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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) This report describes research performed by ARL at the request of the Air Force Logistics Command to develop and apply analytical methodology to characterize the USAF inventory of Herbicide Orange stocks. A computerized Gas Chromatograph-Mass Spectrometer (GC-MS) system was developed which permitted determination of the 15 to 25 major and minor herbicide components which are typically present in the stocks located at Gulfport, Mississippi. For determination of tetrachlorodibenzo-p-dioxin (TCDD), a fully automated GC-Quadrupole MS was developed and used in conjunction with an improved column-chromatography		

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sample-clean-up technique. The analytical methodology is described in detail.

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PREFACE

The research and development described in this report were performed in-house by the Gaseous Ionization and Excitation Processes Group of the Chemistry Research Laboratory, Aerospace Research Laboratories (AFSC), Wright Patterson AFB, Ohio. This work was funded by Air Force Logistics Command, Assistant Deputy Chief of Staff/Distribution, Mr. Karl Merrill. Dr. Billy E. Welch, Special Assistant for Environmental Quality, Office of the Secretary of the Air Force, had overall cognizance for this effort which was undertaken to provide analytical chemistry support of USAF efforts to dispose of excess herbicide stocks in accordance with Environmental Protection Agency guidelines. The in-house work force was augmented during these studies via Contract No. F33615-73-C-4099 with Systems Research Laboratories, Inc., Dayton, Ohio 45440. These studies were performed under Project 7023, Task 702306, Work Unit 70230614, "Advanced Mass Spectrometric Analytical and Diagnostic Techniques for Materials and Research Applications."

The ARL principal investigator in these studies was Dr. Thomas O. Tiernan, ARL (LJ), Wright Patterson AFB, Ohio 45433.

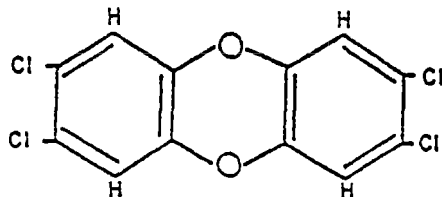
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SECTION I

INTRODUCTION

During the 1960's a herbicide formulation consisting mainly of the n-butyl esters of 2,4-dichlorophenoxyacetic acid (2,4-D) and 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) and designated Herbicide Orange was employed as a defoliant in Southeast Asia. Research performed at Bionetics Laboratories and reported by Courtney et al early in 1970^{1,2} implicated 2,4,5-T as a teratogenic agent. It was later reported³⁻⁵ that the 2,4,5-T formulation employed by Courtney et al contained 30 µg/g of 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD) --one



2,3,7,8-tetrachlorodibenzo-p-dioxin

of the most toxic and and potent teratogenic substances known. Subsequent to these findings, the Environmental Protection Agency promulgated more stringent rules regulating the domestic use of 2,4,5-T, and the Secretary of Defense ordered that use of these herbicide formulations in South Vietnam be discontinued. The abrupt ban on usage of 2,4,5-T defoliants left the Department of Defense (the Department of the Air Force, in particular) with 2.3 million gallons of such defoliants which are still stored in 55-gal. drums in Gulfport, Mississippi, and Johnston Island in the Pacific Ocean. Several methods for disposing of these herbicide stocks from the inventory are now under consideration. In order to secure required data to support use of selected lots of the herbicide inventory, the Air Force Logistics Command requested the Gaseous Excitation and Ionization Processes Group of the Chemistry Research Laboratory at the Aerospace Research Laboratories (Air Force Systems Command) to undertake the development and application of analytical methods for characterizing Air Force herbicide stocks at Gulfport, Mississippi. Prior to the work at ARL

some preliminary analyses had been performed by Dow Chemical Co, and the sample numbering system devised by Dow was retained throughout our studies.

An "Analysis Sequence Number" was assigned to each herbicide Transportation Control Number (TCN). The pertinent TCN's, the manufacturer of each batch, and the related Analysis Sequence Numbers are shown below:

<u>Manufacturer</u>	<u>TCN</u>	<u>Analysis Sequence No.</u>	<u>Gallons on Hand as of 12 Jan 73</u>
Thompson Company	94638155X012	5	44,440
Hercules Company	946481560001	8	27,500
Dow Chemical Company	94638155X052	10	383,680
Hercules Company	94648192001	14	<u>118,360</u>
Total Gallons			573,980

Approximate Market Value @ \$40/gallon \$22,959,200

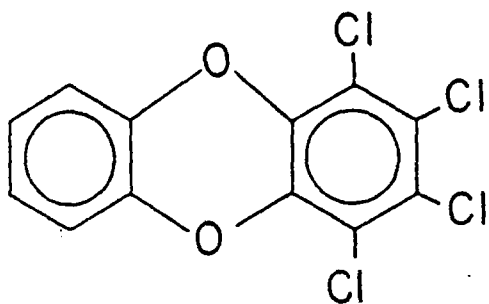
Representative samples from each of the above TCN's were collected by personnel from Kelly AFB/EHL(K) on 10 July 1973. Individual samples were taken by suspending a 1- or 2-oz. glass bottle from a wire and inserting the bottle ~18 in. into the herbicide and swirling the bottle. The bottle was then removed and capped and the exterior was cleaned. Each drum was numbered, and that number was scribed onto the glass bottle. Samples are precisely identified by listing the Analysis Sequence Number and barrel number. The convention adopted is shown here:

7 Hercules 8
 ↑
 Barrel # Manufacturer Analysis Sequence Number

This report describes the development and application of methodology developed for mass-spectrometric characterization of contaminants present in the herbicide samples at levels > 0.1%, including all volatile compounds and the chlorophenoxyacetic acids. The techniques for determining tetrachlorodibenzo-p-dioxin in concentrations > 0.02 ppm (0.02 µg/g) are also described, and the analytical results are summarized.

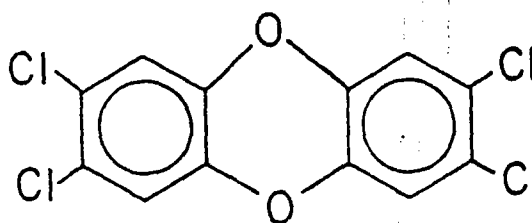
TABLE I (continued)

XXVII



1,2,3,4-Tetrachloro-dibenzo-p-dioxin

XXVIII



2,3,7,8-Tetrachloro-dibenzo-p-dioxin

A second method for identification of small peaks which may be associated with an unknown compound is the mass chromatogram. After studying a normalized background-subtracted scan, very small peaks can be associated with the spectrum of interest by plotting the intensity of a certain mass as a function of chromatographic elution time and comparing the observed behavior either with a more intense peak that is known to arise from the unknown compound or with the total ion chromatogram of the unknown in the mixture. An example of the use of this subroutine is given in Appendix D (see Figure D-11 and D-12). Here total-ion chromatograms, the Mass-196 chromatogram, and the Mass-206 chromatogram for Herbicide Sample #264 are displayed as a function of chromatographic retention time. It is evident that Masses 196 and 206 originate not from the same compound but from two different compounds which elute at slightly different times. In this case, the relative amounts are such that this difference can actually be seen as a shoulder which appears at a longer time on the total-ion chromatogram. However, the compound, if present in smaller quantities, could not be observed visually in the total-ion chromatogram. It could be detected only if one of the masses which are associated with the lesser compound were displayed as a function of retention time. This technique greatly facilitates distinction of background mass-spectrometric peaks from small peaks arising from the unknown compound. This markedly simplifies identification of unknowns.

Qualitative identification of unknown species can be made by first obtaining a listing of spectra at elution times corresponding to maxima or shoulders in the reconstructed total-ion chromatogram, and then searching for a molecular-ion identification using the mass-chromatogram displays to distinguish background from authentic peaks. Mass spectra of components are verified by comparison with standard mass-spectrometric tables. Appendix E is a compilation of standard spectra taken in this laboratory for compounds that are of interest due to their suspected presence in the herbicide samples or due to their possible interference with low-level tetrachlorodibenzo-p-dioxin analysis. In each table the origin of the standard compound is given, along with the retention time of the compound and the time of the background spectrum.

In addition to comparison of unknown spectra with spectra obtained from the literature or with standard spectra obtained under different conditions, it is often necessary to identify an unknown compound by comparison with the standard spectrum of an analogous compound. This method of identification is exemplified in the identification of an impurity present in each of the four herbicide samples analyzed--the butyl ester of monochlorophenoxyacetic acid (XII). As can be seen from a comparison of the mass spectra in Tables A-9 and A-10 (see Appendix A), similarities between the two spectra include large m/e 57, 41, and 29 peaks, indicating the presence of the C_4H_9 group. The heaviest mass found that is associated with the molecular ion is 34 amu lower in Spectrum A-9 than in Spectrum A-10. The spectrum of I (Table A-10) has been identified from standard spectra to be the butyl ester of dichlorophenoxyacetic acid and the difference in the molecular-ion mass of 34 units, along with intense butyl ion fragments, indicates that Spectrum H of Gulfport #7 is a butyl ester of monochlorophenoxyacetic acid. In addition, Spectra I and H both have very intense m/e 91, m/e 101, and m/e 114 peaks. These correspond to loss of C_4H_8Cl , $CO_2C_4H_9$, and $CHCO_2C_4H_9$, respectively, from the molecular ion. Similar analogies are necessary in cases where the exact compound of interest is not readily available.

Two other identification techniques reported here greatly simplify the interpretation of the spectra of unknowns found in the four Gulfport herbicide samples analyzed. These techniques are (1) identification of butyl fragments in the spectrum and (2) the use of the isotope distributions to determine the number of chlorine atoms present in a given fragment. The basis for the butyl-fragment approach is seen in Figure A-6 (Appendix A). It is evident that only those total-ion chromatographic peaks which exhibit Masses 57, 41, and 29 can be associated with a butyl compound. Since the major components of Herbicide Orange are butyl esters, these compounds along with impurities containing butyl groups gave rise to these masses.

The second technique mentioned above--the chlorine-isotope distribution--was also quite useful in classifying unknown compounds. Since the natural-chlorine isotope distribution of ^{35}Cl : ^{37}Cl is approximately 3:1, mass spectra of

widely recognized to be the most toxic small molecule known ($LD_{50} = 0.6 \mu\text{g/kg}$ in guinea pigs); the threat to man must at this point be assumed to be equally great. Thus, analytical methods for determining TCDD have been sought which can be used to detect and quantify TCDD in such samples as food stuffs, water, and soil at extremely low levels--on the order of 1×10^{-12} g TCDD/g or 1 part-per-trillion. Baughman and Meselson^{8,9} have used such a method, and Ryan¹⁰ and Crummett¹¹ have reported somewhat similar methods.

It should be noted at this point that several structural isomers can quite properly be referred to as tetrachlorodibenzo-p-dioxin; thus, it is possible to encounter not only 2,3,7,8-TCDD but also 1,2,3,4-TCDD, 2,3,6,8-TCDD, 2,3,6,9-TCDD, etc. Approximately twenty tetrachlorodibenzo-p-dioxins are possible. Any analytical method which does not involve a very sophisticated scheme for separating highly similar compounds prior to mass-spectral determination or which utilizes solely the molecular-ion region of the mass spectrum cannot possibly be used to make a distinction between the respective tetrachlorodibenzo-p-dioxins which may be present in the sample. Furthermore, depending upon the resolution of the mass spectrometer being employed, such techniques cannot be used to differentiate tetrachlorodibenzo-p-dioxin from other tetrachlorinated hydrocarbons having nearly the same mass (or mass fragments) as the TCDD. Specifically, it is not at all certain at this writing whether the TCDD levels in Gulfport Herbicides reported by Dow in 1971¹² and 1972¹³ represent 2,3,7,8-TCDD or a mixture of TCDD's which may be composed, in part, of the 2,3,7,8-TCDD. At worst, the Dow values represent upper limits.

The emphasis in the work reported herein was the characterization of herbicide stocks stored at Gulfport, Mississippi; in the case of TCDD, a method which could be used to detect reliably and quantify tetrachlorodibenzo-p-dioxin present in Herbicide Orange at levels greater than 0.1 ppm was needed. The methods alluded to above⁸⁻¹¹ were not suitable for our purposes since the levels of TCDD of concern were 10^5 greater than TCDD levels detectable by the techniques referred to above. Rather than ultrasensitive methodology, we sought to develop an approach which has adequate sensitivity and specificity

SECTION III

RESULTS AND DISCUSSION

A. VOLATILE CONSTITUENTS IDENTIFIED IN HERBICIDE ORANGE

Tables IV through VII are lists of the components we have determined to be present in the four representative samples of Gulfport Herbicide Orange. The actual mass-spectral and gas-chromatographic data obtained for each of the four herbicide specimens have been consolidated and included in the report in Appendices A-D. In establishing the identity of components in each of the four herbicide samples, it was also helpful to compare the analytical data from the four samples; in fact, in a qualitative sense these four specimens were found to be very similar. Table VIII contains gas-chromatographic retention times obtained in "fingerprinting" the four Herbicide-Orange specimens (this "fingerprinting" technique is described in detail in Vol. II of this report)¹⁴ along with the identities of the chromatographic peaks assigned following our GC-MS studies. The similarities of the four samples are apparent in Table VIII.

A detailed discussion of the rationale employed in interpreting the large volume of data contained in Appendices A-D is outlined below in two parts: (1) identification of volatile unknowns in Herbicide Orange based upon direct comparison of mass spectra of unknowns with standard mass spectra and (2) identification of volatile unknowns based solely upon mass spectral data obtained for the unknown without confirmation by direct comparison with a standard spectrum.

