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APPLIED SCIENCES REPORT

DETERMINATION OF DECOMPOSITION
PRODUCTS OF THERMINOL VP-1

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DETERMINATION OF DECOMPOSITION PRODUCTS OF THERMINOL VP-1INTRODUCTION

Therminol VP-1 was bomb exposed for 1000 hrs. at 750°C by the Functional Products business group and submitted for GC/MS analysis to determine the identity and concentration levels of the decomposition products. Also submitted was unexposed Therminol VP-1.

SUMMARY

Analysis of the decomposed Therminol VP-1 indicated the presence of over forty compounds. Most of these compounds were high boilers whose general structures appeared to be different combinations of benzene chains and benzene chains with ether linkages. The concentrations of the minor components ranged from 8500 ppm to less than 10 ppm. Undecomposed Therminol VP-1 (diphenyl ether and biphenyl) accounted for about 92% of the sample.

The unexposed Therminol VP-1 had almost no high boilers in detectable amounts and less than ten minor components. Generally the concentrations of the minor components were less than 150 ppm.

EXPERIMENTAL

All samples were analyzed via a Hewlett Packard 5980 GC/MS. Samples which were not analyzed as neat materials were diluted to about 1000 ppm in methylene chloride.

Mass spectra interpretation - The identity of the components of the mixtures analyzed were determined mainly from the mass spectrum associated with a chromatographic peak. The most reliable identifications were those in which there was agreement of both the retention times and mass spectra of the sample peak and a known standard. In cases where known standards were unavailable identity was assigned on agreement between the sample spectrum and a published spectrum. If identification of a chromatographic peak could not be determined using the previous routes, an identification was assigned by the author which was consistent with molecular weight and fragmentation patterns. In all cases tentative identifications were reviewed to see if they were consistent with the sample origin and other identified sample components.

Sample quantitation - Ideally quantitation of all peaks in an unknown should be done against known standards. However in this case less than ten compounds were available as external standards. Therefore quantitation of all peaks was done

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against an average response factor of the known standards. The two major components in both mixtures (biphenyl and diphenyl ether) were quantitized against their respective standards. Use of an average response factor leads to estimations of concentration levels and not exact concentrations.

Instrumental conditions - Mixtures were separated chromatographically under the following GC conditions:

Column: 2M X 2mm 5% silicone UC-W982
on 80/100 mesh Chromosorb Q

Temperature: Oven - 0-300°C @ 8°/min.
Injection port - 250°C

Carrier Gas: Helium @ 30 ml/min.

- The mass spectrometer was operated in the total ion mode of operation with the spectrometer being scanned from 35 to 500 amu in electron ionization and from 50 to 500 amu in chemical ionization.

The decomposed Therminol VP-1 sample was investigated by both electron and chemical ionization. Chemical ionization was used to confirm molecular weights and the presence of co-eluting components. Unexposed Therminol VP-1 was investigated only with electron ionization. Quantitation was done on chromatograms obtained with electron ionization.

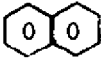
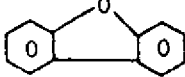
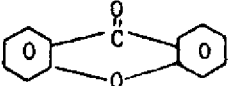
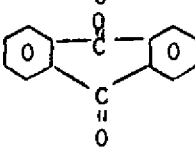
RESULTS AND DISCUSSION

Figures 1 and 2 are the total ion chromatograms of exposed and unexposed Therminol VP-1, respectively. Tables 1 and 2 are the compilation of the peak identifications and concentrations. From the identifications made it appears that Therminol VP-1 decomposes to compounds having either three or four benzene rings, with varying number (0 to 3) of ether groups. Also apparently present are compounds which have two benzene rings which are connected together by a double bridgehead consisting of either or both carbon and oxygen. In cases where identified compounds could have structural isomerization no attempt was made to assign exact structures. (One exception being the terphenyls which were identified with the aid of known standards.)

Compounds which were in the exposed Therminol VP-1 and which had concentrations of less than 50 ppm were probably not detected above baseline noise especially in the high boiler region. Also many of the peaks in the high boiler region consisted of co-eluting compounds which made identification somewhat tenuous and probably masked the presence of some compounds.

