow its detection in the predominantly aqueous system.

Duro FR-HD fluid was the only mineral oil-water composition studied. Under the test conditions employed it lost all of its water into the volatiles; the residue consisted essentially of the mineral oil component. The extent of the oxidation was relatively minor; the products derived from the mineral oil portion of the fluid amounted to 4% of the volatiles collected. A total of 41 compounds were identified and quantitated. The main toxic species found were carbon monoxide and acrolein. The ready volatilization of water, which is the fire retardant ingredient of this fluid, indicates the potential combustion hazard of this composition.

The synthetic aliphatic ester type hydraulic fluid, Quintolubric 822-300, was tested at 370 and 420°C inasmuch as at the lower temperature the extent of decomposition was very low (3.3%). In the volatiles formed following the treatment at 370°C, 52 species were identified and quantitated; traces of toxic compounds such as acrolein, carbon monoxide and benzene (TLV, 30 $mg/m^3$) were detected; the potential presence of formic acid was indicated by traces of methyl formate. At 420°C the extent of degradation was increased by a factor of two; again only traces of toxic species, namely carbon monoxide, benzene, acrolein and formic acid, were detected among the 48 species which were identified and quantitated. The higher degradation temperature apparently reduced the relative proportion of the aliphatics and increased the production of aromatics.

The phosphate ester type compositions present an entirely different system as compared to the other groups of fluids. The four phosphate ester based fluids: Fyrquel 220, Pydraul 50E, Pydraul MC and Dasco FR 300 were studied at two temperatures, 370 and 400-420°C due to the low degree of decomposition at 370°C and production of the highly toxic phosphine (TLV, 0.4 $mg/m^3$) by some of these materials at temperatures around 400°C. The major toxic species formed by all these compositions were phenolic moieties.

For Fyrquel 220 at 370°C a total of 44 compounds were identified and quantitated. The major toxic species were phenol (TLV, 19 mg/m$^3$), cresols (TLV, 22 mg/m$^3$), and to a much smaller degree sulfur-containing species, hydrogen sulfide (TLV, 15 mg/m$^3$) and sulfur dioxide (TLV, 13 mg/m$^3$) in addition to diphenyl (TLV, 1 mg/m$^3$). The phenolic species amounted to 60.3% of the collected volatiles. At 420°C the phenolic species constituted 72% of the collected volatiles and added up to 5.69 mg/g as compared to 3.26 mg/g found at 370°C.

In the case of Pydraul 50E at 370°C among the total of 38 compounds identified and quantitated phenol, which amounted to 42% of the volatiles collected, was the major toxic component accompanied by traces of carbon monoxide and acrolein. At 420°C the quantity of phenol collected increased by a factor of 5 to 34.1 mg/g and it accounted for 50% of the volatiles.

Pydraul MC at 370°C afforded a product mix comparable to that found for Pydraul 50E, although the content of aliphatics derived from the mineral oil constituent was higher. Phenol was the major toxic component (10.3 mg/g) accompanied by traces of carbon monoxide and sulfur dioxide. As in the case of Pydraul 50E at 410°C the quantity of phenol produced increased substantially, approximately six-fold. In addition, the highly toxic phosphine was also formed and at 2.78 mg/g it presented a higher toxic hazard than phenol at 66.3 mg/g.

For Dasco FR 300 at 370°C a total of 56 compounds was identified and quantitated. The toxic species found were carbon monoxide, acrolein, allyl alcohol (TLV, 5 mg/m$^3$), phenol, carbon disulfide (TLV, 60 mg/m$^3$), cresols, and hydrogen sulfide. Since large quantities of propionaldehyde were produced a common precursor would be expected also for acrolein and allyl alcohol. However, the actual ingredient from which these three carbon compounds are derived is unknown. Conducting the degradation process at 400°C failed to afford more extensive degradation and no increase in phenolic species was observed; however, phosphine was detected among the volatiles. Pydraul MC and Dasco FR 300 contain other ingredients, in addition to phosphate esters, mineral oil being one of them, and it is apparently interaction of these with the phosphate esters which results in the production of phosphine. This was proven by thermal oxidative degradation of a synthetic triphenylphosphate/octacosane mixture, which at 404°C did produce phosphine.

Considering the extent of degradation at 370°C and even above 400°C it is apparent that "pure" phosphate esters derived from substituted phenols represent probably the least dangerous of all the compositions tested under this program insofar as flammability and the overall toxicity of the degradation products are concerned, even though these "pure" phosphate esters evolve toxic phenolic species. On the other hand "hydrocarbons" can act as reducing agents towards the phosphate moiety which results in the production of the highly toxic and volatile phosphine. The question remains whether in the case of overheating or a fire, coal itself might not act as a reducing agent.

## 2. INTRODUCTION

Modern mining relies more and more on mechanical devices which require hydraulic fluids, oils and lubricants. Thus fire retardant fluids are being used increasingly underground in mining machinery, hydraulic jacks, drilling equipment, and many other operations. In view of the present energy situation coal is becoming of primary importance as an energy source. To produce coal economically requires increased use of machinery underground as represented by, e.g., the mechanical miner, and this in turn necessitates increased introduction of the various fluids into the mines. It is noteworthy that apparently one gallon of hydraulic fluid or fluids is lost per 10 tons of coal mined; these are significant amounts and it is thus imperative to know in regard to safety what the potential products of thermal oxidative degradation of these fluids are. The possibility just cannot be ignored that these materials can decompose when brought into contact with overheated machinery or potential ignition sources. To eliminate the most dangerous fluids and to formulate meaningful regulations, it is thus necessary to determine the thermal oxidative behavior of these materials.

Work conducted to date, with the exception of the survey approach performed under Contract HO122009 [1] was concentrated on conveyor belts, ventilation pipes, brattice cloths, cable and hose insulations, wood supports, to a very limited degree urethane foams, and on compounding ingredients used in their manufacture. [2,3,4] Hydraulic fluids, lubricants, cleaning liquids, and fire extinguishants present very different types of compositions, which nonetheless are of equally great importance in toxic hazard assessments. This is particularly true in view of the large quantities of certain of these materials used and lost as discussed above, in the mine environment.

Most of the hydraulic fluids are mixtures and the number of the actual undisclosed ingredients is much larger than that usually denoted. It is obvious that it is unlikely for a single pure and inexpensive compound to combine all the characteristics of fire retardancy, lubricity, etc., required of a hydraulic fluid. Furthermore, with the introduction of more sophisticated machinery more extensive formulations of these fluids must be anticipated. Previous work has clearly established [2,3,4] that the presence of the various ingredients can be deduced from the nature and relative concentration of the products formed on thermal oxidative degradation. Furthermore, a survey of the hydraulic fluids approved for underground operation has shown that these belong to five well defined composition classes. Accordingly, this program was undertaken to determine on a gram per gram basis the amounts of individual products formed upon oxidative thermal decomposition of selected representatives of these five classes or groups of hydraulic fluids and to relate these data to established safety regulations or maximum exposure limits.

## 3. PROCEDURES, RESULTS AND DISCUSSION

The selection of materials for these investigations was based on the list of fire resistant hydraulic fluids approved by the Bureau of Mines under Schedule 30 for underground use. The listed fluids can be divided into five broad groups or classes as follows:

I Glycol-water solutions
II Mineral oil-water emulsions
III Synthetics other than phosphate esters
IV Synthetic phosphate esters
V Mixtures of phosphate esters with mineral oils and chlorinated solvents

Regarding the selection of potential candidates to be subjected to thermal oxidative degradation, it is obvious that within the scope of the program it was impossible to study all the 75 or so approved fluids. However, an attempt was made to study at least two representatives of each group and to correlate the generated data. In addition, in the instances where at 370°C the degree of decomposition was very low or where higher temperatures could be suspected to result in the formation of exceptionally toxic species, experiments were performed both at 370 and 420°C. Furthermore, to establish mechanisms and to identify ingredients and the combinations leading to specific toxic substances, a "synthetic" hydraulic composition was prepared and tested.

In Table I the hydraulic fluids studied are listed together with the manufacturer's disclosed composition. The last entry in the Table is the "synthetic" hydraulic fluid composition which was subjected to thermal oxidative degradation to determine the effect of a hydrocarbon diluent upon the phosphate ester decomposition mode.

TABLE I

LIST OF HYDRAULIC FLUIDS STUDIED

Ucon Hydrolube 275 CP; water-ethylene glycol mixture; manufactured by Union Carbide Corporation

Citgo Glycol FR-20XD; water-ethylene glycol mixture; manufactured by Cities Service Oil Company

SNFH Fluid; water-synthetics (glycols) mixture; manufactured by Ore-Lube Corporation

Duro-FR-HD; oil-water emulsion; manufactured by Atlantic Richfield Company

Quintolubric 822-300; non-phosphate synthetic esters; manufactured by Quaker Chemical Corporation

Fyrquel 220; synthetic phosphate esters; manufactured by Stauffer Chemical Company

Pydraul 50E; synthetic phosphate esters; manufactured by Monsanto Corporation

Pydraul MC; mixture of phosphate esters, mineral oils, etc.; manufactured by Monsanto Corporation.

Dasco FR 300; mixture of phosphate esters, mineral oils, etc.; manufactured by D. A. Stuart Oil Company, Ltd.

Phosphate-hydrocarbon mixture; 50% by weight triphenylphosphate/n-octacosane

For ease and clarity of presentation Section 3 was divided into two main sub-sections: 3.1, a description of the experimental and analytical procedures employed, and 3.2, the discussion of the material decomposition studies. The investigated materials were divided into two main groups, namely miscellaneous hydraulic fluids and the phosphate ester based compositions. Accordingly the discussion of the individual fluids will follow the order of this grouping and the order in which the substances are listed in Table I.

## 3.1 EXPERIMENTAL AND ANALYTICAL PROCEDURES

The experimental and analytical methods employed during this phase of the program consisted essentially of: (a) degradation at 370°C and in selected instances at "420°C" using a sealed system, followed by separation of all products by vacuum line fractionation, (b) analysis of the fractions thus obtained by combined gas chromatography-mass spectroscopy, and (c) miscellaneous procedures including infrared spectroscopy and investigation of test samples by differential thermal analysis. These various procedures and methods will be discussed below in detail.

### 3.1.1 Sealed Tube Degradations

All oxidative thermal degradations performed during this phase of the program were carried out in a sealed tube following the procedures employed during the previous contract phases.[2,3,4] Although this system and its operation has been fully reported,[3] an abbreviated description will be repeated here. The sealed tube and the way it was attached to the high vacuum line is depicted in Figure 1. The general method of operation was to place a weighed sample of the test specimen into the heating finger of the decomposition flask, to attach it to the ground joint below stopcock A, to evacuate it through stopcock A, then fill the flask with breathing air to a measured pressure,

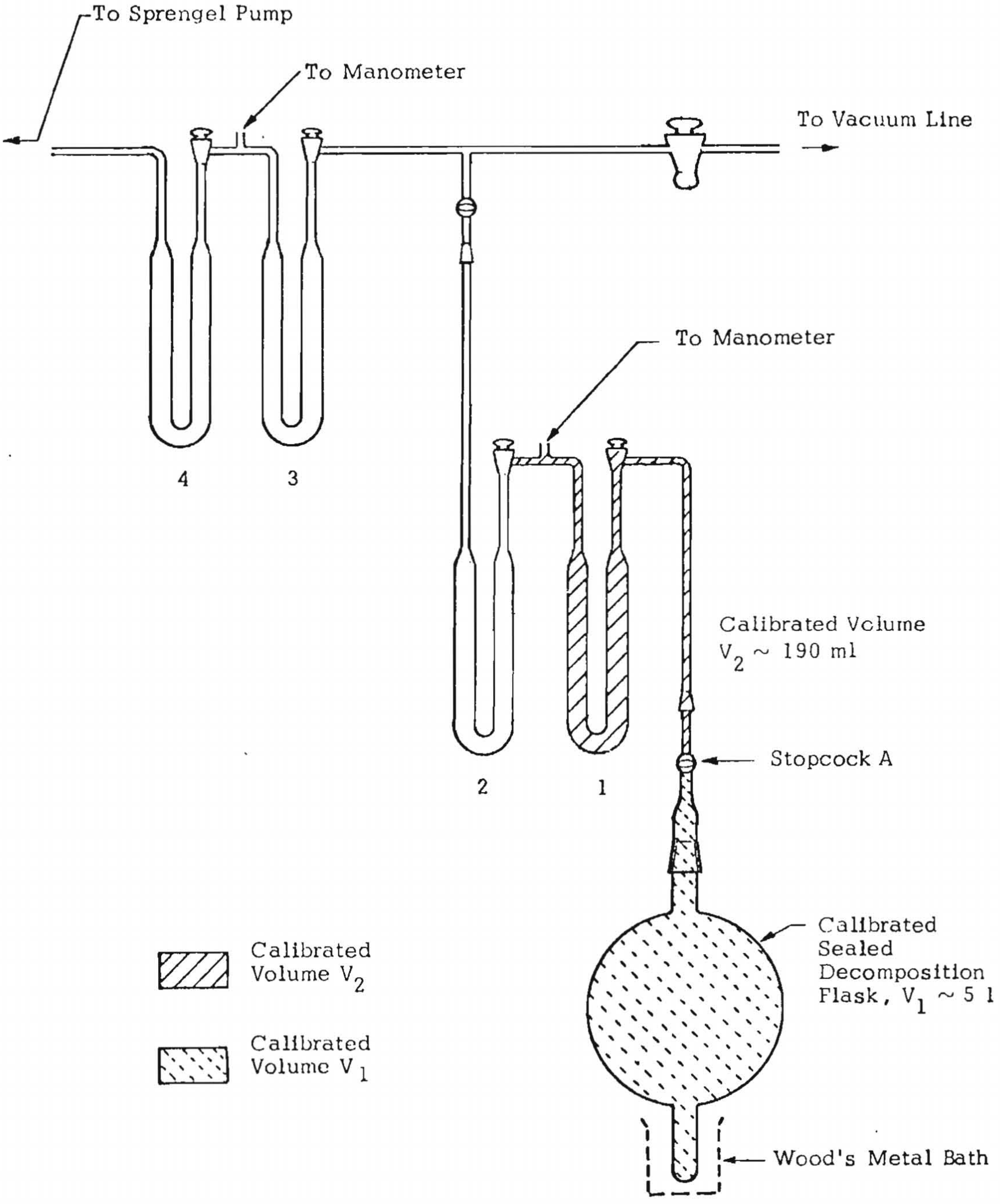


Figure 1: Sealed System for Thermal Oxidative Degradations

and to seal it by closing stopcock A. The degradation then was carried out by immersing the heating finger for 30 min into a Wood's metal bath which was preheated to 370 ± 2°C. After removing the metal bath and cooling the heating finger the gas phase in the 5-l flask was expanded into the calibrated volume $V_2$ (trap 1, in the diagram), the pressure measured, and stopcock A closed again. Then traps 1-4 (see diagram) were cooled with liquid nitrogen and the contents of trap 1 slowly expanded by allowing it to enter trap 2, then trap 3, and finally trap 4 before the components not condensible at liquid nitrogen temperature were collected and measured in a Sprengel pump. The materials condensed in traps 1-4 were then returned to trap 1.

The bulk of the products still contained in the sealed tube ($V_1$) was then freed from the liquid nitrogen noncondensible components (air, CO, $CH_4$, $H_2$) by passing through five liquid nitrogen cooled traps. The condensates in these five traps were returned to trap 1 and then roughly separated by fractional condensation in traps kept at 0, -23, -78, and -196°C. This fractionation was continued until all products had evaporated out of trap 1. Subsequently, the weights of all four fractions thus obtained were taken and the vapor pressures of the -23 and -78°C fractions were measured. In addition, the volume of the -196°C fraction was determined. After thus establishing the quantity on a volume and/or weight basis, each fraction, including the liquid nitrogen noncondensibles collected in the Sprengel pump, was subjected to quantitative analysis as described below.

The residue left in the heating finger was removed and weighed to establish an overall mass balance and subjected to infrared analysis to allow qualitative identification.

### 3.1.2 Gas Chromatographic and Mass Spectral Analyses, Combined GC/MS

The initial step in the analysis of all fractions obtained by vacuum line separation as described above was to record the mass spectrum of the gas phase of each fraction prior to gas chromatographic analysis. The same applied to the liquid portion of all the fractions. The "bulk" mass spectral analysis, prior to gas chromatography, pinpoints clearly the major products present and allows the detection of constituents which might be retained by the gas chromatographic columns. This method in conjunction with infrared spectroscopy and gas chromatography, affords considerably more complete and reliable results. All the mass spectral determinations were performed using a duPont Model 21-491B mass spectrometer. After carrying out these "bulk" mass spectral analyses all fractions obtained via high vacuum separation were subjected to combined GC/MS (gas chromatography/mass spectroscopy).

Gas chromatographic separations were conducted using two basic instrumentations, a Loenco Model 70 and the GC-MS combination. The Loenco Model 70 dual column gas chromatograph was equipped with calibrated gas inlet system; the effluent stream of the sample column was split 1:10 between a flame ionization and a thermal conductivity detector operated at 100 ma. The GC/MS combination consisted of a modified single column Varian Aerograph gas chromatograph with the effluent stream split 1:1.34 between the flame ionization detector and the inlet to the duPont Model 491-B mass spectrometer, which was coupled to a duPont 21-094-91 data acquisition and processing system with library search capability. Three columns were employed in these analyses: (i) a stainless steel, 1/8" x 10' column packed with 4% Apiezon L on Chromosorb G, 80/100 mesh, (ii) a 1/8" x 10' stainless steel column packed with 4% OV-101 on Chromosorb G, 80/100 mesh and (iii) a stainless steel 1/8" x 8' column, packed with Porapak Q, 80/100 mesh. The helium flow used was 37 ml/min and the temperature was programmed from 50 to 220°C at 8°C/min in the case of Porapak Q column and at 4°C/min in the case of the OV-101 and Apiezon L columns.

All organic liquid layers were investigated using the GC/MS combination and either the Apiezon L column or the OV-101 column in the Varian Aerograph. All other fractions and parts of fractions, e.g., gas phase of the -78°C fraction or the aqueous layers, were run over Porapak Q columns twice using first the Loenco Model 70 gas chromatograph and then the GC/MS combination. This duplication was necessary since the latter is equipped only with a flame ionization detector, which does not detect important species such as HCl, HCOOH, COS, $SO_2$, $CS_2$, $CO_2$, and water, all of which had to be quantitated in order to obtain an overall mass balance. The Porapak Q column installed in the GC/MS combination was used mainly for identification purposes, whereas the quantitative determinations were made using the Loenco Model 70. Accordingly, the area factors given for these analyses are those determined on the Loenco gas chromatograph, e.g., for a 1:10 effluent split.

In all the GC/MS analyses a mass spectrometer scanning rate of 2 sec/decade was employed, the mass:charge ratio scanned was from m/e = 12 to m/e = 500. The identification of species was performed by using the spectra library of the data system and by scan printout, followed by manual search and identification. The library search utilizes a reference tape containing the mass spectra of over 6,000 organic compounds which is based on the "Atlas of Mass Spectral Data".[5] In the manual analysis of spectra the reference works by Cornu and Massot, the Mass Spectrometry Data Centre,[7] and Stenhagen[8] were employed in addition to the above referenced Atlas.

### 3.1.3 Miscellaneous Analyses

Infrared spectral analyses were performed on both gas and liquid samples, including all residues. For the gas samples 10 cm gas cells were employed. All condensed phases were run squeezed between sodium chloride windows, if necessary using silver spacers. The spectra were recorded using a Perkin-Elmer Model 21 double beam infrared spectrophotometer.

All materials investigated during this phase of the program were subjected to the differential thermal analysis (DTA) in air, using a duPont 990-951 thermal analysis system programmed from 20 to 400°C at a heating rate of 10°C/min.

## 3.2 MATERIAL DECOMPOSITION STUDIES

### 3.2.1 Glycol-Water Type Hydraulic Fluids

Glycol-water compositions provide effective, economical, non-flammable hydraulic fluids. Accordingly, a large number of these are approved and widely used in underground operations. Ethylene glycol appears to be the most commonly used glycol in these materials. From the list of the approved fluids Ucon Hydrolube 275 CP and Citgo Glycol FR-20XD were selected as the representative members of the series. The SNFH fluid (the symbols denote Synthetic Non-Flammable Hydraulic fluid) was tested at a specific request by the Bureau of Mines. As denoted by the manufacturer (see Table I) it consists of water and synthetics. The latter were found by the current study to be ethylene and propylene glycols.

The DTA curves (see Figures 2-4) of the three fluids, although similar, are by no means identical. In the Citgo Glycol FR-20XD what would appear to be the water plus ethylene glycol boiling endotherm (centered at ca 150°C) is well separated from that

PART NO. 990088

**DTA**
RUN NO 164 DATE 2 Oct 75
OPERATOR F.S.
SAMPLE UCON Hydrolube 275 CP PM-1921 (Union Carbide Corporation)
ATM Air @
FLOW RATE 50 ml/min

**T-AXIS**
SCALE, °C/in 50
PROG RATE, °C/min 10
HEAT ✓ COOL ISO
SHIFT in 0

**DTA-DSC**
SCALE, °C/in
(mcal/sec)/in
WEIGHT, mg
REFERENCE $Al_2O_3$
Red 1.0° C/in
Green 0.2 °C/in

**TGA**
SCALE, mg/in
SUPPRESSION, mg
WEIGHT, mg
TIME CONST sec
dY mg/min) /in

**TMA.**
SCALE, mils/in
MODE
SAMPLE SIZE
LOAD, g
dY,(10X),(mils/min)/in

Thermocouple K
Baseline: 375

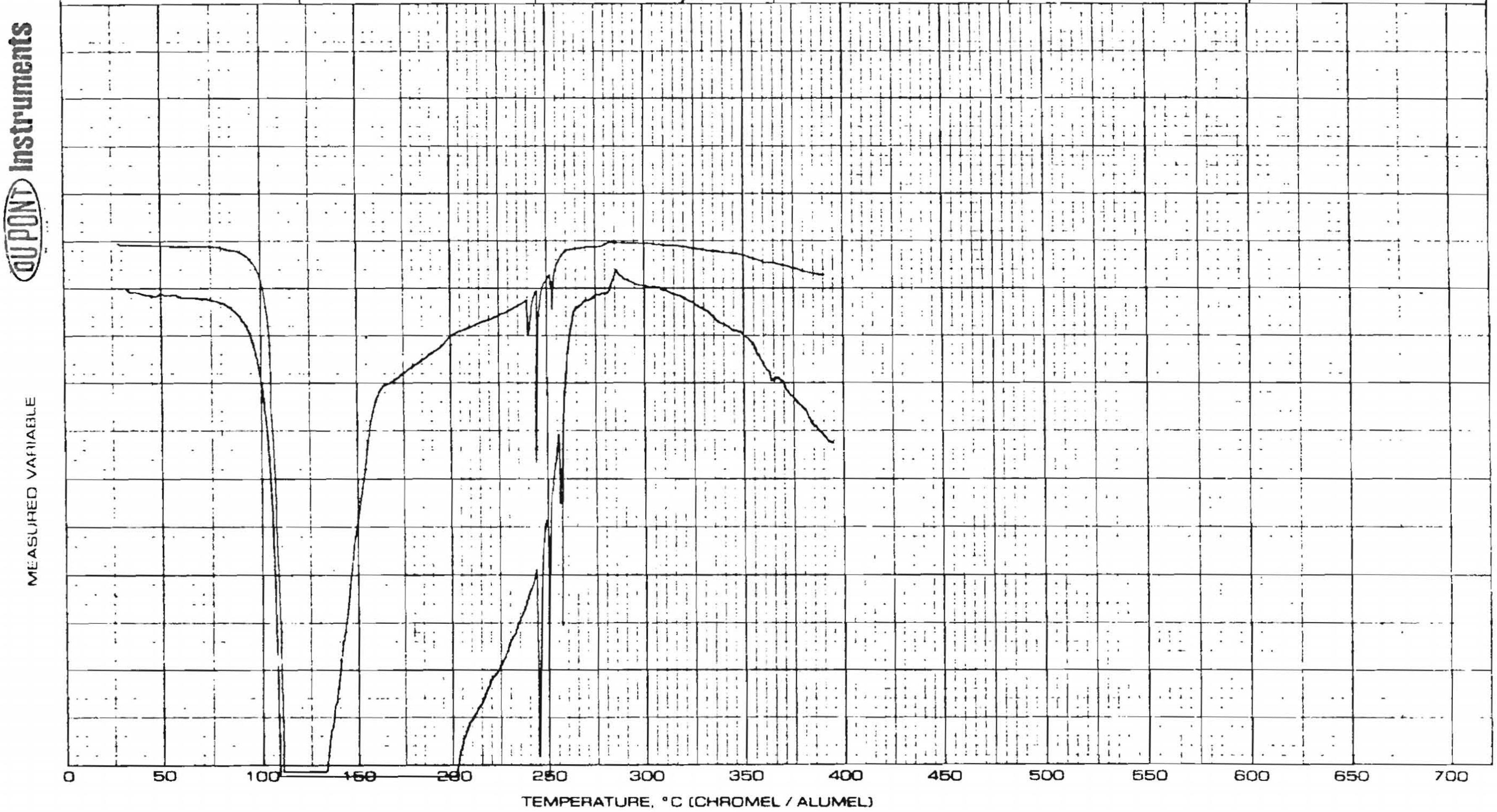
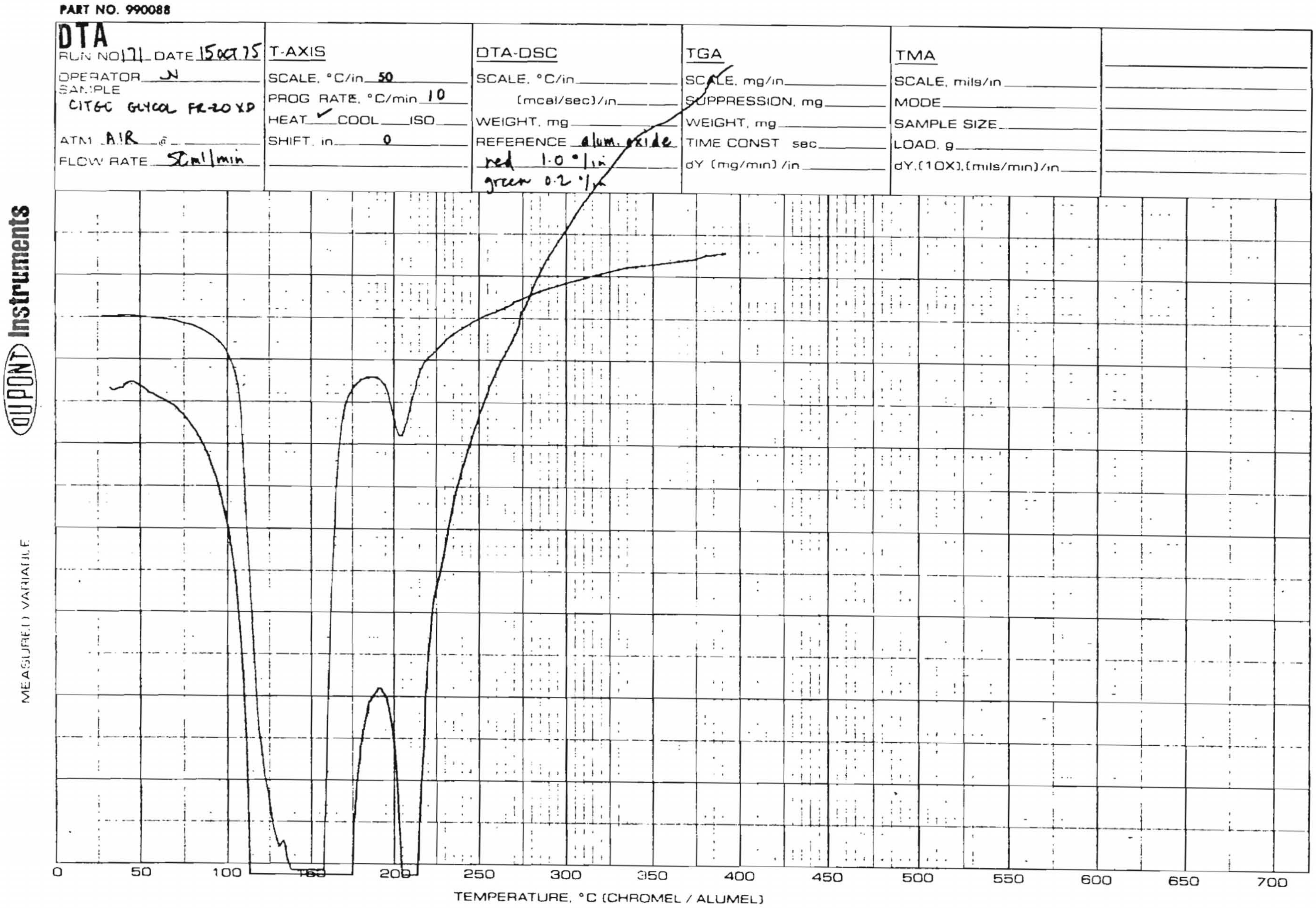


Figure 2: DTA of Ucon F



PART NO. 990088

DTA
RUN NO 171 DATE 15 OCT 75
OPERATOR N
SAMPLE
CITGO GLYCOL FR-20 XD
ATM AIR @
FLOW RATE 50 ml/min

T-AXIS
SCALE, °C/in 50
PROG RATE, °C/min 10
HEAT ✓ COOL ISO
SHIFT, in 0

DTA-DSC
SCALE, °C/in
(mcal/sec)/in
WEIGHT, mg
REFERENCE alum. oxide
red 1.0 °/in
green 0.2 °/in

TGA
SCALE, mg/in
SUPPRESSION, mg
WEIGHT, mg
TIME CONST sec
dY (mg/min)/in

TMA
SCALE, mils/in
MODE
SAMPLE SIZE
LOAD, g
dY,(10X),(mils/min)/in

Figure 3: DTA of Citgo Glycol FR-20XD Fluid

PART NO. 990088

**DTA**

RUN NO. 287 DATE 23A-1976

OPERATOR Rcj

SAMPLE SNFH

ATM Air

FLOW RATE 50 ml/min

T-AXIS

SCALE, °C/in 50

PROG RATE, °C/min 10

HEAT ✓ COOL __ ISO __

SHIFT, in 0

DTA-DSC

SCALE, °C/in

(mcal/sec)/in

WEIGHT mg

REFERENCE $Al_2O_3$

Red 1.0°C/in

Green 0.2°C/in

TGA

SCALE, mg/in

SUPPRESSION, mg

WEIGHT mg

TIME CONST sec

dY (mg/min) /in

TMA

SCALE, mils/in

MODE

SAMPLE SIZE

LOAD, g

dY.(10X).(mils/min)/in

THERMOCOUPLE N.