1. COMPOUNDS IDENTIFIED BY COMPARISON WITH STANDARDS

Butyl Esters of Dichlorophenoxyacetic Acid (XIII) and Trichlorophenoxyacetic Acid (XIV)

The gas chromatograms and total-ion chromatograms obtained for each of the four Herbicide-Orange samples (Figures A-1, A-2, B-1, B-2, C-1, C-2, D-1, and D-2) indicate that each of the four samples

TABLE VIII
RETENTION TIMES^a (SEC) FOR SPECIES IDENTIFIED IN HERBICIDE ORANGE SAMPLES

COMPOUND	GULFPORT DRUM NUMBER ^b			
	<u>7</u>	<u>59</u>	<u>251</u>	<u>264</u>
Butanol (I)	27	27	26	27
Toluene (II)	43	43	- ^c	43
Xylenes (III), Ethylbenzene(XI)	-	-	-	68,76
Butyl Chloride (IV)	136	132	126	-
Dichlorophenol (V)	255	261	252	257
Peak D(#251)	-	-	390	-
Trichlorophenol (VI)	493	506	-	507
Trichloroanisole (IX)	-	-	-	629
Dichloro-Methoxyanisole (X)	-	-	-	713
Dichloro-Methoxyanisole (X)	-	-	-	761
Butoxydichlorophenol (VII)	-	-	757	-
Butoxytrichlorophenol (VIII)	-	-	990	-
Butyl-monochlorophenoxyacetate (XII)	1052	1075	1054	1062
Butyl-dichlorophenoxyacetate (XIII)	1262	-	1265	1140,1205
Butyl-dichlorophenoxyacetate (XIII)	1357	1373	1390	1406
Butyl-trichlorophenoxyacetate (XIV)	1462	1482	1464	1470
Butyl-trichlorophenoxyacetate (XIV)	1614	1620	1618	1626
Butyl-methoxy-dichlorophenoxyacetate (XV)	1650	1671	1646	1657
Octyl-dichlorophenoxyacetate(XVI)	1768	-	-	-
Octyl-dichlorophenoxypropionate(XVII)	1869	-	-	-
Octyl-trichlorophenoxyacetate(XVIII)	1931	-	-	-
1,1-dibutoxy-2-trichlorophenoxyethane (XXII)	-	-	1974	-
Octyl-methoxy-dichlorophenoxyacetate (XXIII)	1966	-	-	-
Butyl-bis-dichlorophenoxyacetate(XIX)	2691	2711	2665	2663

a. See chromatograms in Figures A-1, B-1, C-1 and D-1 of the appendix. Chromatographic parameters are as follows: 8 ft x 1/8" O.D. glass column packed with 10% DC-200 on Gas Chrom Q. Column temperature programmed from 110° to 240°C at 4°C/min. Data acquisition: Autolab System IV computing integrator and 1-mV strip-chart recorder.

b. Drum #7 is one of 500 drums obtained from Hercules Company (TCN 9464 8156 000), Drum #59 is one of 2152 drums obtained from Hercules Chemical Company (TCN 9464 8192 001), Drum #251 is one of 6976 drums obtained from Dow Chemical Company (TCN 9463 8155 X052), Drum #264 is one of 808 drums obtained from Thompson Company (TCN 9463 8155 X012).

c. Denotes none detected at levels greater than 0.1%.

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esters of dichlorophenoxyacetic acid, trichlorophenoxyacetic acid, and dichlorophenoxypropionic acid. These were identified only in Gulfport #7 in quantities greater than 0.1% of the total volatile samples. Mass-spectral data in Tables A-11 through A-13 and Figures A-12 through A-14 can be compared with standard spectra given in Tables E-1 through E-18.

2. IDENTIFICATION OF UNKNOWNNS WITHOUT COMPARISON WITH STANDARDS

In order to identify the remaining components in the four Gulfport samples, analogies with existing spectra shown largely in Appendix E, along with molecular ion and fragmentation patterns, were relied upon heavily. All components present in quantities larger than 0.1% in the pre-butyl^{*} ester of dichlorophenoxyacetic acid region and larger than 0.3% in the post-butyl ester of trichlorophenoxyacetic acid region^{*} were identified, except compounds D and J in Gulfport #251. However, the lack of success in making an unambiguous identification of these two compounds is not due to lack of sensitivity of the instrument, but inability to determine the molecular ion and important fragmentation that would unambiguously identify the unknown. This will be discussed in more detail in a later portion of this section.

Butyl Esters of Monochlorophenoxyacetic Acid and Methoxy-dichlorophenoxyacetic Acid

Two large impurities that are present in all four herbicide samples have been identified as the butyl esters of monochlorophenoxyacetic acid (XII) and methoxy-dichlorophenoxyacetic acid (XV). In Gulfport #7, these compounds appear as peaks H and M (see Table A-9); in Gulfport #59,

*Pre-butyl ester = components eluting from the chromatographic column prior to this ester.

Post-butyl ester = components eluting from the chromatographic column after butyl trichlorophenoxyacetate.

they are J and O (see Table B-9 and Figure B-11); in Gulfport #251, they are K and P (see Table C-13 and Figure C-18; Table C-19 and Figure C-24); and in Gulfport #264, they are K and Q (see Table D-10 and Figure D-14). A complete spectrum of the butyl ester of methoxy-dichlorophenoxyacetic acid superimposed upon the ester of trichlorophenoxyacetic acid was obtained only from #251 (Table C-19), and the other three samples were concluded to have this same contaminant, based upon F.I.D. retention time (see Table VIII). If the spectra of the two butyl esters are compared with those of the butyl esters of dichlorophenoxyacetic acid and trichlorophenoxyacetic acid (Tables E-19 and A-2, respectively), it is apparent that prominent peaks which correspond to the molecular ion and to the molecular ion minus C_4H_8 , C_4H_8Cl , $CO_2C_4H_9$, $HCCO_2C_4H_9$, and $OCH_2CO_2C_4H_9$ (Fragmentation Pathway A outlined, Figure 1b) are present. Based upon these features of the mass spectra, the unknowns are shown to be butyl esters of chlorinated phenoxyacetic acids. The isotope distribution of the molecular ion and the corresponding fragments confirm that these compounds are the monochloro- and dichloro-substituted phenoxyacetic acids.

Compounds D and J in Gulfport #251

Two compounds could not be identified conclusively in Gulfport #251. Compound D is 1.2% of the total, and Compound J is on the order of 0.1%. Data in Tables C-6 and C-11 and Figures C-9 and C-17 indicate that these compounds are very similar. Both compounds give rise to large butyl fragments along with m/e 31 (CH_3O^+), m/e 61, and m/e 116, but the isotope distributions of these major fragments do not indicate the presence of chlorine. These unknowns are possibly some type of butyl ether or ester of an unchlorinated acid, or alcohol. Any further identification would be completely speculative due to the lack of positive identification of a molecular ion in the mass spectra and the absence of reference spectra among the 12,000 standard mass spectra catalogued in the General Electric mass spectral Search Routine computer library.

Octyl Ester of Methoxy-dichlorophenoxyacetic Acid (XXIII)
and 1,1-Dibutoxy-2-Trichlorophenoxyethane (XXII)

A major impurity found in each of the four herbicide samples was determined to be the butyl ester of methoxy-dichlorophenoxyacetic acid. Such a compound could arise if one of the chlorines in trichlorophenoxyacetic acid is replaced by a methoxy group. Such an impurity in the trichlorophenoxyacetic acid would, when the acids are esterified with butanol or octanol, be converted to the corresponding ester during the synthesis of the herbicide. In Gulfport #7 — in addition to the octyl esters of the dichloro- and trichlorophenoxyacetic acids — the octyl ester of methoxy-dichlorophenoxyacetic acid was identified as Compound Q but was not identified in any of the other samples. Table A-14 gives a complete spectrum, and Figure A-15 shows it to elute after the analogous trichlorophenoxyacetic acid ester.

Mass spectrometrically a very similar compound to the octyl ester of methoxy-dichlorophenoxyacetic acid is the 1,1-dibutoxy-2-trichlorophenoxyethane. This compound was identified as Compound R in Gulfport #251. Its identity is based upon the spectrum shown in Table C-18 and mass chromatograms displayed in Figure C-23. The retention times for this compound and the octyl ester of methoxy-dichlorophenoxyacetic acid are very similar; the major differences are: octyl-ion fragmentation is present in the octyl ester but absent in the dibutoxy compound; only di- and monochlorinated fragments are present in the octyl ester, but prominent trichlorophenol and molecular ions indicating a Cl_3 species are present in the dibutoxy spectrum. The identification of these compounds is not based upon a complete mass spectrum; however, their most probable identities are the octyl ester of methoxy-dichlorophenoxyacetic acid and 1,1-dibutoxy-trichlorophenoxy-ethane, respectively.

Butyl Esters of Bis-(chlorophenoxy)acetic Acids

The Herbicide-Orange samples were found to contain the butyl esters of bis-(chlorophenoxy)acetic acids. These compounds can be produced during the synthesis of the herbicide by reaction of the corresponding chlorinated phenol with possible impurities in the 2-chloroacetic acid such as 2,2-dichloroacetic acid. The three impurities found were the butyl esters of bis-(dichlorophenoxy)acetic acid, bis-(trichlorophenoxy)acetic acid, and methoxy-dichlorophenoxy-trichlorophenoxyacetic acid. The last product is due to the methoxy-dichlorophenol impurity in the trichlorophenol, as discussed in the previous section. Each of the four herbicide samples was shown to contain at least two of these bis-compounds. In #7 and #59 all three products were present in levels greater than 0.1%. In addition to the butyl fragments, fragments very similar to the dichlorophenoxy-, trichlorophenoxy-, and methoxy-dichlorophenoxyacetic esters are seen. However, the lack of molecular ions corresponding to the mono-substituted chlorinated phenoxyacetic acid esters and the occurrence of this mass less 1 show the likelihood of a bis-substituted chlorinated phenoxyacetic ester. In addition, (m-101)⁺ ions with proper chlorine distributions were identified for Species A in #7 (see Table A-15), for Species P in #59 (see Table B-14), for Species T in #251 (see Table C-16), and Species R in #264 (see Table D-14). The loss of 100 mass units from the radical ion (m/e 275 for the bis-dichlorophenoxyacetic ester and m/e 309 for the bis-trichlorophenoxyacetic ester) was also seen to involve a rearrangement to yield CO₂ and C₄H₈ as neutral products. Probable Fragmentation Pathway D is illustrated in Figure 4.

B. QUANTITIES OF DICHLOROPHENOXYACETIC ACID AND TRICHLOROPHENOXYACETIC ACID PRESENT IN HERBICIDE ORANGE

Using the procedure for analysis described previously, we determined the amount of di- and trichlorophenoxyacetic acids in the four Gulfport samples. For calibration of the gas chromatograph, chloroform solutions of EPA/FDA-primary-standard methyl dichloro- and methyl

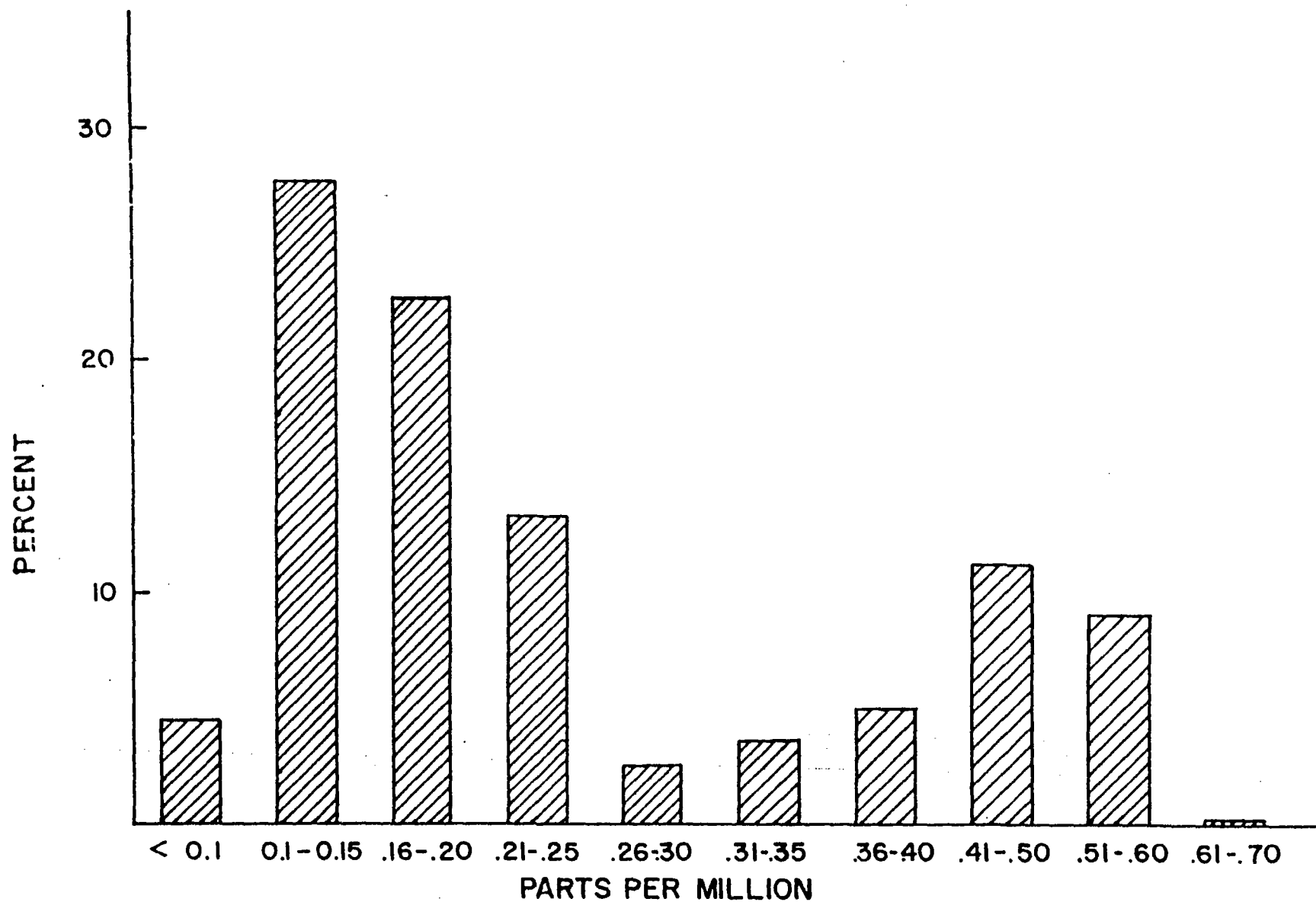


Figure 8. DIOXIN DISTRIBUTION IN 80 BARRELS OF DOW CHEMICAL (ASN-10)