TABLE 1

COMPOUNDS IN DECOMPOSED THERMINOL VP-1. ASSIGNMENTS OF POSSIBLE STRUCTURES WAS CONSISTENT WITH MASS SPECTRA.

PEAK	RETENTION TIME (Min)	MOLECULAR WEIGHT	PROBABLE CHEMICAL FORMULA	POSSIBLE STRUCTURE AND/OR NAME ²	ASSIGNMENT ¹	CONCENTRATION ³
A	4.3	78	C ₆ H ₆	φ-H benzene	1	3760 ppm
B	6.6	92	C ₇ H ₈	φ-CH ₃ toluene	1	34 ppm
C	8.9	106	C ₈ H ₁₀	φ-CH ₂ -CH ₃ ethylbenzene	2	41 ppm
D	10.3	120	C ₈ H ₈ O	φ-C(=O)-CH ₃ acetophenone	2	26 ppm
E	11.6	94	C ₆ H ₆ O	φ-OH phenol	1	8290 ppm
F	15.6	128	C ₁₀ H ₈	 naphthalene	2	<10 ppm
G	19	154	C ₁₂ H ₁₀	φ-φ biphenyl	1	31% ✓
H	21.5	170	C ₁₂ H ₁₀ O	φ-O-φ diphenyl ether	1	61% ✓
I	22.3	168	C ₁₂ H ₈ O	 dibenzofuran	2	1220 ppm ✓
J	24.0	170		Unidentified		36 ppm
K	25.9	196	C ₁₃ H ₈ O ₂	 xanthone	2	16 ppm
		204	C ₁₆ H ₁₂	 dibenzofulvene	2	
L	26.3	230	C ₁₈ H ₁₄	φ-φ-φ o-terphenyl	1	161 ppm
M	27.5	246	C ₁₈ H ₁₄ O	φ-φ-O-φ diphenyl phenyl ether	2	1280 ppm
N	27.7	244	C ₁₉ H ₁₆	φ-C(=O)-φ triphenyl methane	2	289 ppm
O	29.5	230	C ₁₈ H ₁₄	φ-φ-φ m-terphenyl	1	
		246	C ₁₈ H ₁₄ O	φ-O-φ-φ diphenyl phenyl ether	2	3675 ppm

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TABLE II (cont'd)

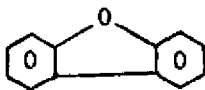
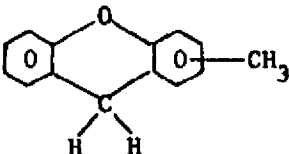
PEAK	RETENTION TIME (Min)	MOLECULAR WEIGHT	PROBABLE CHEMICAL FORMULA	POSSIBLE STRUCTURE AND/OR NAME ²	ASSIGNMENT ¹	CONCENTRATION ³
P	30.0	230	C ₁₈ H ₁₄	◊-◊-◊ p-terphenyl	1	2366 ppm
		246	C ₁₈ H ₁₄ O	◊-◊-◊-◊ diphenyl phenyl ether	2	
Q	30.9	262	C ₁₈ H ₁₄ O ₂	◊-O-◊-◊-◊ diphenoxyben- zene	3	83 ppm
Possible other unidentified components						
R	32.1	306	C ₂₄ H ₁₈	◊-◊-◊-◊ quaterphenyl	3	20 ppm
Possible other unidentified components						
S	32.9	322	C ₂₄ H ₁₈ O	◊-O-◊-◊-◊ phenoxy terphenyl	4	269 ppm
T	33.7	338	C ₂₄ H ₁₈ O ₂	◊-O-◊-◊-◊-◊	4	37 ppm
U	34.3	306	C ₂₄ H ₁₈	◊-◊-◊-◊ quaterphenyl	3	997 ppm
		322	C ₂₄ H ₁₈ O	◊-O-◊-◊-◊ phenoxy terphenyl	4	
		338	C ₂₄ H ₁₈ O ₂	◊-O-◊-◊-◊-◊	4	
V	34.7	306	C ₂₄ H ₁₈	◊-◊-◊-◊ quaterphenyl	3	436 ppm
		322	C ₂₄ H ₁₈ O	◊-O-◊-◊-◊ phenoxy terphenyl	4	
W	35.2	322	C ₂₄ H ₁₈ O	◊-O-◊-◊-◊	4	3452 ppm
		338	C ₂₄ H ₁₈ O ₂	◊-O-◊-◊-◊-◊	4	
X	35.7	322	C ₂₄ H ₁₈ O	◊-O-◊-◊-◊ phenoxy terphenyl	4	1436 ppm
		338	C ₂₄ H ₁₈ O ₂	◊-O-◊-◊-◊-◊	4	
Y	37.3	306	C ₂₄ H ₁₈	◊-◊-◊-◊ quaterphenyl	3	8268 ppm
		322	C ₂₄ H ₁₈ O	◊-O-◊-◊-◊ phenoxy terphenyl	4	
		338	C ₂₄ H ₁₈ O ₂	◊-O-◊-◊-◊-◊	4	