BASELINE SLOPE 15.9

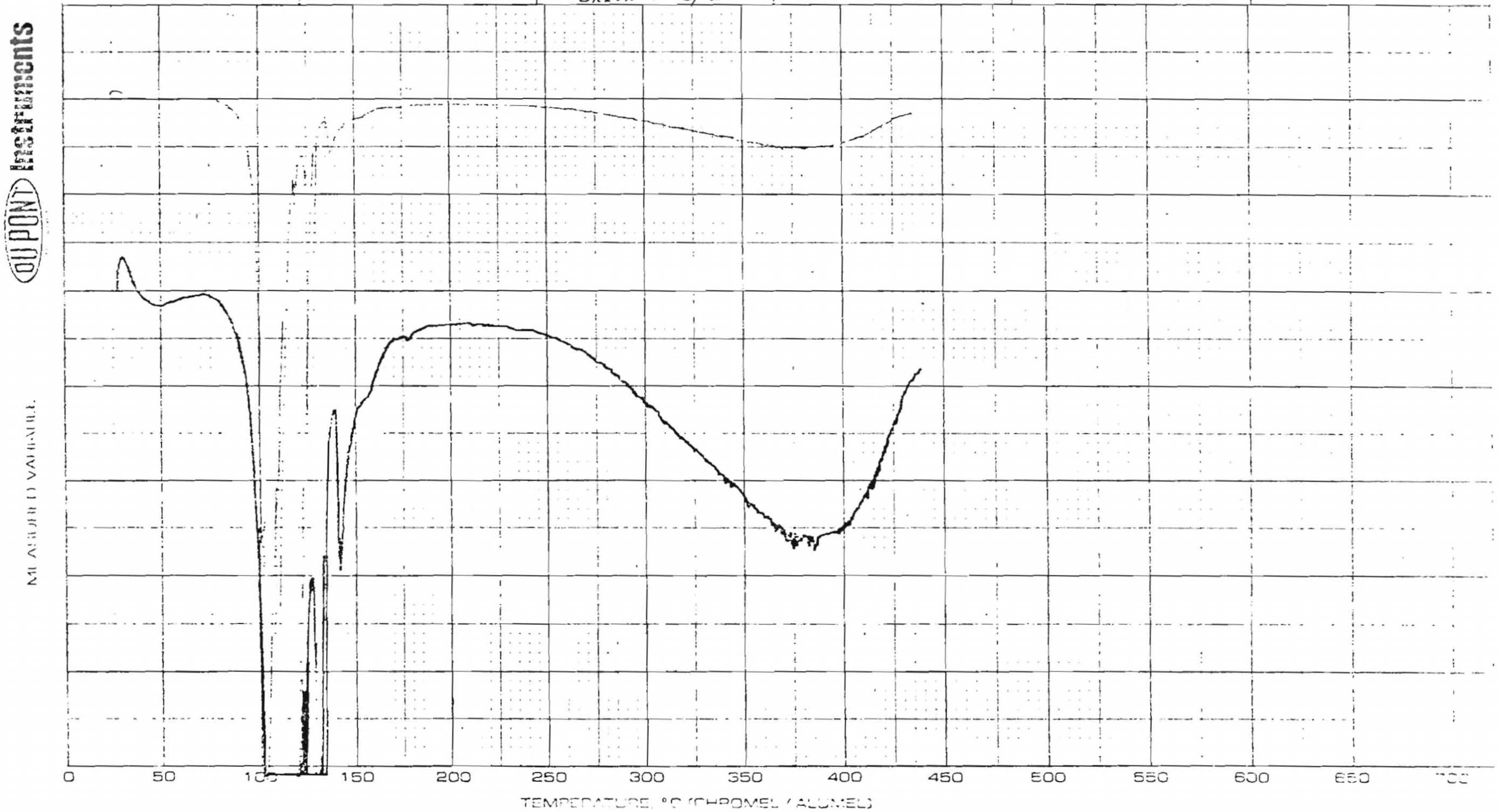


Figure 4: DTA of SNFH Hydraulic Fluid

of glycol itself (centered at 205°C). No such separation exists in the DTA of Ucon Hydrolube 275 CP and the SNFH fluid. In the latter, however, a definite endotherm is visible at approximately 140°C. The absence of a definite endotherm at 200°C in the DTA traces of Ucon Hydrolube 275 CP and SNFH fluid implies that these possibly contain lower proportions of the glycol or glycols than Citgo Glycol FR-20XD.

The experimental details for the degradations are presented in Table II and the product distribution is given in Table III. The degradation temperature chosen was 370°C, (see Section 3.1). However, as it is apparent from Table II, both Ucon Hydrolube 275 CP and Citgo Glycol FR-20XD were actually tested at lower temperatures. This was due to the higher heat of evaporation of water which resulted in cooling of the bath although the latter was initially preheated to 370°C.

In the case of Ucon Hydrolube weight loss under the conditions of the experiment amounted to approximately 50%. The residue was in the form of brown liquid; however, it exhibited an infrared spectrum essentially identical with that of the starting material. The volatile condensibles accounted for 81% of the weight loss; the unaccounted for material was deposited as a coating on the walls of the bulb. This fraction exhibited an infrared spectrum identical to that of the starting material and the residue, which is not surprising inasmuch as at the temperatures involved one would expect distillation and subsequent condensation of the ethylene glycol-water mixture especially since the main constituents of the volatile condensibles were water and ethylene glycol.

The results of the gas chromatographic separations are given in Tables IV and V while the mg/g compilation is presented in Table XIV. Products such as ethylene oxide, formic acid, acetic acid,

## TABLE II

## EXPERIMENTAL DATA FOR THERMAL OXIDATIVE DEGRADATIONS OF MISCELLANEOUS HYDRAULIC FLUIDS

| Sample | Tube V | Initial P | Final P | React Temp | Sample Wt | Residue | | Weight Loss | Oxygen Consumed | | Total Products | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | ml | mm | mm | °C | mg | mg | %[a] | mg | mg | %[b] | mg | %[c] |
| Ucon Hydrolube 275 CP | 5300 | 503.8 | 507.6 | 340 | 5291 | 2911 | 55.0 | 2380 | 72.3 | 7.6 | 1928.0 | 81.1 |
| Citgo Glycol FR-20XD | 5330 | 499.0 | 516.4 | 334 | 5035 | 3635 | 72.2 | 1400 | 25.7 | 2.7 | 1170.9 | 83.6 |
| SNFH | 5300 | 504.1 | 506.0 | 370 | 2917 | 2164 | 74.2 | 753 | 49.0 | 5.1 | 607.2 | 80.6 |
| Duro FR-HD | 5330 | 497.0 | 511.9 | 360 | 4287 | 2353 | 54.9 | 1934 | 66.3 | 7.0 | 1792.1 | 92.7 |
| Quintolubric 822-300 | 5300 | 500.0 | 506.9 | 370 | 4498 | 4350 | 96.7 | 148 | 38.4 | 3.8 | 115.0 | 77.7 |
| Quintolubric 822-300 | 5330 | 503.0 | 516.9 | 405 | 4264 | 3889 | 91.2 | 375 | 39.1 | 4.0 | 356.6 | 95.0 |

a) Percent of the weight of the starting material; this is the residue remaining in the finger and does not include oils and tars deposited on the sides of the 5-liter bulb. b) Percent of oxygen available. c) Percent of total products expected.

## TABLE III

## PRODUCT DISTRIBUTION: DEGRADATIONS OF MISCELLANEOUS HYDRAULIC FLUIDS

| Sample | Noncondensibles | | | | | Condensibles | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Total | CO | | $CH_4$ | | Total | -196°C Frac | | -78°C Frac | | -23°C Frac | | 0°C Frac | |
| | mmoles[a] | mg | %[b] | mg | %[b] | mg | mg | %[b] | mg | %[b] | mg | %[b] | mg | %[b] |
| Ucon Hydrolube 275 CP | 136.89 | 8.0 | 0.2 | T | T | 1920.0 | 24.9 | 0.5 | 230.9 | 4.4 | 1423.5 | 26.9 | 240.7 | 4.5 |
| Citgo Glycol FR-20XD | 140.78 | 9.5 | 0.2 | - | - | 1161.4 | 34.3 | 0.7 | 185.2 | 3.7 | 887.3 | 17.6 | 54.6 | 1.1 |
| SNFH | 137.48 | - | - | - | - | 607.2 | 4.7 | 0.2 | 266.5 | 9.1 | 317.9 | 10.9 | 18.1 | 0.6 |
| Duro FR-HD | 140.80 | 15.0 | 0.3 | - | - | 1777.1 | 31.8 | 0.7 | 312.6 | 7.3 | 1432.7 | 33.4 | -[c] | - |
| Quintolubric 822-300[d] | 145.78 | 6.1 | 0.15 | 2.3 | 0.10 | 106.6 | 26.2 | 0.6 | 67.8 | 1.5 | 6.2 | 0.1 | 6.4 | 0.1 |
| Quintolubric 822-300[e] | 142.96 | 8.0 | 0.20 | 3.4 | 0.15 | 345.2 | 74.4 | 1.7 | 174.4 | 4.1 | 29.6 | 0.7 | 66.8 | 1.6 |

a) This is mainly air. b) Percent of the weight of the starting material. c) The 0° and -23°C fractions were combined. d) This sample was subjected to degradation at 370°C. e) This sample was subjected to degradation at ~ 405°C.

## TABLE IV

## GAS CHROMATOGRAPHY RESULTS: DEGRADATION OF UCON HYDROLUBE 275 CP HYDRAULIC FLUID

(Porapak Q Column)

| -78°C[a,b] Frac | | -78°C[c,d] Frac (vapor) | | -196°C[c,e] Frac | | Peak Identification |
|---|---|---|---|---|---|---|
| r.t.[f] | Area | r.t. | Area | r.t. | Area | |
| | | | | 2.0[g] | 93.4 | $CO_2$ |
| | | | | 2.3[g] | 7.7 | $N_2O$ |
| | | 2.8 | 0.1 | 2.8 | 2.3 | $C_2H_4$ |
| | | | | 3.4 | 0.4 | $C_2H_6$ |
| | | | | 7.4 | 1.7 | $C_3H_6$ |
| | | | | 7.9 | 0.6 | $C_3H_8$ |
| | | | | 9.2 | 0.1 | Methyl ether |
| 11.4 | 0.2 | | | | | Methanol |
| 12.2 | 0.2 | 10.3 | 2.2 | 10.2 | 1.6 | Acetaldehyde |
| | | | | 10.5 | 7.5 | Ethylene oxide |
| | | | | 12.8 | T[h] | $C_4$-species |
| | | | | 13.3 | T | Cyclobutane |
| | | | | 13.8 | 0.3 | Methyl ethyl ether |
| 15.5 | 1.1 | 14.1 | 1.9 | | | Ethanol |
| 18.0 | 0.1 | | | | | Propionaldehyde, formic acid |
| 18.7 | 0.1 | 14.6 | 0.2 | 15.0 | 0.1 | Acetonitrile, acetone |
| | | 15.9 | 1.0 | 15.9 | 0.7 | Acetone |
| | | 17.8 | 0.6 | 17.7 | 0.5 | Thiacyclopropane |
| | | | | 18.3 | 0.1 | Methyl propyl ether |
| | | 18.7 | 0.9 | 19.2 | 0.3 | Propionitrile, 1-propanol |
| 20.5 | 0.1 | | | | | 1-propanol |
| 21.7 | 0.2 | 20.4 | 0.4 | 20.4 | 0.7 | Methyl ethyl ketone |
| 22.8 | 0.4 | 21.9 | 1.7 | | | 2-Methyl-1,3-dioxolane |
| | | 23.4 | 0.1 | | | Methyl isopropyl ketone, divinyl sulfide |
| 24.4 | 0.1 | | | | | 2-Methyl-1-propanol |
| 25.0 | 0.1 | 24.1 | 1.1 | | | 2-Pentanone, p-dioxane, $C_2$-1,3-dioxolane |
| | | 24.8 | 0.1 | | | 1-Cyano-1-butene |
| | | 25.3 | 1.7 | | | 2-Methyl-2-butenal |
| 25.4 | 0.1 | | | | | $C_2$-1,3-dioxolane |
| | | 26.5 | 0.1 | | | Ethyl-n-butyl ether |

TABLE IV - Cont'd.

GAS CHROMATOGRAPHY RESULTS: DEGRADATION OF UCON HYDROLUBE 275 CP HYDRAULIC FLUID

(Porapak Q Column)

| $-78^{\circ}C^{a,b}$ Frac | | $-78^{\circ}C^{c,d}$ Frac (vapor) | | $-196^{\circ}C^{c,e}$ Frac | | Peak Identification |
|---|---|---|---|---|---|---|
| r.t.[f] | Area | r.t. | Area | r.t. | Area | |
| 27.0 | 0.1 | | | | | Cyclopentanone |
| | | 27.1 | 0.7 | | | Toluene |
| | | 28.0 | 0.3 | | | 3-Hexanone |
| | | 29.5 | 1.1 | | | 2-Methyl-2-penten-1-al |
| | | 33.0 | 0.4 | | | |
| | | 34.3 | T | | | |

a) This fraction was examined under the following conditions: Column: stainless steel, 8' x 1/8" Porapak Q, detector: a 10% split into F.I., He flow: 35 ml/min. Column temperature: 50-220°C programmed at 8°/min. b) This was the liquid phase of the fraction. Area is given in square inches x attenuation per microliter of sample. c) This fraction was examined under the following conditions: Column: stainless steel, 8' x 1/8" Porapak Q, detector: a 43% split into F.I., He flow: 35 ml/min, column temperature: 50-220°C programmed at 7°/min. d) This was the gaseous phase of the fraction; a 12 mm pressure was used. e) A 15 mm pressure was used. f) Retention time, min. g) This peak was identified by the TC detector only under testing conditions given in footnote a). h) < 0.05 $in^2/\mu l$ for liquid samples; < 0.05 $in^2$ for gas samples.

# TABLE V

# GAS CHROMATOGRAPHY RESULTS: DEGRADATION OF UCON HYDROLUBE 275 CP HYDRAULIC FLUID

(Porapak Q Column)

| 0°C[a,b] Frac | | -23°C[a,b] Frac | | Peak Identification |
|---|---|---|---|---|
| r.t.[c] | Area | r.t. | Area | |
| 6.8[d] | 360.2 | 6.7[d] | 453.7 | $H_2O$ |
| 11.7 | T[e] | 11.6 | T | $CH_3CHO$ |
| 21.2 | T | | | 2-Methyl-1,3-dioxolane |
| 22.1 | T | | | Acetic acid |
| 23.0 | 2.2 | | | Ethylene glycol |
| 25.0 | T | | | |
| 31.5 | 0.1 | | | |

a) This fraction was examined under the following conditions: Column: stainless steel 8' x 1/8" Porapak Q, detector: a 10% split in F.I., He flow: 35 ml/min., column temperature: 50-220°C programmed at 8°/min. b) Area is given in square inches x attenuation per microliter. c) Retention time, min.
d) This peak was identified by the TC detector only.
e) $< 0.05\ in^2/\mu l$.

acetaldehyde, dioxane, etc., can be readily traced to ethylene glycol. One does suspect that probably additional quantities of formic acid and acetic acid were formed; however, the presence of large amounts of water makes analysis very difficult. It is most likely that formaldehyde was also produced, in particular since formic acid was found. The origin of nitrous oxide, $N_2O$, is unknown; it was identified unequivocally by its gas chromatographic retention time, its mass spectral pattern, and infrared spectrum. The same applies to the other nitrogen-containing species such as acetonitrile, propionitrile, etc. The sulfur-containing compounds were identified only by mass spectrometry; since their breakdown patterns are unique the assignment should be valid. Again their origin is unknown.

To summarize, 41 components were identified and quantitated in the volatiles obtained on thermal oxidative degradation of Ucon Hydrolube 275 CP and these accounted for 99.92% of volatiles liberated. The majority of products could be readily shown as being derived from ethylene glycol; however, the origin of the nitrogen and sulfur containing compounds remains obscure. The toxic species carbon monoxide, formic acid, acetic acid, acetonitrile and ethylene oxide, were found to be produced in very small quantities.

Citgo Glycol exhibited a thermal oxidative behavior strongly reminiscent of Ucon Hydrolube. However, the residue here amounted to 72% of the starting material; possibly due to an originally higher glycol concentration. The volatile condensibles accounted for 84% of the weight loss. The extent of oxidation was relatively minor as indicated by the oxygen consumed.

The results of the gas chromatographic separations are given in Table VI. The gas chromatography of fraction -23°C is not

TABLE VI

GAS CHROMATOGRAPHY RESULTS: DEGRADATION OF CITGO GLYCOL FR20-XD HYDRAULIC FLUID

(Porapak Q Column)

| $-78^\circ C^{a,b}$ Frac | | $-78^\circ C^{c,d}$ Frac (vapor) | | $-196^\circ C^{c,e}$ Frac | | Peak Identification |
|---|---|---|---|---|---|---|
| r.t.[f] | Area | r.t. | Area | r.t. | Area | |
| | | | | 2.0[g] | 72.3 | $CO_2$ |
| | | | | 2.4[g] | 5.3 | $N_2O$ |
| | | 2.8 | T | 2.7 | 20.8 | $C_2H_4$ |
| | | | | 3.4 | 0.2 | $C_2H_6$ |
| 6.5[g] | 749.6 | | | | | $H_2O$ |
| | | | | 7.5 | 1.0 | $C_3H_6$ |
| | | | | 8.0 | 0.1 | $C_3H_8$ |
| | | | | 9.4 | T | Methyl ether |
| 9.7 | 0.3 | | | | | Methanol |
| 10.3 | 0.1 | 10.7 | 1.7 | 10.4 | 1.6 | Acetaldehyde, methanol |
| | | | | 10.7 | 8.3 | Ethylene oxide |
| | | | | 12.8 | 0.1 | $C_4$-species |
| | | | | 13.4 | T | |
| | | | | 13.9 | 0.1 | Methyl ethyl ether |
| 13.2 | 1.1 | 14.5 | 1.9 | | | Ethanol |
| | | 15.2 | T | 15.4 | 0.1 | Acetonitrile |
| | | | | 15.8 | 0.1 | Furan |
| 16.2 | 0.1 | 16.2 | 0.8 | | | Propionaldehyde |
| 17.0 | 0.1 | 16.4 | 0.9 | 16.1 | 0.7 | Acetone |
| | | | | 17.1 | T | |
| | | 18.4 | 0.4 | 17.9 | 0.5 | Thiacyclopropane |
| | | | | 18.3 | 0.1 | Methyl propyl ether |
| | | | | 18.8 | T | |
| | | 19.5 | 0.6 | 19.4 | 0.1 | Propionitrile |
| | | 19.8 | 0.8 | | | Isobutyraldehyde |
| 20.2 | 0.2 | | | | | 1-Propanol |
| 21.0 | 0.2 | 21.1 | 1.9 | 20.5 | 0.4 | Methyl ethyl ketone |
| | | | | 21.7 | 0.1 | $C_5$-ether ? |
| 22.0 | 0.3 | 22.5 | 0.6 | 22.0 | 0.1 | 2-Methyl-1,3-dioxolane |
| | | 23.6 | 0.2 | 23.0 | T | Benzene |
| | | | | 23.3 | 0.1 | Divinyl sulfide |
| 23.8 | 0.7 | 24.3 | 1.9 | 23.8 | T | p-Dioxane, divinyl sulfide |
| 24.4 | T | 24.8 | 1.9 | 24.2 | T | 2-Pentanone, ethyl butyl ether |
| | | 25.5 | 0.2 | | | |
| 25.9 | 0.2 | 26.0 | 2.2 | | | 2-Methyl-2-butenal |
| 27.0 | T | 27.3 | 0.2 | | | Cyclopentanone |
| | | 27.8 | 1.8 | | | Toluene |
| | | 28.8 | 1.3 | | | 3-Hexanone |
| | | 29.5 | 1.0 | | | |
| 30.2 | T | 30.8 | 1.6 | | | 3-Methylcyclopentanone |
| 33.2 | T | 33.8 | 1.3 | | | |
| | | 35.0 | 0.8 | | | |

## TABLE VI - Cont'd.

## GAS CHROMATOGRAPHY RESULTS: DEGRADATION OF CITGO GLYCOL FR20-XD HYDRAULIC FLUID

(Porapak Q Column)

a) This fraction was examined under the following conditions: Column: stainless steel, 8' x 1/8" Porapak Q, detector: a 10% split into F.I., He flow: 35 ml/min. Column temperature: 50-220°C programmed at 8°/min. b) This was the liquid phase of the fraction. Area is given in square inches x attenuation per microliter of sample. c) This fraction was examined under the following conditions: Column: stainless steel, 8' x 1/8" Porapak Q, detector: a 43% split into F.I., He flow: 35 ml/min. Column temperature: 50-220°C programmed at 7°/min. d) This was the gaseous phase of the fraction; an 18 mm pressure was used. e) A 17 mm pressure was used. f) Retention time, min. g) This peak was identified by the TC detector only under testing conditions given in footnote a). h) < 0.05 $in^2/\mu l$ for liquid samples; < 0.05 $in^2$ for gas samples.

tabulated, inasmuch as water and a trace of acetaldehyde were the only products detected. The 0°C fraction consisted mainly of ethylene glycol admixed with a non-identified component (whose main peak in the mass spectrum was m/e 87, pointing to an ester) which could not be separated from ethylene glycol by gas chromatography. It can be seen from the data given in Table VI that the type and relative quantities of products formed by Citgo Glycol FR-20XD correspond closely to those obtained from Ucon Hydrolube 275 CP fluid. No formic acid and acetic acid were detected; yet, based on the other products found, it is most certain that these were produced. However, in view of the presence of water and glycol in the residue these could have been retained there by solution in the former or by ester formation with the latter. The detection of the nitrogen- and sulfur-containing compounds, in particular nitrous oxide is surprising. As discussed for Ucon Hydrolube 275 CP fluid, their origin is obscure. A total of 36 components was identified and quantitated and these accounted for 99.98% of the volatiles collected (see Table XIV).

Results obtained for SNFH fluid paralleled fairly closely those found for the other two water-glycol mixtures. This is evident by examination of the gas chromatographic tabulation given in Table VII and the mg/g tabulation presented in Table XIV. It should be noted that the -23 and 0°C fractions (see Table III) were shown by infrared and mass spectral analyses to consist of water, ethylene glycol, and propylene glycol. These constituents do not lend themselves readily to gas chromatographic quantitative analysis, thus the actual proportions of these compounds were determined by quantitative batch mass spectral analysis.

In the condensible volatiles a total of 31 components were identified and quantitated; water, ethylene glycol, and propylene glycol

TABLE VII

GAS CHROMATOGRAPHY RESULTS: DEGRADATION OF SNFH HYDRAULIC FLUID

(Porapak Q Column)

| $-78^{\circ}C$ [a,b] Frac | | $-78^{\circ}C$ [c,d] Frac (Vapor) | | $-196^{\circ}C$ [c,e] Frac | | Peak Identification |
|---|---|---|---|---|---|---|
| r.t.[f] | Area | r.t. | Area | r.t. | Area | |
| | | | | 2.0[g] | 20.0 | $CO_2$ |
| | | | | 2.8 | 0.9 | $C_2H_4$ |
| | | | | 3.4 | 0.3 | $C_2H_6$ |
| 6.1[g] | 451.0 | | | | | $H_2O$ |
| | | | | 7.3 | 1.0 | $C_3H_6$ |
| | | | | 7.8 | 0.3 | $C_3H_8$ |
| | | | | 8.9 | T[h] | Methyl ether |
| 9.1 | T | | | | | Methanol |
| 10.6 | T | 10.2 | T | 10.1 | 0.2 | Acetaldehyde |
| | | 12.3 | T | 12.5 | 0.9 | $C_4$-ene |
| | | | | 13.1 | 0.1 | $C_4$-ane |
| | | | | 13.6 | 0.1 | $C_4$-ene |
| 15.6 | T | 15.2 | T | | | Acrolein |
| 16.0 | 0.6 | 15.5 | 2.9 | 15.4 | 3.2 | Propionaldehyde, acetone |
| | | | | 16.5 | T | $C_5$-ene |
| 16.9 | T | | | | | Isopropanol |
| | | 17.5 | T | 17.4 | 0.3 | $C_5$-ene |
| | | 18.3 | 0.1 | 17.9 | 0.2 | $C_5$-ene, $C_5$-ane |
| | | 19.2 | T | | | Isobutyraldehyde |
| | | 20.2 | 0.1 | | | n-Butyraldehyde, methyl ethyl ketone |
| | | 20.5 | T | 20.4 | 0.1 | Chloroform |
| | | 21.2 | T | 21.0 | 0.1 | $C_6$-ene |
| | | 21.9 | 0.1 | 21.7 | 0.3 | $C_6$-ene |
| | | 22.4 | 0.4 | 22.1 | 0.1 | $C_6$-ane |
| | | 22.8 | 0.2 | 22.6 | 0.1 | Benzene |
| | | 23.4 | 0.1 | 23.3 | T | Cyclohexene, $C_5$-ketone, $C_5$-aldehyde |
| | | 24.3 | 0.1 | | | $C_5$-aldehyde, $C_5$-ketone |
| | | 25.6 | 0.8 | 25.4 | 0.2 | $C_7$-ene |
| | | 26.1 | 1.0 | 25.8 | 0.1 | $C_7$-ane |

TABLE VII - Cont'd.

GAS CHROMATOGRAPHY RESULTS: DEGRADATION OF SNFH HYDRAULIC FLUID

(Porapak Q Column)

| -78°C[a,b] Frac | | -78°C[c,d] Frac (vapor) | | -196°C[c,e] Frac | | Peak Identification |
|---|---|---|---|---|---|---|
| r.t.[f] | Area | r.t. | Area | r.t. | Area | |
| | | | | 26.9 | 0.1 | $C_7$-species |
| | | 27.3 | 1.5 | | | Toluene, $C_2Cl_4$ |
| | | 28.4 | 0.8 | | | $C_8$-ene |
| 29.3 | T | 29.0 | 0.5 | | | n-Hexanal |
| 30.2 | 0.2 | 29.9 | 2.8 | | | $C_6$-aldehyde |
| | | 30.8 | 1.1 | | | $C_8$-ene |
| | | 31.3 | 1.7 | | | $C_8$-ane |
| 33.5 | 0.2 | 33.3 | 2.3 | | | $C_2$-benzene |
| | | 34.7 | 0.4 | | | $C_9$-species |
| | | 39.1 | 3.7 | | | $C_9$-species |
| | | 41.6 | 0.6 | | | $C_3$-benzene |
| | | 45.5 | 0.2 | | | $C_3$-benzene |

a) This fraction was examined under the following conditions: Column: stainless steel, 8' x 1/8" Porapak Q, detector: a 10% split into F.I., He flow: 35 ml/min. Column temperature: 50-220°C programmed at 8°/min. b) This was the liquid phase of the fraction. Area is given in square inches x attenuation per microliter of sample. c) This fraction was examined under the following conditions: Column: stainless steel, 8' x 1/8" Porapak Q, detector: a 53% split into F.I., He flow: 35 ml/min. column temperature: 50-220°C programmed at 7°/min. d) This was the gaseous phase of the fraction; a 14 mm pressure was used. e) A 20.6 mm pressure was used. Area is given in square inches x attenuation. f) Retention time, min. g) This peak was identified by the TC detector only under testing conditions given in footnote a). h) $< 0.05$ in$^2$/µl for liquid samples; $< 0.05$ in$^2$ for gas samples.

accounted for 99% of these. The relatively high content of propionaldehyde, as compared to the solely ethylene glycol based fluids, reflected the presence of propylene glycol. The only toxic constituent detected was acrolein, most likely derived from the propylene glycol. It is surprising that acrolein was found in the volatiles since under the analysis conditions it would be expected to remain in the "involatile" residue. The latter consisted essentially of the starting ingredients as shown by the infrared spectral analysis. The presence of chloroform and tetrachloroethylene in the volatiles points to the use of highly chlorinated compounds which had been added most likely as fire retardants. No sulfur and nitrogen containing species were detected. Thus it would appear that SNFH is differently compounded than Ucon Hydrolube and Citgo Glycol.

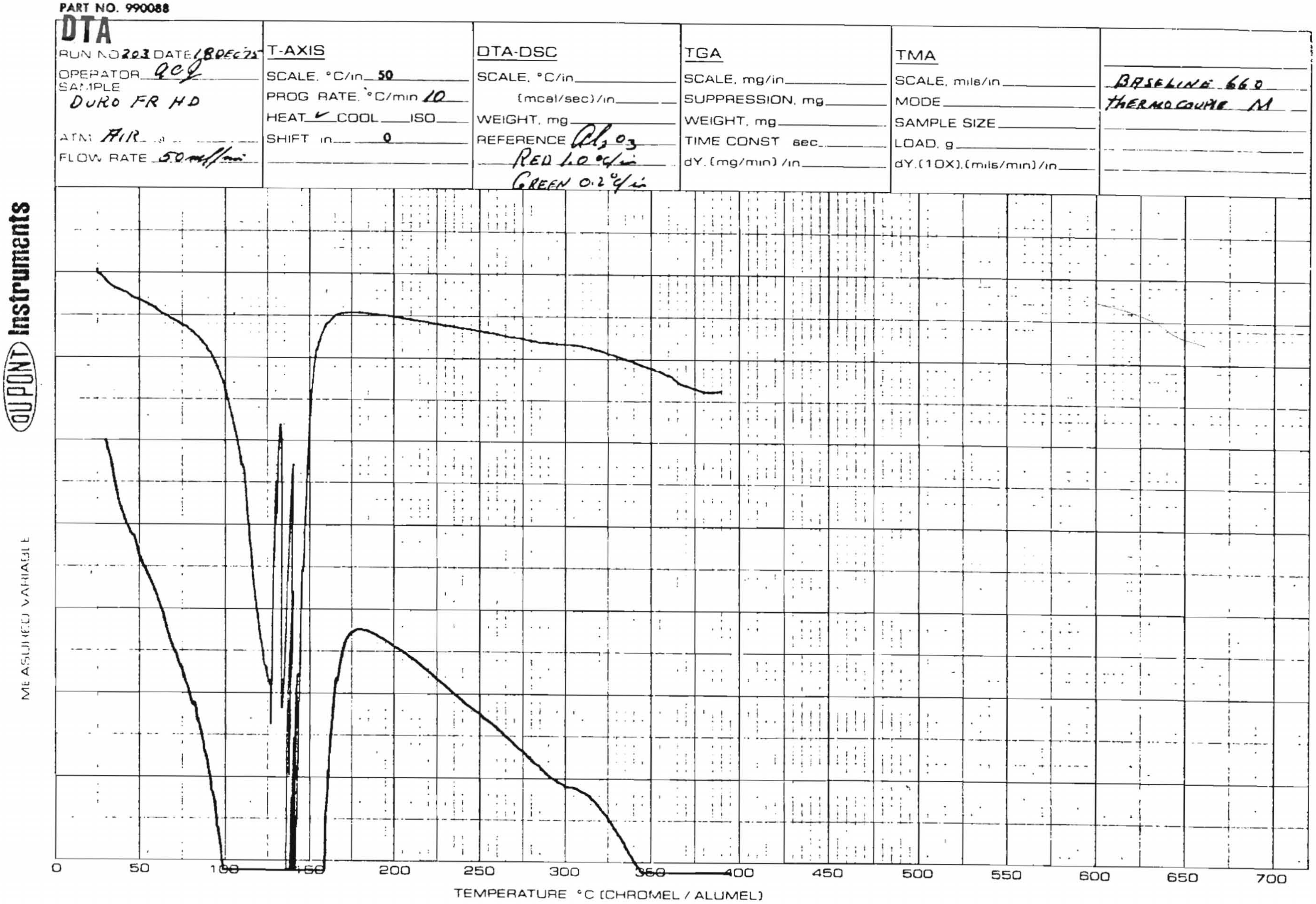
From the data given in Table XIV it is apparent that the majority of species detected in the volatiles were derived from the ethylene and/or propylene glycol portion of the fluid, which is to be expected. As discussed earlier, the toxic components such as formaldehyde, formic acid, acrolein, and allyl alcohol are to a degree most likely retained on the walls of the bulb and in the residue due to the large quantities of glycol and water present. To what extent this type of "trapping" would be effective at temperatures higher than 370°C is unknown. On the other hand if one considers local overheating and spillage in the actual mining environment, the results generated would tend to indicate that this type of hydraulic fluid is relatively "safe" insofar as toxic product generation is concerned.

### 3.2.2 Mineral Oil Emulsion Type Hydraulic Fluids

The mineral oil-water emulsion as represented by Duro-FR-HD fluid, the only one member of this series studied, presents a somewhat different system from that of the ethylene glycol-water compositions.

This is most evident in that after the heat treatment the residue consisted only of the hydrocarbon portion, free of the "fire-retardant", water. Furthermore, examining Table II it is apparent that here the extent of oxidation as shown by oxygen consumed was significantly higher than for the ethylene glycol based fluids. Surprisingly enough, the DTA curve of Duro FR-HD fluid (see Figure 5) resembles strongly that of SNFH fluid (see Figure 4).