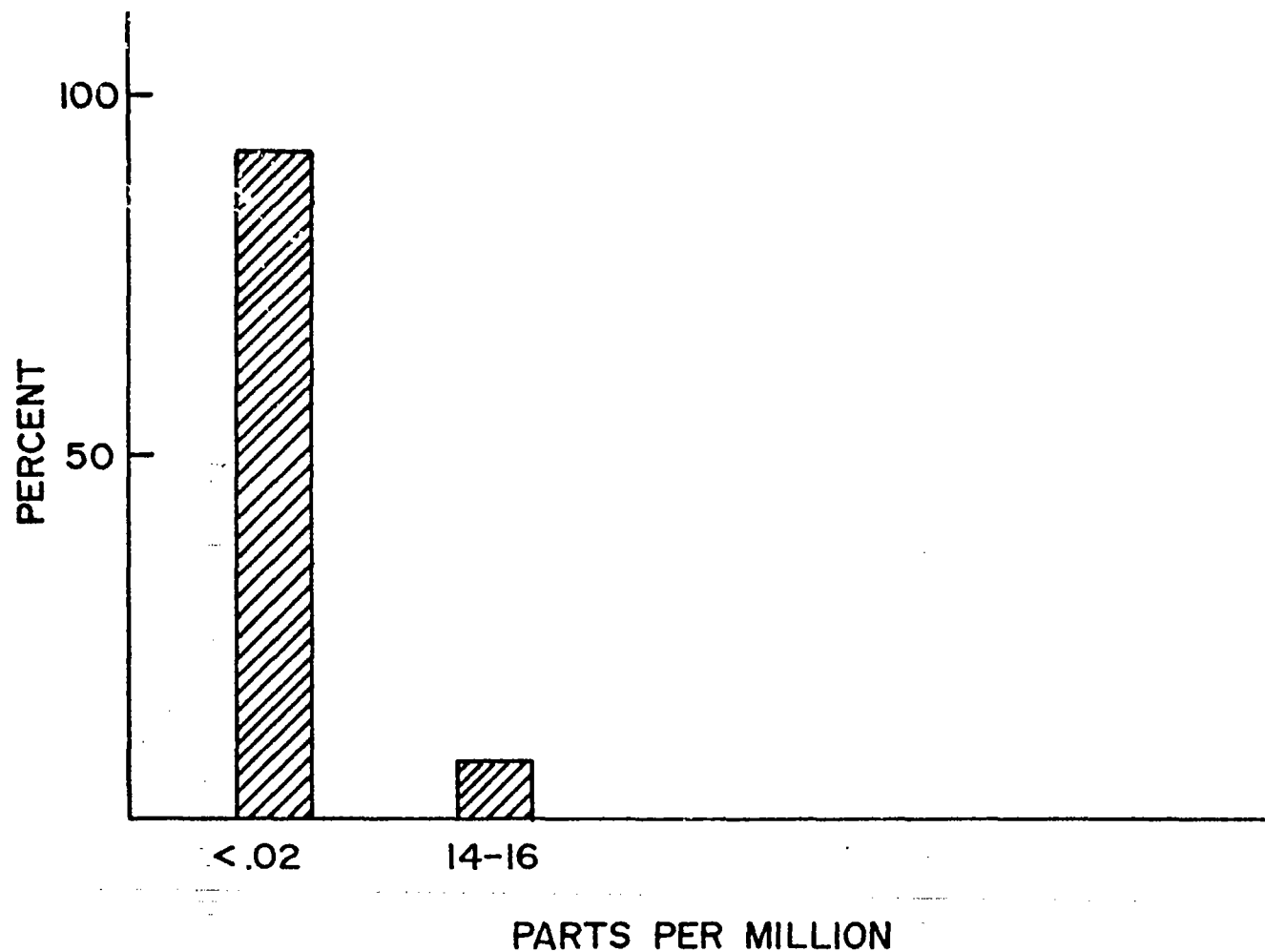


Figure 9. DIOXIN DISTRIBUTION IN 61 BARRELS LABELED HERCULES (ASN-8)

SECTION IV
SUMMARY OF RESULTS

Table XV summarizes the results of the qualitative and quantitative analysis of selected samples of Herbicide Orange. Volatile constituents (with boiling points below 300°C at 1 atm) and the chlorophenoxyacetic acids are the main components in the Herbicide-Orange samples. The absolute response of the flame ionization detector (FID) was determined for the butyl ester of 2,4,-D and the butyl ester of 2,4,5-T through use of the EPA standards. Assuming that all components of the herbicide mixture gave an equal response on the flame ionization detector, we detected an average of 96 $\pm$ 10% of the total herbicide sample injected onto the gas chromatographic column by FID. Thus, the relative amounts of volatile components listed in Tables IV through VII (pp. 32-39) and summarized in Table XV (p. 68) represent the absolute composition of the sample in percent by weight (within the limits of the assumption of equal detector response).

This report describes the in-depth GC-MS qualitative and quantitative analysis of representative samples from four separate drums in Gulfport, Mississippi, which were taken as representative samples of four lots of Herbicide Orange identified on the basis of preliminary Dow Chemical Co. Analyses as "low dioxin herbicide." In addition to the in-depth GC-MS characterization of the four representative samples, a concurrent study¹⁵ described in Vol. II of this report was undertaken in which the homogeneity of the major and minor constituents in the drums representing each of the four Herbicide-Orange batches was examined by using flame-ionization gas chromatography (FID-GC). By correlating the retention times measured for the various components in the FID-GC study (see Vol. II) with those measured in the present detailed GC-MS identification study, it is possible to derive qualitative data for the components of the several barrels of each herbicide lot analyzed. These results are summarized in Tables

TABLE XV
SUMMARY OF COMPOSITION OF HERBICIDE ORANGE

COMPOUND	GULFPORT DRUM NUMBER ^a			
	<u>7</u>	<u>59</u>	<u>251</u>	<u>264</u>
Butanol (I)	0.81	0.75	0.28	1.13
Toluene (II)	1.3	2.2	-- ^b	0.51
Xylenes (III), Ethylbenzene(XI)	--	--	--	2.6
Butyl Chloride (IV)	0.11	0.16	0.14	--
Dichlorophenol (V)	0.19	0.26	--	0.28
Peak D(#251)	--	--	1.2	--
Trichlorophenol (VI)	0.41	0.67	--	3.6
Trichloroanisoie (IX)	--	--	--	0.75
Dichloro-Methoxyanisoie (X)	--	--	--	0.18
Dichloro-Methoxyanisoie (X)	--	--	--	0.31
Butoxydichlorophenol (VII)	--	--	0.22	--
Butoxytrichlorophenol (VIII)	--	--	0.31	--
Butyl-monochlorophenoxyacetate (XII)	0.49	1.16	1.6	0.78
Butyl-dichlorophenoxyacetate (XIII)	0.78	--	4.2	1.0
Butyl-dichlorophenoxyacetate (XIII)	42.4	44.2	43.3	44.9
Butyl-trichlorophenoxyacetate (XIV)	0.92	0.70	0.96	0.44
Butyl-trichlorophenoxyacetate (XIV)	39.0	42.1	44.1	40.1
Butyl-methoxy-dichlorophenoxyacetate (XV)	6.1	5.4	1.9	2.5
Octyl-dichlorophenoxyacetate(XVI)	3.2	--	--	--
Octyl-dichlorophenoxypropionate(XVII)	0.3	--	--	--
Octyl-trichlorophenoxyacetate(XVIII)	2.0	--	--	--
1,1-dibutoxy-2-trichlorophenoxyethane (XXII)	--	--	0.36	--
Octyl-methoxy-dichlorophenoxyacetate (XXIII)	0.37	--	--	--
Butyl-bis-dichlorophenoxyacetate(XIX)	0.41	0.58	0.47	0.27
Butyl ester of bis Trichlorophen- oxyacetic acid (XX)	0.95	1.8	0.19	0.53
Butyl ester of Trichlorophenoxy-	0.16	0.21	--	--
2,4-Dichlorophenoxyacetic acid (free acid)	0.78	0.65	0.19	0.66
2,4,5-Trichlorophenoxyacetic acid (free acid)	0.84	0.78	0.13	0.80
Tetrachlorodibenzo-p-dioxin ($\mu\text{g/g}$) ^c	< 0.05	0.07	0.38	0.18

TABLE XV (continued)

- a. Drum #7 is one of 500 drums obtained from Hercules Company (TCN 9464 8156 000); Drum #59 is one of 2152 drums obtained from Hercules Chemical Company (TCN 9464 8192 001); Drum #251 is one of 6976 drums obtained from Dow Chemical Company (TCN 9463 8155 X052); Drum #264 is one of 808 drums obtained from Thompson Company (TCN 9463 8155 X012).
- b. Denotes none detected at levels greater than 0.1%.
- c. Note well that the tetrachlorodibenzo-p-dioxin content is listed in $\mu\text{g/g}$ (ppm); all other values are listed as relative percent (calculation of relative percent:
$$\frac{\text{peak area of component}}{\text{total area of all volatile components}} \times 100$$
).

XVI, XVII, XVIII, XIX and suggest that each lot is generally quite homogeneous. Furthermore, the feasibility of using the "fingerprint" of major and minor constituents to ascertain the manufacturer of an unidentified specimen of Herbicide Orange was conclusively demonstrated.

The homogeneity of each of the four batches of Herbicide Orange with respect to TCDD concentration is of utmost concern. Our data as shown in bar-graph form (Figures 6-9) lead one to the conclusion that only Thompson Co. ASN 5 (44,440 gallons in storage) and Hercules ASN 14 (118,360 gallons in storage) are sufficiently uniform in TCDD content and other constituents to be considered homogeneous throughout. Hercules ASN 8 (27,500 gallons in storage) is inhomogeneous in TCDD content--8% of the drums sampled were found to contain inordinately high levels of TCDD. It may well be that these "high dioxin specimens" or the drums from which they were obtained are actually mislabeled. This can be determined by the methodology described in Vol. II of this report. The DOW ASN 10 (383,680 gallons in storage) batch appears quite heterogeneous. The data shown in the bar graph (Figure 8) suggest the presence of two or more sub-groups, each with average TCDD content of well over 0.1 µg/g.

It should be noted that the distribution of dioxin levels in Figure 7 is sufficiently narrow (95% of the values obtained were within 20% of the mean value of 0.125 ppm) that it is a measure not only of the actual dioxin-level distribution but also of the precision of the analytical methodology (as discussed in an earlier section, the overall precision of the analysis is 12.5%). For the Dow ASN 10 samples, however, the distribution of dioxin levels is much broader and clearly is indicative of the actual spread of values in the batch itself. Again, the Dow material is certainly very inhomogeneous.

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TABLE XVI

COMPOSITION OF VARIOUS DRUMS OF HERBICIDE ORANGE IN THE LOT
DESIGNATED ANALYSIS SEQUENCE NUMBER 8 (HERCULES CO.)[†]

<u>Compound</u>	<u>Drum Number</u>			<u>Average (a)</u>
	<u>2</u>	<u>7</u>	<u>11B</u>	
Butanol	(b) 0.71	0.81	1.36	0.96
	(c) 26	27	25	26
Toluene	1.47	1.32	1.75	1.51
	43	43	41	42
Butyl Chloride	0.07	0.11	0.11	0.10
	134	136	137	136
Dichlorophenol	0.25	0.19	0.26	0.23
	265	255	256	259
Trichlorophenol	0.43	0.41	0.42	0.42
	511	493	497	500
Butyl monochlorophenoxyacetate	0.59	0.49	0.58	0.55
	1075	1052	1057	1061
Butyl dichlorophenoxyacetate	(d)	0.78	0.37	0.58
		1262	1267	1265
Butyl dichlorophenoxyacetate	42.8	42.5	39.8	41.7
	1382	1357	1367	1369
Butyl trichlorophenoxyacetate	0.90	0.92	0.85	0.89
	1486	1462	1467	1472
Butyl trichlorophenoxyacetate	39.3	39.0	38.6	38.9
	1608	1583	1593	1595
Butyl methoxydichlorophenoxyacetate	5.87	5.40	6.00	5.76
	1673	1650	1656	1660
Octyl dichlorophenoxyacetate	3.32	3.21	3.46	3.33
	1793	1768	1777	1779
Octyl dichlorophenoxypropionate	0.32	0.32	0.35	0.33
	1894	1869	1878	1880
Octyl trichlorophenoxyacetate	2.29	2.05	2.33	2.22
	1957	1931	1941	1943
Octyl methoxydichlorophenoxyacetate	0.38	0.37	0.37	0.37
	2002	1986	1976	1988

TABLE XVI (continued)

<u>Compound</u>	<u>Drum Number</u>			<u>Average</u> ^(a)
	<u>2</u>	<u>7</u>	<u>11B</u>	
Butyl (bis-dichlorophenoxy)acetate	0.34 2691	0.41 2700	0.38 2717	0.38 2703
Butyl (bis-trichlorophenoxy) acetate	(e)	1.8	(e)	
Butyl (methoxydichlorophenoxy) tri-chlorophenoxyacetate	(e)	0.21	(e)	
Tetrachlorodibenzo-p-dioxin (µg/g)	<0.05	<0.05	<0.05	<0.05 ^(f)

[†]This lot obtained from Hercules Company (TCN 9464 8156 0001) contains 500 drums.

(a) Average relative percent and retention time for the respective compounds found in these samples.

Table shows two values for each volatile compound.

(b) Relative amount (%) of the compound

(c) Gas chromatographic retention time of the compound (sec.)

(d) Present in chromatogram but no numerical value obtained. Quantity present appears to be similar to amount found in other samples. The average was determined by dividing the sum of the values obtained by the number of actual observations.

(e) Analyses not performed.

(f) Additional TCDD analyses are summarized in Figure 9, p. 65.

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TABLE XVII

COMPOSITION OF VARIOUS DRUMS OF HERBICIDE ORANGE IN THE LOT
DESIGNATED ANALYSIS SEQUENCE NUMBER 14 (HERCULES COMPANY)

Compound	Drum Number						Average (a)
	17	27	39	42	50	59	
Butanol	(b) 0.79	0.67	0.87	0.77	0.82	0.75	0.78
	(c) 25	27	26	27	31	27	27
Toluene	2.57	2.31	2.75	2.40	2.35	2.24	2.52
	39	43	42	43	49	43	43
Butyl Chloride	0.17	0.17	0.17	0.15	0.14	0.16	0.16
	122	129	126	130	147	132	131
Dichlorophenol	0.34	0.32	0.33	0.30	0.30	0.26	0.31
	249	257	250	258	287	261	260
Trichlorophenol	0.75	0.55	0.77	0.71	0.76	0.67	0.70
	492	487	498	501	543	506	505
Butyl monochlorophenoxyacetate	1.42	1.39	1.44	1.28	1.34	1.16	1.34
	1063	1063	1051	1068	1125	1075	1074
Butyl dichlorophenoxyacetate	1.03	1.09	0.79	0.92	0.65	(d)	0.90
	1274	1273	1260	1278	1338		1285
Butyl dichlorophenoxyacetate	43.1	42.6	42.3	42.7	43.4	44.4	43.2
	1380	1380	1361	1385	1434	1393	1389
Butyl trichlorophenoxyacetate	2.51	2.02	1.82	1.79	1.65	0.70	1.75
	1473	1471	1461	1476	1538	1482	1484
Butyl trichlorophenoxyacetate	40.6	41.2	40.3	41.1	40.4	42.1	41.0
	1606	1607	1588	1612	1662	1620	1616
Butyl methoxydichlorophenoxy- acetate	5.62	5.71	6.16	5.70	6.69	5.44	5.89
	1665	1662	1653	1666	1731	1671	1675
Butyl (bis-dichlorophenoxy)- acetate	0.45	0.46	0.53	0.39	0.38	0.58	0.47
	2687	2706	2670	2704	2814	2711	2715
Butyl (bis-trichlorophenoxy)- acetate	(e)	(e)	(e)	(e)	(e)	1.8	
Butyl (methoxydichlorophenoxy)- trichlorophenoxyacetate	(e)	(e)	(e)	(e)	(e)	0.21	
Tetrachlorodibenzo-p-dioxin (ug/g)	<0.05	<0.05	0.08	0.06	0.07	0.07	(f)

[†] This lot obtained from Hercules Company (TCN 9464 8192 001) contains 2152 drums.

(a) Average relative percent and retention time for the respective compounds found in these samples.

Table shows two values for each volatile compound.