Table 1 (cont'd)

PEAK	RETENTION TIME (MIN)	MOLECULAR WEIGHT	PROBABLE CHEMICAL FORMULA	POSSIBLE STRUCTURE AND/OR NAME ²	ASSIGNMENT ¹	CONCENTRATION ³
Z	38.2	306	C ₂₄ H ₁₈	φ-φ-φ-φ quater- phenyl	2	7313 ppm
		322	C ₂₄ H ₁₈ O	φ-O-φ-φ-φ-φ phenoxyterphenyl	4	
		338	C ₂₄ H ₁₈ O ₂	φ-O-φ-φ-O-φ	4	
AA	38.6	306	C ₂₄ H ₁₈	φ-φ-φ-φ quater- phenyl	3	2509 ppm
		322	C ₂₄ H ₁₈ O	φ-O-φ-φ-φ phenoxy terphenyl	4	
		338	C ₂₄ H ₁₈ O ₂	φ-O-φ-φ-O-φ	4	
		354	C ₂₄ H ₁₈ O ₃	φ-O-φ-O-φ-O-φ	4	

- (1) 1 retention time and mass spectrum consistent with standard compound.
 2 mass spectrum consistent with published spectrum.
 3 best judgment based on similarities between this mass spectrum and others observed in the experiment.
 4 best judgment based on interpretation of mass spectrum alone.
- (2) structures assigned to oxygen containing compounds based on lack of ion fragments for other possible positions of oxygen.
- (3) concentration for whole peak based on an average response factor.

TABLE 2

PEAK	RETENTION TIME (MIN)	MOLECULAR WEIGHT	COMPOUNDS IN THERMINOL VP-1		ASSIGNMENT ⁽¹⁾	CONCENTRATION ⁽³⁾
			PROBABLE CHEMICAL FORMULA	POSSIBLE(2) STRUCTURE AND/OR NAME		
A	2.1	84	$C_2H_2Cl_2$	methylene chloride	2	10 ppm
B	4.3	78	C_6H_6	benzene	1	31 ppm ✓
C	6.8	92	C_7H_8	toluene	1	10 ppm
D	8.5	Column decomposition product				
E	11.8	94	C_6H_6O	phenol	1	111 ppm ✓
F	15.7	128	$C_{10}H_8$	naphthalene	2	19 ppm
G	Therminol VP-1 biphenyl diphenyl ether		37% 64%			
H	22.3	168	$C_{12}H_8O$	 dibenzofuran	2	53 ppm
I	23.5	196	$C_{14}H_{13}O$	 methyl xanthane	4	35 ppm

- (1) 1 retention time and mass spectrum consistent with standard compound.
 2 mass spectrum consistent with published spectrum.
 3 best judgment based on similarities between this mass spectrum and others observed in the experiment.
 4 best judgment based on interpretation of mass spectrum alone.
- (2) structures assigned to oxygen containing compounds based on lack of ion fragments for other possible positions of oxygen.
- (3) concentration for whole peak based on an average response factor.