The results of the gas chromatographic separations are summarized in Tables VIII and IX and the mg/g compilation is given in Table XIV. The gas chromatographic analyses of the combined -23° and 0°C fractions are not included, since these consisted essentially of water admixed with a trace of the higher hydrocarbons ($C_{11}$ - $C_{12}$ - species) and substituted aromatics. The residue amounted to 55% of the sample originally employed and as indicated above consisted of hydrocarbons. It can be seen from the mg/g compilation that water accounted for at least 40% of the sample subjected to decomposition, thus it can be deduced that the fluid is an approximately 1:1 water/mineral oil mixture. Under the conditions of the test the mineral oil portion apparently was relatively unaffected although a total of 41 components derived from this constituent were identified and quantitated in the volatiles. However, these amounted only to 4% of the volatiles, the remainder being water. The presence in the volatiles of carbonyl sulfide, thiophene, and thiacyclopropane shows clearly that sulfur-containing species were present in the fluid but in what form is unknown. The toxic species found were carbon monoxide and acrolein. Although the quantity of acrolein found was very low, one must assume that the major portion of the acrolein formed was retained in water, of which a large quantity was present. Consequently, it is believed that much larger amounts of acrolein were produced than reported in Table XIV. No acetic acid, formaldehyde and formic acid were detected in the volatiles.



PART NO. 990088

**DTA**

RUN NO 203 DATE 18 DEC 75
OPERATOR QCQ
SAMPLE
DURO FR HD
ATM AIR
FLOW RATE 50 ml/min

**T-AXIS**
SCALE, °C/in 50
PROG RATE, °C/min 10
HEAT ✓ COOL ___ ISO ___
SHIFT in 0

**DTA-DSC**
SCALE, °C/in
(mcal/sec)/in
WEIGHT, mg
REFERENCE $Al_2O_3$
RED 1.0 °C/in
GREEN 0.2 °C/in

**TGA**
SCALE, mg/in
SUPPRESSION, mg
WEIGHT, mg
TIME CONST sec
dY, (mg/min)/in

**TMA**
SCALE, mils/in
MODE
SAMPLE SIZE
LOAD, g
dY, (10X), (mils/min)/in

BASELINE 660
THERMOCOUPLE M

Figure 5: DTA of Duro FR-HD Fluid

TABLE VIII

GAS CHROMATOGRAPHY RESULTS: DEGRADATION OF DURO FR-HD HYDRAULIC FLUID

(Porapak Q Column)

| $-78^{\circ}C^{a,b}$ Frac (bottom layer) | | $-78^{\circ}C^{a,b}$ Frac (top layer) | | $-78^{\circ}C^{c,d}$ Frac (vapor) | | $-196^{\circ}C^{c,e}$ Frac | | Peak Identification |
|---|---|---|---|---|---|---|---|---|
| r.t.[f] | Area | r.t. | Area | r.t. | Area | r.t. | Area | |
| | | | | | | 2.0[g] | 5.5 | $CO_2$ |
| | | 3.0 | 0.1 | 2.8 | 0.9 | 2.8 | 16.6 | $C_2H_4$ |
| | | | | | | 3.6 | 3.8 | $C_3H_6$ |
| | | | | | | 6.5[g] | 0.1 | COS |
| 6.8 | 174.3 | | | | | | | $H_2O$ |
| | | | | 7.5 | T[h] | 7.6 | 8.8 | $C_3H_6$ |
| | | | | 8.0 | T | 8.2 | 3.8 | $C_3H_8$ |
| 10.8 | 0.2 | | | | | | | Methanol |
| 11.5 | 1.0 | 12.2 | T | 10.2 | 6.1 | 10.6 | 10.1 | Acetaldehyde |
| | | | | 12.7 | 0.4 | 12.9 | 36.0 | $C_4$-ene |
| | | | | 13.3 | 0.1 | 13.6 | 7.3 | $C_4$-ene, $C_4$-ane |
| 15.4 | 0.1 | | | | | | | Ethanol |
| | | | | | | 15.5 | 0.1 | Acrolein |
| 16.5 | 0.4 | 16.5 | 0.1 | 15.6 | 8.5 | 16.1 | 6.7 | Propionaldehyde, furan,acetone |
| 16.8 | 0.7 | 16.8 | 0.1 | | | | | Acetone |
| 17.8 | 0.1 | | | | | 17.0 | 1.1 | $C_5$-ene |
| | | | | | | 17.8 | 16.2 | $C_5$-ene, thiacyclopropane |
| 18.2 | 0.2 | 18.2 | 0.9 | 17.7 | 16.4 | | | Thiacyclopropane |
| | | | | | | 18.3 | 4.2 | $C_5$-ene |
| 19.7 | 0.2 | 19.6 | 0.2 | 19.1 | 4.1 | 19.4 | 0.8 | Crotonaldehyde, isobutyraldehyde |
| 20.6 | 0.4 | 20.4 | 1.2 | 20.1 | 13.7 | 20.5 | 2.3 | Methyl ethyl ketone, n-butyraldehyde |
| 20.8 | 0.6 | 20.6 | 0.9 | | | | | Methyl ethyl ketone |
| 21.5 | T | 21.4 | 1.0 | 21.0 | 0.3 | 21.3 | 3.0 | $C_6$-ene |
| | | | | 21.7 | 4.5 | 22.0 | 9.1 | $C_6$-ene |
| | | 22.0 | 0.6 | 22.4 | 4.2 | 22.4 | 3.4 | $C_6$-species, thiophene |
| 22.0 | 0.1 | | | | | | | |
| 22.6 | T | 22.4 | 0.7 | 22.6 | 1.3 | | | Benzene |
| 23.4 | 0.4 | 23.2 | 2.4 | 23.2 | 7.8 | 23.5 | 0.6 | 2-Methyltetrahydrofuran,cyclohexane, 3-methylbutanal, 2-pentanone |
| 24.4 | 0.7 | 24.2 | 6.1 | 24.1 | 12.6 | | | n-Pentanal |

## TABLE VIII - Cont'd.

## GAS CHROMATOGRAPHY RESULTS: DEGRADATION OF DURO FR-HD HYDRAULIC FLUID

(Porapak Q Column)

| $-78^{0}C^{a,b}$ Frac (Bottom layer) | | $-78^{\circ}C^{a,b}$ Frac (Top layer) | | $-78^{\circ}C^{c,d}$ Frac (Vapor) | | $-196^{\circ}C^{c,e}$ Frac | | Peak Identification |
|---|---|---|---|---|---|---|---|---|
| r.t.$^{f}$ | Area | r.t. | Area | r.t. | Area | r.t. | Area | |
| | | | | | | 24.6 | 1.2 | $C_7$-ane, $C_7$-ene |
| 25.5 | 0.2 | 25.0 | 7.2 | 25.4 | 23.0 | 25.2 | 1.8 | $C_7$-ane, $C_7$-ene |
| | | 25.4 | 3.5 | 25.8 | 6.6 | 25.7 | 2.5 | $C_7$-ane, $C_7$-ene |
| 26.6 | T | 26.4 | 1.8 | 26.5 | 3.4 | 26.1 | 0.5 | $C_7$-ane |
| | | | | | | 27.0 | 0.1 | $C_7$-species |
| 27.7 | 0.1 | 27.2 | 7.9 | 27.0 | 6.3 | | | Toluene |
| | | | | 27.8 | 0.8 | 27.5 | 0.1 | $C_8$-ene |
| | | | | | | 28.3 | 0.1 | |
| 28.8 | T | 28.4 | 3.2 | | | | | 2-Methyl-3-pentanone, $C_7$-ene |
| 29.5 | 0.2 | 29.2 | 12.4 | 28.8 | 5.6 | | | n-Hexanal |
| 30.7 | 0.2 | 30.3 | 13.7 | 29.9 | 16.2 | | | $C_8$-species, 3-Methylcyclopentanone |
| | | 31.0 | 4.3 | 30.7 | 4.1 | | | $C_8$-species |
| 32.5 | T | | | | | | | |
| | | | | 33.0 | 2.4 | | | $C_9$-ane |
| | | 34.0 | 3.6 | | | | | $C_2$-benzene, $C_9$-ane |
| 34.5 | 0.1 | | | | | | | Cyclohexanone |
| | | | | 35.2 | 5.9 | | | $C_9$-ene |
| 36.0 | 0.1 | 36.7 | 15.7 | 37.2 | 3.3 | | | $C_9$-ene, 2-heptanone |
| | | | | 38.2 | 0.8 | | | |
| | | 39.0 | 12.8 | | | | | $C_9$-ene |
| | | 42.0 | 0.7 | | | | | |
| | | 47.8 | 3.2 | | | | | $C_3$-benzene, 2-octanone |
| | | 51.0 | 5.4 | | | | | |
| | | 55.0 | 1.4 | | | | | |

a) This fraction was examined under the following conditions: Column: stainless steel, 8' x 1/8" Porapak Q, detector: a 10% split into F.I., He flow: 35 ml/min. Column temperature: 50-220°C programmed at 8°/min. b) This was the liquid phase of the fraction. Area is given in square inches x attenuation per microliter of sample. c) This fraction was examined under the following conditions: Column: stainless steel, 8' x 1/8" Porapak Q, detector: a 43% split into F.I., He flow: 35 ml/min, column temperature: 50-220°C programmed at 7°/min. d) This was the gaseous phase of the fraction; a 14 mm pressure was used. e) A 21 mm pressure was used. f) Retention time, min. g) This peak was identified by the TC detector only under testing conditions given in footnote a). h) $< 0.05\ in^2/\mu l$ for liquid samples: $< 0.05\ in^2$ for gas samples.

## TABLE IX

## GAS CHROMATOGRAPHY RESULTS: DEGRADATION OF DURO FR-HD HYDRAULIC FLUID

(Apiezon L Column)

| -78°C[a,b] Frac (Top Layer) | | Peak Identification |
|---|---|---|
| r.t.[c] | Area | |
| 0.9 | 0.3 | |
| 1.0 | 0.2 | |
| 1.4 | 0.2 | |
| 4.5 | 0.5 | |
| 4.8 | 1.6 | |
| 5.6 | 1.6 | $C_7$-species |
| 5.8 | 1.1 | |
| 6.4 | 5.4 | $C_7$-species |
| 6.8 | 5.5 | Hexanone |
| 7.2 | 0.8 | |
| 7.7 | 0.9 | |
| 8.5 | 6.5 | $C_8$-species |
| 9.2 | 14.3 | |
| 9.4 | 17.1 | |
| 10.0 | 56.3 | Toluene, $C_8$-species |
| 10.6 | 24.0 | $C_8$-ane |
| 11.0 | 8.5 | |
| 11.4 | 0.8 | |
| 11.9 | 3.7 | $C_9$-species |
| 12.2 | 31.7 | $C_9$-species |
| 12.5 | 17.3 | $C_9$-species |
| 12.9 | 29.6 | $C_9$-species |
| 13.5 | 16.5 | $C_9$-species |
| 13.9 | 25.6 | $C_9$-species |
| 14.2 | 26.7 | $C_9$-species |
| 14.7 | 25.1 | $C_9$-ane |
| 15.9 | 11.2 | $C_{10}$-species |
| 16.4 | 4.8 | |
| 16.6 | 21.3 | $C_{10}$-species |
| 17.2 | 1.1 | |
| 17.6 | 0.5 | |
| 18.0 | 6.4 | $C_{10}$-species |
| 18.3 | 29.9 | $C_{10}$-species |
| 18.9 | 32.5 | $C_{10}$-ane |
| 19.6 | 7.5 | |
| 20.1 | 9.6 | $C_{11}$-species |
| 20.5 | 2.7 | $C_3$-benzene |
| 21.1 | 11.7 | |
| 22.0 | 8.0 | |
| 22.3 | 23.5 | $C_{11}$-species |
| 22.8 | 13.9 | $C_{11}$-ane |
| 23.2 | 11.2 | |
| 23.8 | 1.6 | |
| 24.3 | 1.1 | |
| 24.7 | 1.6 | |
| 25.1 | 7.5 | $C_4$-benzene |
| 25.8 | 11.2 | $C_{12}$-species |
| 26.2 | 11.2 | $C_{12}$-species |
| 26.6 | 16.5 | $C_{12}$-ane |
| 27.4 | 0.5 | |
| 28.0 | 1.6 | |
| 29.4 | 3.5 | |
| 29.6 | 1.6 | 1,2,3,4-Tetrahydronapthalene |
| 30.2 | 4.8 | |
| 31.4 | 4.5 | |
| 31.9 | 1.9 | |
| 32.5 | 2.7 | |
| 33.2 | 0.3 | |
| 34.2 | 4.8 | |
| 36.2 | 0.5 | |
| 36.9 | 1.1 | |

## TABLE IX- Cont'd.

## GAS CHROMATOGRAPHY RESULTS: DEGRADATION OF DURO FR-HD HYDRAULIC FLUID

(Apiezon L Column)

a) This fraction was examined under the following conditions: Column: stainless steel, 10' x 1/8" 4% Apiezon L on Chromosorb G, detector: a 43% split into F.I. He flow: 35 ml/min, column temperature: 35 to 220°C programmed at 4°C/min. b) This was the liquid phase of the fraction. Area is given in square inches x attenuation per microliter of sample. c) Retention time, min.

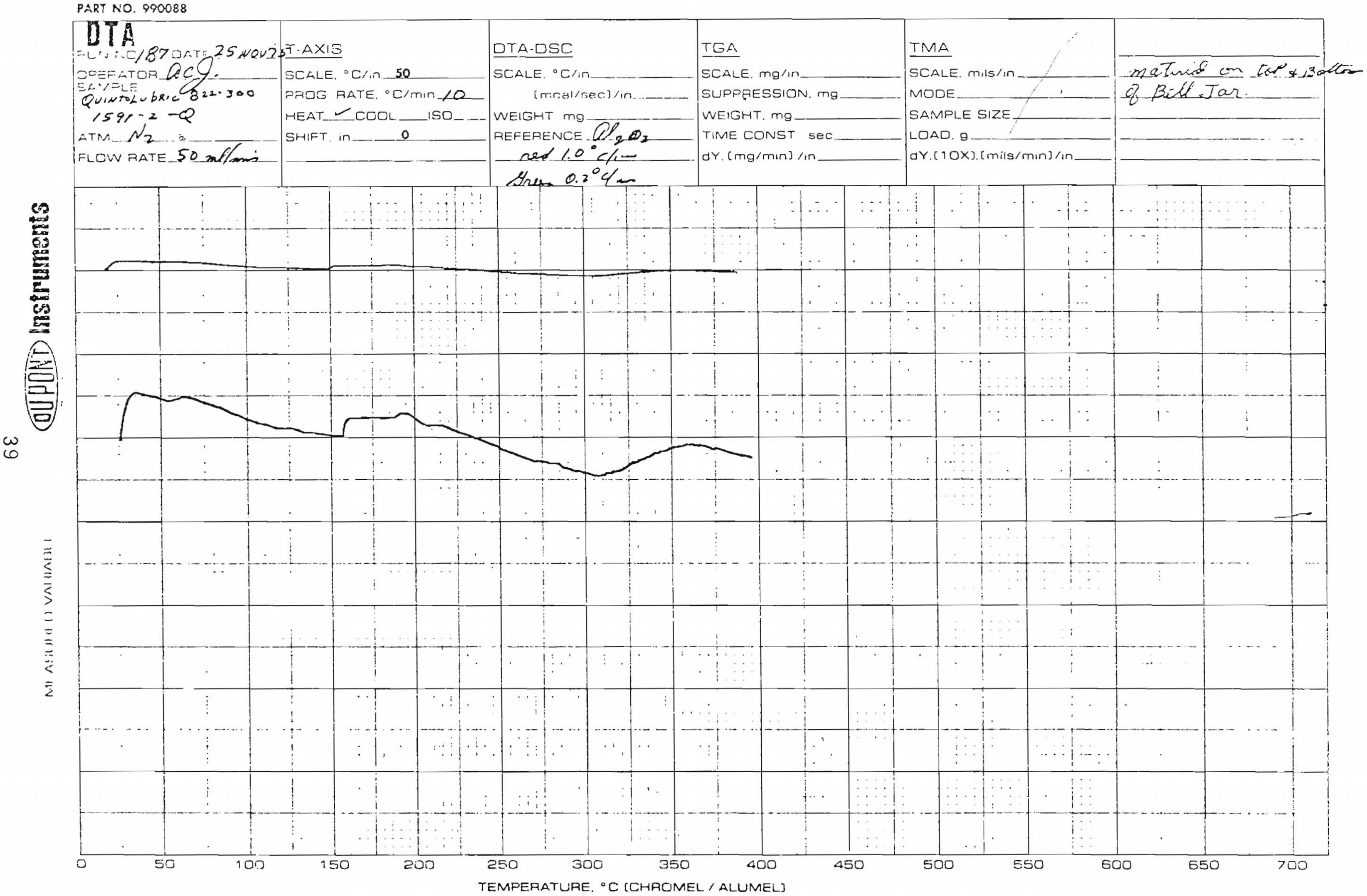
Acetic acid, however, was most certainly formed inasmuch as acetaldehyde was found. Since methanol was also detected one would assume that formic acid and formaldehyde were also produced. It has to be stressed that the large quantity of water present makes the analyses of these compounds exceedingly difficult.

The quantity of toxic products generated was relatively small, yet larger than that found for the glycol-water compositions. Furthermore, the preferential distillation of water, which functions as the flame retardant in the system, leaves the mineral oil, a hydrocarbon fuel, free to decompose oxidatively and ultimately to burn. The situation is different in glycol-water compositions since here the glycol is to a degree chemically associated with water and thus it is almost impossible by distillation to free the glycol from water. Thus, based on the current study, it would appear that mineral oil-water emulsions present a greater hazard both from toxicity and flammability aspects than the water-glycol based fluids.

### 3.2.3 Synthetics Other Than Phosphate Esters

The only fluid investigated in this class of materials was Quintolubric 822-300. According to the manufacturer, this fluid is composed of synthetic organic esters which is supported by the material's infrared spectrum and the type of products obtained on thermal oxidative degradation.

The extent of decomposition at 370°C, as shown by the volatiles formed and residue recovered (see Table II), was very minor, in agreement with the differential thermal analysis (DTA) given in Figure 6 wherein up to 390°C no significant endotherms or exotherms are evident. Based on its infrared spectrum, the residue appeared to consist of unchanged starting material. From the sides of the bulb a



PART NO. 990088

**DTA**

RUN NO. 187 DATE 25 NOV 75

OPERATOR ACJ.

SAMPLE QUINTOLUBRIC 822-300 1591-2-Q

ATM N2

FLOW RATE 50 ml/min

T-AXIS

SCALE, °C/in 50

PROG RATE, °C/min 10

HEAT ✓ COOL ___ ISO ___

SHIFT, in 0

DTA-DSC

SCALE, °C/in

(mcal/sec)/in

WEIGHT, mg

REFERENCE $Al_2O_3$

red 1.0 °C/in

Green 0.2 °C/in

TGA

SCALE, mg/in

SUPPRESSION, mg

WEIGHT, mg

TIME CONST sec

dY, (mg/min) /in

TMA

SCALE, mils/in

MODE

SAMPLE SIZE

LOAD, g

dY, (10X), (mils/min) /in

material on top + Bottom of Bell Jar.

Figure 6: DTA of Quintolubric 822-300 Hydraulic Fluid

liquid, 15 mg (10% of the weight loss), was recovered. Its infrared spectrum indicated the presence of Quintolubric 822-300 admixed with what appeared to be a long chain aliphatic alcohol.

Examining the tabulations of gas chromatographic analyses given in Tables X and XI in conjunction with the mg/g compilation summarized in Table XIV, it can be seen that among the 52 compounds or family of compounds identified and quantitated (which accounted for 99.10% of volatiles collected), the main species found were aliphatic hydrocarbons, aldehydes, ketones, esters, and alcohols. These would be the expected decomposition products formed from an aliphatic ester system. The trace of COS, which was detected, indicates the presence of sulfur-containing components. The quantity of CO formed is surprisingly low. The only toxic species in addition to CO were acrolein and benzene. On the other hand, since formate esters were identified it has to be assumed that formic acid and possibly formaldehyde were also produced.

To determine the effect of higher temperatures a test analogous to that conducted at 370°C was performed at "420°C". It should be stressed that although the metal bath was at 420°C prior to immersing the finger with the sample, during the actual test the temperature was 405°C. It is evident from the data given in Table II that the extent of decomposition for Quintolubric 822-300 at "420°C" was only somewhat higher than that observed at 370°C (8.8% weight loss versus 3.3%). The type of products formed (see Table XIV) and their relative proportion were also comparable, although at the higher temperature the relative quantities of substituted aromatics and e.g., carbonyl sulfide were increased, whereas that of the simple compounds such as acrolein and propionaldehyde, were

## TABLE X

## GAS CHROMATOGRAPHY RESULTS: DEGRADATION OF QUINTOLUBRIC 822-300 HYDRAULIC FLUID AT 370°C

(Porapak Q Column)

| $-78^{\circ}C$ [a,b] Frac (Bottom Layer) | | $-78^{\circ}C$ [a,b] Frac (Top Layer) | | $-78^{\circ}C$ [c,d] Frac (Vapor) | | $-196^{\circ}C$ [c,e] Frac | | Peak Identification |
|---|---|---|---|---|---|---|---|---|
| r.t.[f] | Area | r.t. | Area | r.t. | Area | r.t. | Area | |
| | | | | | | 2.3[g] | 24.3 | $CO_2$ |
| | | | | | | 2.9 | 2.8 | $C_2H_4$ |
| | | | | | | 3.6 | 2.5 | $C_2H_6$ |
| | | | | | | 5.0[g] | 0.3 | COS |
| 6.8[g] | 349.6 | | | | | | | $H_2O$ |
| | | | | 7.5 | 0.4 | 7.5 | 8.0 | $C_3H_6$ |
| | | | | | | 8.0 | 3.6 | $C_3H_8$ |
| 9.8 | 3.0 | | | 10.0 | 0.5 | | | Methanol |
| 11.3 | 0.5 | | | 10.6 | 0.6 | 10.5 | 3.4 | Acetaldehyde |
| | | | | 12.4 | 0.2 | 12.5 | 0.2 | $C_4$-ane |
| | | | | 12.9 | 0.3 | 12.9 | 18.6 | $C_4$-ene |
| | | | | 13.5 | 0.1 | 13.5 | 8.1 | $C_4$-ane |
| 14.7 | 0.5 | | | | | | | Ethanol |
| 16.3 | 0.1 | 16.0 | T[h] | 16.1 | 4.7 | 16.1 | 2.3 | Propionaldehyde, acetone, furan, acrolein |
| 16.6 | 0.8 | 16.4 | 0.1 | | | | | Acetone |
| | | | | | | 16.9 | 0.1 | $C_5$-species |
| | | 17.2 | 0.1 | 17.3 | T | | | Methyl acetate, methyl propyl ether |
| 17.3 | 0.4 | | | | | | | Propanol |
| | | | | 17.8 | 0.3 | 17.8 | 9.5 | $C_5$-ene |
| | | | | 18.3 | 0.5 | 18.3 | 12.0 | $C_5$-ane |
| 18.4 | 1.1 | 18.9 | 5.1 | 19.4 | 37.1 | 19.1 | 6.8 | Isobutyraldehyde |
| 20.4 | 1.0 | 19.9 | 2.9 | 20.4 | 7.5 | 20.5 | 0.4 | Methyl ethyl ketone, n-butyraldehyde |
| | | 20.7 | 1.1 | 21.4 | 4.9 | 21.4 | 11.4 | $C_6$-ene |
| 21.2 | 0.1 | | | | | | | |
| | | 21.0 | 1.7 | 22.1 | 10.3 | 22.1 | 8.1 | $C_6$-ene |
| 22.0 | 0.3 | | | | | | | |
| | | 21.8 | 1.6 | 22.5 | 13.1 | 22.5 | 7.6 | $C_6$-ane |
| | | 22.4 | 2.8 | 23.1 | 1.1 | | | Benzene |
| 23.0 | 0.7 | 22.6 | 2.7 | 23.7 | 12.6 | 23.7 | 3.2 | 2-Methylbutyraldehyde, cyclohexene |
| 24.2 | 0.6 | 23.5 | 3.7 | 24.5 | 4.6 | | | n-Pentanal |
| | | 24.3 | 26.4 | 25.8 | 63.0 | 25.7 | 2.1 | $C_7$-species |
| 25.3 | 0.3 | | | | | | | |

## TABLE X-Cont'd.

## GAS CHROMATOGRAPHY RESULTS: DEGRADATION OF QUINTOLUBRIC 822-300 HYDRAULIC FLUID AT $370^{\circ}$C

(Porapak Q Column)

| $-78^{\circ}$C[a,b] Frac (Bottom Layer) | | $-78^{\circ}$C[a,b] Frac (Top Layer) | | $-78^{\circ}$C[c,d] Frac (Vapor) | | $-196^{\circ}$C[c,e] Frac | | Peak Identification |
|---|---|---|---|---|---|---|---|---|
| r.t.[f] | Area | r.t. | Area | r.t. | Area | r.t. | Area | |
| | | 25.7 | 0.7 | 26.1 | 25.3 | 26.1 | 0.7 | $C_7$-ane |
| | | 26.7 | 5.9 | 27.4 | 3.0 | | | Toluene |
| 27.2 | 0.5 | | | | | | | Cyclopentanone |
| 28.5 | 1.3 | 27.7 | 11.6 | | | | | 2-Hexanol |
| | | 28.7 | 8.8 | 29.0 | 1.6 | | | n-Hexanal |
| 29.5 | 0.3 | | | | | | | |
| | | | | 29.7 | 5.1 | | | $C_8$-diene |
| | | 29.8 | 37.5 | 30.7 | 17.2 | | | $C_8$-ene |
| | | | | 31.1 | 13.7 | | | $C_8$-ane |
| | | 32.8 | 4.7 | 33.1 | 1.3 | | | $C_2$-benzene |
| | | | | 34.6 | 0.2 | | | Styrene |
| | | 35.0 | 1.3 | | | | | n-Heptanal |
| 35.5 | 0.1 | | | | | | | Cyclohexanone |
| | | 37.0 | 3.6 | | | | | $C_9$-ene |
| 38.5 | 1.6 | 38.7 | 17.9 | 38.5 | 2.6 | | | $C_9$-ene |
| | | 40.6 | 0.7 | | | | | |
| | | 43.5 | 1.2 | | | | | |
| | | 46.5 | 5.6 | | | | | |
| | | 53.0 | 12.0 | | | | | $C_{10}$ species,<br>$C_4$-benzene |
| | | 62.0 | 2.0 | | | | | |

a)This fraction was examined under the following conditions: Column: stainless steel, 8' x 1/8" Porapak Q, detector: a 10% split into F.I., He flow: 35 ml/min. Column temperature: 50-220°C programmed at 8°/min. b) This was the liquid phase of the fraction. Area is given in square inches x attenuation per microliter of sample. c) This fraction was examined under the following conditions: Column: stainless steel, 8' x 1/8" Porapak Q, detector: a 43% split into F.I., He flow: 35 ml/min. column temperature: 50-220°C programmed at 7°/min. d) This was the gaseous phase of the fraction; a 12 mm pressure was used. e) A 14 mm pressure was used. f) Retention time, min. g) This peak was identified by the TC detector only under testing conditions given in footnote a). h) < 0.05 in$^2$/$\mu$l for liquid samples: < 0.05 in$^2$ for gas samples.

## TABLE XI

## GAS CHROMATOGRAPHY RESULTS: DEGRADATION OF QUINTOLUBRIC 822-300 HYDRAULIC FLUID AT 370°C

(Apiezon L Column)

| $0^{\circ}C^{a,b}$ Frac | | $-23^{\circ}C^{a,b}$ Frac | | $-78^{\circ}C^{a,b}$ Frac (Top Layer) | | Peak Identification |
|---|---|---|---|---|---|---|
| r.t.[c] | Area | r.t. | Area | r.t. | Area | |
| | | | | 3.2 | 1.0 | $C_6$-ene |
| | | | | 4.0 | 29.8 | Isobutyraldehyde |
| | | | | 4.7 | 15.9 | |
| | | | | 5.6 | 9.0 | |
| | | | | 6.3 | 96.5 | $C_7$-ene |
| 7.3 | 2.5 | | | 6.8 | 94.6 | $C_7$-ane |
| | | | | 8.6 | 6.4 | |
| | | | | 9.4 | 99.2 | $C_8$-diene |
| | | | | 10.1 | 92.3 | $C_8$-ene |
| 11.2 | 1.4 | | | 10.7 | 126.2 | $C_8$-ane |
| 11.9 | 5.2 | | | 12.0 | 8.5 | |
| | | 13.0 | 18.1 | 13.0 | 1.6 | |
| | | | | 13.4 | 11.0 | |
| | | | | 14.2 | 49.8 | $C_9$-ene |
| | | | | 14.8 | 97.8 | $C_9$-ane |
| 15.5 | 3.8 | 15.4 | 38.5 | | | |
| | | | | 15.8 | 8.2 | Styrene |
| 17.2 | 7.8 | 17.1 | 0.8 | 17.0 | 49.4 | $C_9$-species |
| | | | | 17.7 | 16.5 | $C_3$-benzene |
| | | | | 18.3 | 48.0 | $C_{10}$-ene |
| 18.8 | 5.6 | 18.6 | 8.5 | | | |
| 19.3 | 7.2 | 19.1 | 10.8 | 18.9 | 51.2 | $C_{10}$-ane |
| | | | | 19.9 | 5.0 | |
| | | 20.1 | 1.2 | 20.2 | 9.6 | $C_4$-benzene |
| | | 20.7 | 2.8 | | | |
| 21.5 | 7.8 | 21.5 | 19.8 | 21.1 | 8.7 | $C_4$-benzene |
| | | 21.9 | 45.6 | 21.8 | 7.3 | $C_{11}$-species |
| 22.7 | 5.0 | 22.5 | 160.0 | 22.3 | 10.9 | $C_{11}$-ene |
| 23.3 | 56.4 | 23.1 | 371.2 | 22.8 | 52.3 | $C_{11}$-ene |
| | | 23.4 | 160.0 | 23.2 | 2.3 | $C_{11}$-species |
| 24.2 | 4.4 | 24.0 | 22.4 | 24.2 | 11.4 | $C_{11}$-species |
| 24.7 | 13.2 | 24.5 | 67.2 | | | $C_{11}$-species |
| 25.1 | 4.0 | 25.3 | 65.6 | 25.1 | 1.7 | $C_{11}$-species |

TABLE XI - Cont'd.

GAS CHROMATOGRAPHY RESULTS: DEGRADATION OF QUINTOLUBRIC 822-300 HYDRAULIC FLUID AT 370°C

(Apiezon L Column)

| $0^{\circ}C^{a,b}$ Frac | | $-23^{\circ}C^{a,b}$ Frac | | $-78^{\circ}C^{a,b}$ Frac (Top Layer) | | Peak Identification |
|---|---|---|---|---|---|---|
| r.t.[c] | Area | r.t. | Area | r.t. | Area | |
| 25.5 | 29.6 | | | | | 1,1-Dimethylindan |
| 26.0 | 53.2 | 25.9 | 76.8 | 25.7 | 2.5 | $C_5$-benzene, $C_{10}$-ketone |
| 26.6 | 69.6 | 26.4 | 56.0 | 26.2 | 1.1 | $C_{12}$-ene |
| 27.1 | 62.8 | 26.8 | 47.2 | 26.6 | 0.3 | $C_{12}$-ane |
| 28.0 | 19.2 | 27.8 | 6.8 | | | |
| 28.5 | 7.6 | 28.3 | 5.6 | | | $C_{11}$-ketone |
| 28.7 | 6.0 | 29.0 | 6.0 | | | |
| 29.7 | 29.2 | | | | | $C_6$-benzene |
| 30.0 | 68.0 | 29.7 | 9.0 | | | $C_{13}$-ene |
| 30.7 | 52.0 | 30.5 | 6.8 | | | $C_{13}$-ane |
| 31.7 | 6.4 | | | | | $C_6$-benzene |
| 32.2 | 14.4 | 31.8 | 3.2 | | | $C_{12}$-ketone |
| 33.0 | 72.8 | 32.8 | 5.6 | | | 3,4,7-Trimethyl-1-indanone |
| 33.5 | 33.6 | | | | | $C_7$-benzene, $C_{14}$-ene |
| 34.0 | 20.0 | 34.0 | 15.0 | | | |
| 35.1 | 8.2 | | | | | Diphenyl ether |
| 36.2 | 1.2 | | | | | |
| 36.5 | 2.8 | | | | | |
| 36.7 | 0.6 | | | | | |
| 37.4 | 52.8 | 37.2 | 15.0 | | | |
| 39.2 | 0.5 | | | | | |
| 39.7 | 0.8 | | | | | |
| 40.8 | 7.5 | | | | | |
| 45.2 | 2.6 | | | | | |

a) This fraction was examined under the following conditions: Column: stainless steel, 10' x 1/8" 4% Apiezon L on Chromosorb G, detector: a 43% split into F.I. He flow: 35 ml/min, column temperature: 35 to 220°C programmed at 4°C/min. b) This was the liquid phase of the fraction. Area is given in square inches x attenuation per microliter of sample. c) Retention time, min.