TABLE XVII (continued)

- (b) Relative amount (%) of the compound.
- (c) Gas chromatographic retention time (sec).
- (d) Present in chromatogram but no numerical value obtained. Quantity present appears to be similar to amount found in other samples. In this case the average value was calculated by dividing the sum of the values obtained by the number of actual observations.
- (e) Analyses not performed.
- (f) Additional TCDD analyses are summarized in Figure 6, p. 62.

TABLE XVIII

COMPOSITION OF VARIOUS DRUMS OF HERBICIDE ORANGE IN
THE LOT DESIGNATED ANALYSIS SEQUENCE NUMBER 10
(DOW CHEMICAL CO.)[†]

Compound	Drum Number												Average (a)
	249	250	251	252	253	254	255	256	257	258	275	276	
Butanol	(b) 0.29 (c) 27	0.30 27	0.28 26	0.25 27	0.61 27	0.24 26	0.25 27	0.23 26	0.30 26	0.35 27	0.30 27	0.23 27	0.30 27
Toluene	0.17 43	0.23 42	* 42	0.15 42	0.61 42	* 42	* 42	* 42	* 42	* 42	* 42	* 42	0.10 (d) 42
Xylenes, Ethylbenzene	0.08 77	0.04 75	* 75	* 75	0.08 75	* 75	* 75	* 75	* 75	* 75	* 75	* 75	0.03 76
Butyl Chloride	* 126	* 126	0.14 126	* 126	* 126	* 126	* 126	* 126	* 126	0.17 128	0.14 128	* 128	0.05 127
Dichlorophenol	0.11 261	0.10 255	0.10 252	0.10 261	0.24 257	0.10 257	0.10 252	0.10 254	0.13 254	0.14 256	0.10 255	0.10 258	0.12 256
Peak D	0.23 403	0.28 392	1.24 390	0.23 404	0.22 398	0.33 397	0.33 389	0.33 393	0.40 392	1.52 389	1.26 393	0.33 398	0.57 395
Trichlorophenol**	0.38 492	0.48 492	0.15 478	0.39 492	0.24 487	0.12 486	0.12 477	0.12 483	0.17 481	0.21 480	0.21 482	0.11 487	0.23 485
Butoxydichlorobenzene	0.10 772	0.13 760	0.22 757	0.11 773	0.04 791	0.14 768	0.14 756	0.13 764	0.14 761	0.28 753	0.31 761	0.13 768	0.16 765
Butoxytrichlorobenzene	0.10 1029	0.13 1014	0.40 1012	0.16 1030	0.10 1024	0.09 1025	0.08 1011	0.08 1021	0.12 1015	0.20 1009	0.37 1017	0.07 1025	0.16 1019
Butyl monochloro- phenoxyacetate	1.08 1069	1.42 1054	1.59 1054	1.08 1070	1.01 1062	1.25 1066	1.27 1052	1.25 1062	1.55 1056	2.24 1049	1.59 1060	1.26 1066	1.38 1060
Butyl dichloro- phenoxyacetate	2.15 1282	2.69 1268	3.07 1265	1.87 1280	0.92 1274	2.85 1280	2.79 1266	2.70 1277	4.26 1270	4.15 1260	2.99 1272	2.78 1280	2.77 1273

TABLE XVIII (continued)

Compound	Drum Number												Average (a)
	249	250	251	252	253	254	255	256	257	258	275	276	
Butyl dichloro- phenoxyacetate	43.2 1404	43.8 1358	43.3 1390	43.8 1406	44.3 1370	44.7 1403	44.4 1389	45.5 1403	44.1 1363	42.2 1353	44.2 1398	45.7 1408	44.1 1387
Butyl trichloro- phenoxyacetate	1.23 1482	2.23 1464	0.96 1464	1.45 1484	0.83 1471	0.82 1478	0.85 1464	0.85 1475	1.32 1465	1.46 1454	0.99 1470	0.85 1479	1.22 1471
Butyl trichloro- phenoxyacetate	43.2 1632	40.9 1582	44.1 1618	42.8 1635	41.9 1596	45.6 1633	45.6 1619	44.8 1631	42.1 1589	41.1 1577	43.6 1625	44.5 1635	43.4 1614
Butyl methoxydichloro- phenoxyacetate	3.48 1662	3.70 1642	1.97 1646	1.80 1663	3.34 1652	2.18 1662	2.21 1648	2.19 1659	3.73 1646	3.33 1632	1.99 1654	2.19 1663	2.68 1652
Octyl dichloro- phenoxyacetate**	0.40 1726	0.70 1708	0.25 1717	0.37 1728	0.27 1723	0.15 1731	0.18 1717	0.19 1728	0.27 1718	0.30 1706	0.21 1724	0.18 1732	0.29 1722
Octyl trichloro- phenoxyacetate**	1.19 1826	* 	* 	1.40 1830	1.64 1822	0.12 1819	0.12 1804	0.15 1816	0.18 1801	* 	0.07 1812	0.14 1819	0.42 1817
1,1-dibutoxy-2-tri- chlorophenoxyethane	0.24 1990	* 	0.36 1974	0.27 1995	0.65 1986	0.29 1990	0.29 1974	0.29 1987	0.40 1976	0.46 1966	0.36 1982	0.29 1990	0.33 1983
Butyl (bis-dichloro- phenoxy)acetate	0.42 2682	* 	0.47 2665	0.44 2735	0.85 2694	0.29 2679	0.40 2652	0.29 2680	0.55 2682	0.56 2674	0.33 2677	0.39 2680	0.42 2682
Tetrachlorodibenzo-p- dioxin (µg/g)	0.13	0.20	0.38	0.17	0.11	0.22	0.22	0.30	0.21	0.41	0.22	0.29	(c)

[†]This lot obtained from Dow Chemical Co. (TCN 9463 8155 X052) contains 6976 drums.

(a) Average relative percent and retention time for the respective compounds found in these samples.

Table shows two values for each volatile compound

(b) The relative amount (%) of the compound.

(c) Gas chromatographic retention time (sec).

TABLE XVIII (continued)

(d) In the cases where a compound was detected in only a few of the samples and not in others, the average was calculated by dividing the sum of the values by 12.

(e) Additional TCDD analyses are summarized in Figure 8, p. 64.

*None detected.

**Tentative identification based solely on gas chromatographic retention time.

Drums 249, 250, 251, and 252 contain an unidentified component at an average retention time of 790 sec and average relative percent concentration of 0.14; Drums 251, 254, 255, 256, 257, 258, 275, and 276 contained another unidentified component with retention time of 888 sec and 0.07 retention time and average relative percent concentration. Also, Drum 253 exhibited an unidentified component at 291 sec, relative intensity, 0.13% and Drum 252 was found to contain a component with a retention time of 1502 sec and relative intensity of 1.78%.

TABLE XIX

COMPOSITION OF VARIOUS DRUMS OF HERBICIDE ORANGE IN THE LOT
DESIGNATED ANALYSIS SEQUENCE NUMBER 5 (THOMPSON CO.)†

<u>Compound</u>	<u>Drum Number</u>				<u>Average (a)</u>
	<u>262</u>	<u>263</u>	<u>264</u>	<u>274</u>	
Butanol	(b) 2.1	1.6	1.1	1.8	1.7
	(c) 26	27	27	27	27
Toluene	0.78	0.68	0.51	0.62	0.65
	42	42	43	43	43
Xylenes, ethyl benzene	3.8	3.5	2.6	3.5	3.4
	71	71	72	72	72
Butyl chloride	0.15	0.14	0.10	0.14	0.13
	104	103	104	105	104
Dichlorophenol	0.38	0.35	0.28	0.36	0.34
	257	254	257	259	257
Unknown	0.15	0.14	0.11	0.14	0.14
	291	287	289	293	290
Trichlorophenol	4.7	4.3	3.6	4.3	4.2
	506	501	507	510	506
Dichloromethoxyanisole	0.17	0.16	0.13	0.16	0.16
	599	594	601	603	599
Trichloroanisole	0.99	0.90	0.75	0.91	0.89
	629	625	629	634	629
Dichloromethoxyanisole	0.23	0.21	0.18	0.21	0.21
	712	708	713	717	713
Dichloromethoxyanisole	0.45	0.42	0.31	0.42	0.40
	760	756	761	766	761
Butyl monochlorophenoxyacetate	1.1	0.96	0.78	0.97	0.95
	1060	1057	1062	1066	1061
Butyl dichlorophenoxyacetate	0.36		0.29		0.16 (d)
	1148		1145		1147
Butyl dichlorophenoxyacetate		0.28	0.16	0.30	0.19
		1200, 1212	1205	1209, 1220	1209
Unknown	0.11	0.40		0.39	0.23
	1238	1236		1245	1240

TABLE XIX (continued)

Compound	Drum Number				Average ^(a)
	262	263	264	274	
Butyl dichlorophenoxyacetate	0.21 1267	0.54 1264	0.53 1268	0.52 1276	0.45 1269
Butyl dichlorophenoxyacetate	42.1 1389	41.2 1387	44.9 1406	41.3 1397	42.4 1395
Butyl trichlorophenoxyacetate	0.37 1465	0.36 1464	0.44 1470	0.36 1473	0.38 1468
Butyl trichlorophenoxyacetate	41.1 1605	38.4 1605	40.1 1626	38.3 1619	39.5 1614
Butyl methoxydichlorophenoxyacetate		4.6 1649	2.5 1657	4.6 1659	2.9 ^(d) 1655
Unknown		0.33 2296			0.1 2296
Unknown	0.12 2379				0.03 2379
Butyl-bis-dichlorophenoxyacetate		0.38 2689	0.27 2663		0.16 2676
Tetrachlorodibenzo-p-dioxin ($\mu\text{g/g}$)	(e)	(e)	0.18	(e)	(e)

[†] This lot obtained from Thompson Company (TCN 9463 8155 X012) contains 808 drums.

(a) Average relative percent and retention time for the respective compounds found in these samples.

Table shows two values for each volatile compound.

(b) Relative amount (%) of the compound.

(c) Gas chromatographic retention time of the compound (sec).

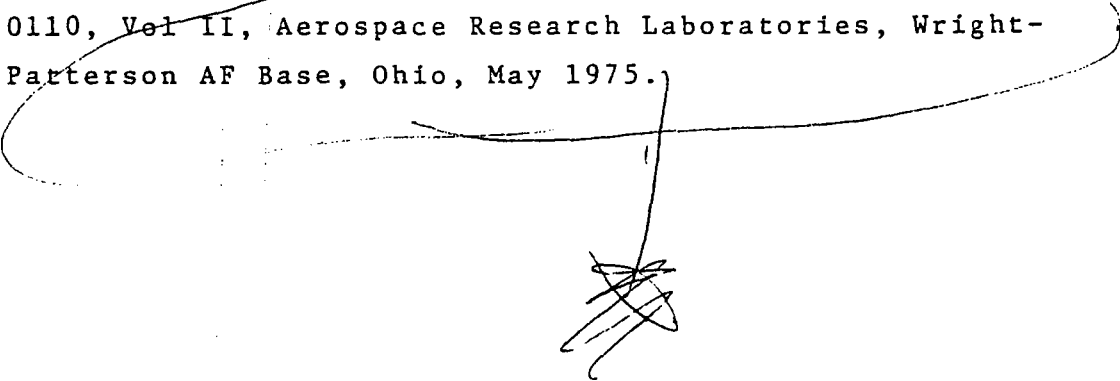
(d) In the case where a compound was detected in only a few of the samples and not in others, the average was calculated by dividing the sum of the values by 4.

(e) Additional TCDD analyses are summarized in Figure 7, p. 63.

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HERCULES POWDER COMPANY

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Mr. Charles Maddock - Legal
Dr. Lemuel C. McGee - Medical
Mr. P. J. Reno - Synthetics
Mr. R. T. Yates - Synthetics
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Wilmington, Delaware
March 26, 1965

TO: Mr. John G. Copeland - Synthetics Department

FROM: John P. Frawley - Medical Department

Report of Meeting with Dow Chemical Company on the
Toxicity of Trichlorophenol Impurities

At the invitation of Mr. V. K. Rowe, Biochemical Research Department, Dow Chemical Company, Mr. C. L. Dunn and the writer (along with representatives of other TCP producers--see letter attached) met in Midland on March 24, 1965, to discuss impurities in TCP.

Mr. Rowe and Dr. Holder of Dow reported that 60 to 70 employees of Dow over the past two years have developed chloracne from exposures to materials in their TCP operation. Chloracne is a disfiguring disease involving blockage and inflammation of the sebaceous glands of the skin, particularly of the face. It is believed to be a systemic disease and requires several years after exposure for the condition to disappear.

Dow has conducted considerable research to identify the cause of this condition and has concluded that several impurities, sometimes present in TCP, are responsible. They have identified one of these impurities which they believe is the principal acnegen--2,3,7,8-tetrachlorodibenzo-p-dioxin. They have developed (and supplied to all attendees) a chemical method for the detection of this material which is sensitive to 1 ppm (gas chromatography and flame ionization).

There was considerable discussion of the clinical aspects of the disease and the toxicological research Dow has conducted. In brief, 2,3,7,8-TCDD has been shown to produce the disease in rabbits at a concentration of 40 ppm after one application of 0.1 ml to the ear, and at a concentration of 0.4 ppm after eight applications. No evidence of the disease has been produced by concentrations up to 20 ppm for a single application and up to 0.1 ppm for twenty-five applications to rabbit ears. The compound has also been demonstrated to be a potent liver toxicant by oral or skin exposure. As little as 0.017 mg/kg is lethal to rabbits by the oral route.

Dow has analyzed commercial samples of TCP of all producers and has found up to 20 ppm of 2,3,7,8-TCDD in some. In finished samples of 2,4,5-T-acid they have found up to 10 ppm. No Hercules sample analyzed contained any significant acnegen. Dow has reduced their TCP capacity and is checking all production to be certain that it contains less than 1 ppm 2,3,7,8-TCDD. Currently, Dow is burying all wastes and contaminated material from their TCP plant since they are

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Mr. John G. Copeland

Page 2

March 26, 1965

not positive that burning will completely destroy the acnegens. Dow's intention in requesting this meeting was to inform all TCP producers of this information so that they can take steps to control the quality of their TCP production. A sample of 2,3,7,8-TCDF for analytical control was supplied to each company.

The Michigan State Department of Health has been consulted on this problem because of labor relations problems. Dow suspects that the Federal Government has become aware of the problem.

I recommend that Hercules take immediate steps to determine whether any acnegens are formed in our TCP process. This should be determined by chemical analyses and biological assays. If any such materials are formed, we should determine the fate of these materials in our plant--whether they are chemically destroyed, burned, or discharged in the waste stream, etc. We should also consider the desirability of constant monitoring of our TCP or 2,4,5-T-acid production by chemical methods to protect against illegitimate claims of acne from users of our 2,4,5-T products.

John G. Copeland

JPC/eww

18879



Mr. J. C. Copeland, Jr.