TABLE XII

GAS CHROMATOGRAPHY RESULTS: DEGRADATION OF QUINTOLUBRIC 822-300 HYDRAULIC FLUID AT "420°C"

(Porapak Q Column)

| $-78^{\circ}C^{a,b}$ Frac (Bottom Layer) | | $-78^{\circ}C^{a,b}$ Frac (Top Layer) | | $-78^{\circ}C^{c,d}$ Frac (Vapor) | | $-196^{\circ}C^{a,e}$ Frac | | Peak Identification |
|---|---|---|---|---|---|---|---|---|
| r.t.[f] | Area | r.t. | Area | r.t. | Area | r.t. | Area | |
| | | | | | | 2.0[g] | 1.1 | $CO_2$ |
| | | | | 2.8 | T[h] | 3.3 | 3.9 | $C_2H_4$ |
| | | | | 3.4 | T | 4.1 | 7.8 | $C_2H_6$ |
| 6.5[g] | 320.0 | | | | | | | $H_2O$ |
| | | | | 7.4 | 0.3 | 8.4 | 13.0 | $C_3H_6$ |
| | | | | 7.9 | 0.1 | 8.8 | 17.3 | $C_3H_8$ |
| 10.4 | 0.8 | | | | | | | Methanol |
| 11.3 | T | | | 10.3 | 0.1 | | | Acetaldehyde |
| | | 12.0 | 0.1 | 12.2 | T | 13.1 | 0.5 | $C_4$-ane |
| | | | | 12.7 | 0.5 | 13.3 | 35.2 | $C_4$-ene |
| | | | | 13.3 | 0.5 | 13.8 | 29.1 | $C_4$-ene, $C_4$-ane |
| 16.0 | 0.1 | | | | | | | Ethanol, formic acid |
| 16.7 | 0.3 | 16.2 | 0.1 | 15.8 | 1.0 | 16.3 | 0.5 | Propionaldehyde, acrolein, acetone |
| | | 16.4 | 0.1 | | | | | Methyl acetate |
| | | | | 16.7 | 0.2 | 17.2 | 0.5 | $C_5$-ene |
| | | 17.2 | 0.9 | 17.1 | 0.2 | 17.8 | 21.3 | $C_5$-ene |
| 17.7 | 0.1 | | | | | | | Isopropanol |
| | | 17.4 | 2.5 | 17.5 | 8.1 | 18.2 | 37.4 | $C_5$-ane |
| | | 17.8 | 1.5 | 18.0 | 19.7 | 18.7 | 5.4 | $C_5$-species |
| 18.9 | 1.4 | | | | | | | Acetic acid |
| 19.4 | 0.1 | 18.7 | 4.4 | 19.1 | 27.7 | 20.1 | 1.1 | Isobutyraldehyde |
| 20.5 | T | | | 20.2 | 0.4 | | | Methyl ethyl ketone, n-butyraldehyde |
| | | 20.2 | 2.5 | | | | | $C_6$-ene |
| | | 20.6 | 13.5 | 21.1 | 4.8 | 21.2 | 3.4 | $C_6$-ene |
| | | 20.8 | 29.7 | 21.8 | 27.0 | 21.8 | 9.0 | $C_6$-ene |
| | | 21.6 | 1.4 | 22.2 | 38.9 | 22.2 | 11.4 | $C_6$-ane, benzene |
| | | 22.0 | 1.0 | | | | | Benzene |
| 21.7 | T | | | | | | | |
| 22.4 | 0.2 | | | | | | | n-Butanol |
| 23.2 | T | 22.5 | 10.8 | 23.4 | 6.8 | 23.5 | 0.6 | Cyclohexene, 2-methyl butyraldehyde |
| 23.8 | 1.0 | | | | | | | Propionic acid |
| | | | | 24.4 | 0.2 | | | n-Pentanal |
| | | | | 25.5 | 28.8 | | | $C_7$-ene |
| | | 23.7 | 103.1 | 25.9 | 16.8 | 25.3 | 1.1 | $C_7$-ane |
| 25.6 | 0.4 | | | | | | | $C_5$-ketone |

TABLE XII-Cont'd.

GAS CHROMATOGRAPHY RESULTS: DEGRADATION OF
QUINTOLUBRIC 822-300 HYDRAULIC FLUID
AT "420°C"
(Porapak Q Column)

| -78°C [a,b] Frac (Bottom Layer) | | -78°C [a,b] Frac (Top Layer) | | -78°C [c,d] Frac (Vapor) | | -196°C [a,e] Frac | | Peak Identification |
|---|---|---|---|---|---|---|---|---|
| r.t.[f] | Area | r.t. | Area | r.t. | Area | r.t. | Area | |
| | | 25.0 | 5.2 | 27.0 | 1.2 | | | Toluene, $C_7$-species |
| 26.5 | 0.3 | | | | | | | $C_5$-alcohol |
| 27.7 | 0.2 | | | | | | | Cyclopentanone |
| 28.6 | 0.2 | 25.7 | 9.8 | | | | | 2-Hexanol |
| | | 26.7 | 4.6 | 29.2 | 0.7 | | | $C_8$-species |
| | | 27.8 | 93.8 | 30.2 | 5.8 | | | $C_8$-ene |
| | | 29.5 | 1.5 | 30.6 | 5.9 | | | $C_8$-ane |
| | | 30.6 | 12.7 | 32.3 | 0.6 | | | $C_2$-benzene |
| | | 32.2 | 13.3 | 33.7 | 0.2 | | | Styrene |
| 33.3 | 0.1 | | | | | | | Cyclohexanone |
| | | 34.4 | 50.6 | 35.5 | 0.4 | | | $C_9$-species |
| | | 37.5 | 0.7 | 37.5 | 1.8 | | | $C_9$-species |
| | | 39.0 | 1.1 | | | | | $C_9$-ene, $C_9$-ane |
| | | 40.8 | 0.6 | | | | | $C_9$-species |
| | | 47.2 | 12.3 | | | | | $C_{10}$-species |

a) This fraction was examined under the following conditions: Column: stainless steel, 8' x 1/8" Porapak Q, detector: a 10% split into F.I., He flow: 35 ml/min. Column temperature: 50-220°C programmed at 8°/min. b) This was the liquid phase of the fraction. Area is given in square inches x attenuation per microliter of sample. c) This fraction was examined under the following conditions: Column: stainless steel, 8' x 1/8" Porapak Q, detector: a 43% split into F.I., He flow: 35 ml/min. column temperature: 50-220°C programmed at 7°/min. d) This was the gaseous phase of the fraction; a 13 mm pressure was used. e) A 106 mm pressure was used. Area is given in square inches x attenuation. f) Retention time, min. g) This peak was identified by the TC detector only under testing conditions given in footnote a). h) < 0.05 $in^2/\mu l$ for liquid samples; < 0.05 $in^2$ for gas samples.

TABLE XIII

GAS CHROMATOGRAPHY RESULTS: DEGRADATION OF QUINTOLUBRIC 822-300 HYDRAULIC FLUID AT "420°C"

(Apiezon L Column)

| $0^{o}$ Frac[a,b] | | $-23^{o}C$ Frac | | $-78^{o}C$ Frac (Top Layer) | | Peak Identification |
|---|---|---|---|---|---|---|
| r.t.[c] | Area | r.t. | Area | r.t. | Area | |
| | | | | 2.0 | 6.8 | $C_5$-species |
| | | | | 3.0 | 11.6 | $C_6$-species |
| | | | | 3.9 | 39.0 | $C_6$-species |
| | | | | 4.1 | 138.9 | $C_6$-species |
| | | | | 5.4 | 4.0 | |
| | | | | 6.1 | 128.0 | $C_7$-ene |
| | | | | 6.6 | 163.8 | $C_7$-ane |
| | | | | 8.0 | 4.0 | |
| | | | | 8.4 | 5.4 | |
| | | | | 9.2 | 18.9 | |
| | | | | 9.8 | 143.4 | $C_8$-ene |
| | | | | 10.5 | 189.4 | $C_8$-ane |
| | | | | 11.9 | 8.6 | |
| | | | | 12.6 | 8.5 | |
| | | | | 13.2 | 6.6 | |
| | | 14.2 | 22.1 | 13.9 | 107.5 | $C_9$-ene |
| 15.0 | 1.1 | 14.6 | 80.5 | 14.5 | 152.3 | $C_9$-ene |
| | | | | 15.5 | 28.5 | Styrene |
| 16.9 | 10.0 | 16.7 | 68.8 | 16.6 | 32.6 | $C_9$-ene, diester ? |
| 17.7 | 2.3 | 17.5 | 16.0 | 17.3 | 8.0 | $C_9$-species, $C_3$-benzene |
| 18.3 | 24.5 | 18.1 | 166.4 | 18.0 | 16.6 | $C_{10}$-ene |
| 18.8 | 44.0 | 18.7 | 270.9 | 18.5 | 22.4 | $C_{10}$-ane |
| | | 19.6 | 32.0 | | | $C_{10}$-species |
| 20.4 | 24.3 | 19.9 | 26.1 | | | $C_4$-benzene |
| 21.1 | 45.6 | 20.8 | 64.5 | 20.7 | 3.0 | $C_{10}$-species |
| 21.7 | 42.1 | 21.5 | 38.9 | 21.5 | 14.4 | $C_{10}$-species |
| 22.3 | 156.8 | 22.1 | 123.7 | 22.0 | 1.0 | $C_{11}$-ene |
| 22.8 | 441.6 | 22.6 | 371.2 | 22.5 | 3.6 | $C_{11}$-ane, $C_{11}$-ene |
| 23.7 | 44.8 | 23.5 | 20.8 | | | $C_{11}$-species |
| 24.2 | 20.8 | 24.0 | 12.3 | | | |
| 24.5 | 11.7 | 24.3 | 3.7 | | | |
| 25.0 | 103.5 | 24.8 | 23.2 | | | 1,2-Dimethylindan |
| 25.6 | 35.2 | 25.4 | 17.1 | | | $C_5$-benzene |
| 26.1 | 64.0 | 25.9 | 13.3 | | | $C_{12}$-ene |
| 26.5 | 101.3 | 26.3 | 17.1 | | | $C_{12}$-ane |
| 27.5 | 49.6 | | | | | $C_{12}$-species |
| 28.2 | 1.1 | | | | | |

TABLE XIII-Cont'd.

GAS CHROMATOGRAPHY RESULTS: DEGRADATION OF
QUINTOLUBRIC 822-300 HYDRAULIC FLUID
AT "420°C"
(Apiezon L Column)

| 0° Frac[a,b] | | -23°C Frac | | -78°C Frac (Top Layer) | | Peak Identification |
|---|---|---|---|---|---|---|
| r.t.[c] | Area | r.t. | Area | r.t. | Area | |
| 28.7 | 41.1 | 28.6 | 1.7 | | | $C_{12}$-species |
| 29.4 | 30.9 | 29.2 | 0.6 | | | $C_{12}$-species |
| 29.6 | 16.0 | | | | | $C_{13}$-ene |
| 30.1 | 30.9 | 30.1 | 1.9 | | | $C_{13}$-ane |
| 31.1 | 4.3 | 31.6 | 6.2 | | | |
| 32.3 | 31.9 | | | | | 3,4,7-Trimethylindanone |
| 33.0 | 19.5 | | | | | |
| 33.4 | 3.7 | | | | | |
| 33.6 | 3.1 | | | | | |
| 35.6 | 4.5 | | | | | |
| 37.0 | 2.1 | | | | | |
| 42.3 | 0.8 | | | | | |

a) This fraction was examined under the following conditions: Column: stainless steel, 10' x 1/8" 4% Apiezon L on Chromosorb G, detector: a 43% split into F.I., He flow: 35 ml/min, column temperature: 35 to 220°C programmed at 4°C/min.
b) This was the liquid phase of the fraction. Area is given in square inches x attenuation per microliter of sample. c) Retention time, min.

## TABLE XIV

## VOLATILE PRODUCTS OBTAINED ON THERMAL OXIDATIVE DEGRADATION OF MISCELLANEOUS HYDRAULIC FLUIDS

| Products | Ucon Hydrolube 275 CP mg/g | Citgo Glycol FR-20 XD mg/g | SNFH mg/g | Duro FR-HD mg/g | Quintolubric 822-300 | |
|---|---|---|---|---|---|---|
| | | | | | 370°C mg/g | "420°C" mg/g |
| CO | 1.51 | 1.89 | - | 3.50 | 1.36 | 1.87 |
| $CH_4$ | T[a] | - | - | - | 0.511 | 0.797 |
| $H_2O$ | 347 | 212 | 200 | 400 | 8.39 | 8.32 |
| $CO_2$ | 3.26 | 4.15 | 1.50 | 1.79 | 1.39 | 2.95 |
| COS | - | - | - | 0.032 | 0.016 | 0.106 |
| $N_2O$ | 0.344 | 0.295 | - | - | - | - |
| $C_2$-species | 0.071 | 0.901 | 0.011 | 0.650 | 0.187 | 0.867 |
| $C_3$-species | 0.056 | 0.045 | 0.011 | 0.392 | 0.410 | 2.23 |
| $C_4$-species | 0.002 | 0.004 | 0.009 | 1.34 | 0.958 | 4.64 |
| $C_5$-species | - | - | 0.005 | 0.409 | 0.761 | 5.21 |
| $C_6$-species | - | - | 0.008 | 0.519 | 1.20 | 5.88 |
| $C_7$-species | - | - | 0.017 | 0.628 | 1.15 | 8.32 |
| $C_8$-species | - | - | 0.025 | 0.262 | 1.27 | 7.22 |
| $C_9$-species | - | - | 0.037 | 1.11 | 0.890 | 6.34 |
| $C_{10}$-species | - | - | - | 0.61 | 0.464 | 5.48 |
| $C_{11}$-species | - | - | - | 0.277 | 1.52 | 9.74 |
| $C_{12}$-species | - | - | - | 0.232 | 0.383 | 3.36 |
| $C_{13}$-species | - | - | - | - | 0.253 | 0.525 |
| $C_{14}$-species | - | - | - | - | 0.026 | - |
| Benzene | T | 0.002 | 0.002 | 0.008 | 0.098 | 0.205 |
| Toluene | 0.003 | 0.007 | 0.009 | 0.088 | 0.157 | 0.332 |
| $C_2$-benzenes | - | - | 0.028 | 0.012 | 0.122 | 0.663 |
| $C_3$-benzenes | - | - | 0.007 | 0.013 | 0.056 | 0.063 |
| $C_4$-benzenes | - | - | - | 0.003 | 0.074 | 0.121 |
| $C_5$-benzenes | - | - | - | - | 0.118 | 0.447 |
| $C_6$-benzenes | - | - | - | - | 0.016 | - |
| $C_7$-benzenes | - | - | - | - | 0.033 | - |
| Styrene | - | - | - | - | T | 0.694 |
| Tetrahydronapthalenes | - | - | - | 0.006 | - | - |
| Dimethylindans | - | - | - | - | 0.056 | 1.19 |
| 3,4,7-Trimethyl-1-indanone | - | - | - | - | 0.138 | 0.357 |
| Chloroform | - | - | 0.005 | - | - | - |

TABLE XIV-Cont'd.

VOLATILE PRODUCTS OBTAINED ON THERMAL OXIDATIVE DEGRADATION OF MISCELLANEOUS HYDRAULIC FLUIDS

| Products | Ucon Hydrolube 275 CP mg/g | Citgo Glycol FR-20XD mg/g | SNFH mg/g | Duro FR-HD mg/g | Quintolubric 822-300 | |
|---|---|---|---|---|---|---|
| | | | | | 370°C mg/g | "420°C" mg/g |
| Tetrachloroethylene | - | - | 0.007 | - | - | - |
| Methanol | 0.052 | 0.066 | 0.009 | 0.068 | 0.215 | 0.045 |
| Ethanol | 0.239 | 0.167 | - | 0.027 | 0.019 | 0.003 |
| $C_3$-alcohols | 0.025 | 0.029 | T | - | 0.011 | 0.002 |
| $C_4$-alcohols | 0.009 | - | - | - | - | 0.003 |
| $C_5$-alcohols | - | - | - | - | - | 0.001 |
| $C_6$-alcohols | - | - | - | - | 0.447 | 0.964 |
| Ethylene glycol | 9.83 | 10.3 | 2.70 | - | - | - |
| 1,2-Propanediol | - | - | 3.59 | - | - | - |
| Acetaldehyde | 0.330 | 0.297 | 0.007 | 1.58 | 0.397 | 0.003 |
| Propionaldehyde | 0.004 | 0.017 | 0.168 | 0.284 | 0.084 | 0.029 |
| Acrolein | - | - | T | 0.006 | 0.017 | T |
| $C_4$-aldehydes | - | 0.005 | 0.001 | 0.315 | 0.830 | 1.54 |
| $C_5$-aldehydes | 0.015 | 0.028 | 0.001 | 0.262 | 0.337 | 1.24 |
| $C_6$-aldehydes | 0.009 | - | 0.050 | 0.186 | 0.321 | - |
| $C_7$-aldehydes | - | - | - | - | 0.046 | - |
| Acetone | 0.058 | 0.086 | 0.010 | 0.500 | 0.130 | 0.078 |
| Methyl ethyl ketone | 0.081 | 0.051 | T | 0.266 | 0.137 | 0.002 |
| $C_5$-ketones | 0.005 | 0.015 | 0.001 | 0.117 | - | 0.008 |
| $C_6$-ketones | 0.002 | 0.007 | - | 0.033 | - | - |
| $C_7$-ketones | - | - | - | 0.064 | - | - |
| $C_8$-ketones | - | - | - | 0.025 | - | - |
| $C_{10}$-ketones | - | - | - | - | 0.052 | - |
| $C_{11}$-ketones | - | - | - | - | 0.015 | - |
| $C_{12}$-ketones | - | - | - | - | 0.028 | - |
| Cyclopentanone | 0.004 | 0.005 | - | - | 0.013 | 0.004 |
| Cyclohexanone | - | 0.009 | - | 0.034 | 0.004 | 0.003 |
| Methyl ether | 0.004 | 0.003 | T | - | - | - |
| Methyl ethyl ether | 0.011 | 0.007 | 0.001 | - | - | - |
| Methyl propyl ether | 0.003 | 0.005 | - | - | 0.003 | - |
| Methyl butyl ether | 0.024 | 0.003 | - | - | - | - |
| Ethyl butyl ether | 0.001 | 0.005 | - | - | - | - |

TABLE XIV-Cont'd.

VOLATILE PRODUCTS OBTAINED ON THERMAL OXIDATIVE DEGRADATION OF MISCELLANEOUS HYDRAULIC FLUIDS

| Products | Ucon Hydrolube 275 CP mg/g | Citgo Glycol FR-20XD mg/g | SNFH mg/g | Duro FR-HD mg/g | Quintolubric 822-300 | |
|---|---|---|---|---|---|---|
| | | | | | 370°C mg/g | "420°C" mg/g |
| Diphenyl ether | - | - | - | - | 0.013 | - |
| Ethylene oxide | 0.693 | 1.04 | - | - | - | - |
| Furan | - | 0.008 | - | T | T | - |
| 2-Methyltetrahydrofuran | - | - | - | 0.062 | - | - |
| 2-Methyl-1,3-dioxolane | 0.028 | 0.049 | - | - | - | - |
| $C_2$-1,3-Dioxolanes | 0.004 | - | - | - | - | - |
| p-Dioxane | 0.013 | 0.125 | - | 0.034 | - | - |
| Formic acid | 0.004 | - | - | - | - | 0.001 |
| Acetic acid | 0.018 | - | - | - | - | 0.061 |
| Propionic acid | - | - | - | - | - | 0.026 |
| Long chain aliphatic acids | - | - | - | - | 0.147 | 1.07 |
| Methyl formate | - | - | - | - | T | - |
| Methyl acetate | - | - | - | - | 0.003 | 0.016 |
| Aliphatic diesters | - | - | - | - | 0.062 | 0.308 |
| Thiacyclopropane | 0.015 | 0.056 | - | 0.804 | - | - |
| Thiophene | - | - | - | 0.010 | - | - |
| Divinyl sulfide | 0.004 | 0.008 | - | - | - | - |
| Acetonitrile | 0.022 | 0.006 | - | - | - | - |
| Propionitrile | 0.020 | 0.009 | - | - | - | - |
| 1-Cyano-1-butene | 0.001 | - | - | - | - | - |

a) < 0.0005 mg/g

decreased. Inasmuch as the relative proportions of the acids, such as formic, acetic and propionic were significantly increased it can be deduced that at the higher temperature the aldehydes were preferentially oxidized. As would be expected $CO_2$ was somewhat increased. The presence of aliphatic diesters was shown by observing in the analysis of a series of compounds exhibiting high abundances at m/e = 115 ($C_5H_7O_3$ or $C_6H_{11}O_2$) associated with the presence of peaks differing by m/e = 14 ($CH_2$) in what is assumed to be the higher members of the series. The latter observation is in agreement with the nature of Quintolubric 822-300 which consists of organic esters. The residue after treatment at "420°C", based on infrared spectral analysis was composed of the unchanged starting material which was also the case in the test conducted at 370°C. A total of 48 species were identified and quantitated in the volatiles formed at "420°C" and these amounted to 99.6% of the materials collected.

Based on the above studies and on the quantities of toxic species such as carbon monoxide, acrolein, formic acid, formaldehyde, etc., measured, it can be deduced that at least at the temperatures investigated Quintolubric 822-300 fluid does not pose a grave hazard insofar as toxic offgassing is concerned.

### 3.2.4 Phosphate Ester Based Hydraulic Fluids

Phosphate ester based hydraulic fluids encompass a wide variety of compositions since not only a large number of different phosphate esters exist and are employed in the manufacture or compounding of hydraulic fluids but also the nature of the hydrocarbon constituents and their proportions as well as those of the chlorinated additives, which are frequently employed, can vary widely. The simplest aromatic phosphate ester is triphenylphosphate, which is also the most volatile of this series.

The four phosphate ester based fluids studied under this program included what were supposed to be hydrocarbon free phosphate esters namely Fyrquel-220 and Pydraul 50E and phosphate ester - hydrocarbon compositions represented by Pydraul MC and Dasco FR 300. In addition a "synthetic" phosphate ester - hydrocarbon "fluid" composed of triphenylphosphate and n-octacosane was also investigated to elucidate the effect of a hydrocarbon upon the mode of decomposition of a phosphate ester, specifically with respect to the production of toxic species. All these materials are listed in Table I.

To determine the type of phosphate ester present in a given fluid these compositions were subjected to gas chromatographic analysis utilizing 10% solution, in 1:1 benzene-toluene and a 1/8" x 10' 1% OV-17 on Chromosorb G-AW (80/100 mesh) column heated isothermally at 250°C. The procedure adopted was developed at the Bureau of Mines by J. Snyder and L. Hofer.[9] Based on these analyses Fyrquel apparently does not contain any triphenylphosphate as shown by the absence of a peak at 26 min in the data given in Table XVI. Pydraul 50 E is composed at least of 40% triphenylphosphate; no other constituents were eluted under the gas chromatographic conditions employed. Pydraul MC also contained at least 44% triphenylphosphate, eighteen additional components were eluted (these were not identified). The retention times and relative areas are given in Table XV. It should be noted that the infrared spectra of Pydraul 50E and MC fluids confirmed the presence of triphenylphosphate. In addition, as will become apparent from later discussion, the exclusive production of phenol (and absence of cresols and other substituted phenolic species) further confirmed that phenylphosphate is the sole phosphate ester ingredient of these fluids. No gas chromatographic peaks were observed for Dasco FR 300 fluid up to 150 min indicating that the phosphate esters present in this composition and the other ingredients were not eluted

## TABLE XV

## GAS CHROMATOGRAPHY RESULTS FOR PYDRAUL MC FLUID[a]

| r.t. min | Area |
|---|---|
| 3.0 | 0.10 |
| 4.0 | 0.64 |
| 5.0 | 0.39 |
| 5.3 | 0.06 |
| 6.3 | 0.04 |
| 7.5 | 0.04 |
| 15.7 | 0.53 |
| 19.7 | 1.26 |
| 20.0 | 0.27 |

| r.t. min | Area |
|---|---|
| 26.0 | 14.97, $(\Phi O)_3P(O)$ |
| 30.6 | 0.10 |
| 33.6 | 1.64 |
| 40.2 | 0.77 |
| 43.0 | 2.36 |
| 49.1 | 1.38 |
| 53.5 | 2.60 |
| 59.5 | 0.10 |
| 66.8 | 2.47 |
| 77.5 | 0.50 |

a) The material was examined under the following conditions: Column: stainless steel, 10' x 1/8" 1% OV-17 on Chromosorb-G-AW, 80/100 mesh a 10% split into F.I., He flow 35 ml/mm. Column temperature 250°C. Area is given in inches x attenuation per microliter of solution.

## TABLE XVI

## GAS CHROMATOGRAPHY RESULTS FOR FYRQUEL 220[a]

| r.t. min | Area |
|---|---|
| 59 | 0.10 |
| 66 | 0.41 |
| 72 | 0.70 |
| 82 | 2.53 |
| 93 | 2.42 |
| 105 | 2.08 |
| 118 | 0.93 |
| 131 | 0.07 |

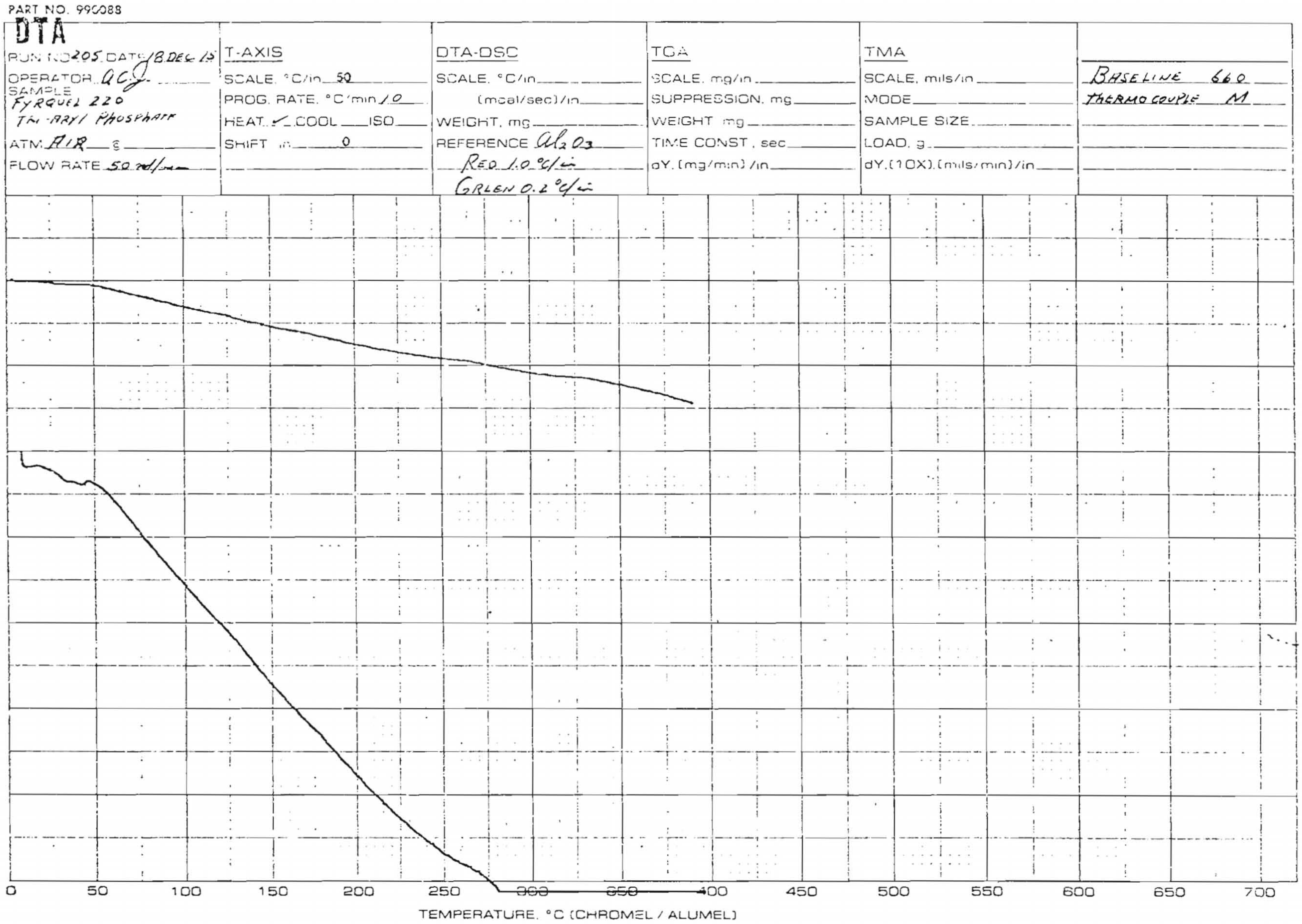
a) The material was examined under the following conditions: Column: stainless steel, 10' x 1/8" 1% OV-17 on Chromosorb-G-AW, 80/100 mesh a 10% split into F.I., He flow 35 ml/mm. Column temperature 250°C. Area is given in inches x attenuation per microliter of solution.

under the conditions used.

In Figures 7-11 are presented the DTA traces of the phosphate ester based fluids as well as the trace for the "synthetic" fluid. The relatively flat curve obtained for Fyrquel 220 indicates that at least up to 400°C the fluid is stable and relatively involatile. In Pydraul 50E some exothermic reaction, most likely oxidation, is evident above 200°C while in Pydraul MC the endotherm at 260-265°C points to distillation of a component. Similar action can be observed around 380°C for Dasco FR 300. The DTA curve (see Figure 11) of the "synthetic" triphenylphosphate n-octacosane mixture (both compounds are solids at room temperature) exhibits two endotherms at 50 and 60°C corresponding to melting points of triphenylphosphate and n-octacosane, respectively, whereas the endotherm centered at 405°C is due to the boiling points (400 and 430°C, respectively) of the two ingredients.

The experimental details of the degradation studies performed on the phosphate ester - containing hydraulic fluids are summarized in Table XVII and the volatile product distribution is presented in Table XVIII. The results of the gas chromatographic analyses are given in Tables XIX-XXXVII and the mg/g compilation is presented in Table XXXVIII. Inasmuch as all the phosphate ester based hydraulic fluids appeared to undergo relatively minor decomposition at 370°C, tests were also performed above or at 400°C. For clarity of presentation the results of the degradation investigations for each of the fluids will be discussed separately following the order given in Tables XVII, XVIII and XXXVIII.

In agreement with DTA data (see Figure 7) the extent of decomposition at 370°C for Fyrquel 220 was very minor, which is shown by the volatiles formed and confirmed by the residue recovered (see


PART NO. 990088

DTA

RUN NO 205 DATE 18 DEC 75
OPERATOR QCJ
SAMPLE Fyrquel 220
Tri-Aryl Phosphate
ATM AIR @
FLOW RATE 50 ml/min

T-AXIS
SCALE, °C/in 50
PROG. RATE, °C/min 10
HEAT ✓ COOL ISO
SHIFT in 0

DTA-DSC
SCALE, °C/in
(mcal/sec)/in
WEIGHT, mg
REFERENCE $Al_2O_3$
Red 1.0 °C/in
Green 0.2 °C/in

TGA
SCALE, mg/in
SUPPRESSION, mg
WEIGHT mg
TIME CONST, sec
dY, (mg/min)/in

TMA
SCALE, mils/in
MODE
SAMPLE SIZE
LOAD, g
dY, (10X), (mils/min)/in

Baseline 660
Thermocouple M

Figure 7: DTA of Fyrquel 220 Hydraulic Fluid

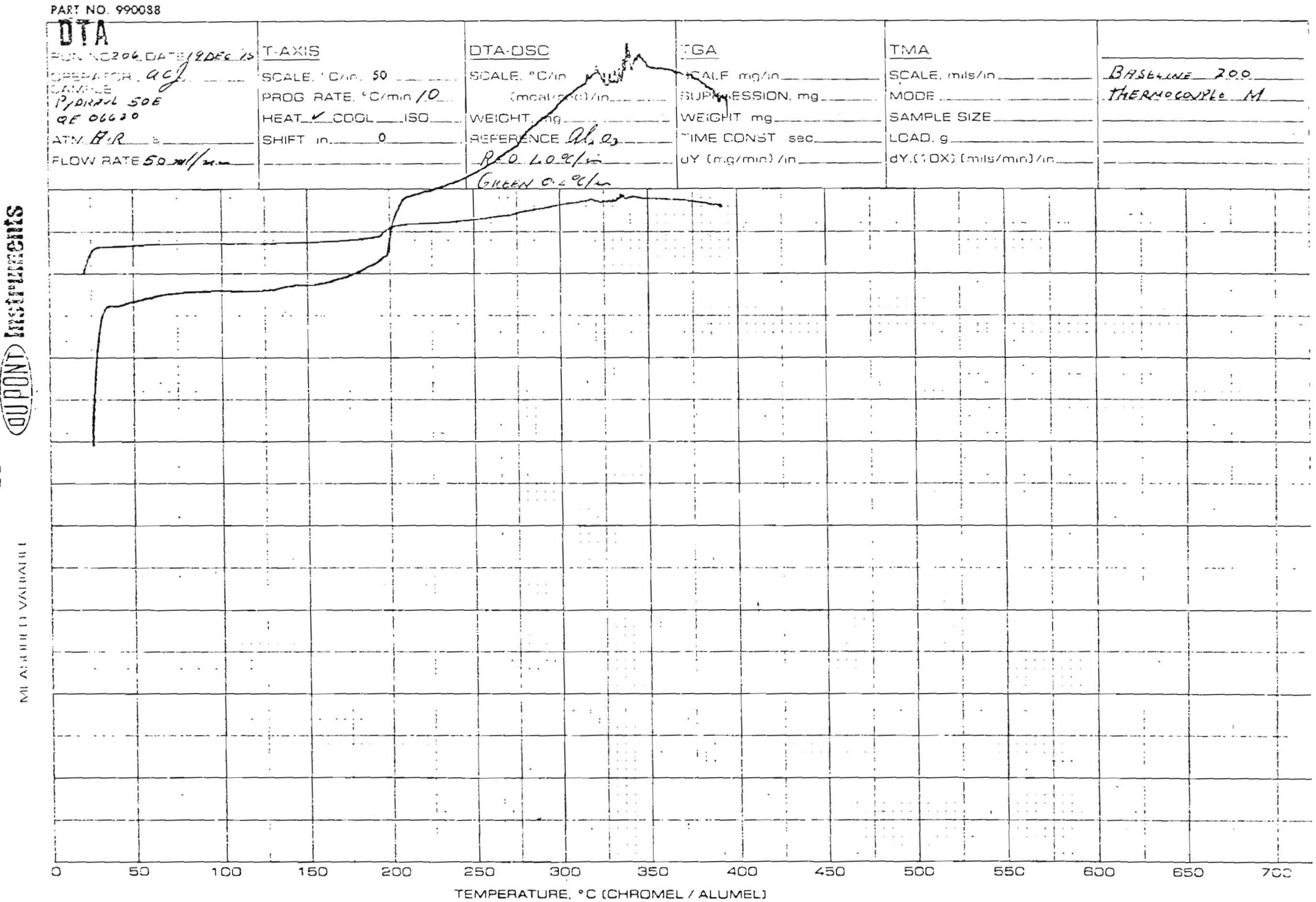
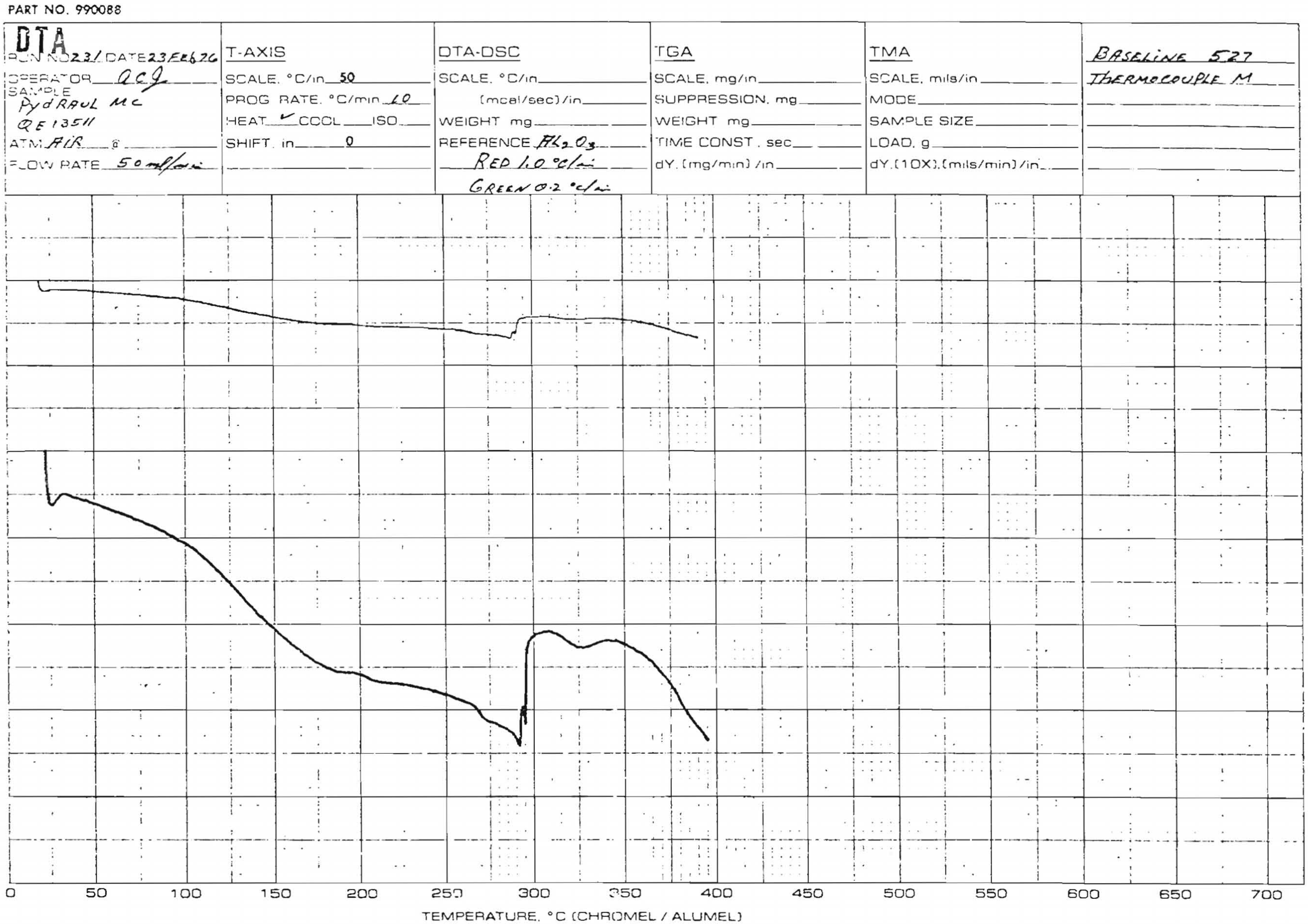


Figure 8: DTA of Pydraul 50E Hydraulic Fluid



DTA
RUN NO 231 DATE 23 Feb 76
OPERATOR QCJ
SAMPLE Pydraul MC QE 13511
ATM AIR @
FLOW RATE 50 ml/min

T-AXIS
SCALE, °C/in 50
PROG RATE, °C/min 10
HEAT ✓ COOL ISO
SHIFT, in 0

DTA-DSC
SCALE, °C/in
(mcal/sec)/in
WEIGHT mg
REFERENCE $Al_2O_3$
Red 1.0 °C/in
Green 0.2 °C/in

TGA
SCALE, mg/in
SUPPRESSION, mg
WEIGHT mg
TIME CONST., sec
dY, (mg/min)/in

TMA
SCALE, mils/in
MODE
SAMPLE SIZE
LOAD, g
dY, (10X), (mils/min)/in

Baseline 527
Thermocouple M

Figure 9: DTA of Pydraul MC QE 13511 Hydraulic Fluid

PART NO. 990088

**DTA**
RUN NO 161 DATE 30 Sept.75
OPERATOR F.S.
SAMPLE Dasco FR300 Hydraulic Oil (Stuart Oil Co.)
ATM Air
FLOW RATE 50 ml/min

T-AXIS
SCALE, °C/in 50
PROG RATE, °C/min 10
HEAT ✓ COOL ISO
SHIFT in 0

DTA-DSC
SCALE, °C/in
(mcal/sec)/in.
WEIGHT, mg
REFERENCE $Al_2O_3$
Red 1.0 °c/in
Green 0.2 °c/in

TGA
SCALE, mg/in
SUPPRESSION, mg
WEIGHT, mg
TIME CONST., sec
dY, (mg/min)/in

TMA
SCALE, mils/in
MODE
SAMPLE SIZE
LOAD, g
dY,(10X),(mils/min)/in

Baseline: 375
Thermocouple K

DU PONT Instruments

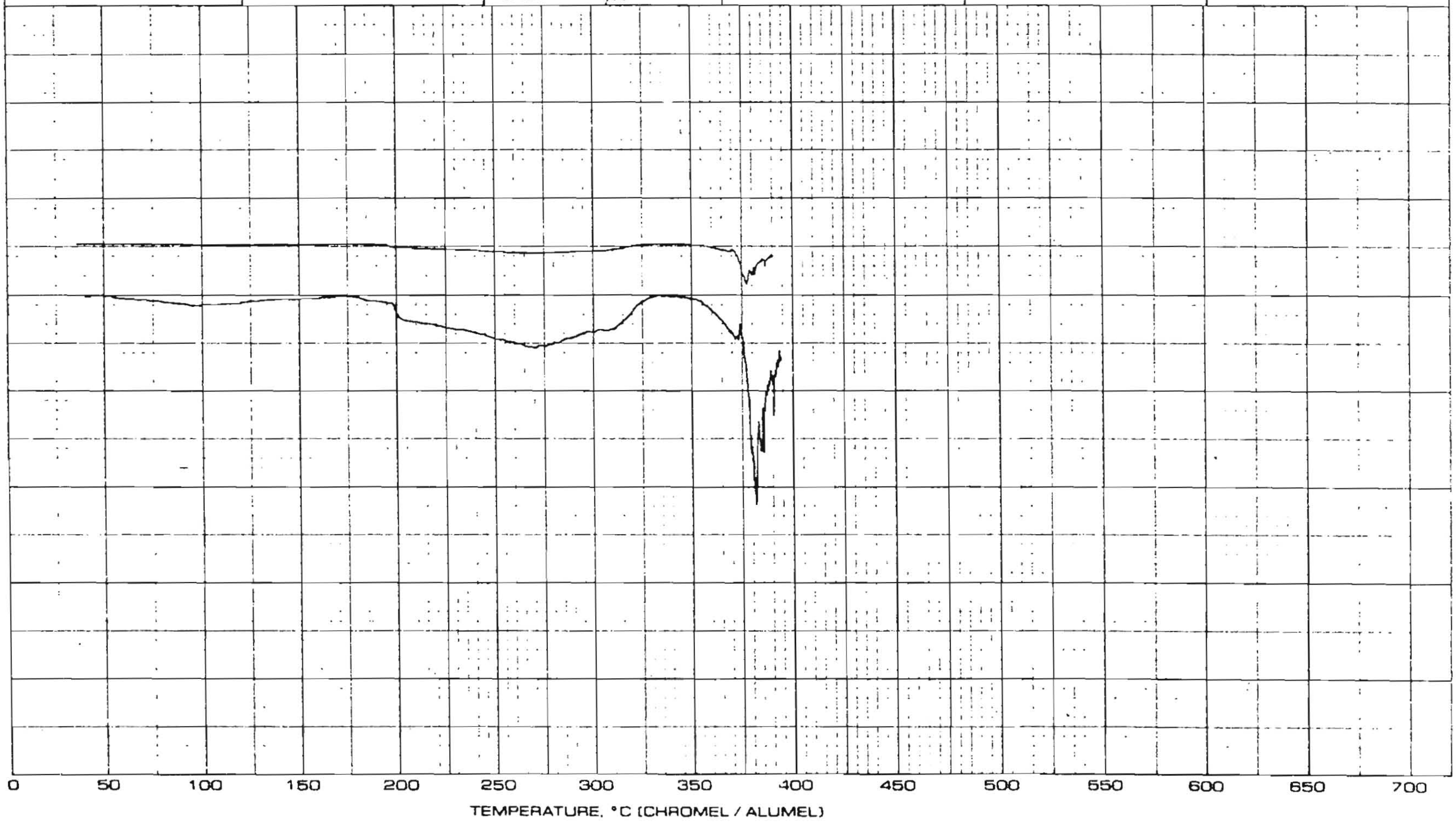


Figure 10: DTA of DASCO FR 300 Hydraulic Fluid

PART NO. 990088

DTA
RUN NO 290 DATE 10 SEPT 76
OPERATOR ACJ
SAMPLE
n-octacosane + Triphenylphos-
-phate (1:1 by wt.)
ATM Air @
FLOW RATE 50 ml/min

T-AXIS
SCALE, °C/in 50
PROG RATE, °C/min 10
HEAT ✓ COOL ISO
SHIFT in 0

DTA-DSC
SCALE, °C/in
(mcal/sec)/in
WEIGHT mg
REFERENCE Al2O3
Red 1.0°C/in
Green 0.2°C/in

TGA
SCALE, mg/in
SUPPRESSION mg
WEIGHT mg
TIME CONST sec
dY (mg/min)/in

TMA
SCALE mils/in
MODE
SAMPLE SIZE
LOAD, g
dY (10X) (mils/min)/in

Thermocouple N
Baseline Slope 159

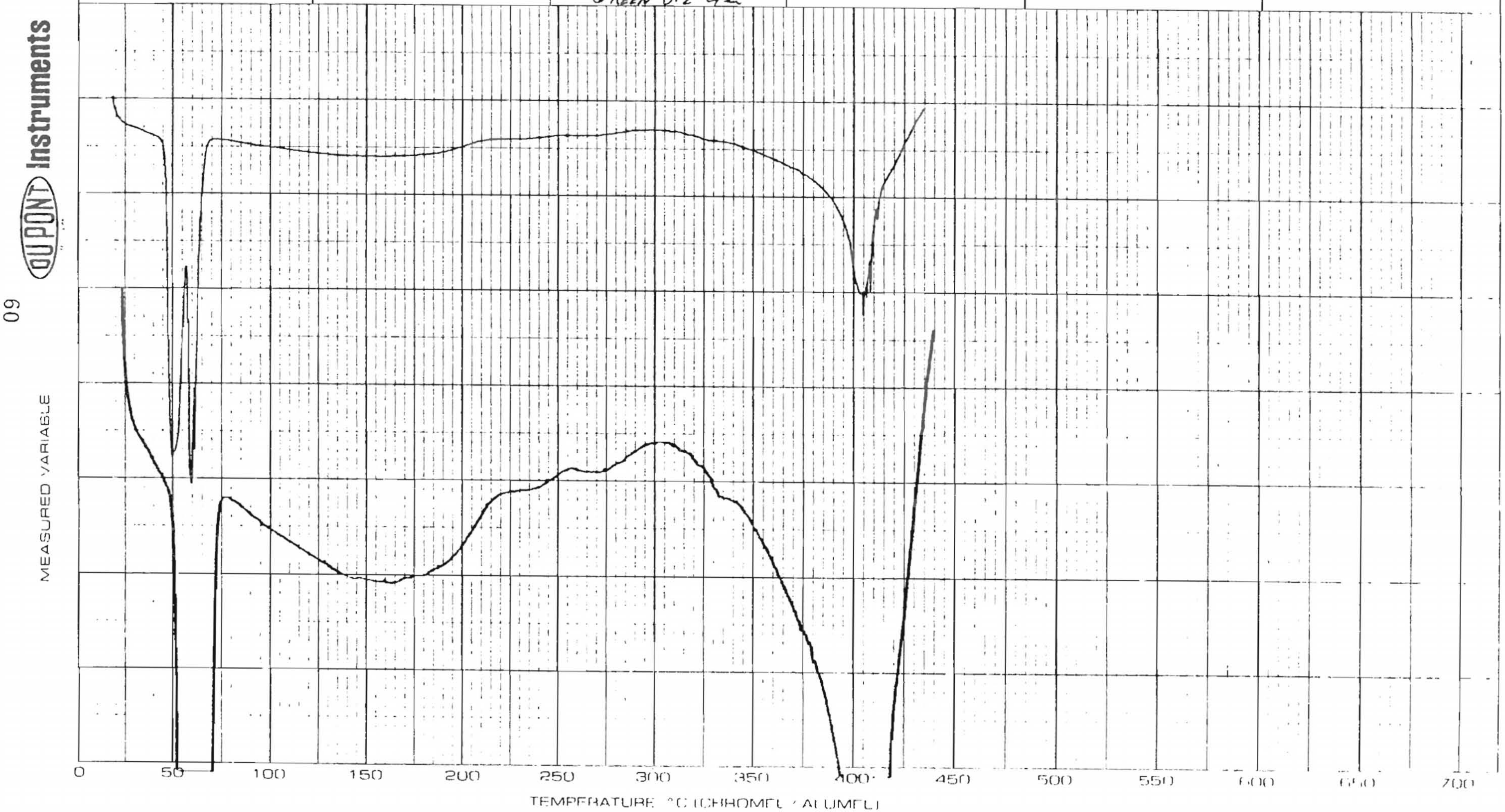


Figure 11: DTA of Triphenylphosphate/n-Octacosane Mixture

## TABLE XVII

## EXPERIMENTAL DATA FOR THERMAL OXIDATIVE DEGRADATIONS OF PHOSPHATE ESTER BASED HYDRAULIC FLUIDS

| Sample | Tube V | Initial P | Final P | React Temp | Sample Wt | Residue | | Weight Loss | Oxygen Consumed | | Total Products | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | ml | mm | mm | °C | mg | mg | %[a] | mg | mg | %[b] | mg | %[c] |
| Fyrquel 220 | 5330 | 502.9 | 504.5 | 370 | 5601 | 5523 | 98.6 | 78 | 14.6 | 1.5 | 30.3 | 38.8 |
| Fyrquel 220 | 5330 | 502.9 | 500.5 | 420 | 5316 | 5236 | 98.5 | 80 | 39.3 | 4.2 | 42.1 | 52.6 |
| Pydraul 50E | 5330 | 500.6 | 499.3 | 370 | 5696 | 5566 | 97.7 | 130 | 30.7 | 3.2 | 97.7 | 75.2 |
| Pydraul 50E | 5300 | 500.9 | 510.9 | 420 | 5411 | 4953 | 91.5 | 458 | 22.8 | 2.4 | 365.8 | 79.9 |
| Pydraul MC | 5300 | 500.9 | 509.0 | 370 | 5335 | 5070 | 95.0 | 265 | 30.5 | 3.2 | 260.8 | 98.4 |
| Pydraul MC | 5330 | 501.8 | 515.9 | 410 | 5154 | 4127 | 80.1 | 1027 | 25.5 | 2.7 | 831.6 | 81.0 |
| Dasco FR 300 | 5330 | 502.9 | 521.3 | 370 | 4790 | 4456 | 93.0 | 334 | 8.2 | 0.9 | 255.2 | 76.4 |
| Dasco FR 300 | 5330 | 498.7 | 516.2 | 400 | 4564 | 4123 | 90.3 | 441 | 22.1 | 2.4 | 282.7 | 64.1 |
| $(\Phi O)_3PO + C_{28}H_{58}$ | 5330 | 502.0 | 503.9 | 404 | 4771 | 4470 | 93.7 | 301 | 33.7 | 3.6 | 257.1 | 85.4 |

a) Percent of the weight of the starting material; this is the residue remaining in the finger and does include oils and tars deposited on the sides of the 5-liter bulb. b) Percent of oxygen available. c) Percent of total products expected.

TABLE XVIII

PRODUCT DISTRIBUTION: DEGRADATIONS OF PHOSPHATE ESTER BASED HYDRAULIC FLUIDS

| Sample | Temp | Noncondensibles | | | | | Condensibles | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Total | CO | | $CH_4$ | | Total | -196°C Frac | | -96°C Frac | | -78°C Frac | | -63°C Frac | | -23°C Frac | | 0°C Frac | |
| | °C | mmoles[a] | mg | %[b] | mg | %[b] | mg | mg | %[b] | mg | %[b] | mg | %[b] | mg | %[b] | mg | %[b] | mg | %[b] |
| Fyrquel 220 | 370 | 145.86 | - | - | 0.7 | 0.03 | 29.6 | 1.4 | 0.02 | - | - | 9.8 | 0.2 | - | - | -[c] | - | 18.4 | 0.3 |
| Fyrquel 220 | 420 | 142.67 | T | T | 0.9 | 0.04 | 41.2 | 1.8 | 0.03 | - | - | 9.3 | 0.2 | - | - | -[c] | - | 30.1 | 0.6 |
| Pydraul 50E | 370 | 144.89 | 3.2 | 0.08 | T | T | 94.5 | 24.3 | 0.4 | - | - | 24.9 | 0.4 | - | - | 5.6 | 0.1 | 39.7 | 0.7 |
| Pydraul 50E | 420 | 143.32 | T | T | 1.6 | 0.07 | 364.2 | 100.4 | 1.9 | - | - | 70.9 | 1.3 | - | - | 13.4 | 0.2 | 179.5 | 3.3 |
| Pydraul MC | 370 | 145.49 | 3.7 | 0.1 | T | T | 257.1 | 3.2 | 0.1 | - | - | 192.7 | 3.6 | - | - | 14.0 | 0.3 | 47.2 | 0.9 |
| Pydraul MC | 410 | 143.84 | T | T | 0.5 | 0.02 | 831.1 | 32.1 | 0.6 | - | - | 404.3 | 7.8 | - | - | 57.1 | 1.1 | 337.6 | 6.6 |
| Dasco FR 300 | 370 | 144.02 | 6.0 | 0.12 | 0.5 | 0.01 | 248.7 | 27.1 | 0.6 | 23.9 | 0.5 | 58.3 | 1.2 | 83.8 | 1.8 | 9.8 | 0.2 | 45.8 | 1.0 |
| Dasco FR 300 | 400 | 142.79 | 10.0 | 0.22 | 0.9 | 0.02 | 271.8 | 81.1 | 1.8 | - | - | 148.9 | 3.3 | - | - | 10.1 | 0.2 | 31.7 | 0.7 |
| $(\Phi O)_3PO + C_{28}H_{58}$ | 404 | 140.03 | 8.2 | 0.21 | 0.7 | 0.03 | 248.2 | 30.4 | 0.6 | - | - | 78.8 | 1.6 | - | - | 17.5 | 0.4 | 121.5 | 2.5 |

a) This is mainly air. b) Percent of the weight of the starting material. c) The -23° and -78°C fractions were combined.

## TABLE XIX
## GAS CHROMATOGRAPHY RESULTS: DEGRADATION OF FYRQUEL 220 HYDRAULIC FLUID AT 370°C

(Porapak Q Column)

| -23 + -78°C[a,b] Frac | | -23 + -78°C[c,d] Frac (Vapor) | | -196°C[c,e] Frac | | Peak Identification |
|---|---|---|---|---|---|---|
| r.t.[f] | Area | r.t. | Area | r.t. | Area | |
| | | | | 2.8 | 3.4 | $C_2H_4$ |
| | | | | 3.4 | 10.4 | $C_2H_6$ |
| | | | | 7.4 | 3.2 | $C_3H_6$ |
| | | | | 7.9 | 1.5 | $C_3H_8$ |
| 9.0 | 14.6 | | | | | Methanol |
| 10.4 | 0.2 | 10.3 | 2.7 | 10.2 | 13.4 | $CH_3CHO$ |
| | | 12.2 | 0.1 | | | Methyl formate |
| | | | | 12.6 | 1.7 | $C_4$-species |
| | | | | 13.3 | 0.9 | $C_4$-species |
| | | | | 15.7 | 0.5 | Furan |
| | | 16.0 | 2.0 | 16.0 | 0.9 | Propionaldehyde, acetone |
| | | | | 16.5 | 0.1 | Acetone |
| | | 17.3 | T[g] | | | Methyl acetate |
| | | | | 17.5 | 0.6 | $C_5$-species |
| | | | | 18.1 | 1.2 | $C_5$-species |
| 18.2 | 0.5 | | | | | Acetic acid |
| | | 19.4 | 0.1 | | | 1,3-Dioxolane |
| | | 20.4 | 0.6 | 20.5 | 0.2 | Methyl ethyl ketone, butyraldehyde |
| | | | | 21.1 | 0.2 | $C_6$-ene |
| | | | | 21.9 | 2.1 | $C_6$-ene, $C_6$-ane |
| | | | | 22.1 | 2.1 | Cyclo-$C_6$-ene |
| | | 22.9 | 0.1 | 22.7 | 0.8 | Benzene |
| | | 23.5 | 0.1 | 23.4 | 0.3 | Cyclohexene, 2-methyl-2-butanone |
| 24.2 | 0.1 | 24.3 | 0.2 | | | p-Dioxane, 2-pentanone, n-pentanal |
| | | | | 24.4 | 0.2 | $C_7$-ene |
| 24.8 | 0.2 | | | | | 2-Pentanone |
| 25.5 | 0.1 | 25.7 | 2.4 | 25.5 | 2.4 | $C_7$-ene |
| 26.3 | 0.1 | | | | | 2-Methyl-2-butenal |
| 27.4 | 0.1 | 27.1 | 3.1 | 27.1 | 0.2 | Toluene |
| | | 28.3 | T | 28.2 | 0.1 | $C_8$-ene |

## TABLE XIX- Cont'd.

## GAS CHROMATOGRAPHY RESULTS: DEGRADATION OF FYRQUEL 220 HYDRAULIC FLUID AT 370°C

## (Porapak Q Column)

| $-23 + -78^\circ C^{a,b}$ Frac | | $-23 + -78^\circ C^{c,d}$ Frac (Vapor) | | $-196^\circ C^{c,e}$ Frac | | Peak Identification |
|---|---|---|---|---|---|---|
| r.t.[f] | Area | r.t. | Area | r.t. | Area | |
| 29.0 | 0.1 | | | | | 2-Methyl pentanal |
| | | 29.1 | 1.1 | 29.1 | T | $C_8$-ene |
| 30.5 | 0.2 | 30.3 | 29.8 | 30.3 | 3.4 | $C_8$-ene |
| 33.2 | 0.6 | 33.0 | 33.6 | | | $C_2$-benzene |
| 34.5 | 0.1 | 34.3 | 5.2 | | | $C_2$-benzene |
| 35.8 | 64.8 | | | | | Phenol |
| | | 38.0 | 11.6 | | | $C_9$-ene |
| 41.3 | 4.4 | 41.0 | 10.5 | | | $C_3$-benzene |
| 43.8 | 3.8 | 43.7 | 4.1 | | | $C_3$-benzene |
| 47.5 | 3.1 | | | | | Cresol |
| 55.0 | 5.9 | | | | | $C_4$-benzene, cinnamaldehyde ? |
| 60.5 | 3.7 | | | | | Xylenol |

a) This fraction was examined under the following conditions: Column: stainless steel, 8' x 1/8" Porapak Q, detector: a 10% split into F.I., He flow: 35 ml/min. Column temperature: 50-220°C programmed at 8°/min. b) This was the liquid phase of the fraction. Area is given in square inches x attenuation per microliter of sample. c) This fraction was examined under the following conditions: Column: stainless steel, 8' x 1/8" Porapak Q, detector: a 43% split into F.I., He flow: 35 ml/min. column temperature: 50-220°C programmed at 7°/min. d) This was the gaseous phase of the fraction ; a 12 mm pressure was used. e) A 15 mm pressure was used. f) Retention time, min. g) < 0.05 in$^2$/$\mu$l for liquid samples; < 0.05 in$^2$ for gas samples.

## TABLE XX

## GAS CHROMATOGRAPHY RESULTS: DEGRADATION OF FYRQUEL 220 HYDRAULIC FLUID AT 370°C

## (OV-101 Column)

| 0°C[a] Frac | | Peak Identification |
|---|---|---|
| r.t.[b] | Area | |
| 15.8 | 52.2 | Phenol |
| 18.2 | 3.8 | |
| 20.0 | 60.2 | Cresol |
| 20.7 | 53.3 | Cresol |
| 24.3 | 198.7 | Xylenol |
| 25.2 | 116.5 | Xylenol |
| 25.5 | 1.9 | $C_3$-phenol |
| 25.8 | 0.6 | $C_3$-phenol |
| 26.5 | 7.6 | $C_3$-phenol |
| 27.0 | 0.8 | $C_3$-phenol |
| 27.4 | 0.3 | Napthalene |
| 28.4 | 3.6 | Methylnapthalene |
| 28.8 | 2.2 | Methylnapthalene |
| 29.8 | 0.1 | Methylnapthalene |
| 30.8 | 3.3 | Phenyl ether |
| 31.5 | 7.2 | Biphenyl |

a) This fraction was examined under the following conditions: Column: stainless steel, 10' x 1/8" 4% OV-101 on Chromosorb G, detector: a 10% split into F.I., programmed at 4°/min. b) Retention time, min. Area is given in square inches x attenuation per microliter of sample.