• 2 •

March 26, 1968

The chief toxic impurity identified by Dow is 2,3,7,8-tetrachloro-*p*-dicoumarin:



Acute oral LD₅₀ to rabbits:
17 micrograms/Kg body wt.
(extremely toxic)

RECEIVED (12) 0 5 9 0

There is evidence that the 1,3,7,8 isomer and other closely related toxic compounds may also be present, although in smaller quantities. As little as four micrograms applied in 0.1 ml benzene to the ear of a test rabbit will give a characteristic skin response (folliculitis). Multiple applications (up to 25) at daily intervals show a no-folliculitis-effect level of 100 parts per billion. In addition to the skin effect, liver damage is severe, and a no-effect level based on liver response has not yet been established. Even vigorous washing of the skin fifteen minutes after application will not prevent damage, and may possibly enhance absorption of the material. There is some evidence that it is systemic.

Analytical method for the detection of the impurities is based on gas chromatography. Using a flame ionization detector, Dow has established lower detection limits of 10 p.p.m. in the unseparable oils from 2,4,8-TCP, and 1 p.p.m. in 2,4,9-TCP, 2,4,5-T acid, or 2,4,5-TP acid. It is likely that the method can be further refined to give even lower limits of detection. Upon our request, an analytical reference sample of 2,3,7,8-tetrachlorodibenzo-p-dioxin was furnished by Dow.

Plant waste from the TCP process in the Dow operation is now being encapsulated and buried.

I would like to discuss this matter with you at an early time.

E. L. Dunn

CLD:kn
AMch.

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On March 24 Dr. J. P. Frawley and I attended a meeting at the Dow Chemical Company Biochemical Research Laboratory at the invitation of Mr. V. K. Rowe, Assistant Director of the laboratory. At that meeting we were informed of Dow's findings relating to highly toxic impurities that may occur in 2,4,5-trichlorophenol. Methods for detecting these impurities in 2,4,5-trichlorophenol and products such as 2,4,5-T were also given.

Dow discovered that a change in their manufacturing process caused the appearance of chloroacene in their trichlorophenol. Plant personnel have shown mild to severe cases of chloroacene as a consequence of exposure to small amounts of tars from the process. Recovery from chloroacene may require several years, there is no effective therapy. Since diagnosing the cause, Dow has modified its process and has been operating without incident for the past five months.

Dow says that their examination of their own and competitors 2,4,5-T products shows that some may contain what they term "surprisingly high" amounts of the toxic impurities. Their analysis of Hercules 2,4,5-T has given a low value for these toxic impurities. In view of the serious problems that can arise from the presence of even minute quantities of such impurities, I recommend that a program designed to examine and test current production of trichlorophenol and TCP process waste be started, and that a system of sample retention and periodic testing of TCP and/or 2,4,5-T be set up for future production.



HO1327

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2017

HERCULES POWER COMPANY

TO: Mr. J. C. Copeland, Jr.
FROM: C. L. Dunn

cc:

Dr. R. S. George
Dr. R. B. Scott
Mr. E. S. P. Bellinger
Mr. J. M. Eagan
Mr. R. T. Yates
Mr. J. M. Neal
Dr. J. P. Fawley - Medical
Mr. J. C. Kumbel - Legal
Miss Jan Hestler

Wilmington, Delaware
March 26, 1965

Highly Toxic Impurities in 2,4,3-Trichlorophenol

DOW

DOW CHEMICAL U.S.A.

AN OPERATING UNIT OF THE DOW CHEMICAL COMPANY

PURCHASING DEPARTMENT

2030 DOW CENTER MIDLAND, MICH. 48660

PURCHASE ORDER/RELEASE

SUPPLIER	Vertac, Inc. Suite 2414 5100 Poplar Avenue Memphis, Tenn. 38137 Attn: Mr. Wilkerson				PURCHASE ORDER NO. US-1418542	
	SHIP TO: Jacksonville, Fla.				AGREEMENT NO.	
SHIP TO	TERMS: Net 30				DATE: 1-17-78	
	SHIP TO: by and Jan 1978				DATE: 1-17-78	
SHIP TO	DOW CHEMICAL INTERNATIONAL P.A.S. U.S. PORT (Will advise port)				ACKNOWLEDGMENT AND INVOICING INFORMATION	
	NOT APPLICABLE - FOR EXPORT				ATTN: J. A. Mattle	
ITEM	PRICE/UNIT OF PURCHASE	QUANTITY IN UNITS OF PURCHASE	UNIT OF PURCH	DOW CROSS AND CODE	DESCRIPTION	
A	\$1170/lb.	45	M.T.	072-917900	Trichlorophenoxy Acetic Acid Specifications: Assay 98.0% min Free phenol 0.5 Pct. max Dioxin 1.0 Pct. max NaCl 1.0 Pct. max Packaging: A) 50 lb. bags or pallets - shrinkwrapped B) 25 lb. bags - 148-60292/Cat. 1	

Feb - Sep 1978

March 30, 1973

CERTIFIED AIR MAIL

Environmental Protection Agency
Pesticides Office
Criteria and Evaluation Division
Washington, D. C. 20250

Attention: Mr. Carroll W. Collier
Chief Chemist
Chemistry Branch

Gentlemen:

Re: Your letter of March 16, 1973
requesting information on "dioxin" content of
Transvaal 2,4,5-T Butyl Ester EPA Reg. No. 11687-31 and
Transvaal 2,4,5-T Low Volatile Ester EPA Reg. No. 11667-33

The subject ester products are manufactured from the appropriate purchased alcohols and 2,4,5-T acid of our plant production. The 2,4,5-T acid is produced from the coupling of monochloro-acetic acid and 2,4,5-Trichlorophenol produced in our plant.

1. The "dioxin" with which we are concerned is 2,3,7,8-tetrachloro-dibenzo-p-dioxin, since it is the most likely "dioxin" to be expected in 2,4,5-T acid. Accordingly, we examine our 2,4,5-T acid production.

The level of 2,3,7,8-TCDD found in our 2,4,5-T acid ranges from amounts classed as undetected to a high of 2 ppm as determined in our laboratory. The average amount found is below 1 ppm.

Since the operating conditions employed to manufacture our esters involves relatively lower temperatures than those which are necessary for the generation of "dioxin" from ortho-substituted chlorophenols in alkaline media, and employ an acid catalyst, we do not routinely examine our esters for dioxin content. Samples of esters which we have examined from time to time have yielded results which range from "undetected" to a high of 1.5 ppm.

2. The analytical procedure which we use is based upon that published by C. A. Elvidge (THE ANALYST, Oct. 1971, Vol. 96, pp. 721-727) for the analysis of esters, formulated products and free acid.

NOTE: REQUISITIONER TO FILL IN AREAS WITH CORNER SIGNALS IF APPLICABLE TO THIS ORDER

 New U.

V E N D O R	871320004		SUGGESTED OR LAST VENDOR IF KNOWN Transroll Inc. Attn Mr. M.F. Wilkerson Suite 2414 5100 Poplar Ave. Memphis, Tenn 38137		LAST P.O. NO.		REQUISITION NO. 08227 923942 STICK P.O. NUMBER HERE	
	DOW CHEMICAL U.S.A.		☐ CHECK FOR EXTRA EXPEDITING This means that the Requisition Approver AUTHORIZES additional charges for Premium Follow-up, Higher price, Premium freight, and/or any other special methods to meet requested delivery date.		REQUISITIONED BY BE Dersnah ADDITIONAL COPIES TO C Prior G. LECHONE R. Russell		PHONE 489 489 2030	
S H I P T O	ATTENTION OF CLARE PRIOR CONFIRMING CFO. To Mr. M.F. Wilkerson 10-23-77		BLDG. 489 DOOR		DATE 10-28-77		SHIP TO PHONE 6-2092 REQUISITION DATA	
	SHIPPING INFORMATION F.O.B. POINT Jacksonville Ark		FREIGHT TERMS Collect		TAX CODE 1		DATE REQUIRED 2030	
M I S C.	SHIP VIA Rail SSN 5500, CNA CFO		PAYMENT TERMS N30		SHIP TO ARRIVE 12-1-77		WORK ORDER 170 71700	
	Truck - IHFS						AUTH. NO. 000	
I T E M	PRICE/UNIT OF PURCHASE	% DIS-COUNT	QUANTITY	UNIT OF PURCHASE	DOW CLASS & CODE	DESCRIPTION		
	125		123000	LB.	072-907900	TRICHLOROPHENOXY ACETIC ACID (2,4,5T ACID)		
18887						SPECS:		
						ASSAY 98.0% MINIMUM		
						FREE PHENOLS 0.5% MAXIMUM		
						DIOXIN 1/2 0.1 PPM		
						MOISTURE 1.0% MAXIMUM		
						NAEL 19. MAX		
						208090NW		
- ROUTING NOTICE - AFTER OBTAINING NECESSARY DEPARTMENTAL APPROVAL PUT REQUISITION IN PLANT MAIL. NO ENVELOPE REQUIRED.						APPROVED BY BE Dersnah		
						* APPROVAL INCLUDES ASSURANCE THAT THE ORDERED MATERIAL HAS BEEN CHECKED AND MEETS APPROVED STANDARDS FOR: 1. RADIATION SOURCES 2. NOISE CONTROL 4. INDUSTRIAL HYGIENE CONTROL		

TRANSVAAL, INC.

Information Regarding Products Manufactured

- A. The phenoxy herbicides, 2,4-D, 2,4,5-T, 2,4-DP, silvex (2,4,5-TP), and related salts and esters, are called selective herbicides which are widely used in crop production and in the careful management of forest, rangeland and industrial, urban and aquatic sites. They each kill plants by causing malfunctions in plant growth processes. Broad-leaved plants are generally susceptible to the phenoxy herbicides. Most grasses, coniferous trees and certain legumes are relatively resistant to their action.

The phenoxy herbicides, while predominantly toxic to green plants, are much less toxic to birds, fish, insects, mammals, reptiles, shellfish, worms, fungi, and bacteria. When properly used, they do not occur in soils and water at levels which would harm animals and micro-organisms. They do not concentrate in food chains and do not persist from year to year in croplands. They are detected only rarely in food and, when so found, are present only in insignificant amounts.

A highly poisonous substance, a kind of dioxin called TCDD (short for the compound 2,3,7,8-tetrachlorodibenzo-p-dioxin), is an unavoidable contaminant of commercial supplies of 2,4,5-T and silvex (2,4,5-TP). The amount present in currently produced formulations of 2,4,5-T and silvex, less than 0.1 part per million, is not enough to alter the toxicological properties of these preparations nor to affect plants or animals in the environment or to endanger human life.

The phenoxy herbicides are widely used because they are more efficient and usually less hazardous and less injurious to the environment than alternative methods. The use of such chemicals is a factor in reducing the cost of agricultural crops and their use in forest, rangeland and non-crop situations provides additional savings.

- B. Dalapon, the name for technical 2,2-dichloropropionic acid, is used as the sodium salt in water solution for the control of annual and perennial grasses. It kills grasses by absorption through roots and leaves causing malfunctions of growth. While it is not readily degraded in plants, it leaches into soil and is rapidly and completely broken down by microbial action.

March 11, 1976

Mr. Jarrell Southall
Director, Air Division
State of Arkansas
Department of Pollution Control and Ecology
3001 National Drive
Little Rock, AR 72209

Dear Mr. Southall:

Enclosed with this letter are several pieces of information about the raw materials and products manufactured by Transvaal, Inc.

Rather than attempt to write a "white paper", which might overlook something, my choice has been to Xerox copy some published information with respect to the materials.

The report entitled "The Phenoxy Herbicides" recently prepared by the Council for Agricultural Science and Technology (CAST) provides a general discussion. These pages are supplemented by material on individual phenoxy herbicides taken from "Herbicide Handbook of the Weed Science Society of America", Third Edition, 1974.

Information on the various chemicals used in the manufacture of products at this plant is reproduced from "Dangerous Properties of Industrial Materials" by N. Irving Sax, Fourth Edition, 1975 (Van Nostrand Reinhold Company). Also included is a copy of our method for the determination of TCDD in 2,4,5-T acid.

After you have had an opportunity to go over this material, and especially if more information is desired, we would appreciate discussing any or all of it with you at your convenience.

With respect to 2,4,5-T, a report by J. Robert Hasness of Transvaal, Inc. and some information from Weeds Today and Farm Chemicals should be of interest.

18886

Mr. Jarrell Southall
Department of Pollution Control
and Ecology

March 15, 1976
Page 2

In my opinion much "scare head" information has been extant about TCDD and the use of 2,4,5-T. A report from the National Academy of Sciences states in conclusion that:

"The Committee could find no conclusive evidence of association between exposure to herbicides and birth defects in humans. Available records of two major Saigon hospitals and evaluation of records in a third, as far as they go, showed no consistent pattern of association between rates of congenital malformations and annual amounts of herbicides sprayed. The Committee recognizes however that the material is not adequate for definite conclusions."

It is of interest to note in this regard that there were no reports of chloracne from persons interviewed by the Committee, although qualified medical pathologists who have studied TCDD and chloracne believe that the first symptoms resulting from exposure to TCDD by humans is the manifestation of chloracne on exposed portions of the body.

Sincerely,

TRANSVAAL, INC.

A. E. Sidwell
Director of Research, Emeritus

AES:ew

Enclosures (6)

18887



INTERNAL CORRESPONDENCE

0000103

DATE: December 12, 1984

TO: ALL VERTAC EMPLOYEES

FROM: C. P. Bomar, Jr.

CC:

SUBJECT: Year End Summary

The same excellent momentum and effort which allowed us to meet our Profit Plan for 1983 set the stage for Vertac's continued success in 1984. We have made hard fought but sustained progress throughout the year, and I want to outline for you some of the obstacles and opportunities which we have faced together and some of the accomplishments which we have made.

PHENOXYIES

Vertac's 1983 acquisition of Dow Chemical Company's formulated phenoxy business gave us the opportunity to capture a dominant phenoxy market share in 1984, although other companies seeking to capture the same market share created lower than hoped for prices. When Dow failed to furnish sufficient technical phenoxyies to supply our customers, we reacted immediately by supplying the necessary funds to rehabilitate and restart the Jacksonville plant and bring it up to full capacity. In fact, within three months after this effort began, we were setting new production records. The exceptional efforts and teamwork at Jacksonville helped us to avert a major marketing disaster and maintain Vertac's credibility as a principal supplier of 2,4-D products in the United States.

POTASSIUM NITRATE

We have had an almost unprecedented opportunity to excel in the area of potassium nitrate and chlorine. Both of these products have been sold out since the beginning of the year, and we have been able to increase prices to very attractive levels. The potassium nitrate complex has made an excellent contribution this year; and if we had been able to produce at past production levels, we could have substantially exceeded our Profit Plan for this year. Unfortunately, production for the first half of the year was only average; and we have lost a month's production in the second half due to plant problems, creating difficulties for many of our customers. We hope that we have solved the problems associated with this unit and look forward to taking advantage of this unique opportunity in future months.

PROPANIL AND CUSTOM MANUFACTURING

Many of you are aware of our 1981 litigation which allowed Vertac to benefit from the Rohm and Haas propanil patent. This patent was overturned by the Courts in 1984, resulting in a significant drop in propanil pricing

18808

and reducing our profit margin by a third. Fortunately, this loss in profits has been offset by the addition of other important contract manufacturing projects at West Helena and Vicksburg, and we expect to add several new custom projects in the next few months.

EPA LITIGATION

Another major item for Vertac was the EPA litigation over Jacksonville. Vertac has spent millions of dollars and several years of effort to correct past problems at the site and, in 1984, set forth a proposed final remedial plan based on the last two years of studies. Although EPA had earlier approved this plan in principle, a change in the bureaucratic structure caused a reversal of EPA's position. This was not because our plan was inadequate scientifically, but simply because they felt it to be politically desirable to see us spend more money. Vertac challenged EPA in Court and, after a very major battle, won the Court's approval to proceed with our remedial plan. While on the one hand this was a great victory for Vertac, the implementation of the remedial plan is a very costly process which will continue into 1985.

FINANCING

We were successful in increasing Vertac's bank credit line from \$14 million to \$20 million while reducing our interest rates. This additional borrowing power has allowed us to continue to expand our business base and to handle a severe overrun in capital spending at Jacksonville and Vicksburg. The ability to obtain this financing is an example of the renewed confidence in Vertac as a result of our more recent performance.

~~There have been other important achievements too numerous to mention in detail here, including major new advancements in employee safety.~~

While we cannot be certain what our final year-end results will be, we are confident that with good production and continued strong sales in December, we can meet or exceed our 1984 Profit Plan. As I am sure you know by now, there is a direct relationship between profitability and the income and benefits afforded to each of us at Vertac. Accordingly, I am pleased to announce that, effective December 3, we are increasing wages for our hourly employees by six per cent. Further, during the next month we will review the individual performance of our salaried employees (exempt and non-exempt) with the goal of making appropriate merit increases in the three to seven percent range in January. In this action we will be returning almost a fourth of Vertac's 1984 profits to our employees through increased wages and benefits in 1985.

As a member of the Vertac team, I hope you feel pride in the progress which we have made and confidence in our potential for the future. We are constantly seeking out new ventures which will strengthen our present position and further expand our future opportunities. I look forward to informing you as these new ventures are finalized. Meanwhile, please accept our sincerest appreciation for your continued contribution to the success of Vertac and our very best wishes for a Happy Holiday Season and a mutually Prosperous New Year.

CPB:ap

C. F. Boman Jr.
18889



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0000103

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FROM: C. P. Bomar, Jr.

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18890

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CPB:ap

C. F. Bonney Jr.
18891

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THE GOVERNMENT OF
CANADA

FREDERICTON

DEPARTMENT OF HEALTH

MINISTÈRE DE LA SANTÉ

Warm Greetings

WARM WISHES TO THE NEW YEAR

December 17, 1964

Mr. J. H. Tseedale
Chairman
N.B. Electric Power Commission
Fredericton, N.B.

Dear Mr. Tseedale:

*under what
concern was*

You are well aware that there is increasing interest in Canada today over the use of pesticides and herbicides. Many inquiries on this subject come to the Department of Health, and in view of our lack of information your help and advice is needed.

The Minister of Health, The Hon. Georges L. Dumont, C.B., has asked me to arrange a meeting in Fredericton so that the various Departments and Organizations using pesticides and herbicides, or having some jurisdiction over their use, may be brought together for discussions. As it is felt that your Organization would have a valuable contribution to make to the discussions, the attendance of your representative would be greatly appreciated.

While we are not bound by any specific terms of reference, we would like to arrive at recommendations upon which policy could be made. In order to expedite the work of the committee, a prepared outline of your interest in the subject is requested for discussion purposes in committee.

If you would like to assist us at this time, we would be pleased to hear from you as soon as possible, so that our first meeting can be scheduled during the first week of January.

Yours very truly,

Alwyn J. Cameron

Alwyn J. Cameron, P. Eng.
Director
Military Engineering Division

18892



VERTAC CHEMICAL CORPORATION

24th Floor • 5100 Poplar • Memphis, TN 38137 • 901-767-6851

TELEX 53927

MEMORANDUM

To: All Jacksonville Plant Employees

August 11, 1983

Subject: Shift in Production Emphasis

Effective September 1, 1983, we will shift our emphasis at Jacksonville from the operation of the primary 2,4-D processing unit to the full-scale utilization of the 2,4-D waste recovery unit. This will necessitate a shutdown of certain production facilities associated with the primary processing unit. Since we are uncertain as to when these facilities will come back into full utilization, some reduction in personnel cannot be avoided. We will utilize as many employees as possible in the operation of the recovery unit and in the research projects which are being transferred to the Jacksonville laboratories. We will give principal consideration to seniority and acquired skills in filling these positions.

In the interim, all hourly employees affected will receive at least two week's notice plus accumulated vacation pay and the following severance pay upon completion of their duties throughout the notice period:

<u>Date of Employment</u>	<u>Amount of Severance</u>
After January 1, 1983	1 week's pay
After January 1, 1978, but prior to January 1, 1983	2 week's pay
Prior to January 1, 1978	3 week's pay

Salaried employees affected will receive severance pay based on age and tenure in accordance with Company policy. Again, in accordance with Company policy, all affected personnel will be asked to take an exit physical.

If your position is to be changed or you are to be affected by this layoff, you will be notified by August 15, 1983.

As you are aware, this plant has come under unwarranted pressure as a result of newspaper sensationalism and distortions which have frightened many citizens. It is our sincere hope that over the next several months we can convince the residents of Jacksonville that Vertac's present and future operations pose no threat to the community so that you can continue your jobs in peace.

To those employees whose layoff cannot be avoided, you have our sincere regrets. We will attempt in every way possible to assist you in locating new employment. When circumstances permit us to increase production levels, we hope that you will want to return to Vertac.

RAG:ap

18893

R. A. Guidi
R. A. Guidi



INTERNAL CORRESPONDENCE

DATE: December 12, 1984

TO: ALL VERTAC EMPLOYEES

FROM: C. P. Bomar, Jr.

CC:

SUBJECT: Year End Summary

The same excellent momentum and effort which allowed us to meet our Profit Plan for 1983 set the stage for Vertac's continued success in 1984. We have made hard fought but sustained progress throughout the year, and I want to outline for you some of the obstacles and opportunities which we have faced together and some of the accomplishments which we have made.

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Many of you are aware of our 1981 litigation which allowed Vertac to benefit from the Rohm and Haas propanil patent. This patent was overturned by the Courts in 1984, resulting in a significant drop in propanil pricing

18894

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ARKANSAS (From SODA)
MOYER V DOW

09

09

ARKANSAS

18837

ATTACHMENT Y



THE DOW CHEMICAL COMPANY

~~September 26, 1967~~

Colonel E. C. Sheed (SAD)
Directorate of Air Force Aerospace Fuels
Kelly Air Force Base, Texas 78241

1953 (2)

Dear Colonel Sheard:

We have been asked to bid on the design, conversion and operation of an 8,000,000 gallon per year "Orange" plant at the Government owned chemical plant at Weldon Spring, Missouri.

This is to inform you that we have advised W. G. Kratz, Colonel, Corps of Engineers in Kansas City, Missouri, that we do not intend to bid on their solicitation No. DCA41-68-R-0001, dated September 7, 1967.

The basic reason for our decision is due to critical factors outlined below:

"The time allotted for submission of bids, September 8, 1967 to October 12, 1967, is not ample for preparation of bids on a project of this magnitude.

"The presentation of alternative design at locations other than Eldon Spring were precluded because of the time allowed for preparation of a responsive bid in answer to your solicitation.

"We would like to sum up some other reasons for not presenting a bid at this time, as follows:

1. The Weldon Spring site, located as it is between the University of Missouri Experimental Farm and the August Busch Reserve, presents too much of a hazard to the plant life in these areas, in case of an accidental release of products from the Orange Plant.
2. The requirement of 13 months start up and full operation in 18 months on the Weldon Spring site appears almost impossible to meet without excessive overtime.
3. The labor situation in the St. Louis area would present too many problems.
4. It would be almost impossible to solve the pollution problems in the area.

C0270802 BATCH 513 15A JUS 0063

1889

ORANGE - 8 Million Gallons/Year
 (Basis: 6.0 million gallons/year estimate dated March 17, 1967)

27,600,000 #/yr. =	2,300,000 #/mo.	(2,000 gal.)	17,000 #/batch
21,000,000 #/yr. =	1,750,000 #/mo.	(2,000 gal.)	20,000 #/batch
20,200,000 #/yr. =	1,685,000 #/mo.	(750 gal.)	2,000 #/batch
26,400,000 #/yr. =	2,200,000 #/mo.	(3,000 gal.)	4,600 #/batch
27,600,000 #/yr. =	2,300,000 #/mo.	(3,000 gal.)	4,600 #/batch
64,500,000 #/yr. =	5,370,000 #/mo.	(4,000 gal.)	16,500 #/batch

ors for 8 million gallons Orange:

Basis: Government Specifications - by volume

4 million gals. Bu-D @ 1.245 sp. gr. = 10.35#/gal.

4 million gals. Bu-T @ 1.325 sp. gr. = 11.02#/gal.

$$D = 1.245 \times 8.33 \times 4,000,000 = 41,500,000 \text{ #/year Butyl "D" Ester}$$

$$T = 1.325 \times 8.33 \times 4,000,000 = 44,200,000 \text{ #/year Butyl "T" Ester}$$

$$\underline{85,700,000 \text{ #/year Total Mixed Ester}}$$

	<u>6MM</u>		<u>8MM</u>
Ester	64,500,000 # mixed	x 1.328	85,700,000 # mixed
"D" Acid	26,400,000 # (2.44)	=	$\frac{85,700,000}{2.44} = 35,100,000 \text{ #/yr.}$
"T" Acid	27,600,000 # (2.34)	=	$\frac{85,700,000}{2.34} = 36,600,000 \text{ #/yr.}$

$$\underline{54,000,000 \text{ #}}$$

$$\underline{71,700,000 \text{ #/yr.}}$$

Total "D" and "T" Acid

Ester 85,700,000 #/year mixed 50/50 by weight.
 Acid 71,700,000 #/year mixed "D" and "T".
 D 35,100,000 #/year
 T 36,600,000 #/year

$$TCP = 20,200,000 \text{ #} \times \frac{36,600,000 \text{ # T @ } 8 M^2}{27,600,000 \text{ # T @ } 6 M^2} = \underline{\underline{26,700,000 \text{ #/year TCP}}}$$

$$DCP = 21,200,000 \text{ #} \times \frac{35,100,000 \text{ # D @ } 8 M^2}{26,400,000 \text{ # D @ } 6 M^2} = \underline{\underline{28,200,000 \text{ #/year DCP}}}$$

$$MCA = 27,600,000 \text{ #} \times \frac{71,700,000 \text{ # Total Acid (8M}^2\text{)}}{54,000,000 \text{ # Total (6M}^2\text{)}} = \underline{\underline{36,600,000 \text{ #/year MCA}}}$$

Orange - MCA

$$36,600,000 \text{ \#/yr.} = 3,050,000 \text{ \#/mo.} = 102,000 \text{ \#/day} = 4,250 \text{ \#/hr.}$$

$$\frac{3,050,000 \text{ \#MCA/mo.}}{17,000 \text{ \# MCA/batch}} = 180 \text{ Batches/month}$$

$$\frac{720 \text{ hrs./mo.}}{65 \text{ hrs./batch/unit}} = 11 \text{ Batches/Unit/Month}$$

Chlorinators:	$\frac{180 \text{ Batches/Month}}{11 \text{ Batch/Unit/Month}}$	=	16.4 Units on MCA
@ 2,000 gallons			
(@ 4,000 gallons		=	8 Units?)

- 2 - Rows of 8-2,000 gallon glass-lined, jacketed agitated reactors.
- 7 - Chlorinating each bank - 1 prechlorinating.
- 2 - Weigh tanks - acetic acid with plate coils, glass-lined.
- 16 - Primary condensers.
- 16 - Secondary condensers.
- 2 - Weigh tanks - phosphorous trichloride - stainless.
- 2 - Chillers - one for each chlorinator bank.
- 8 - Pumps - 1 for each 2 chlorinators.
- 2 - Absorbers - 1 for each 8 chlorinator row.

Orange - DCP

$$28,200,000 \text{ \#/yr.} = 2,350,000 \text{ \#/mo.} = 78,200 \text{ \#/day} = 3,260 \text{ \#/hr.}$$

$$\frac{2,350,000 \text{ \# DCP/mo.}}{20,000 \text{ \# DCP/batch}} = 117 \text{ Batches/month.}$$

$$\frac{720 \text{ Hrs./mo.}}{60 \text{ Hrs./Batch/Unit}} = 12 \text{ Batches/Unit/Month}$$

$$\frac{117 \text{ Batches/Month}}{12 \text{ Batches/Unit/Month}} = 9.8 \text{ -- Say 10 Units on DCP @ 2,000 gal.}$$

- 2 - Rows of 5-2,000 gal. glass-lined, jacketed, agitated reactors.
- 2 - Absorbers - 1 for each bank of 5 chlorinators with temperature controls on makeup water.
- 5 - Pumps - 1 for each 2 chlorinators.
- 2 - Chillers - for chilled tempered jacket water, 1 for each 5 units.
Also chilled tempered water on absorber condensers (2).
- 2 - Weigh tanks - 2,000 gals. glass-lined with plate coil vent tied into absorbers.

Orange - Chlorination - Outside Tanks

Chlorine: 58,500,000 #Cl₂/yr. = 4,880,000 #/mo. = 162,000 #/day = 6,800 #/hr.

$$\frac{162,000}{2,000} = 81 \text{ tons/day} = \frac{81}{55} = 1.5 \text{ cars/day} \quad (55 \text{ tons/car})$$

Use railcars to store chlorine

Vaporizers: 8 - 2 for each of 4 chlorinator banks

Phenol: 1,500,000 #/mo. = 17.3 cars/mo. @ 10,000 gal. each
4 - 12,500 gal.-glass Chemstor storage tanks - (50,000 gal.)

Acetic: 1,700,000 to 2,000,000 #/mo. = 25.3 cars/mo. @ 10,000 gal. each
(Mix) 6 - 12,500 gal. - (75,000 gal.)

DCP: 28,200,000 #/yr. = 2,350,000 #/mo. = 78,200 #/day = 3,260 #/hr.
(11.6 #/gal.) 2,430,000 gal./yr. = 202,500 gal./mo. = 6,750 gal./day = 280 gal./hr.
4 - 12,500 gal.-glass lined tanks (50,000 gal. = 7.4 days)

MCA: 36,600,000 #/yr. = 3,050,000 #/mo. = 102,000 #/day = 4,250 #/hr.
(11.5 #/gal.) 3,180,000 gal./yr. = 265,000 gal./mo. = 8,800 gal./day = 366 gal./hr.
4 - 12,500 gal.-glass lined tanks (50,000 gal. = 5.7 days)

HCl: 20° (32%) - Average from MCA = 122,000 #/day
" " DCP = 105,000 #/day
 $\frac{227,000 \text{ #/day}}{9.7} = 23,500 \text{ gal./day}$ containing phenolics, etc.