## TABLE XXI

## GAS CHROMATOGRAPHY RESULTS: DEGRADATION OF FYRQUEL 220 HYDRAULIC FLUID AT 420°C

(Porapak Q Column)

| -23°,+-78°C[a,b] Frac (top layer) | | -23°,+-78°C[a,c] Frac (vapor) | | -196°C[a,d] Frac | | Peak Identification |
|---|---|---|---|---|---|---|
| r.t.[e] | Area | r.t. | Area | r.t. | Area | |
| | | | | 2.7 | 5.1 | $C_2H_4$ |
| | | | | 3.3 | 9.9 | $C_2H_6$ |
| | | | | 7.3 | 6.3 | $C_3H_6$ |
| | | | | 7.8 | 2.4 | $C_3H_8$ |
| | | 10.5 | 0.3 | 10.1 | 5.4 | $CH_3CHO, CH_3OH$ |
| | | | | 12.2 | 0.7 | $C_4$-ane |
| | | | | 12.5 | 1.7 | $C_4$-ene |
| | | | | 13.2 | 1.5 | $C_4$-ene |
| | | | | 15.7 | 0.2 | Propionaldehyde |
| 16.3 | 0.2 | 16.1 | 0.4 | 15.9 | 0.6 | Propionaldehyde, acetone |
| | | | | 16.6 | 0.1 | $C_5$-ene |
| | | | | 17.5 | 0.1 | $C_5$-ene |
| | | | | 18.0 | 1.3 | $C_5$-ene |
| 20.6 | 0.4 | 20.6 | 0.2 | 20.4 | 0.1 | Methyl ethyl ketone, n-butyraldehyde |
| | | | | 21.0 | 0.1 | $C_6$-ene |
| | | | | 21.6 | 0.3 | $C_6$-ene |
| | | 21.9 | 0.1 | 21.9 | 0.4 | $C_6$-ene |
| | | 22.7 | 0.3 | 22.3 | 1.1 | $C_6$-species |
| 23.1 | 0.4 | 23.0 | 1.4 | 22.7 | 1.8 | Benzene |
| 23.7 | 0.3 | 23.6 | 0.9 | 23.3 | 1.0 | Cyclohexene |
| 24.4 | 0.4 | 24.4 | 0.1 | | | n-Pentanal |
| | | | | 24.3 | 0.1 | $C_7$-ene |
| 25.7 | 0.7 | 25.9 | 1.3 | 25.5 | 1.3 | $C_7$-ene |
| 27.4 | 20.5 | 27.4 | 10.4 | 27.0 | 1.4 | Toluene |
| 29.4 | 1.4 | 29.5 | 0.6 | 29.0 | 0.1 | $C_8$-ene |
| 30.1 | 14.2 | 30.7 | 6.1 | 30.3 | 1.8 | $C_8$-ene |
| 32.8 | 610.9 | 33.4 | 97.4 | 33.2 | 0.2 | $C_2$-benzene |
| 34.5 | 114.2 | 34.9 | 15.0 | 34.0 | 0.2 | $C_2$-benzene |
| 35.9 | 87.4 | | | | | Phenol |
| 38.8 | 7.7 | 38.5 | 0.6 | | | $C_3$-benzene, $C_9$-ene |
| 40.6 | 655.1 | 41.9 | 28.8 | | | $C_3$-benzene |
| 43.2 | 783.1 | 44.8 | 17.4 | | | $C_3$-benzene |
| 46.4 | 84.4 | 48.5 | 0.5 | | | $C_3$-benzene |
| 55.5 | 260.9 | | | | | $C_4$-benzene |
| 60.0 | 512.0 | | | | | $C_4$-benzene |

### TABLE XXI-Cont'd.

### GAS CHROMATOGRAPHY RESULTS: DEGRADATION OF FYRQUEL 220 HYDRAULIC FLUID AT 420°C

### (Porapak Q Column)

a) This fraction was examined under the following conditions: Column: stainless steel, 8' x 1/8" Porapak Q, detector: a 43% split into F.I., He flow: 35 ml/min. column temperature: 50-220°C programmed at 7°/min. b) This was the liquid phase of the fraction. Area is given in square inches x attenuation per microliter of sample. c) This was the gaseous phase of the fractions; a 12 mm pressure was used. Area is given in square inches x attenuation. d) A 15 mm pressure was used. e) Retention time, min.

## TABLE XXII

## GAS CHROMATOGRAPHY RESULTS: DEGRADATION OF FYRQUEL 220 HYDRAULIC FLUID AT 420°C

(OV-101 Column)

| 0° [a] Frac | | -23° + -78°C [a] Frac (Bottom Layer) | | Peak Identification |
|---|---|---|---|---|
| r.t. [b] | Area | r.t. [b] | Area | |
| 11.3 | 0.2 | 11.3 | 0.8 | $C_2$-benzene |
| 12.2 | T | 12.2 | 0.2 | $C_2$-benzene |
| 14.7 | 0.1 | 14.5 | 1.8 | $C_3$-benzene |
| 14.9 | 46.6 | 14.7 | 0.4 | Phenol |
| | | 15.9 | 2.4 | $C_3$-benzene |
| 16.7 | 0.4 | 17.1 | 1.4 | $C_3$-benzene |
| 17.7 | 5.4 | | | Cresol |
| | | 18.2 | 3.0 | $C_4$-benzene |
| 18.4 | 123.2 | | | Cresol |
| | | 19.1 | 6.2 | Ethylstyrene |
| 19.4 | 12.8 | | | Xylenol |
| | | 19.6 | 11.4 | Dimethylstyrene |
| 20.4 | 7.8 | | | Xylenol |
| | | 20.5 | 2.9 | Dimethylstyrene |
| 21.0 | 280.0 | | | Xylenol |
| 21.7 | 220.0 | | | Xylenol |
| 22.5 | 7.2 | | | |
| 22.8 | 5.6 | | | |
| 23.7 | 14.8 | | | $C_3$-phenol |
| 25.9 | 0.5 | | | Methylnapthalene |
| 26.4 | 0.7 | | | |
| 28.3 | 1.2 | | | Biphenyl |
| 28.9 | 2.7 | | | Diphenyl ether |
| 29.3 | 1.0 | | | |
| 29.7 | 0.6 | | | |
| 32.2 | 0.2 | | | |

a) This fraction was examined under the following conditions: Column:stainless steel, 10' x 1/8" 4% OV-101 on Chromosorb G, detector: a 43% split into F.I., programmed at 4°/min from 35-220°C.

b) Retention time, min. Area is given in square inches x attenuation per microliter of sample.

TABLE XXIII

GAS CHROMATOGRAPHY RESULTS: DEGRADATION OF PYDRAUL 50E HYDRAULIC FLUID AT 370° C

(Porapak Q Column)

| $-78^{\circ}C^{b,c}$ Frac (Bottom Layer) | | $-78^{\circ}C^{a,b}$ Frac (Top Layer) | | $-78^{\circ}C^{c,d}$ Frac (Vapor) | | $-196^{\circ}C^{c,e}$ Frac | | Peak Identification |
|---|---|---|---|---|---|---|---|---|
| r.t.[f] | Area | r.t. | Area | r.t. | Area | r.t. | Area | |
| | | | | | | 2.2[g] | 14.9 | $CO_2$ |
| | | | | | | 2.7 | 1.9 | $C_2H_4$ |
| | | | | | | 3.4 | 1.7 | $C_2H_6$ |
| | | | | | | 7.3 | 4.4 | $C_3H_6$ |
| | | | | | | 7.9 | 2.7 | $C_3H_8$ |
| 9.8 | 7.5 | | | | | | | Methanol |
| | | | | 10.5 | 0.3 | 10.2 | 1.9 | Acetaldehyde |
| | | | | 12.4 | 0.2 | 12.2 | 0.6 | $C_4$-ane |
| | | | | 12.8 | 0.1 | 12.6 | 76.2 | $C_4$-ene |
| | | 13.2 | 0.1 | 13.5 | 0.1 | 13.2 | 35.8 | $C_4$-ene |
| | | | | 13.7 | 0.1 | 13.5 | 23.0 | $C_4$-ene |
| | | | | | | 15.7 | 0.8 | Acrolein, furan, propionaldehyde |
| 17.7 | 1.9 | 15.4 | 0.1 | 15.9 | 7.7 | 15.8 | 1.4 | Propionaldehyde, acetone, ethanol |
| | | | | | | 16.6 | 1.3 | $C_5$-ene |
| | | 17.2 | 0.1 | 17.8 | 0.1 | 17.5 | 6.2 | $C_5$-ene |
| | | 18.6 | 0.1 | 18.3 | 0.5 | 18.0 | 11.3 | $C_5$-species |
| 19.2 | 0.4 | 19.2 | 0.1 | 19.3 | 0.8 | 19.2 | T[h] | Isobutyraldehyde |
| | | 19.8 | 0.1 | | | 19.9 | 0.3 | $C_6$-ene |
| 21.5 | 0.7 | 20.7 | 0.5 | 20.4 | 6.6 | 20.3 | 0.2 | n-Butyraldehyde, methyl ethyl ketone |
| | | | | 21.2 | 0.4 | 21.0 | 3.1 | $C_6$-ene |
| | | 21.8 | 1.4 | | | 21.8 | 10.6 | $C_6$-ene, $C_6$-ane |
| | | 22.9 | 1.1 | 22.3 | 17.5 | 22.1 | 7.2 | $C_6$-ene, $C_6$-ane |
| 23.1 | 0.1 | 23.6 | 0.2 | 22.9 | 3.8 | 22.7 | 1.0 | Benzene |
| 23.8 | 3.7 | | | | | | | n-Butanol |
| | | | | | | 23.8 | 0.2 | $C_7$-ene |
| | | 24.1 | 0.4 | 23.5 | 1.4 | | | 2-Pentanone, cyclohexene, 3-methylbutyraldehyde |
| | | 24.6 | 0.3 | 25.0 | 12.2 | 24.8 | 2.1 | $C_7$-ene, n-pentanal |
| | | 25.5 | 2.3 | 25.8 | 25.8 | 25.4 | 1.2 | $C_7$-ene |
| | | 26.7 | 4.9 | | | | | $C_7$-species |
| | | 27.8 | T | | | | | $C_7$-species |
| | | 28.6 | 1.2 | 27.3 | 3.1 | | | Toluene |

TABLE XXIII-Cont'd.

GAS CHROMATOGRAPHY RESULTS: DEGRADATION OF PYDRAUL 50E HYDRAULIC FLUID AT 370° C

(Porapak Q Column)

| -78°C [b,c] Frac (Bottom Layer) | | -78°C [a,b] Frac (Top Layer) | | -78°C [c,d] Frac (Vapor) | | -196°C [c,e] Frac | | Peak Identification |
|---|---|---|---|---|---|---|---|---|
| r.t.[f] | Area | r.t. | Area | r.t. | Area | r.t. | Area | |
| | | | | 29.2 | 5.8 | | | $C_8$-ene |
| | | 29.4 | 0.3 | | | | | 2-Hexanol |
| | | 30.3 | 3.0 | 30.5 | 21.4 | | | $C_8$-species |
| | | 31.4 | 12.7 | | | | | $C_8$-species |
| | | 34.1 | 62.4 | 34.1 | 63.8 | | | $C_2$-benzene, $C_9$-ene |
| | | 35.6 | 65.7 | 35.5 | 106.7 | | | $C_9$-ene |
| 36.8 | 5.8 | | | | | | | Phenol |
| | | 37.0 | 75.9 | | | | | $C_9$-ene |
| | | 39.2 | 16.6 | | | | | $C_9$-ene |
| | | 40.7 | 35.6 | 39.0 | 10.8 | | | $C_3$-benzene |
| | | 43.5 | 132.8 | 42.4 | 12.9 | | | α-Methylstyrene |

a) This fraction was examined under the following conditions: Column: stainless steel, 8' x 1/8" Porapak Q, detector: a 10% split into F.I., He flow: 35 ml/min. Column temperature: 50-220°C programmed at 8°/min. b) This was the liquid phase of the fraction. Area is given in inches x attenuation per microliter of sample. c) This fraction was examined under the following conditions: Column: stainless steel, 8' x 1/8" Porapak Q, detector: a 43% split into F.I., He flow: 35 ml/min, column temperature 50-220°C programmed at 7°/min. d) This was the gaseous phase of the fraction; a 14 mm pressure was used. e) An 18 mm pressure was used. f) Retention time, min. g) This peak was identified by the TC detector only under testing conditions given in footnote a).
h) < 0.05 $in^2/\mu l$ for liquid samples: < 0.05 $in^2$ for gas samples.

## TABLE XXIV

## GAS CHROMATOGRAPHY RESULTS: DEGRADATION OF PYDRAUL 50E HYDRAULIC FLUID AT 370°C

(OV-101 Column)

| -23°C[a,b] Frac | | Peak Identification |
|---|---|---|
| r.t.[c] | Area | |
| 6.6 | 0.5 | |
| 7.5 | 3.5 | |
| 8.2 | 0.6 | |
| 8.6 | 0.4 | |
| 9.6 | 0.1 | |
| 10.5 | 3.1 | |
| 11.2 | 7.3 | $C_3$-benzene |
| 11.7 | 1.6 | |
| 12.3 | 1.9 | Styrene |
| 12.9 | 17.3 | Methyl phenyl ether |
| 13.4 | 98.7 | $C_3$-benzene |
| 14.6 | 3.1 | $C_3$-benzene |
| 15.6 | 1354.7 | α-Methylstyrene |
| 16.6 | 3.3 | |
| 17.0 | 3.3 | α-Dimethylstyrene |
| 17.8 | 0.7 | |
| 18.2 | 3.7 | |
| 19.8 | 45.0 | Cinnamaldehyde, $C_5$-benzene |

a) This fraction was examined under the following conditions: Column: stainless steel, 10' x 1/8" 4% OV-101 on Chromosorb G, detector: a 43% split into F.I. He flow: 35 ml/min, column temperature: 35 to 220°C programmed at 4°C/min. b) This was the liquid phase of the fraction. Area is given in square inches x attenuation per microliter of sample. c) Retention time, min.

TABLE XXV

## GAS CHROMATOGRAPHY RESULTS: DEGRADATION OF PYDRAUL 50E HYDRAULIC FLUID AT 420°C

(Porapak Q Column)

| -78°C[a,b] Frac | | -78°C[c,d] Frac (vapor) | | -196°C[c,e] Frac | | Peak Identification |
|---|---|---|---|---|---|---|
| r.t.[f] | Area | r.t. | Area | r.t. | Area | |
| | | | | 2.2[g] | 1.3 | $CO_2$ |
| | | | | 2.7 | 3.7 | $C_2H_4$ |
| | | | | 3.4 | 7.3 | $C_2H_6$ |
| | | 7.5 | T[h] | 7.3 | 13.1 | $C_3H_6$ |
| | | 8.0 | T | 7.8 | 9.9 | $C_3H_8$ |
| | | 10.8 | 0.1 | | | $CH_3CHO$ |
| | | | | 12.1 | 2.6 | $C_4$-ane |
| | | 12.8 | 0.1 | 12.5 | 22.6 | $C_4$-ene |
| | | 13.4 | 0.2 | 13.1 | 22.4 | $C_4$-ene |
| | | | | 15.6 | 0.4 | $C_5$-ane |
| | | 15.9 | 0.2 | | | Propionaldehyde |
| | | 16.2 | 0.1 | | | Acetone |
| 17.6 | T | 16.9 | T | 16.5 | 1.2 | $C_5$-ane |
| 18.5 | 0.1 | 17.7 | 0.9 | 17.2 | 9.4 | $C_5$-ene |
| 18.8 | 1.0 | 18.2 | 7.6 | 17.9 | 20.2 | $C_5$-ene |
| | | | | 19.8 | 0.2 | $C_6$-ene |
| 20.5 | T | 20.5 | 0.7 | | | n-Butyraldehyde, methyl ethyl ketone |
| | | | | 20.9 | 2.6 | $C_6$-ene |
| 21.4 | 1.7 | 21.2 | 8.0 | 21.4 | 3.3 | $C_6$-ane |
| | | | | 21.7 | 3.4 | Cyclo-$C_6$-ene |
| 22.2 | 53.5 | 22.3 | 154.2 | 22.0 | 7.4 | $C_6$-ane |
| 23.5 | 4.8 | 23.0 | 6.3 | 22.6 | 0.5 | Benzene |
| 24.0 | 0.3 | 23.6 | 0.4 | | | Cyclo-$C_6$-ene |
| | | 24.1 | 0.5 | | | $C_7$-ene |
| 24.5 | 0.1 | 25.1 | 16.8 | | | $C_7$-ene |
| 25.7 | 11.8 | 25.6 | 26.6 | | | $C_7$-ene |
| 26.3 | 33.7 | 27.3 | 4.7 | | | Toluene |
| 28.5 | T | 28.5 | 0.3 | | | $C_8$-ene |
| 29.4 | 10.7 | 29.5 | 3.2 | | | $C_8$-ene |
| 31.0 | 0.6 | 30.1 | 8.3 | | | $C_8$-ene |
| 31.8 | 7.3 | | | | | $C_8$-ene |
| 32.6 | 15.6 | 33.0 | 2.2 | | | $C_2$-benzene |
| 33.2 | 19.5 | | | | | $C_9$-ene |
| 36.1 | 53.4 | 34.4 | 8.2 | | | $C_9$-ene |
| 37.8 | 54.7 | 35.8 | 14.0 | | | $C_9$-ene |
| 38.0 | 33.3 | | | | | $C_9$-ene |
| 41.7 | 1.6 | | | | | $C_9$-ene |
| 43.3 | 19.5 | 39.2 | 1.4 | | | $C_3$-benzene |
| 46.8 | 63.7 | 42.5 | 1.4 | | | α-Methylstyrene |
| 59.5 | 3.3 | | | | | $C_{10}$-ene |

TABLE XXV-Cont'd.

GAS CHROMATOGRAPHY RESULTS: DEGRADATION OF PYDRAUL 50E HYDRAULIC FLUID AT 420°C

(Porapak Q Column)

a) This fraction was examined under the following conditions: Column: stainless steel, 8' x 1/8" Porapak Q, detector: a 10% split into F.I., He flow: 35 ml/min. Column temperature: 50-220°C programmed at 8°/min. b) This was the liquid phase of the fraction. Area is given in square inches x attenuation per microliter of sample. c) This fraction was examined under the following conditions: Column: stainless steel, 8' x 1/8" Porapak Q, detector: a 43% split into F.I., He flow: 35 ml/min. column temperature: 50-220°C programmed at 7°/min. d) This was the gaseous phase of the fraction; a 10 mm pressure was used. e) A 11 mm pressure was used. Area is given in square inches x attenuation. f) Retention time, min. g) This peak was identified by the TC detector only under testing conditions given in footnote a). h) $< 0.05$ in$^2$/µl for liquid samples; $< 0.05$ in$^2$ for gas samples.

## TABLE XXVI

## GAS CHROMATOGRAPHY RESULTS: DEGRADATION OF PYDRAUL 50E HYDRAULIC FLUID AT 420°C

(Apiezon L Column)

| -23°C[a,b] Frac | | Peak Identification |
|---|---|---|
| r.t.[c] | Area | |
| 9.5 | 2.5 | |
| 11.2 | 3.5 | $C_9$-ene |
| 12.3 | 6.9 | $C_9$-ene |
| 13.1 | 5.8 | $C_{10}$-ene |
| 14.0 | 2.6 | $C_2$-benzene |
| 14.3 | 9.7 | $C_2$-benzene |
| 14.9 | 3.8 | $C_9$-ene |
| 16.0 | 555.2 | $C_3$-benzene, phenol |
| 17.4 | 24.0 | |
| 18.3 | 11.2 | $C_{10}$-ene |
| 18.9 | 44.0 | $C_{10}$-ene |
| 19.5 | 142.4 | $C_4$-benzene |
| 21.4 | 4.8 | Indan |
| 21.7 | 35.2 | Propenyl benzene |
| 22.3 | 66.0 | $C_{11}$-ene |
| 22.8 | 37.2 | $C_{11}$-ene |
| 23.2 | 130.4 | $C_5$-benzene |
| 24.2 | 11.2 | $C_5$-benzene |
| 24.9 | 14.6 | |
| 25.7 | 17.0 | $C_6$-benzene |
| 26.2 | 11.2 | $C_5$-benzene, $C_{12}$-species |
| 26.7 | 38.6 | $C_{12}$-ene |
| 27.2 | 5.2 | |
| 29.6 | 4.4 | Methyltetrahydronapthalene |
| 30.3 | 2.1 | $C_{13}$-ene |

a) This fraction was examined under the following conditions: Column: stainless steel, 10' x 1/8" 4% Apiezon L on Chromosorb G, detector: a 43% split into F.I. He flow: 35 ml/min, column temperature: 35 to 220°C programmed at 4°C/min. b) This was the liquid phase of the fraction. Area is given in square inches x attenuation per microliter of sample. c) Retention time, min.

## TABLE XXVII

## GAS CHROMATOGRAPHY RESULTS: DEGRADATION OF PYDRAUL MC HYDRAULIC FLUID AT 370°C

(Porapak Q Column)

| -78°C[a,b] Frac | | -78°C[c,d] Frac (vapor) | | -196°C[c,e] Frac | | Peak Identification |
|---|---|---|---|---|---|---|
| r.t.[f] | Area | r.t. | Area | r.t. | Area | |
| | | | | 2.8 | 5.7 | $C_2H_4$ |
| | | | | 3.4 | 1.6 | $C_2H_6$ |
| 6.5[g] | | | | | | $H_2O$ |
| | | | | 7.4 | 4.9 | $C_3H_6$ |
| | | | | 7.9 | 2.2 | $C_3H_8$ |
| | | 10.8 | 0.1 | 10.5 | 0.8 | Acetaldehyde |
| | | | | 12.3 | 0.6 | $C_4$-ane |
| | | 12.8 | 0.1 | 12.7 | 9.8 | $C_4$-ene |
| | | 13.4 | 1.0 | 13.3 | 8.5 | $C_4$-ane |
| | | 13.7 | 0.1 | 13.6 | 3.5 | $C_4$-ene |
| | | 15.9 | T[h] | | | Propionaldehyde |
| | | 16.2 | 0.4 | 16.0 | 1.8 | Propionaldehyde, acetone, furan |
| 17.4 | T | | | 16.7 | 0.6 | $C_5$-ene |
| 17.8 | T | 17.7 | 0.3 | 17.6 | 4.0 | $C_5$-ene |
| 18.3 | 0.1 | 18.3 | 1.2 | 18.2 | 8.7 | $C_5$-ene, $C_5$-ane |
| | | | | 20.2 | 0.1 | $C_6$-ene |
| 20.8 | 0.1 | 20.6 | 0.3 | 20.5 | 0.3 | Methyl ethyl ketone |
| 21.5 | 0.4 | 21.3 | 0.1 | 21.2 | 0.7 | $C_6$-ene |
| 21.8 | 0.3 | 21.8 | 1.6 | 21.7 | 2.9 | $C_6$-ene, $C_6$-ane, $C_6$-yne |
| 22.2 | 0.8 | 22.7 | 4.2 | 22.5 | 3.2 | Cyclo-$C_6$-ene |
| 22.6 | 1.0 | 22.9 | 3.6 | 22.8 | 3.4 | Benzene |
| 23.0 | 2.6 | 23.6 | 7.8 | 23.4 | 4.2 | Cyclohexene |
| 24.2 | 2.8 | 25.0 | 5.0 | 24.9 | 1.7 | $C_7$-ene |
| 24.5 | 57.8 | 25.7 | 96.6 | 25.6 | 8.5 | $C_7$-ene |
| 26.7 | 0.2 | 27.4 | 0.3 | | | Toluene |
| | | 29.1 | 13.8 | 29.1 | 0.2 | $C_8$-ene |
| 27.7 | 303.8 | 30.1 | 305.9 | 30.3 | 2.7 | $C_8$-ene |
| 33.8 | 10.1 | 34.1 | 7.8 | | | $C_9$-ene |
| 35.2 | 13.6 | 35.6 | 15.5 | | | $C_9$-ene |
| 36.2 | 9.8 | | | | | $C_9$-ene |
| 37.5 | 17.6 | | | | | $C_9$-ene |
| 40.4 | 14.4 | 38.1 | 30.9 | | | $C_3$-benzene, $C_9$-ene |
| 45.8 | 3.9 | | | | | α-Methylstyrene |

TABLE XXVII-Cont'd.

GAS CHROMATOGRAPHY RESULTS: DEGRADATION OF PYDRAUL MC HYDRAULIC FLUID AT 370°C

(Porapak Q Column)

a) This fraction was examined under the following conditions: Column: stainless steel, 8' x 1/8" Porapak Q, detector: a 10% split into F.I., He flow: 35 ml/min. Column temperature: 50-220°C programmed at 8°/min. b) This was the liquid phase of the fraction. Area is given in square inches x attenuation per microliter of sample. c) This fraction was examined under the following conditions: Column: stainless steel, 8' x 1/8" Porapak Q, detector: a 43% split into F.I., He flow: 35 ml/min, Column temperature: 50-220°C programmed at 7°/min. d) This was the gaseous phase of the fraction; a 10 mm pressure was used. e) An 8 mm pressure was used. f) Retention time, min. g) This peak was identified by the TC detector only under testing conditions given in footnote a). h) $< 0.05$ in$^2$/$\mu$l for liquid samples; $< 0.05$ in$^2$ for gas samples.

### TABLE XXVIII

### GAS CHROMATOGRAPHY RESULTS: DEGRADATION OF PYDRAUL MC HYDRAULIC FLUID AT 370°C

(Apiezon L Column)

| -23°C[a,b,] Frac | | -78°C[a,b] Frac | | Peak Identification |
|---|---|---|---|---|
| r.t.[c] | Area | r.t. | Area | |
| | | 3.5 | 0.2 | $C_6$ |
| | | 4.6 | 0.8 | $C_6$ |
| | | 5.9 | 12.1 | $C_7$-ene |
| | | 6.6 | 103.2 | $C_7$-ene |
| | | 7.1 | 98.5 | $C_7$-ene |
| | | 8.5 | 23.2 | $C_8$-ene |
| | | 10.2 | 576.0 | $C_8$-ene |
| | | 10.5 | 265.5 | $C_8$-ene |
| 11.3 | 11.7 | 10.9 | 384.0 | $C_8$-ene |
| | | 12.4 | 19.8 | $C_9$-ene |
| 13.5 | 0.4 | 13.2 | 16.5 | $C_9$-ene |
| | | 14.4 | 129.5 | $C_9$-ene |
| 15.3 | 29.7 | 15.1 | 68.0 | $C_9$-ene |
| 17.0 | 2.7 | 16.4 | 24.8 | $C_3$-benzene |
| 19.8 | 36.9 | | | $C_{11}$-ene |
| 20.5 | 37.9 | 20.6 | 7.4 | $C_{11}$-ene, α-methylstyrene |
| 20.7 | 40.5 | | | $C_{11}$-ene |
| 21.0 | 45.9 | | | $C_{11}$-ene |
| 21.4 | 68.3 | | | $C_{11}$-ene |
| 21.8 | 123.7 | | | $C_{11}$-ene |
| 22.7 | 1386.7 | 22.7 | 1.9 | $C_{11}$-ene |
| 23.2 | 602.7 | | | $C_{11}$-ene |
| 30.0 | 0.5 | | | |
| 31.2 | 0.1 | | | |
| 33.0 | 4.7 | | | Cyclohexylcyclohexane |

a) This fraction was examined under the following conditions: Column: stainless steel, 10' x 1/8" 4% Apiezon L on Chromosorb G, detector: a 43% split into F.I. He flow: 35 ml/min, column temperature: 35 to 220°C programmed at 4°C/min. b) This was the liquid phase of the fraction. Area is given in square inches x attenuation per microliter of sample. c) Retention time, min.

## TABLE XXIX

## GAS CHROMATOGRAPHY RESULTS: DEGRADATION OF PYDRAUL MC HYDRAULIC FLUID AT "420°C"

(Porapak Q Column)

| -78°C [a,b] Frac | | -78°C [c,d] Frac (vapor) | | -196°C [c,e] Frac | | Peak Identification |
|---|---|---|---|---|---|---|
| r.t.[f] | Area | r.t. | Area | r.t. | Area | |
| | | | | 2.1[h] | 1.5 | $CO_2$ |
| | | 2.7 | T[g] | 2.6 | 7.4 | $C_2H_4$ |
| | | | | 3.2 | 1.3 | $C_2H_6$ |
| | | | | 4.2[h] | 83.8 | $PH_3$ |
| | | 7.1 | T | 6.9 | 4.4 | $C_3H_6$ |
| | | 7.6 | T | 7.4 | 2.1 | $C_3H_8$ |
| | | | | 11.8 | 0.7 | $C_4$ |
| | | 12.3 | 0.2 | 12.1 | 7.5 | $C_4$ |
| 13.5 | 0.1 | 13.0 | 0.3 | 12.7 | 8.0 | $C_4$ |
| 15.5 | 0.2 | 15.5 | 0.1 | 15.4 | 0.1 | Acetone, $C_5$-ane |
| 16.4 | T | 16.3 | T | 16.2 | 0.3 | $C_5$-ene |
| 17.6 | 0.3 | 17.2 | 1.3 | 17.0 | 4.4 | $C_5$-ene |
| 18.0 | 1.7 | 17.8 | 9.6 | 17.6 | 14.6 | $C_5$-ene, $C_5$-ane |
| 18.7 | 0.2 | 18.6 | 0.4 | 18.5 | 0.2 | Cyclo-$C_5$-ane |
| 19.8 | 0.3 | 20.0 | 0.1 | | | Methyl ethyl ketone, n-butyraldehyde |
| 20.6 | 0.2 | 20.7 | 0.8 | 20.7 | 0.8 | $C_6$-ene, $C_6$-ane |
| 21.0 | 8.7 | 21.2 | 24.6 | 21.1 | 6.2 | $C_6$-diene or cyclo-$C_6$-ene |
| 21.6 | 35.3 | 22.0 | 56.3 | 22.0 | 5.7 | $C_6$-diene or cyclo-$C_6$-ene |
| 22.2 | 15.3 | 22.3 | 58.8 | 22.3 | 2.6 | Benzene |
| 22.4 | 68.6 | 22.9 | 80.0 | 22.9 | 3.4 | Cyclohexene |
| 24.0 | 1.3 | 24.5 | 1.0 | 23.8 | 0.2 | $C_7$-ene |
| 24.5 | 28.2 | 25.6 | 28.0 | 25.9 | 0.5 | $C_7$-ene |
| 26.4 | 4.8 | 26.6 | 2.8 | | | Toluene |
| 27.5 | 5.7 | 28.5 | 3.3 | | | $C_8$-ene |
| 28.0 | 141.4 | 29.7 | 47.0 | | | $C_8$-ene |
| 31.8 | 37.7 | 33.3 | 8.7 | | | $C_7$-benzene, $C_9$-ene |
| 33.3 | 49.2 | | | | | $C_9$-ene |
| 34.5 | 35.9 | 34.7 | 11.8 | | | $C_9$-ene |
| 36.5 | 26.8 | 37.5 | 4.4 | | | $C_3$-benzene |
| 38.3 | 35.6 | | | | | $C_3$-benzene |
| 43.5 | 3.5 | | | | | α-Methylstyrene |
| 47.0 | 0.2 | | | | | $C_{10}$-species |

## TABLE XXIX-Cont'd.

## GAS CHROMATOGRAPHY RESULTS: DEGRADATION OF PYDRAUL MC HYDRAULIC FLUID AT "420°C"

(Porapak Q Column)

a) This fraction was examined under the following conditions: Column: stainless steel, 8' x 1/8" Porapak Q, detector: a 10% split into F.I., He flow: 30 ml/min. Column temperature: 50-220°C programmed at 8°/min. b) This was the liquid phase of the fraction. Area is given in square inches x attenuation per microliter of sample. c) This fraction was examined under the following conditions: Column: stainless steel, 8' x 1/8" Porapak Q, detector: a 43% split into F.I., He flow: 35 ml/min. column temperature: 50-220°C programmed at 7°/min. d) This was the gaseous phase of the fraction; a 19 mm pressure was used. e) A 14 mm pressure was used. Area is given in square inches x attenuation. f) Retention time, min. g) $< 0.05$ in$^2$ for gas samples. h) This peak was identified by the TC detector only under testing conditions given in footnote a).

## TABLE XXX

## GAS CHROMATOGRAPHY RESULTS: DEGRADATION OF PYDRAUL MC HYDRAULIC FLUID AT "420°C"

(Apiezon L Column)

| $-23^{\circ}C$[a] Frac | | Peak Identification |
|---|---|---|
| r.t.[b] | Area | |
| 10.6 | 10.9 | $C_8$-ene |
| 10.9 | 19.2 | $C_8$-ene |
| 11.4 | 19.6 | $C_8$-ene |
| 11.7 | 57.4 | $C_8$-ene |
| 12.8 | 100.8 | $C_9$-ene |
| 13.6 | 176.0 | $C_9$-ene |
| 14.4 | 32.8 | $C_9$-ene |
| 14.8 | 216.0 | $C_9$-ene |
| 15.4 | 137.6 | $C_9$-ene |
| 16.5 | 412.8 | $C_3$-benzene, phenol |
| 19.4 | 171.0 | $\alpha$-Methylstyrene |
| 20.7 | 4.8 | $C_{11}$-species |
| 21.3 | 1.2 | $C_{11}$-species |
| 21.7 | 2.0 | $C_{11}$-species |
| 22.2 | 9.0 | $C_{11}$-species |
| 22.9 | 208.0 | $C_{11}$-ene |
| 23.4 | 49.6 | $C_{11}$-ene |
| 23.7 | 24.0 | $C_{11}$-ene |

a) This fraction was examined under the following conditions: Column: stainless steel, 10' x 1/8" 4% Apiezon L on Chromosorb G, detector: a 43% split into F.I., programmed at 4°/min. b) Retention time, min. Area is given in square inches x attenuation per microliter of sample.

## TABLE XXXI

## GAS CHROMATOGRAPHY RESULTS: DEGRADATION OF DASCO FR 300 HYDRAULIC FLUID AT 370°C

(Porapak Q Column)

| $-78^{\circ}C^{a,b}$ Frac | | $-78^{\circ}C^{c,d}$ Frac (vapor) | | $-96^{\circ}C^{c,e}$ Frac | | $-196^{\circ}C^{c,f}$ Frac | | Peak Identification |
|---|---|---|---|---|---|---|---|---|
| r.t.[g] | Area | r.t. | Area | r.t. | Area | r.t. | Area | |
| | | | | | | 1.9[h] | 11.7 | $CO_2$ |
| | | | | | | 2.7 | 7.4 | $C_2H_4$ |
| | | | | | | 3.3 | 8.4 | $C_2H_6$ |
| | | | | | | 6.5[h] | 3.3 | COS |
| | | | | 6.5 | T[i] | 7.1 | 67.2 | $C_3H_6$ |
| | | | | | | 7.6 | 8.0 | $C_3H_8$ |
| 10.3 | T | 10.7 | 0.1 | 10.4 | 0.4 | 10.0 | 1.9 | $CH_3CHO$ |
| | | | | | | 11.9 | 0.8 | $C_4$-ane |
| | | | | | | 12.2 | 40.6 | $C_4$-ene |
| | | | | | | 12.8 | 26.9 | $C_4$-ene |
| | | | | | | 13.1 | 12.2 | $C_4$-ene |
| 14.9 | 1.6 | 15.4 | 5.1 | 15.3 | 3.0 | | | Acrolein |
| 16.0 | 58.3 | 15.8 | 107.5 | 15.6 | 119.0 | 15.2 | 5.8 | Propionaldehyde, acetone |
| | | | | | | 16.2 | 0.2 | $CS_2$ |
| | | 17.9 | T | 17.7 | 0.1 | 17.1 | 6.9 | $C_5$-ene |
| | | | | | | 17.6 | 22.2 | $C_5$-species |
| 18.4 | T | 18.7 | 0.6 | 18.6 | 6.3 | | | Isoprene |
| 19.2 | 0.1 | 19.5 | 0.2 | | | | | Crotonaldehyde, Isobutyraldehyde |
| | | | | | | 19.5 | T | $C_6$-species |
| 20.3 | 0.2 | 20.6 | 0.3 | | | | | Butyraldehyde |
| 21 | 18.6 | | | | | | | $C_6$-species |
| | | 21.5 | 0.3 | 21.4 | 1.5 | 20.6 | 0.6 | $C_6$-ene |
| | | | | | | 21.0 | 1.6 | $C_6$-ane |
| | | | | | | 21.7 | 1.3 | $C_6$-ane |
| | | 22.3 | 4.0 | 22.3 | 7.6 | | | $C_6$-diene |
| | | 22.8 | 6.0 | 22.5 | 10.5 | | | 1-Methylcyclopentene |
| | | 23.2 | 0.7 | | | | | Benzene |
| | | 23.8 | 0.6 | 23.7 | 0.3 | | | Cyclohexene, cyclohexane |
| | | 24.8 | 0.5 | 24.7 | 0.4 | | | $C_7$-ene, $C_7$-ane |
| 25.2 | 1.5 | 25.5 | 1.8 | 25.6 | 1.5 | | | $C_7$-diene |

## TABLE XXXI-Cont'd.

## GAS CHROMATOGRAPHY RESULTS: DEGRADATION OF DASCO FR 300 HYDRAULIC FLUID AT 370°C

(Porapak Q Column)

| -78°C[a,b] Frac | | -78°C[c,d] Frac (vapor) | | -96°C[c,e] Frac | | -196°C[c,f] Frac | | Peak Identification |
|---|---|---|---|---|---|---|---|---|
| r.t.[g] | Area | r.t. | Area | r.t. | Area | r.t. | Area | |
| 25.7 | 5.1 | 25.9 | 3.7 | | | | | $C_7$-species |
| | | 26.2 | 2.7 | 26.2 | 0.5 | | | $C_7$-ane, $C_7$-ene |
| 26.8 | 0.8 | 26.9 | 0.2 | 26.8 | T | | | $C_7$-ane, $C_7$-ene |
| 27.8 | 0.9 | 27.5 | 0.4 | | | | | Toluene |
| 28.4 | 8.6 | 28.3 | 9.3 | 28.3 | 1.2 | | | $C_8$-ene |
| 29.5 | 1.4 | | | | | | | $C_8$-ane |
| 31.0 | 2.4 | | | | | | | $C_8$-ane, $C_8$-ene, $C_8$-diene ? |
| 32.6 | T | | | | | | | $C_2$-benzene |

a) This fraction was examined under the following conditions: Column: stainless steel, 8' x 1/8" Porapak Q, detector: a 43% split into F.I., He flow: 35 ml/min. Column temperature: 50-220°C programmed at 7°/min. b) This was the liquid phase of the fraction. Area is given in square inches x attenuation per microliter of sample. c) This fraction was examined under the following conditions: Column: stainless steel, 8' x 1/8" Porapak Q, detector: a 10% split into F.I., He flow 35 ml/min, column temperature: 50 to 220°C programmed at 8°/min. d) This was the gaseous phase of the fraction; a 16 mm pressure was used. Area is given in square inches x attenuation. e) A 17 mm pressure was used. Area is given in square inches x attenuation. f) A 20 mm pressure was used. Area is given in square inches x attenuation. g) Retention time, min. h) This peak was identified by the TC detector only under testing conditions given in footnote c). i) < 0.05 in²/µl for liquid samples; < 0.05 in² for gas samples.

TABLE XXXII

GAS CHROMATOGRAPHY RESULTS : DEGRADATION OF DASCO FR 300 HYDRAULIC FLUID AT 370°C

(Porapak Q Column)

| $-23^{\circ}$C [a,c] Frac | | $-63^{\circ}$C [b,c] Frac (bottom layer) | | $-63^{\circ}$C [b,c] Frac (top layer) | | $-63^{\circ}$C [a,d] Frac (vapor) | | Peak Identification |
|---|---|---|---|---|---|---|---|---|
| r.t.[e] | Area | r.t. | Area | r.t. | Area | r.t. | Area | |
| | | | | | | 2.7 | 0.2 | $C_2H_4$ |
| | | | | | | 3.3 | 0.2 | $C_2H_6$ |
| | | 6.6[f] | 237.9 | | | | | $H_2O$ |
| | | | | | | 7.5 | 0.9 | $C_3H_6$ |
| | | | | | | 8.0 | 0.1 | $C_3H_8$ |
| | | 9.8 | 0.5 | | | | | Methanol |
| | | 10.3 | T[g] | | | 10.6 | 0.2 | $CH_3CHO$ |
| | | | | | | 12.5 | 0.1 | $C_4$-ane |
| | | | | | | 12.9 | 0.7 | $C_4$-ene |
| | | | | | | 13.6 | 0.5 | $C_4$-ene |
| | | | | | | 13.9 | 0.3 | $C_4$-ene |
| | | 14.4 | T | | | | | Ethanol |
| 16.0 | 8.3 | 16.3 | 3.2 | 16.7 | 5.1 | 15.8 | 70.4 | Propionaldehyde, Acrolein, acetone |
| | | | | | | 17.5 | 0.1 | Methyl acetate |
| | | | | | | 18.0 | 0.1 | Isoprene, $C_5$-ene |
| | | | | 19.5 | T | 18.7 | 0.6 | Isobutyraldehyde, Crotonaldehyde |
| 20.6 | 0.6 | 20.3 | 0.6 | | | | | Allyl alcohol |
| | | 21.2 | 0.8 | 20.5 | T | 19.6 | 0.3 | Butyraldehyde |
| | | | | ~ 21 | 5.3 | | | $C_6$-species |
| | | | | | | 20.6 | 1.5 | $C_6$-species |
| | | | | | | 22.4 | 0.6 | $C_6$-ene |
| 22.8 | 0.1 | | | | | | | |
| | | | | | | 22.9 | 2.9 | 1-Methylcyclopentene |
| | | | | | | 23.2 | 2.6 | Benzene |
| 23.7 | 0.8 | | | | | | | Butanols |
| | | | | | | 23.8 | 1.3 | Cyclohexene |
| 24.5 | 0.7 | 26.0 | 0.2 | | | | | 2-Pentanone |
| | | | | 24.8 | 0.3 | 24.6 | 1.8 | $C_7$-ene |
| | | | | 25.3 | 1.2 | 25.6 | 2.3 | $C_7$-diene |
| 25.8 | 0.8 | | | | | | | |

TABLE XXXII-Cont'd.

GAS CHROMATOGRAPHY RESULTS: DEGRADATION OF DASCO FR 300 HYDRAULIC FLUID AT 370°C

(Porapak Q Column)

| $-23^{\circ}C$ [a,c] Frac | | $-63^{\circ}C$ [b,c] Frac (bottom layer) | | $-63^{\circ}C$ [b,c] Frac (top layer) | | $-63^{\circ}C$ [a,d] Frac (vapor) | | Peak Identification |
|---|---|---|---|---|---|---|---|---|
| r.t.[e] | Area | r.t. | Area | r.t. | Area | r.t. | Area | |
| | | | | 26.0 | 8.5 | 26.0 | 8.4 | $C_7$-ene, $C_7$-diene |
| | | | | 26.4 | 3.3 | 26.2 | 5.6 | $C_7$-ane, $C_7$-diene |
| | | | | 27.0 | 1.3 | | | $C_7$-species |
| 26.9 | 6.3 | 27.7 | 0.4 | 27.8 | 14.6 | 27.5 | 6.5 | Toluene, cyclopentanone |
| 28.7 | 2.9 | | | | | | | |
| | | 28.5 | 0.8 | 28.7 | 21.2 | 28.4 | 24.8 | $C_8$-ene |
| 29.5 | 56.3 | 30.7 | 2.0 | 31.2 | 14.2 | 29.8 | 8.0 | Dimethyl dioxanes |
| 30.7 | 56.5 | 32.5 | 1.0 | 32.2 | 17.0 | 30.8 | 3.0 | Dimethyl dioxanes, $C_8$-ane |
| 33.1 | 6.7 | | | | | | | Cyclohexanone |
| | | 35.2 | 0.5 | 35.7 | 13.4 | 33.2 | 2.8 | $C_2$-benzene |
| 34.8 | 578.7 | 37.4 | 0.1 | | | | | Phenol |
| | | | | 38.0 | 4.2 | | | $C_2$-benzene |
| | | 42.7 | 1.2 | | | | | |
| | | | | 43.0 | 11.5 | | | $C_9$-ane |
| 43.7 | 33.1 | | | | | | | Cresols |
| | | | | 47.4 | 13.6 | | | $C_3$-benzene |
| 45.9 | 31.1 | | | | | | | Cresols |
| | | | | 49.7 | 5.0 | | | $C_3$-benzene |
| | | | | 52.0 | 3.1 | | | Indan |
| 53.0 | n.d.[h] | | | | | | | |
| 56.0 | n.d. | | | 55.7 | 5.2 | | | $C_{10}$-ane |
| | | | | 61.5 | 4.1 | | | |
| 65.5 | n.d. | | | | | | | |
| 69.5 | n.d. | | | | | | | |
| 79.5 | n.d. | | | | | | | |

## TABLE XXXII-Cont'd.

## GAS CHROMATOGRAPHY RESULTS: DEGRADATION OF DASCO FR 300 HYDRAULIC FLUID AT 370°C

(Porapak Q Column)

a) This fraction was examined under the following conditions: Column: stainless steel, 8' x 1/8" Porapak Q, detector, a 43% split into F.I., He flow: 35 ml/min, column temperature: 50 to 220°C programmed at 7°/min. b) This fraction was examined under the following conditions: Column: stainless steel, 8' x 1/8" Porapak Q, detector: a 10% split into F.I., He flow: 35 ml/min, column temperature: 50 to 220°C programmed at 8°/min. c) This was the liquid phase of the fraction. Area is given in square inches x attenuation per microliter of sample. d) This was the gaseous phase of the fraction; a 14 mm pressure was used. Area is given in square inches x attenuation. e) Retention time, min. f) This peak was identified by the TC detector only. g) $< 0.05$ in$^2$/$\mu$l. h) Not determined.

## TABLE XXXIII

## GAS CHROMATOGRAPHY RESULTS: DEGRADATION OF DASCO FR 300 HYDRAULIC FLUID AT 370°C

(Apiezon L Column)

| $0^\circ C$ Frac[a,b] | | $-63^\circ C$ Frac (top layer)[a,b] | | Peak Identification |
|---|---|---|---|---|
| r.t.[c] | Area | r.t. | Area | |
| | | 6.0 | 1.2 | |
| 7.0 | 0.9 | 7.0 | 51.3 | $C_7$-species |
| | | 8.8 | 2.5 | $C_8$-ene |
| | | 9.2 | 9.8 | $C_8$-species |
| | | 10.1 | 10.5 | $C_7$-diene |
| | | 10.4 | 12.2 | Toluene |
| 10.8 | 32.2 | 10.7 | 35.3 | Dimethyl dioxane |
| 12.0 | 51.0 | 12.3 | 3.8 | Dimethyl dioxane |
| | | 12.5 | 7.7 | $C_9$-species |
| | | 13.1 | 9.9 | $C_9$-ene |
| | | 13.7 | 9.6 | |
| | | 14.1 | 14.2 | |
| | | 14.5 | 16.0 | $C_9$-ene |
| | | 14.9 | 19.2 | |
| | | 15.8 | 9.3 | $C_2$-benzene |
| 16.2 | 558.2 | | | Phenol |
| | | 18.0 | 148.9 | Propionaldehyde trimer $(C_3H_6O)_3$ |
| | | 18.6 | 14.2 | |
| | | 19.2 | 22.7 | $C_{10}$-species |
| | | 19.8 | 0.9 | |
| | | 20.5 | 19.8 | $C_3$-benzene |
| 21 | 25.6 | | | Cresol |
| 21.5 | 16.4 | | | |
| 21.8 | 37.0 | 22.0 | 16.6 | Indan |
| | | 22.6 | 7.3 | $C_4$-benzene |
| | | 22.7 | 5.2 | |
| 23.2 | 27.7 | 23.1 | 11.3 | $C_4$-benzene, $C_{11}H_{24}$ |
| | | 23.7 | 5.2 | Ethyl styrene, $C_4$-benzene |
| 24.0 | 5.7 | | | Methyl p-cresyl ether |
| 24.8 | 31.3 | 24.7 | 3.6 | 2,6-Xylenol ? |
| 25.9 | 1.4 | 25.5 | 3.3 | |

### TABLE XXXIII-Cont'd.
### GAS CHROMATOGRAPHY RESULTS: DEGRADATION OF DASCO FR 300 HYDRAULIC FLUID AT 370°C
### (Apiezon L Column)

| $0^{\circ}C$ [a,b] Frac | | $-63^{\circ}C$ [a,b] Frac (top layer) | | Peak Identification |
|---|---|---|---|---|
| r.t.[c] | Area | r.t. | Area | |
| 26.4 | 3.6 | 26.4 | 1.6 | Dimethylstyrene |
| 26.9 | 10.7 | 26.9 | 0.6 | $C_{12}H_{26}$ |
| 27.4 | 5.0 | 27.6 | 1.1 | 1,2,3,4-Tetrahydronapthalene |
| 28.0 | 0.4 | | | 2-Phenyl-2-butenal |
| 28.4 | 2.5 | | | $C_5$-benzene |
| 29.1 | 2.8 | | | Napthalene |
| 29.7 | 13.2 | | | Methyltetrahydronapthalene |
| 30.5 | 10.3 | | | $C_{13}H_{28}$ |
| 30.8 | 2.1 | | | |
| 31.5 | 3.2 | | | |
| 32.0 | 1.1 | | | Trimethylindan |
| 32.5 | 1.6 | | | Dimethyltetrahydronapthalene |
| 33.5 | 0.9 | | | |
| 33.8 | 1.6 | | | $C_{14}H_{30}$ |
| 37.1 | 2.0 | | | $C_{15}H_{32}$ |
| 41.0 | 0.3 | | | |
| 45.7 | 1.7 | | | |
| 51.7 | 12.8 | | | |
| 59.5 | 18.8 | | | |

a) This fraction was examined under the following conditions: Column: stainless steel, 10' x 1/8" 4% Apiezon L on Chromosorb G, detector: a 43% split into F.I., He flow: 35 ml/min, column temperature: 35 to 220°C programmed at 5°C/min. b) This was the liquid phase of the fraction. Area is given in square inches x attenuation per microliter of sample. c) Retention time, min.

## TABLE XXXIV

## GAS CHROMATOGRAPHY RESULTS: DEGRADATION OF DASCO FR 300 HYDRAULIC FLUID AT "420°C"

(Porapak Q Column)

| $-78^\circ$C [a,b] Frac (Bottom Layer) | | $-78^\circ$C [a,b] Frac (Top Layer) | | $-78^\circ$C [c,d] Frac (Vapor) | | $-196^\circ$C [c,e] Frac | | Peak Identification |
|---|---|---|---|---|---|---|---|---|
| r.t.[f] | Area | r.t. | Area | r.t. | Area | r.t. | Area | |
| | | | | | | 2.1[g] | 4.0 | $CO_2$ |
| | | | | | | 2.9 | 6.0 | $C_2H_4$ |
| | | | | | | 3.5 | 7.2 | $C_2H_6$ |
| | | | | | | 4.4[g] | 0.5 | $PH_3$ |
| | | | | | | 7.0[g] | 0.9 | COS |
| 7.3[g] | 449.0 | | | | | | | $H_2O$ |
| | | | | 7.4 | 0.3 | 7.4 | 37.1 | $C_3H_6$ |
| | | | | 7.9 | 0.1 | 7.9 | 9.3 | $C_3H_8$ |
| 10.8 | 0.1 | | | | | | | Methanol |
| 11.7 | 0.3 | | | 10.2 | 0.5 | 10.3 | 0.2 | Acetaldehyde |
| | | | | | | 12.3 | 1.7 | $C_4$-ane |
| | | | | 12.6 | 2.1 | 12.7 | 14.9 | $C_4$-ene |
| | | | | 13.3 | 2.2 | 13.3 | 15.3 | $C_4$-ene, $C_4$-ane |
| 15.4 | T | | | | | | | Ethanol |
| | | | | 15.2 | 0.9 | | | Acrolein |
| 16.0 | 26.6 | 16.1 | 28.1 | 15.5 | 59.8 | 15.6 | 8.9 | Propionaldehyde, Acrolein |
| | | 17.4 | T[h] | 16.7 | 1.0 | 16.8 | 0.2 | $C_5$-ene |
| | | 18.1 | 1.0 | 17.5 | 72.0 | 17.6 | 4.0 | $C_5$-ene |
| | | 18.3 | 1.0 | 18.2 | 8.4 | 18.2 | 10.5 | $C_5$-ene, $C_5$-ane |
| | | 18.8 | T | | | | | 2-Methyl propenal |
| | | | | 19.0 | 0.2 | 19.0 | 0.2 | $C_5$-species |
| 19.4 | T | | | | | | | |
| 19.8 | 0.2 | | | | | | | Allyl alcohol |
| 21.2 | 0.1 | 19.6 | 0.5 | 20.2 | 0.1 | | | n-butyraldehyde, methyl ethyl ketone, t-butyl alcohol |
| | | 20.7 | 3.3 | | | | | $C_6$-ene |
| | | 21.5 | 20.3 | 21.1 | 1.3 | 21.2 | 0.6 | $C_6$-species |
| | | 21.8 | 10.9 | 22.2 | 20.9 | 22.3 | 4.8 | $C_6$-species, benzene |
| | | 22.5 | 4.9 | | | | | Benzene |
| | | 22.8 | 1.9 | 23.5 | 0.7 | 23.5 | 0.1 | Cyclo-$C_6$-ene |
| 23.8 | 0.2 | | | | | | | |
| | | | | 24.5 | 0.6 | | | $C_7$-ene |
| | | 24.7 | 18.5 | 25.6 | 7.0 | 25.7 | 0.5 | $C_7$-ene |
| | | 24.9 | 28.7 | 26.0 | 5.3 | | | $C_7$-ane |

TABLE XXXIV-Cont'd.

GAS CHROMATOGRAPHY RESULTS: DEGRADATION OF DASCO FR 300 HYDRAULIC FLUID AT "420°C"

(Porapak Q Column)

| $-78^{\circ}C^{a,b}$ Frac (Bottom Layer) | | $-78^{\circ}C^{a,b}$ Frac (Top Layer) | | $-78^{\circ}C^{c,d}$ Frac (Vapor) | | $-196^{\circ}C^{c,e}$ Frac | | Peak Identification |
|---|---|---|---|---|---|---|---|---|
| r.t.[f] | Area | r.t. | Area | r.t. | Area | r.t. | Area | |
| | | | | 26.7 | 0.7 | | | $C_7$-species |
| | | 26.7 | 17.4 | 27.3 | 1.4 | | | Toluene |
| 27.5 | 0.1 | | | | | | | Cyclopentanone |
| 28.8 | 0.1 | 27.2 | 19.3 | | | | | 4-methyl-2-ethyl-1,3-dioxolane |
| | | | | 28.4 | 3.2 | 28.5 | 0.2 | $C_8$-ene |
| | | 28.3 | 8.0 | 29.4 | 0.6 | | | $C_8$-species |
| | | 29.2 | 25.0 | 30.2 | 1.8 | | | $C_8$-ene |
| | | 30.2 | 32.6 | 31.3 | 1.5 | | | $C_8$-ane |
| 30.2 | 0.3 | | | | | | | Dimethyl dioxane |
| 31.8 | 0.1 | | | | | | | Dimethyl dioxane |
| | | 33.1 | 25.5 | 33.5 | 0.4 | | | $C_2$-benzene |
| | | 35.0 | 10.9 | | | | | |

a) This fraction was examined under the following conditions: Column: stainless steel, 8' x 1/8" Porapak Q, detector: a 10% split into F.I., He flow: 35 ml/min. Column temperature: 50-220°C programmed at 8°/min. b) This was the liquid phase of the fraction. Area is given in square inches x attenuation per microliter of sample. c) This fraction was examined under the following conditions: Column: stainless steel, 8' x 1/8" Porapak Q, detector: a 43% split into F.I., He flow 30 ml/min. column temperature: 50-220°C programmed at 7°/min. d) This was the gaseous phase of the fraction; a 14 mm pressure was used. e) A 16 mm pressure was used. Area is given in square inches x attenuation. f) Retention time, min. g) This peak was identified by the TC detector only under testing conditions given in footnote a). h) $< 0.05$ $in^2/\mu l$ for liquid samples; $< 0.05$ $in^2$ for gas samples.

## TABLE XXXV

## GAS CHROMATOGRAPHY RESULTS: DEGRADATION OF DASCO FR 300 HYDRAULIC FLUID AT "420°C"

(OV-101 Column)

| 0°C [a] Frac | | -23°C [a] Frac | | -78°C [a] Frac (Top Layer) | | Peak Identification |
|---|---|---|---|---|---|---|
| r.t. [b] | Area | r.t. | Area | r.t. | Area | |
| 1.4 | 0.1 | | | 1.6 | T | $C_5$-species |
| | | | | 1.9 | 0.2 | Acrolein |
| | | | | 2.0 | 88.6 | Propionaldehyde |
| 2.4 | 0.1 | | | 2.9 | 7.6 | $C_6$-species |
| | | | | 3.2 | 9.5 | $C_6$-species |
| | | | | 3.5 | 11.9 | $C_6$-species |
| 3.9 | 0.1 | | | 3.8 | 53.7 | $C_6$-species |
| | | | | 4.2 | 13.8 | $C_6$-species |
| | | | | 4.4 | 7.1 | $C_7$-species |
| 4.9 | 0.1 | | | 5.0 | 44.8 | Benzene |
| | | | | 5.4 | 20.7 | $C_7$-species |
| | | 5.5 | 0.2 | 5.7 | 14.8 | $C_7$-species |
| | | | | 6.0 | 20.2 | |
| 6.3 | 0.1 | 6.3 | 0.2 | 6.4 | 113.2 | $C_7$-species |
| 6.5 | 0.2 | | | 6.7 | 102.4 | $C_8$-species |
| 7.8 | 0.1 | 7.5 | 0.2 | 7.2 | 16.7 | $C_7$-species |
| 8.3 | 0.4 | 8.3 | 0.1 | 8.1 | 128.0 | Toluene |
| | | | | 8.5 | 52.2 | $C_8$-species |
| | | 8.8 | 0.5 | 8.8 | 13.8 | |
| 9.3 | 11.2 | 9.2 | 22.9 | 9.3 | 21.7 | Dimethyl dioxane |
| | | | | 9.7 | 163.4 | $C_8$-species |
| 10.2 | 14.6 | 10.2 | 18.3 | 10.5 | 7.9 | Dimethyl dioxane |
| | | | | 10.9 | 4.2 | |
| | | 11.3 | 0.9 | | | Cyclopentanone |
| 11.7 | 0.9 | 11.6 | 2.9 | 11.5 | 45.8 | $C_2$-benzene |
| | | | | 11.8 | 126.0 | $C_2$-benzene |
| 12.5 | 2.4 | | | 12.6 | 51.2 | $C_2$-benzene |
| 13.0 | 1.9 | 13.0 | 0.6 | 13.3 | 92.6 | $C_9$-species |
| 13.4 | 0.2 | 13.5 | 2.1 | | | |
| 13.7 | 4.0 | 13.8 | 1.6 | 14.1 | 0.5 | $C_3$-benzene, cyclohexanone |
| | | | | 14.6 | 3.7 | |
| 15.0 | 0.3 | 14.9 | 0.5 | 15.2 | 94.0 | $C_3$-benzene |
| 15.4 | 972.8 | 15.4 | 740.6 | | | Phenol |
| | | | | 16.3 | 43.8 | $C_3$-benzene |
| | | 16.6 | 7.3 | 16.9 | 72.4 | $C_{10}$-species |

TABLE XXXV-Cont'd.

GAS CHROMATOGRAPHY RESULTS: DEGRADATION OF DASCO FR 300 HYDRAULIC FLUID AT "420°C"

(OV-101 Column)

| 0°C [a] Frac | | -23°C [a] Frac | | -78°C [a] Frac (Top Layer) | | Peak Identification |
|---|---|---|---|---|---|---|
| r.t. [b] | Area | r.t. | Area | r.t. | Area | |
| | | 17.0 | 1.4 | | | $C_4$-benzene |
| | | 17.5 | 3.7 | | | Methylstyrene |
| | | | | 17.5 | 141.8 | Propionaldehyde trimer |
| 17.9 | 77.3 | 17.9 | 14.6 | | | Cresol |
| 18.6 | 260.3 | 18.3 | 3.7 | | | Cresol |
| | | | | 18.5 | 5.7 | |
| | | | | 18.9 | 2.7 | |
| | | 19.2 | 54.8 | 19.3 | 6.6 | $C_4$-benzene |
| 19.7 | 24.8 | | | | | Xylenol |
| | | 19.8 | 8.2 | 20.0 | 4.9 | $C_{11}$-species |
| 20.1 | 5.1 | 20.2 | 206.6 | 20.3 | 13.0 | $C_{11}$-species |
| 20.7 | 24.1 | | | | | $C_4$-benzene |
| 21.1 | 137.6 | | | | | Xylenol |
| | | 21.1 | 20.1 | | | Ethylstyrene |
| | | 21.5 | 25.6 | | | Ethylstyrene |
| 21.8 | 134.4 | | | | | Xylenol |
| | | 21.8 | 69.5 | | | 1,2,3,4-Tetrahydronapthalene |
| 23.1 | 17.1 | 23.1 | 32.0 | | | $C_{12}$-species |
| 23.5 | 20.3 | 23.4 | 70.4 | 23.5 | 0.2 | $C_{12}$-species |
| | | 23.9 | 6.4 | 24.3 | 0.1 | |
| 24.8 | 1.3 | 24.7 | 1.4 | 24.8 | 0.1 | |
| 25.2 | 13.6 | 25.2 | 2.7 | 25.3 | 0.1 | |
| 26.2 | 3.2 | 26.2 | 1.1 | | | $C_{13}$-species |
| 26.6 | 46.4 | 26.5 | 3.2 | | | $C_{13}$-species |
| 27.1 | 10.7 | | | | | |
| 28.1 | 6.7 | | | | | |
| 29.3 | 3.7 | | | | | |
| 29.6 | 16.8 | | | | | $C_{14}$-species |

a) This fraction was examined under the following conditions: Column: stainless steel, 10' x 1/8" 4% OV-101 on Chromosorb G, detector: a 43% split into F.I., programmed at 4°/min from 35-220°C.

b) Retention time, min. Area is given in square inches x attenuation per microliter of sample.

## TABLE XXXVI

## GAS CHROMATOGRAPHY RESULTS: DEGRADATION OF TRIPHENYL PHOSPHATE- n-OCTACOSANE MIXTURE

(Porapak Q Column)

| -78°C[a,b] Frac (Bottom Layer) | | -78°C[a,b] Frac (Top Layer) | | -78°C[c,d] Frac (Vapor) | | -196°C[c,e] Frac | | Peak Identification |
|---|---|---|---|---|---|---|---|---|
| r.t.[f] | Area | r.t. | Area | r.t. | Area | r.t. | Area | |
| | | | | | | 2.0[g] | 11.0 | $CO_2$ |
| | | | | 2.9 | T[h] | 2.9 | 6.1 | $C_2H_4$ |
| | | | | 3.5 | T | 3.5 | 6.7 | $C_2H_6$, $PH_3$ |
| 6.4[g] | 444.9 | | | | | | | $H_2O$ |
| 7.5 | T | | | | | | | Formaldehyde |
| | | | | 7.5 | 0.1 | 7.5 | 10.8 | $C_3H_6$ |
| | | | | 8.0 | T | 8.0 | 8.6 | $C_3H_8$ |
| 9.0 | 3.2 | | | | | | | Methanol |
| 10.4 | 0.7 | | | 10.4 | 2.0 | 10.3 | 2.0 | Acetaldehyde |
| 12.2 | 0.1 | | | 12.3 | 1.2 | | | Methyl formate |
| | | | | 13.0 | 0.2 | 12.8 | 12.2 | $C_4$-ene |
| | | | | 13.5 | 0.2 | 13.5 | 10.1 | $C_4$-ane |
| 13.7 | 1.0 | | | | | | | Ethanol |
| | | | | 15.5 | 0.2 | 15.5 | 0.3 | Acrolein |
| 15.4 | 0.8 | 15.8 | 0.1 | 15.9 | 10.1 | 15.8 | 2.3 | Propionaldehyde |
| 15.9 | 0.9 | 16.2 | 0.1 | | | | | Acetone |
| | | 16.7 | T | | | | | |
| 17.0 | 0.1 | 17.2 | 0.1 | 17.2 | 0.5 | | | Ethyl formate |
| | | | | 17.9 | 0.6 | 17.9 | 11.7 | $C_5$-ene |
| 18.0 | T | | | | | | | Allyl alcohol |
| | | 18.8 | T | 18.5 | 0.7 | 18.4 | 10.3 | $C_5$-ane |
| 18.4 | 0.3 | | | | | | | Acetic acid, n-propanol |
| | | | | 19.6 | 0.2 | | | Isobutyraldehyde |
| 20.6 | 1.4 | 20.7 | 2.7 | 20.5 | 19.6 | 20.6 | 0.5 | n-Butyraldehyde, methyl ethyl ketone |
| | | | | 21.7 | 0.1 | 21.6 | 0.1 | $C_6$-ene, n-propyl formate |
| 22.3 | 0.4 | | | | | | | Crotonaldehyde, s-trioxane |
| | | 22.5 | 3.6 | 22.3 | 22.7 | 22.3 | 13.9 | $C_6$-ene |
| | | 22.9 | 4.2 | 22.7 | 19.7 | 22.7 | 7.0 | $C_6$-ane |
| | | 23.5 | 0.6 | 23.3 | 2.1 | | | Benzene |
| 23.8 | 0.6 | 23.9 | 3.2 | 23.7 | 6.4 | | | 2-Methyltetrahydrofuran |
| | | | | | | 24.0 | 0.1 | Cyclohexene |

TABLE XXXVI-Cont'd.