240,000 gal. (6 - 40,000 gal) Rubber Lined Tanks

125,000 gal. (10 - 12,500 gal.) Glass Lined Tanks

32% HCl purchased = 415,000 gals./yr. = 415 T/C's = 1.1 T/C per day

Acetic Anhydride:

Phosphorus Trichloride:

Brine: For Secondary MCA condensers
2 - 4,000 gal. wood (1 - for each chiller)

Orange - Chlorination - Outside Tanks (Cont'd.)

Tempered water: For phenol condensers

2 - 4,000 gal. wood (1 - for each tempered system)

Unloading Stations - Chlorination

3 - Chlorine - Tank car
1 - Acetic - Tank car
1 - Phenol - Tank car
1 - HCl - Tank Car
1 - Acetic anhydride tank truck

Orange - TCP

$$26,700,000\#/yr. = 2,250,000\#/mo. = 74,500\#/day = 3,100\#/hr.$$

$$\frac{2,250,000\#/mo.}{2,000\#/batch} = 1,110 \text{ Batches/month} = \underline{37.2 \text{ batches/day}}$$

$$\frac{720 \text{ Hrs./Mo.}}{8 \text{ Hrs./batch/unit}} = 90 \text{ batches/unit/Mo.}$$

$$\text{Dechlorinators: } \frac{1,110 \text{ batches/Mo.}}{90 \text{ batches/unit/Mo.}} = 12.4 \text{ units on TCP}$$

14 - Dechlorinators @ 750 Gal.-nickel clad, jacketed, agitated
Shell: 350 psig. oper. press; Jacket: 150 psig. oper. press.
3 Rows - 4 dechlorinators - barricaded with rupture disc vent liner
TCB (Ground) = 88,000#/day = 440 Drums @ 200# = 147/shift

$$\text{NaOH (Flake)} = 53,000\#/day = 110 \text{ drums @ } 400\# \\ 110 \text{ drums @ } 100\#$$

MeOH (fresh make-up) = 5,400 Gal./day

2-25,000 Gal. Alcohol Storage -

Drum handling facilities for dechlorinator charging.

3 - 10,000 Gal. NaTCP (dirty) Storage -304 S/S, agitated w/coil.

2 Hold Tanks - 6,000 Gals. with vent condensers

2 Stills - 3,000 Gal. Monel clad, agitated, jacketed (150 psig)
still pots - 316 S/S column

2 Still condensers

1 Alcohol Hold Tank - 304 S/S

Orange - Acid

2,4-D

35,100,000 #/yr.
2,930,000 #/mo.
97,500 #/day
32,500 #/shift
4,050 #/hr.

2,4,5-T

36,600,000 #/yr.
3,050,000 #/mo.
102,000 #/day
33,800 #/shift
4,230 #/hr.

- 10 - 3,000 Gal. brick lined, agitated (Titanium) Reactors
5 Units on D and 5 Units on T - normally
Weigh tank and piping arranged for flexibility
for ratio of units on D and T.
Basis : Approx. 95% operating time.
- 8 - 4,000 Gal. Glass Lined, agitated, jacketed crystallizers
2 - Refrigeration units -
2 - 10,000 Gal. Slurry Hold Tanks - heavy duty - agitated
5 - 6,000 Gal. Slurry Feed Tanks - heavy duty - agitated - jacketed
4 - Brine Extraction Column (1 for D and 1 for T) Haveg
4 - Brine Storage Tanks - 10,000 Gal. Haveg
Independent weigh tanks for each reactor
- 10 - NaTCP weigh tanks - 304 S/S
10 - DCP weigh tanks - glass lined - jacketed
10 - MCA weigh tanks - glass lined - jacketed
10 - caustic weigh tanks - steel
6 - recycle liquor measuring tanks - glass lined 2,000 gal.
6 - HCL measuring tanks - Haveg
2 - brine solvent separators - 1,000 Gal. - glass lined
10 - Centrifuges 48 in. - 316L S/S, Kynar Coated
5 - Blenders
4 - Conveyor/Dryers (for flexibility between D&T
316 SS/ 2,000 - 2,500 #/hour
5 - Filtrate Tanks (1 for each 2 centrifuges)
- 400 - Tote Bins (97,500 #/day x 7 = 682,000 #/Wk. 195 Tote Bins @ 3,500 #)
(102,000 #/day x 7 = 714,000 #/Wk. = 204 Tote Bins @ 3,500 #)
Aluminum - 90 cu. ft. capacity

Orange - Ester

85,700,000 #/yr. $\neq$ 7,140,000 #/mo. $\neq$ 238,000 #/day $\neq$ 9,900 #/hr.
@ 330 days/yr. 265,000 #/day $\neq$ 11,000 #/hr.

- 10 - 4,000 gal. 316 L S/S, agitated, jacketed, vacuum esterifiers
- 5 - 4,000 gal. 316 L S/S " " preesterifiers
- 2 - 4,000 gal. Glassed lined agitated, jacketed recovered acid esterifiers
- 2 - Vacuum systems (for each 5 esterifiers)
- 10 - Karbate esterifier condensers
- 2 - 30,000 gal. Butanol storage tank
- 265,000 #/day BuE-Mixed
- 132,500 #/day Bu-T ester = 35,400
- 132,500 #/day Bu-D ester = 35,000
- 70,400 #n-Butanol/day

$$\frac{70,400}{6.76} = 10,500 \text{ gals. n-Butanol/day}$$

- 5 - 10,000 gal. Spent Butanol Storage - Steel (1 for each 2 esterifiers)
- 4 - 20,000 gal. - Butyl D Ester Storage - steel w/coil
- 4 - 20,000 gal. - Butyl T Ester Storage - steel w/coil

Orange - Solvent Clean Up

NaTCP clean up 4 - 6,000 Gal. agitated tanks
NaTCP clean 6- 10,000 Gal. agitated w/plate coils

2 - D - Clean Solvent	15,000 Gal. -
2 - D - Spent Solvent	15,000 Gal. -
2 - T - Clean Solvent	15,000 Gal. -
2 - T - Spent Solvent	15,000 Gal. -
4 - Separator - Decanters	6,000 Gal. -
4 - Clean Up Tanks	6,000 Gal. agitated - heavy duty

Unloading Stations

1 - Toluene
1 - Methanol
1 - Butanol

18907

Orange - Waste

Basis: 85,700,000 # mixed D and T Butyl ester/year

61,000,000 # NaOH (100%)/yr.

NaCl - 90,000,000 # NaCl/yr.

7,500,000 # NaCl/mo.

250,000 # NaCl/day

10,400 # NaCl/hr (5.4 tons/hr.)

Glycollic Acid

5,500,000 #/yr. = 458,000 #/mo. = 15,300 #/day = 638 #/hr.

Oxalic Acid

129,000 #/yr. = 10,800 #/mo. = 360 #/day = 15 #/hr.

Acetic Acid

1,100,000 #/yr. = 91,800 #/mo. = 3,050 #/day = 137 #/hr.

plus all acetyls carried from plant generated HCl.

Still Bottoms - Toluene Recovery Still

1,530,000 #/yr. = 128,000 #/mo. = 4,250 #/day = 177 #/hr.

Still Bottoms - Methanol Still

990,000 #/yr. = 82,500 #/mo. = 2,750 #/day = 115 #/hr.

Combined Bottoms: 7,000 #/day = 292 #/hr.

Approximate composition

35% Toluene

32.5% TCP Anisole

13.0% Trichlorobenzene

19.5% Tetrachlorobenzene

This would generate about 3,200 #/day HCl.

By A. E. Sidwell

3/18/67

18908

Orange - Utilities

	<u>Required for Orange - 8.0</u>	<u>Available at Weldon Spring</u>
Steam (Salt evaporation not included)	200,000 lb./hr.	216,000 lb./hr. (240,000 lb./hr max.)
Air	1,500 CFM	2,000 CFM
Water - make up	10,000,000 Gal./Mo.	10,000,000 Gal./day (wells-treated)
Water - Cooling tower	20,000 GPM	
Electric	9,000 KVA	
Gas		Liquid Propane
Inert Gas	20,000 CFH	Not Available

18819

Orange - Services (Existing at Weldon Spring, Missouri)

Railroads - existing, may need minor additions

Roads - adequate

Office - adequate

Cafeteria - adequate

Shop - adequate

Storeroom - adequate

Warehouse - existing, may be too small and not convenient to process.

Laboratory - existing but not available for Orange

Locker - Change Facility - adequate

TRANSVAAL, INC.

THE GAS CHROMATOGRAPHIC DETERMINATION
OF 2,3,7,8-TETRACHLORODIBENZO-P-DIOXIN
IN 2,4,5-TRICHLOROPHENOXYACETIC ACID (2,4,5-T),
2,4,5-T BUTYL ESTER, AND 2,4,5-T 2-ETHYLHEXYL ESTER

Edward M. Harris

August 13, 1974

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DIGEST

Objective

This is the report of an investigation to determine the 2,3,7,8-Tetrachlorodibenzo-p-dioxin (TCDD) content of 2,4,5-T and 2,4,5-T butyl and 2-ethylhexyl esters manufactured by Transvaal, Inc. at Jacksonville, Arkansas.

The compound of interest, TCDD, may be produced as a by-product in the manufacture of 2,4,5-T, and is of significance due to its, alleged high toxicity to humans.

The objective of this investigation was to determine the amount of TCDD produced in the 2,4,5-T and its butyl and 2-ethylhexyl esters manufactured by Transvaal, Inc.

Results and Conclusions

The analytical method developed in this investigation was based on methods by Dow Chemical Company, Hercules Incorporated, and D. A. Elvidge.¹

Samples of 2,4,5-T acid were dissolved in aqueous acetonitrile and extracted with hexane. The extracts were concentrated and then analyzed for TCDD by gas chromatography using a flame ionization detector.

Analysis of samples of esters involved a preliminary saponification procedure followed by extraction of TCDD from aqueous dimethylformamide

¹ Elvidge, D. A., Analyst, 96, 721-727 (1971).

with hexane. The concentrated hexane extracts of the esters were analyzed by gas chromatography using an electron capture detector.

None of the samples of 2,4,5-T acid and 2,4,5-T esters examined contained TCDD at a concentration greater than 0.1 ppm.

EXPERIMENTAL SECTION

Reagents

n-Hexane

Quality suitable for pesticide residue analyses. (Burdick and Jackson Laboratories, Muskegon, Michigan)

Acetonitrile

Quality suitable for pesticide residue analyses. (Matheson, Coleman, and Bell)

Aqueous Acetonitrile

Solution of 90% acetonitrile and 10% distilled water by volume.

Equilibrated n-Hexane

n-Hexane saturated with the aqueous acetonitrile solvent.

Diethyl Ether

Quality suitable for pesticide residue analyses. (Burdick and Jackson Laboratories, Muskegon, Michigan)

<u>Chloroform</u>	Quality suitable for pesticide residue analyses. (Matheson, Coleman, and Bell)
<u>Ethanol</u>	Reagent alcohol (Anderson Laboratories, Ft. Worth, Texas)
<u>Methanol</u>	Anhydrous, Reagent grade (Mallinckrodt)
<u>25% Ether-Hexane</u>	
<u>Chloroform-Ether, 1:1</u>	
<u>Double Distilled Water</u>	
<u>N,N-Dimethylformamide</u>	A. C. S. Reagent Grade (Baker and Adamson)
<u>Methylene Chloride</u>	Spectroquality Reagent (Matheson, Coleman, and Bell)
<u>Sodium Sulfate</u>	Anhydrous, Granular, A. C. S. Reagent Grade (Mallinckrodt)
<u>Potassium Hydroxide</u>	Reagent grade pellets (Mallinckrodt)
<u>Ammonium Hydroxide: Water Solutions</u>	1:1 and 1:2 by volume (using 25% NH_4OH and double distilled water)
<u>Aluminum Oxide</u>	Woelm, basic (cationotropic), Activity Grade I
<u>Florisil</u>	PR Grade, 60/100 mesh (Supelco, Inc.)

TCDD Reference Material - Obtained from D. Firestone, U. S. Food and Drug Administration.

TCDD Standard Solution: 2.5 milligrams of TCDD were dissolved, with warming, in 10 ml of diethyl ether contained in a 25 ml volumetric flask and adjusted to volume with ether. Dilutions were made, with

25% ether-hexane to yield solutions containing TCDD at concentrations of 20 ng per microliter and 0.2 ng per microliter.

Apparatus

All glassware was cleaned in chromic-sulfuric acid mixture, washed with water, dried and rinsed with hexane prior to use.

A Tracor MT-220 gas chromatograph, equipped with a flame ionization detector, an electron capture detector (with a 10 mCi ^{63}Ni source), a 1-mV Honeywell Elektronik 194 Recorder, and an Infotronics automatic digital integrator, was used.

Chromatographic Columns - Two six-foot glass columns of 2 mm i.d. were packed with 3 percent OV-17 (Pierce Chemical Company) on 80/100 mesh Chromosorb G (Johns-Manville Company) and conditioned at 250° C. for 24 hours before use. One column was attached to the flame ionization detector and the other to the electron capture detector.

Operating Conditions

The following operating conditions were used:

(A) For 2,4,5-T:

Detector temperature - 260° C.

Recorder chart speed - 12 inches per hour

Carrier gas - Nitrogen (Prepurified grade)

Column temperature - 200° C.

Injection port temperature - 250° C.

Carrier gas flow rate - 30 ml per minute

Hydrogen flow rate - 60 ml per minute

Air flow rate - 1.2 cu. ft. per minute

Attenuation settings were adjusted to give at least a 25 percent full-scale recorder deflection for an injection of 40 ng 2,3,7,8-TCDD.

(B) For the butyl and 2-ethylhexyl esters: (Electron capture detector):

Detector voltage - 12V

Detector temperature - 280⁰ C.

Chart speed - 12 inches per hour

Carrier gas and purge gas - Nitrogen (Prepurified Grade)

Column temperature - 200⁰ C.

Injection port temperature - 250⁰ C.

Carrier gas flow rate - 30 ml per minute

Purge flow - 20 ml per minute

Attenuation settings were adjusted to give at least a 25 percent full-scale recorder deflection for an injection of 0.4 ng 2,3,7,8-TCDD.

Methods and Procedures

Procedure for Preliminary Treatment of the Sample: (1) For 2,4,5-T:

Extraction: Twenty grams of sample were weighed in a 500 ml. separatory funnel and dissolved in 100 ml of warm aqueous acetonitrile. Then 100 ml of equilibrated hexane were added, and the funnel shaken vigorously for 30 seconds. After the phases separated, the lower phase

(Acetonitrile) was transferred to a second 500 ml funnel. The first 500 ml funnel was swirled to recover traces of acetonitrile adhering to the funnel walls, and these drainings were transferred to the acetonitrile phase. The hexane phase was added to a 1-liter funnel containing 500 ml of distilled water.