GAS CHROMATOGRAPHY RESULTS: DEGRADATION OF TRIPHENYL PHOSPHATE-n-OCTACOSANE MIXTURE

(Porapak Q Column)

| -78°C[a,b] Frac (Bottom Layer) | | -78°C[a,b] Frac (Top Layer) | | -78°C[c,d] Frac (Vapor) | | -196°C[c,e] Frac | | Peak Identification |
|---|---|---|---|---|---|---|---|---|
| r.t.[f] | Area | r.t. | Area | r.t. | Area | r.t. | Area | |
| 23.3 | 0.8 | 25.0 | 6.4 | 24.8 | 11.4 | | | n-Pentanal |
| | | 26.4 | 50.6 | 26.2 | 52.0 | 26.3 | 1.1 | $C_7$-ene, $C_7$-ane |
| 26.4 | 0.3 | | | | | | | |
| | | | | 26.6 | 31.4 | | | $C_7$-ane |
| 27.4 | 0.1 | | | | | | | |
| | | 28.1 | 3.6 | 27.9 | 2.4 | | | Toluene |
| 28.2 | 0.1 | | | | | | | |
| 29.8 | 0.2 | 29.8 | 1.2 | 29.7 | 2.6 | | | n-Hexanal |
| | | 31.6 | 71.5 | 31.5 | 40.1 | | | $C_8$-ene, $C_8$-ane |
| 34.2 | T | 34.2 | 4.3 | 34.0 | 1.3 | | | $C_2$-benzene |
| 37.2 | 1.4 | 37.2 | 1.3 | | | | | Phenol |
| | | 39.5 | 82.7 | 39.7 | 16.5 | | | $C_9$-ene, $C_9$-ane |
| | | 43.0 | 2.2 | | | | | $C_3$-benzene |
| | | 53.2 | 80.1 | | | | | $C_{10}$-ene, $C_{10}$-ane |

a) This fraction was examined under the following conditions: Column: stainless steel, 8' x 1/8" Porapak Q, detector: a 10% split into F.I., He flow: 35 ml/min. Column temperature: 50-220°C programmed at 8°/min. b) This was the liquid phase of the fraction. Area is given in square inches x attenuation per microliter of sample. c) This fraction was examined under the following conditions: Column: stainless steel, 8' x 1/8" Porapak Q, detector: a 43% split into F.I., He flow: 35 ml/min. column temperature: 50-220°C programmed at 7°/min. d) This was the gaseous phase of the fraction; a 14 mm pressure was used. e) A 15 mm pressure was used. Area is given in square inches x attenuation. f) Retention time, min. g) This peak was identified by the TC detector only under testing conditions given in footnote a). h) < 0.05 $in^2/\mu l$ for liquid samples; < 0.05 $in^2$ for gas samples.

TABLE XXXVII

GAS CHROMATOGRAPHY RESULTS: DEGRADATION OF TRIPHENYL PHOSHATE-n -OCTACOSANE MIXTURE

(OV-101 Column)

| $0^{\circ}C$ [a] Frac | | $-23^{\circ}C$ [a] Frac | | $-78^{\circ}C$ [a] Frac (Top Layer) | | Peak Identification |
|---|---|---|---|---|---|---|
| r.t.[b] | Area | r.t. | Area | r.t. | Area | |
| | | | | 1.5 | T[c] | |
| | | | | 2.3 | 0.1 | |
| | | | | 3.1 | T | |
| | | | | 3.3 | T | |
| | | | | 3.6 | 14.5 | $C_6$-ene |
| | | | | 3.8 | 17.7 | $C_6$-ane |
| | | | | 4.4 | 0.2 | n-Butyraldehyde |
| | | | | 5.1 | 12.7 | Benzene |
| | | | | 5.4 | 3.3 | |
| | | 6.0 | 4.1 | 5.7 | 11.7 | 2-Methyltetrahydrofuran |
| | | 6.5 | 3.2 | 6.1 | 117.3 | $C_7$-ene |
| | | 6.8 | 6.3 | 6.4 | 121.6 | $C_7$-ane |
| 6.9 | 0.3 | | | | | |
| | | | | 7.6 | 1.9 | $C_7$-yne |
| | | 8.1 | 1.9 | 8.1 | 6.1 | |
| | | 8.4 | 1.2 | 8.3 | 11.5 | Toluene, n-pentanal |
| | | | | 8.6 | 4.0 | |
| | | 8.8 | 5.6 | 8.8 | 5.6 | |
| 9.3 | 0.3 | 9.5 | 6.4 | 9.4 | 184.5 | $C_8$-ene |
| 9.6 | 0.6 | 9.8 | 22.0 | 9.8 | 185.6 | $C_8$-ane |
| 10.0 | 1.3 | | | | | |
| | | 11.2 | 0.4 | 11.0 | 5.3 | |
| 11.5 | 0.4 | 11.6 | T | 11.7 | 23.2 | $C_2$-benzene |
| 12.5 | 0.6 | 12.4 | 6.1 | 12.2 | 13.6 | |
| 13.0 | 0.9 | 13.1 | 11.2 | 13.1 | 279.5 | $C_9$-ene |
| 13.5 | 2.1 | 13.5 | 26.2 | 13.5 | 192.0 | $C_9$-ane |
| 14.0 | 3.1 | | | | | |
| | | | | 14.7 | 1.9 | |
| | | | | 15.1 | 19.7 | $C_3$-benzene |
| 15.3 | 0.2 | | | 15.5 | 8.0 | |
| 16.2 | 1941 | 16.1 | 800.0 | 16.3 | 11.1 | Phenol |
| | | 16.9 | 97.8 | 16.9 | 258.1 | $C_{10}$-ene |
| | | 17.4 | 107.4 | 17.3 | 181.3 | $C_{10}$-ane |
| | | | | 18.0 | 1.1 | |
| 18.5 | 0.1 | 18.6 | 0.5 | 18.4 | 0.9 | |
| 19.0 | 0.4 | 19.1 | 13.0 | 18.9 | 9.6 | $C_4$-benzene |

TABLE XXXVII-Cont'd

GAS CHROMATOGRAPHY RESULTS: DEGRADATION OF TRIPHENYL PHOSPHATE-n-OCTACOSANE MIXTURE

(OV-101 Column)

| $0^\circ C$ [a] Frac | | $-23^\circ C$ [a] Frac | | $-78^\circ C$ [a] Frac (Top Layer) | | Peak Identification |
|---|---|---|---|---|---|---|
| r.t.[b] | Area | r.t. | Area | r.t. | Area | |
| 19.6 | 7.3 | 19.4 | 2.3 | 19.3 | 3.1 | |
| | | | | 20.0 | 1.5 | |
| 20.5 | 25.3 | 20.7 | 448.0 | 20.4 | 65.6 | $C_{11}$-ene |
| 20.9 | 18.9 | 21.1 | 435.0 | 20.8 | 53.9 | $C_{11}$-ane |
| | | | | 22.1 | T | |
| 22.6 | 3.7 | 22.7 | 31.0 | 22.5 | 0.2 | $C_5$-benzene |
| 23.0 | 2.5 | | | | | |
| 23.4 | 5.3 | | | | | |
| 24.0 | 68.3 | 24.2 | 185.6 | 23.9 | 3.3 | $C_{12}$-ene |
| 24.4 | 97.6 | 24.5 | 176.5 | 24.2 | 3.1 | $C_{12}$-ane |
| 25.7 | 0.1 | | | | | |
| 26.3 | 4.2 | 26.3 | 2.0 | 26.0 | 0.4 | $C_6$-benzene |
| 27.2 | 51.2 | 27.5 | 9.5 | 27.5 | 1.3 | $C_{13}$-ene |
| 27.6 | 67.2 | 27.8 | 16.2 | | | $C_{13}$-ane |
| 29.1 | 0.7 | | | | | |
| 29.4 | 1.0 | | | 29.7 | 0.2 | |
| 30.4 | 44.0 | 30.6 | 1.0 | 30.5 | 0.7 | $C_{14}$-ene |
| 30.7 | 53.9 | 30.9 | 1.5 | | | $C_{14}$-ane |
| 32.5 | 0.2 | | | 32.5 | 0.2 | |
| 33.4 | 0.9 | | | | | $C_{15}$-ene |
| 33.6 | 1.4 | | | | | $C_{15}$-ane |
| | | 34.2 | 0.5 | | | |
| | | | | 35.0 | 0.2 | |
| | | 36.2 | 0.2 | | | |
| | | | | 37.3 | 0.2 | |
| | | 39.0 | 0.7 | | | |
| | | 40.8 | 1.1 | | | |

a) This fraction was examined under the following conditions: Column: stainless steel, 10' x 1/8" 4% OV-101 on Chromosorb G, detector: a 43% split into F.I., programmed at 4°/min from 35-220°C. b) Retention time, min. Area is given in square inches x attenuation per microliter of sample. c) $< 0.05\ in^2/\mu l$.

TABLE XXXVIII

VOLATILE PRODUCTS OBTAINED ON THERMAL OXIDATIVE DEGRADATION OF PHOSPHATE ESTER BASED HYDRAULIC FLUIDS

| Products | Fyrquel 220 | | Pydraul 50E | | Pydraul MC | | Dasco FR 300 | | $(\Phi O)_3PO$ $+C_{28}H_{58}$ |
|---|---|---|---|---|---|---|---|---|---|
| | 370°C mg/g | 420°C mg/g | 370°C mg/g | 420°C mg/g | 370°C mg/g | "420°C" mg/g | 370°C mg/g | "420°C" mg/g | "420°C" mg/g |
| CO | - | T[a] | 0.596 | T | 0.694 | T | 1.25 | 2.19 | 1.72 |
| $CH_4$ | 0.125 | 0.169 | - | 0.296 | T | 0.097 | 0.104 | 0.197 | 0.147 |
| $H_2O$ | 1.16 | 1.04 | 0.979 | 0.004 | 0.324 | - | 8.92 | 10.5 | 7.72 |
| $CO_2$ | 0.116 | 0.085 | 0.494 | 0.197 | 0.060 | 0.076 | 0.850 | 1.43 | 0.480 |
| COS | 0.001 | T | - | - | T | - | 0.214 | 0.299 | - |
| $CS_2$ | - | - | - | - | - | - | 0.022 | T | - |
| $SO_2$ | 0.001 | T | - | - | 0.069 | T | - | - | - |
| $H_2S$ | 0.003 | T | - | - | - | - | 0.113 | T | - |
| $PH_3$ | - | - | - | - | - | 2.78 | - | 0.141 | T |
| $C_2$-species | 0.024 | 0.067 | 0.068 | 1.47 | 0.042 | 0.413 | 0.351 | 1.64 | 0.697 |
| $C_3$-species | 0.008 | 0.038 | 0.131 | 3.03 | 0.032 | 0.301 | 1.54 | 5.61 | 1.04 |
| $C_4$-species | 0.004 | 0.017 | 2.55 | 6.33 | 0.131 | 0.788 | 1.58 | 3.93 | 1.19 |
| $C_5$-species | 0.003 | 0.007 | 0.351 | 4.93 | 0.092 | 1.33 | 0.683 | 2.80 | 1.18 |
| $C_6$-species | 0.008 | 0.014 | 0.435 | 6.99 | 0.435 | 21.8 | 1.72 | 2.29 | 1.45 |
| $C_7$-species | 0.015 | 0.007 | 0.166 | 0.519 | 5.22 | 5.07 | 1.09 | 1.91 | 1.55 |
| $C_8$-species | 0.147 | 0.015 | 0.158 | 0.685 | 25.0 | 24.7 | 1.26 | 2.28 | 1.75 |
| $C_9$-species | 0.053 | T | 1.93 | 5.68 | 4.65 | 23.4 | 0.056 | 1.16 | 1.88 |
| $C_{10}$-species | - | - | T | 0.203 | T | 0.996 | 0.048 | 0.915 | 1.99 |

### TABLE XXXVIII-Cont'd.

### VOLATILE PRODUCTS OBTAINED ON THERMAL OXIDATIVE DEGRADATION OF PHOSPHATE ESTER BASED HYDRAULIC FLUIDS

| Products | Fryquel 220 | | Pydraul 50E | | Pydraul MC | | Dasco FR 300 | | $(\Phi O)_3PO + C_{28}H_{58}$ " 420°C " mg/g |
|---|---|---|---|---|---|---|---|---|---|
| | 370°C mg/g | 420°C mg/g | 370°C mg/g | 420°C mg/g | 370°C mg/g | "420°C" mg/g | 370°C mg/g | "420°C" mg/g | |
| $C_{11}$-species | - | - | T | 0.149 | 1.14 | 1.91 | 0.052 | 0.527 | 2.36 |
| $C_{12}$-species | - | - | T | 0.062 | 0.002 | T | 0.029 | 0.278 | 2.48 |
| $C_{13}$-species | - | - | - | 0.003 | - | - | 0.028 | 0.191 | 1.39 |
| $C_{14}$-species | - | - | - | - | - | - | 0.004 | 0.065 | 1.12 |
| $C_{15}$-species | - | - | - | - | - | - | 0.006 | T | 0.025 |
| Benzene | 0.001 | 0.004 | 0.022 | 0.192 | 0.084 | 1.61 | 0.004 | 0.165 | 0.034 |
| Toluene | 0.014 | 0.014 | 0.011 | 0.856 | 0.011 | 0.471 | 0.372 | 0.432 | 0.060 |
| $C_2$-benzenes | 0.166 | 0.180 | 0.045 | 0.412 | T | 0.235 | 0.376 | 2.64 | 0.068 |
| $C_3$-benzenes | 0.063 | 0.293 | 0.280 | 1.21 | 0.527 | 7.52 | 0.032 | 1.63 | 0.047 |
| $C_4$-benzenes | 0.001 | 0.136 | - | 0.184 | - | - | 0.050 | 0.219 | 0.085 |
| $C_5$-benzenes | - | - | 0.011 | 0.191 | - | - | 0.005 | - | 0.048 |
| $C_6$-benzenes | - | - | - | 0.022 | - | - | - | - | - |
| Styrene | - | - | 0.001 | - | - | - | - | - | - |
| α-Methylstyrene | - | - | 1.52 | 1.65 | - | 1.32 | - | 0.006 | - |
| $C_2$-styrenes | - | 0.019 | 0.002 | - | - | - | 0.012 | 0.073 | - |
| Biphenyl | 0.026 | 0.009 | - | - | - | - | - | - | - |
| Napthalene | 0.001 | - | - | - | - | - | 0.006 | - | - |
| Methylnapthalene | 0.021 | 0.013 | - | - | - | - | - | - | - |

## TABLE XXXVIII - Cont'd.

## VOLATILE PRODUCTS OBTAINED ON THERMAL OXIDATIVE DEGRADATION OF PHOSPHATE ESTER BASED HYDRAULIC FLUIDS

| Products | Fyrquel 220 | | Pydraul 50E | | Pydraul MC | | Dasco FR 300 | | $(\Phi O)_3PO$ $+C_{28}H_{58}$ |
|---|---|---|---|---|---|---|---|---|---|
| | 370°C mg/g | 420°C mg/g | 370°C mg/g | 420°C mg/g | 370°C mg/g | "420°C" mg/g | 370°C mg/g | "420°C" mg/g | "420°C" mg/g |
| Tetrahydronapthalenes | - | - | - | - | - | - | 0.011 | 0.112 | - |
| Methyltetrahydronapthalenes | - | - | - | 0.006 | - | - | 0.031 | T | - |
| Dimethyltetrahydronapthalenes | - | - | - | - | - | - | 0.004 | - | - |
| Indan | - | - | - | 0.006 | - | - | 0.141 | T | - |
| Trimethylindans | - | - | - | - | - | - | 0.003 | - | - |
| Methanol | 0.054 | 0.001 | 0.008 | - | - | - | 0.036 | 0.008 | 0.112 |
| Ethanol | T | - | T | - | - | - | T | 0.001 | 0.026 |
| $C_3$-alcohols | - | - | - | - | - | - | - | - | 0.002 |
| $C_4$-alcohols | - | - | 0.001 | - | - | - | 0.025 | 0.008 | 0.001 |
| $C_6$-alcohols | - | - | 0.003 | - | - | - | - | - | - |
| Phenol | 0.394 | 0.439 | 7.12 | 34.1 | 10.3 | 66.3 | 10.6 | 5.14 | 21.6 |
| Cresols | 0.758 | 1.02 | - | - | - | - | 0.214 | 1.33 | - |
| Xylenols | 2.04 | 4.11 | - | - | - | - | 0.149 | 1.10 | - |
| $C_3$-phenols | 0.069 | 0.116 | - | - | - | - | - | 0.033 | - |
| Formaldehyde | - | - | - | - | - | - | - | - | 0.002 |
| Acetaldehyde | 0.106 | 0.072 | 0.105 | 0.001 | 0.014 | - | 0.180 | 0.120 | 0.368 |
| Propionaldehyde | 0.003 | 0.002 | 0.022 | 0.001 | 0.003 | - | 12.2 | 5.88 | 0.346 |
| Acrolein | - | - | 0.003 | - | - | - | 0.433 | 0.107 | 0.034 |

TABLE XXXVIII-Cont'd.

VOLATILE PRODUCTS OBTAINED ON THERMAL OXIDATIVE DEGRADATION OF PHOSPHATE ESTER BASED HYDRAULIC FLUIDS

| Products | Fyrquel 220 | | Pydraul 50E | | Pydraul MC | | Dasco FR 300 | | $(\Phi O)_3PO$ $+C_{28}H_{58}$ |
|---|---|---|---|---|---|---|---|---|---|
| | 370°C mg/g | 420°C mg/g | 370°C mg/g | 420°C mg/g | 370°C mg/g | "420°C" mg/g | 370°C mg/g | "420°C" mg/g | "420°C" mg/g |
| 2-Methyl propenal | - | - | 0.001 | - | - | - | - | 0.002 | - |
| $C_4$-aldehydes | - | T | 0.005 | 0.001 | - | - | 0.085 | 0.001 | 0.254 |
| $C_5$-aldehydes | T | T | 0.007 | - | - | - | - | - | 0.252 |
| $C_6$-aldehydes | - | - | - | - | - | - | - | - | 0.043 |
| Cinnamaldehyde | - | - | 0.014 | - | - | - | - | - | - |
| 2-Phenyl-2-butenal | - | - | - | - | - | - | 0.001 | - | - |
| Propionaldehyde trimer, $(C_3H_6O)_3$ | - | - | - | - | - | - | 6.90 | 2.51 | - |
| Acetone | 0.049 | 0.005 | 0.066 | 0.001 | 0.018 | 0.039 | 0.007 | 0.762 | T |
| Methyl ethyl ketone | 0.016 | T | 0.024 | 0.002 | 0.018 | 0.071 | - | 0.034 | 0.024 |
| $C_5$-ketone | 0.008 | - | 0.003 | - | - | - | 0.013 | - | - |
| Cyclopentanone | T | - | - | - | - | - | 0.014 | 0.005 | - |
| Cyclohexanone | - | - | - | - | - | - | 0.004 | 0.024 | - |
| Methyl phenyl ether | - | - | 0.009 | - | - | - | - | - | - |
| Diphenyl ether | - | 0.020 | - | - | - | - | - | - | - |
| Methyl p-cresyl ether | - | - | - | - | - | - | 0.027 | - | - |
| Furan | 0.001 | - | - | - | 0.001 | - | - | - | - |
| Dimethylfurans | - | - | 0.010 | - | - | - | 0.013 | - | - |
| 2-Methyltetrahydrofuran | - | - | - | - | - | - | - | - | 0.141 |

TABLE XXXVIII-Cont'd.

VOLATILE PRODUCTS OBTAINED ON THERMAL OXIDATIVE DEGRADATION OF PHOSPHATE ESTER BASED HYDRAULIC FLUIDS

| Products | Fyrquel 220 | | Pydraul 50E | | Pydraul MC | | Dasco FR 300 | | $(\Phi O)_3PO + C_{28}H_{58}$ |
|---|---|---|---|---|---|---|---|---|---|
| | 370°C mg/g | 420°C mg/g | 370°C mg/g | 420°C mg/g | 370°C mg/g | "420°C" mg/g | 370°C mg/g | "420°C" mg/g | " 420°C " mg/g |
| 1,3-Dioxolane | T | - | T | - | - | - | - | - | - |
| 2-Ethyl-4-methyl-1,3-dioxolane | - | - | - | - | - | - | - | 0.970 | - |
| p-Dioxane | T | - | T | - | - | - | - | - | - |
| Dimethyl dioxanes | - | - | - | - | - | - | 1.41 | 0.259 | - |
| s-Trioxane | - | - | - | - | - | - | - | - | 0.002 |
| Acetic acid | T | - | - | - | - | - | - | - | 0.004 |
| Methyl formate | 0.002 | - | - | - | - | - | - | - | 0.022 |
| Ethyl formate | - | - | - | - | - | - | - | - | 0.028 |
| n-Propyl formate | - | - | - | - | - | - | - | - | 0.001 |
| Methyl acetate | T | - | - | - | - | - | T | - | - |

a) < 0.0005 mg/g

Regarding the other products identified and quantitated in the volatiles, biphenyl presents a potential toxic hazard; however, in view of its very low concentration as compared to phenolic compounds it can be really neglected. Since methyl formate was detected among Fyrquel decomposition products, it is apparent that formic acid must have also been formed. The origin of the sulfur - containing compounds, particularly after the lower temperature treatment, is obscure.

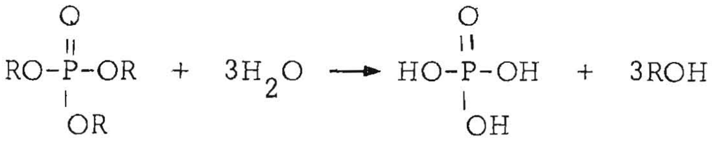
The extent of degradation observed for Pydraul 50E at 370°C, in analogy to Fyrquel 220, was very minor (see Table XVII). The collected volatiles accounted for approximately 75% of the material weight loss and of these phenol constituted approximately 42%. The exclusive presence of phenol is in agreement with the starting material analysis which showed triphenylphosphate to be the phosphate ester ingredient of Pydraul 50E. It is safe to assume that additional quantities of phenol were retained by the residue as indicated by the infrared absorption at 3.0μ. The finding of relatively high proportions of hydrocarbons, in particular the $C_4$-$C_9$ species, tends to indicate that this fluid contains hydrocarbon additive or additives.

From the data presented in Table XVII it is apparent that at 420°C the extent of decomposition of Pydraul 50E was significantly higher than that observed at 370°C. Most of the weight loss (80%) was translated into the room temperature volatiles; the residue itself, based on infrared spectral analysis, contained substantial quantities of phenolic species. Phenol was the major (50%) constituent of the volatiles, it was found mainly in the 0°C fraction (see Table XVIII). It is noteworthy that at 370°C phenol accounted for 42% of the volatiles. Thus it would appear that with increased temperatures only the absolute quantity of phenol increases, the relative proportion in the volatiles remaining essentially the same. Comparing the product distribution

Table XVII). This residue was composed essentially of the starting material admixed with phenolic species as indicated by the presence of a band at 3.0μ. It is noteworthy that only approximately 39% of the material weight loss was recovered in the volatiles. This is not unexpected if one considers that although 44 species were identified and quantitated, phenol and the very involatile cresols, xylenols and $C_3$-phenols (see Table XXXVIII) constituted more than 60 weight percent of the products. These types of materials would be most likely retained on the walls of the reaction tube. The phenolic compounds are formed by hydrolysis of the phosphate esters [4] whereas the water necessary for this process is produced by oxidation of hydrocarbon side chains or additives. The consumption of water by this reaction explains the low water content observed in the volatiles. Inasmuch as xylenols were found in the highest proportion in the collected products in spite of their lower volatility (as compared to the other phenolic species) it can be deduced that either the highly substituted phosphate esters predominate in this hydraulic fluid or that these are preferentially decomposed.

Fyrquel 220, based on volatiles collected and weight loss, did not appear to undergo significantly more extensive decomposition at 420°C than at 370°C. The phenolic species constituted 72% of the collected volatiles and added up to 5.69 mg/g as compared to 3.26 mg/g found at 370°C. It should be noted that the involatile residue, after thermal oxidative degradation at 420°C, exhibited in its infrared spectrum a strong band in the vicinity of 3μ showing the presence of phenolic entities. Thus the actual degradation of the fluid is more extensive than indicated by the weight loss and volatiles production. On the other hand, it can be argued that the products formed are involatile at 420°C, otherwise these would be deposited on the walls of the 5-liter bulb.

at 370 and 420°C, it is apparent that at 420°C the quantity of water found in the volatiles was much lower than that obtained at 370°C The opposite would be usually expected. However, if one considers that the water formed is used to hydrolyze the phosphate ester, i.e.,



$$RO-\overset{\overset{O}{\|}}{\underset{\underset{OR}{|}}{P}}-OR + 3H_2O \longrightarrow HO-\overset{\overset{O}{\|}}{\underset{\underset{OH}{|}}{P}}-OH + 3ROH$$

and that this process will be greatly accelerated at the elevated temperature then the virtual absence of water in the volatiles can be explained. In the volatiles 31 compounds were identified and quantitated and these accounted for 99.94% of the material obtained. Phenol, as noted, was the major toxic product formed. No phosphine could be detected.

For Pydraul MC the extent of decomposition at 370°C as shown by the volatiles formed and residue recovered (see Table XVII) was relatively minor. Based on the infrared spectrum of the residue it appeared to be composed essentially of the starting material admixed with some phenolic species as indicated by the appearance of a band at 3.0μ.

The main products formed were phenol and hydrocarbons $(C_7 - C_9, C_{11})$. It is safe to assume that additional quantities of phenol are dissolved in the liquid residue and would be vaporized either at higher temperature or under dynamic conditions. The $C_7$-$C_9$ and $C_{11}$ hydrocarbons as well as the lower members of the series originate most likely from the mineral oil component or components of the hydraulic fluid, whereas the aromatics result from degradation of the phosphate ester or esters. Inasmuch as $SO_2$ and COS were detected in the volatiles, sulfur-containing components must be present in the original fluid but in what form is unknown. To summarize, a total of 26 species or series of species were identified and quantitated and these accounted for 99.9% of volatiles collected.

Examining Table XVII it is apparent that the extent of decomposition at 420°C for Pydraul MC was significantly higher than that observed at 370°C. Most of the weight loss (81%) was translated into the room temperature volatiles; the residue itself, based on infrared spectral analysis, contained substantial quantities of phenolic species. Phenol was the major (41%) constituent of the volatiles; it was found mainly in the 0°C fraction (see Table XVIII). It is noteworthy that at 370°C phenol accounted for 21% of the volatiles (see Table XXXVIII). Thus it would appear that with increased temperatures not only the absolute but also the relative quantity of phenol in the volatiles increases. The highly toxic phosphine was also found in the volatiles. At 370°C this material, if at all produced, was formed in trace quantities only, since it was not detected by infrared spectral analysis nor by GC-MS techniques. In none of the degradation products of the previously discussed phosphate esters was phosphine found. It should be noted that although the quantity of phosphine produced was relatively low, 2.70 mg/g, as compared to phenol, 66 mg/g, in view of its high toxicity and volatility it presents a greater toxic hazard than phenol. Inasmuch as no phosphine was detected in the products formed by Fyrquel 220 and Pydraul 50E it would seem that an interaction of an ingredient present in the additive or additives of Pydraul MC is responsible for the observed phosphine production.

Dasco FR-300 hydraulic fluid, as discussed earlier, according to the manufacturer is a mixture of phosphate esters, mineral oils and other undisclosed ingredients. The phosphate esters present must be derived from alkyl phenols higher than cresols (methyl-phenols) since no compounds were eluted up to 120 min. Under analogous conditions the isomeric tri-tolyl-phosphate esters were eluted from 24-72 min.

At 370°C Dasco FR-300 appeared to undergo a relatively minor degradation as shown by 93% starting material recovery (see Table XVII). The two main products formed were phenol and propionaldehyde, the latter both in the form of the monomer and trimer. The origin of propionaldehyde is obscure since it is not a likely product of long chain hydrocarbons. It would thus appear that DASCO FR 300 contains an ingredient which degrades relatively readily to propionaldehyde.

The toxic compounds such as acrolein and allyl alcohol, being three carbon species are most likely derived from the same precursor as propionaldehyde or from propionaldehyde itself. The same applies to dimethyl dioxanes. The aliphatic materials as evidenced by the presence of the higher members of the series ($C_{14}$, etc.) most likely originate from the mineral oil constituent or constituents, whereas the aromatics result from degradation of the phosphate esters. Inasmuch as $CS_2$, $H_2S$, and COS were detected in the volatiles sulfur containing components must be present in the original fluid but in what form is again unknown.

The extent of decomposition at "420°C" or rather 400°C was not that much more extensive than at 370°C. The presence of phosphine in the volatile degradation products was the most significant occurrence. Although only 0.141 mg/g of this substance was found, in the actual toxic hazard assessment, phosphine presented an equivalent hazard to phenolic materials. The actual hazard is even greater if one considers the relative volatilities. It should be noted that under the current program four phosphate ester type hydraulic fluids were investigated. Only in the materials wherein the phosphate ester was admixed with other constituents, mainly mineral oil, was phosphine detected and then only at the higher temperatures. Thus it becomes of interest whether long chain hydrocarbons at these elevated temperatures do act as reducing agents for phosphate esters.

The other compounds listed in Table XXXVIII are comparable to those produced at 370°C. On the other hand, the increase in the degree of oxidation is shown by the ten-fold increased proportion of $CO_2$ and the increased oxygen consumption. In addition, the proportion of compounds such as, e.g., acrolein and propionaldehyde, is definitely decreased under the more drastic conditions, whereas the content of substituted aromatics is increased. These results are in agreement with those found for Quintolubric 822-300 (see Section 3.2.3).

The forty-nine species identified and quantitated accounted for 99.9% of the volatiles collected. It should be noted that the volatiles corresponded to 64%of starting material weight loss, it is most likely that the unaccounted for material was composed of phenolic type compounds of molecular weights higher than cresols, which were deposited on the walls of the degradation tube. This would account for the difference between sample weight loss and volatiles recovered. The presence of a relatively strong absorption at 3.0μ in the material left in the reaction finger, which otherwise appears to be the unchanged Dasco FR 300, further supports this stipulation. The drastic decrease in production of propionaldehyde, its trimer, and dimethyl dioxanes at "420°C" as compared to 370°C may be attributed to oxidation of these species at the higher temperature which is substantiated by the increased amounts of carbon dioxide and water formed. The lower quantity of phenol (by approximately 50%) found in the volatiles from the "420°C" treatment as compared to the 370°C exposure, is unexplained.

The thermal oxidative degradation of the n-octacosane-triphenylphosphate mixture (see Tables XVII and XXXVIII) was primarily performed to determine whether the presence of a hydrocarbon constituent does indeed promote phosphine formation. Although less than 0.0005 mg/g of phosphine was detected its presence among the degradation products was definitely established both by infrared spectral analysis and by GC-MS techniques. None of the compositions did appear to form phosphine at 370°C and only the "mineral oil" or "hydrocarbon" containing fluids liberated phosphine at "420°C". Thus it is tempting to speculate that at sufficiently high temperatures hydrocarbons do tend to reduce phosphate esters to phosphine which does not seem very plausible to take place in oxidizing atmospheres such as air. On the other hand the reduction occurs most likely in the solution and not in the vapor phase. The ease of phosphine formation is apparently dependent mainly on the nature of the "hydrocarbon", not the phosphate ester, since no triphenylphosphate was present in Dasco FR 300 whereas triphenylphosphate was the phosphate ester in Pydraul MC and in the octocosane-triphenylphosphate mixture.

Comparing the mg/g compilations given for e.g., Pydraul MC and octacosane-triphenylphosphate even though both compositions contained essentially equal proportions of triphenylphosphate the amounts of phenol produced were higher by a factor of three in the case of Pydraul MC. This finding points to an effect of the nature of the additive on the degradation rate and/or mechanism of the phosphate ester.

## 4. REFERENCES

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