The partition step was repeated twice more, using 100 ml of n-hexane each time. The acetonitrile phase was transferred between the two 500 ml funnels and the hexane phase added to the 1-liter funnel after each partition. Following the third partition, the acetonitrile phase was discarded. The three combined hexane phases in the 1-liter funnel were then washed by shaking with distilled water for 30 seconds.

After the phases separated, the aqueous wash was drained off and discarded. The hexane phase was dried by passing it through a four-inch glass funnel containing a small cotton plug and 50 g of anhydrous Na_2SO_4 . The hexane was collected in a 400 ml beaker and the separator was rinsed with several 10 ml washes of hexane. The washes were passed through the funnel to wash the Na_2SO_4 and collected in the same beaker.

The hexane phase was evaporated just to dryness on a steam bath using a gentle stream of dry nitrogen to aid in the evaporation.

Alumina Column Chromatography - A column was prepared in a glass tube, 150 x 10 mm, having a porous glass plug, by filling the tube with ether and adding alumina while gently tapping the tube to release any air bubbles. The alumina was added until it reached a height of 8 cm. The column was then washed with 50 ml of ether, followed by 50 ml of n-hexane.

The residue from the evaporated hexane phase in the extraction step was dissolved in a small volume (about 1-2 ml) of diethyl ether and transferred to the alumina column. The beaker was rinsed with several additional ether washes, and these were added to the column. The column was then eluted with 50 ml of 25% ether-hexane solution.

The ether-hexane fraction was evaporated just to dryness on a steam bath under a gentle stream of dry nitrogen. The residue was quantitatively transferred to a 4 ml screw cap vial, using a mixture of 1:1 Chloroform-Ether to accomplish the transfer. The sample was evaporated just to dryness once more, and the final residue dissolved in 0.5 ml of 25% ether-hexane solution.

Procedure for Preliminary Treatment of the Sample: (2) For 2,4,5-T Esters:

Saponification: About 10 g of ester sample was accurately weighed in a 400 ml beaker and dissolved in 50 ml of ethanol. After the sample was dissolved, 10 g of potassium hydroxide dissolved in a few ml of water were added, followed by the addition of 50 ml of double distilled water. The solution was heated under reflux for three hours, shaking occasionally. The solution was then evaporated on a hot plate until no noticeable odor of butyl or 2-ethylhexyl alcohol was present. The residual solids were dissolved in 100 ml of N,N-dimethylformamide and 200 ml of double distilled water with slight warming and transferred to a 500 ml separatory funnel.

Extraction: The solution was then extracted with 5 x 50 ml portions of n-hexane, the combined extracts being collected in a 500 ml

separatory funnel. The combined hexane extracts were then washed with 60 ml of 1:1 NH_4OH and 30 ml of 1:2 NH_4OH in that order, and finally washed three to five times with 50 ml of double distilled water (until wash water was neutral). The extracts were dried by the addition of 30 g of sodium sulfate to the separatory funnel and the funnel contents swirled and allowed to remain in contact with the sodium sulfate for 30 minutes. The extracts were then filtered through a funnel containing a cotton plug and about 3 g of sodium sulfate into a 600 ml beaker, and evaporated to dryness on a steam bath under a gentle stream of dry nitrogen.

Florisil Column Chromatography: A column was prepared by filling a glass tube, 150 x 10 mm, having a porous glass plug, with n-hexane and adding Florisil while gently tapping to release any air bubbles. The Florisil was added until it reached a height of 8 cm. The column was then washed with 50 ml of n-hexane, followed by 50 ml of 20% methylene chloride-hexane solution.

The residue from the evaporated hexane extracts was dissolved in a small volume (1-2 ml) of n-hexane and transferred to the Florisil column. The beaker was rinsed with several additional hexane washes, and these were added to the column. The column was then eluted with 50 ml of 20% methylene chloride-hexane solution.

The methylene chloride-hexane fraction was evaporated just to dryness on a steam bath under a gentle stream of dry nitrogen. The residue was quantitatively transferred to a 10 ml volumetric flask using the 20% methylene chloride-hexane solution to accomplish the transfer, and the solution was diluted to volume.

Procedure for the Gas-Chromatographic Determination of 2,3,7,8-Tetrachlorodibenzo-p-dioxin:

Standard TCDD Solutions:

Solutions were prepared containing 20 ng of TCDD per μl in 25% ether-hexane and 0.2 ng of TCDD per μl in 25% ether-hexane. These solutions were used as standards for flame ionization detection and electron capture detection, respectively. The standard used in flame ionization detection corresponds to a TCDD content in 2,4,5-T of 0.5 ppm, and the standard for electron capture detection corresponds to a TCDD content in 2,4,5-T esters of 0.2 ppm.

Extract solutions of samples of 2,4,5-T and 2,4,5-T esters prepared as described were chromatographed under the conditions described. For 2,4,5-T samples, a 2 μl injection of standard TCDD was followed by injection of a 2 μl aliquot of sample solution. For the esters, the injection volume for standard and samples was 1 μl . The retention time for TCDD in 2,4,5-T samples was about ten minutes and in the ester samples about six minutes. The concentration of TCDD in the samples was calculated using the following formula:

$$C_u = \frac{A_u V_s C_s}{A_s V_u} \times f$$

where $f = \frac{10}{w}$ for esters, $f = \frac{0.5}{w}$ for 2,4,5-T,

and

C_u = concentration of TCDD in original sample, ppm

A_u = peak area of TCDD in aliquot of sample injected

As = peak area of TCDD in aliquot of standard injection

Vs = injection volume of standard, μ l

Vu = injection volume of sample, μ l

Cs = concentration of TCDD in standard, ng/ μ l

W = weight of sample taken, g

Results and Discussion:

A total of 15 samples of 2,4,5-T and 15 samples of 2,4,5-T esters were analyzed for 2,3,7,8-tetrachlorodibenzo-p-dioxin. The ester samples chosen for analysis were of esters manufactured from 2,4,5-T analyzed in this work, with the exception of one sample of agent orange herbicide. The date of manufacture of the samples ranges from 1966 to the present. Only four butyl esters were analyzed, whereas ten 2-ethylhexyl esters were analyzed. This is proportional to the quantity of manufacture and use of the two esters.

The esters required a more efficient clean-up procedure than did the 2,4,5-T samples, owing to the use of the electron-capture detector which has greater sensitivity, but is more easily contaminated than the flame ionization detector. Clean-up by Florisil column chromatography proved to be very satisfactory in removing interfering substances.

All of the samples contained less than 0.1 ppm of 2,3,7,8-tetrachlorodibenzo-p-dioxin, except the sample of agent orange herbicide, which contained 6.21 ppm. The agent orange was received from the Air Force and has been stored for about two years at this location.

Recovery of 2,3,7,8-Tetrachlorodibenzo-p-dioxin:

One ml of a solution containing 2 μ g of TCDD per ml was added to 20 g portions each of four samples of 2,4,5-T that were free from the impurity (less than 0.1 ppm), and the samples were analyzed by the method described. The addition produced the equivalent of 0.1 ppm TCDD in the 2,4,5-T, which was detected by the flame ionization detector.

A 0.5 ml aliquot of standard solution containing 0.7 μ g TCDD per ml was added to 10 g portions of each of two butyl and two 2-ethylhexyl esters that were free from the impurity (less than 0.1 ppm), dissolved in 50 ml ethanol, and the samples were analyzed by the method described. The spiked samples contained the equivalent of 0.35 ppm TCDD in the esters. Recoveries of 43 to 60 percent were obtained.

Recovery of 2,3,7,8-Tetrachlorodibenzo-p-dioxin from Florisil Column Chromatography:

A 2 μ l aliquot of standard solution containing 0.7 ng TCDD per μ l was spotted on a Florisil column prepared as described earlier. The sample was then eluted with 50 ml of 25% methylene chloride-hexane solution. After evaporation to near dryness and dissolving the residue with 0.5 ml of 25% methylene chloride-hexane solution, a 2 μ l aliquot was injected into the gas chromatograph. A recovery of 95% was obtained.

Linearity of Response of the Electron Capture Detector:

Portions of 0.4, 1.0, 1.2, 1.4, and 2.0 μ l of a standard solution containing 7.0 ng of TCDD per μ l were injected on to the OV-17 column connected to the electron capture detector. The attached graph of peak area versus nanograms of TCDD on column appears to be linear up to 8.4 ng TCDD over the range examined and passes through the origin.

Limits of Detection:

Under the conditions of the method the lowest level of TCDD detectable corresponded to a sample concentration of 0.1 ppm TCDD in 2,4,5-T and its esters.

Typical chromatograms are attached.

MERCURUS POWDER COMPANY

CC: A. M. CLEVELAND - Jacksonville
J. J. Ford - Research Center
J. M. Eagan - Synthetics

0000342 K

Return to
Research Center
CORRESPONDENCE UNIT
Technical Information
MERCURUS POWDER COMPANY
Wilmington, Delaware
February 24, 1966

TO: E. E. Wilder - Jacksonville
FROM: E. E. Christofano - Medical - Home Office

I'd like to express my appreciation to you and Dr. Sidwell for the time and effort you spent explaining the plant efforts in environmental control. There has been a marked improvement during the past year and if the program continues at this rate even minor problems will be under control. One potential hazard stems from the use of supplied air masks when cleaning the Sharples centrifuge. Under certain circumstances it is possible to generate carbon monoxide in oil lubricated air compressors. If men breathe this air for extended periods their acuity might be impaired, but the effects would not be pronounced if the breathing air contained less than 100 ppm of CO. Determination of the CO content of breathing air is justified, and the enclosed literature describes a system for monitoring breathing air.

Dr. Zayon and Mr. Cholak (representing the NAC feasibility study team) appeared satisfied with the precautions taken to prevent occupational illness at Jacksonville. They noted a unique opportunity to study possible health implications because this plant is the only one entirely devoted to phenyl herbicides. They are not aware of occupational illness associated with the manufacture or use of these materials but they will probably recommend a more thorough study of exposure to raw materials, solvents intermediates and finished products. In addition they would like to see some medical data such as urine analysis. Their report will be sent to you when it is received.

Dr. Sidwell agreed to forward samples of 1,4,5,-T production streams and recycle or waste streams. One pound of each sample should be sent to J. J. Ford at the Research Center. These samples will then be used in preparing material for test by bioassay techniques for chlorine or BCP retention.

EEC:vvh
Enclosure



18925



HERCULES POWDER COMPANY

INCORPORATED

JACKSONVILLE, ARKANSAS

FIRST AID

FOR

CAUSTIC

"MONOCHLOR"

PHENOL

If splashed with any of these materials,

- 1.) Go as quickly as possible to a Safety Shower.
- 2.) Call for help on the way.
- 3.) Get under the shower.
- 4.) Wash repeatedly with water. Rub lightly over areas affected to hasten the removal of caustic or monochlor.
- 5.) While being rinsed with the water, have someone help remove clothing which may be contaminated with the splashed material.
- 6.) Wash for at least five (5) minutes. Continuous washing and rinsing with water is best for the removal of caustic or monochlor, or solutions of these.

For phenols or phenol solutions, after flushing with water and removal of affected clothing, pat dry the areas immediately affected -- do not rub -- and apply a generous layer of glycerin. Allow this to stay on for approximately one (1) minute and then flush off with water. Repeat this at least two (2) to three (3) times. Finally, pat dry and apply a layer of glycerin.

If any of the materials are accidentally splashed on the eye lids or into the eye, immediately flush with water, using an eye fountain. If splashed generally and incidentally in the eyes, rinse eyes while in the shower. Never rub an eye to help remove something, only flush it. Have a helper hold the eyes open if you find it impossible to force yourself to do this.

Report all accidents to supervisor or have someone do it.

Remember!

Prompt Flushing with Water,

Removal of Affected Clothing,

Care to be sure that all body areas are washed, otherwise an area may be overlooked which may cause more trouble than the area first noticed.

18926



THE DOW CHEMICAL COMPANY

WILMINGTON, DELAWARE 19899

December 23, 1968

Emil E. Christofano
Industrial Hygienist
Hercules Incorporated
Hercules Tower
910 Market Street
Wilmington, Delaware 19899

Dear Chris:

This is a belated reply to your letter of October 16, 1968. A delay in replying is for two reasons. First, I wanted a chance to evaluate some of the information we had to see how it agreed with your conclusions and second, to consider further, the advisability of publication of such information at this time.

In regard to the first question I am not at all surprised at your conclusions with regard to the liver function tests for we have observed essentially the same inconsistency in responses. I do not believe this is unique for the acagen you mentioned for I think it is true of many other hepatotoxic substances. I feel quite confident that if one wants to rely on such tests, then a good sized group of animals would have to be used at each dosage level. Individual variation is simply too great to permit using the data from small groups. On the other hand we have still found that the rabbit ear tests to be quite consistent and evaluation of perhaps three animals seems to give us very good assays.

In regard to publication I am not satisfied that we are ready to publish on the subject yet. I think this requires a considerable amount of thought and premeditation with regard to possible consequences. I feel that it would be a mistake to kick this in the public eye until such time as we have answers to obvious questions.

Best wishes for a Happy Holiday and a Prosperous New Year.

Sincerely yours,

V. K. Rowe
Biochemical Research Laboratory
1403 Building

VKR:cc

h0:504

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"Influence of Dioxin on Liver Function in the Rabbit,"
by M. L. Kerpfinger, G. P. Schoenig, O. E. Fancher,
E. E. Christolano, and J. P. Frawley,
Industrial Bio-Test Laboratories, Inc., Northbrook,
Illinois 60062 and Hercules Incorporated, Wilmington,
Delaware 19899

It was suggested that the presence of dioxin (2, 3, 7, 8 tetrachloro-dibenzobenz-p-dioxin) as a contaminant at very low concentrations in industrial chemicals can be detected by changes in liver function following oral administration to rabbits. It was thought that this might be a sensitive bioassay for the presence of dioxin. Therefore dioxin was added to industrial chemicals at concentrations of 0, 0.1, 1.0, 3.0 and 10.0 ppm and the contaminated materials were administered orally, in doses of 80 or 100 mg/kg, to rabbits.

Determinations of SCOT, SCPT and BSP retention were made before administration and at 5 and 15 days after administration. No effects indicating clinical evidence of liver damage were found.

In a second experiment dioxin itself was administered at doses of 0.01 or 0.1 mg/kg (10 and 100 times the highest dose above). Carbon tetrachloride was administered at doses of 100, 250 and 500 mg/kg as a positive control. The SCOT, SCPT and BSP retention were measured every 2 or 3 days for 18 days. All three doses of carbon tetrachloride caused significant increases in SCOT, SCPT and BSP retention. Increases in these three were found in some, but not all animals receiving dioxin.

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The changes were neither well correlated with dose nor consistent in onset and duration, even in animals showing apparently significant effects.

Although some positive results were obtained with dioxin itself, the usefulness of this technique as a bioassay for the presence of dioxin is questionable.

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Industrial BIO-TEST Laboratories, Inc.

1810 FRONTAGE ROAD
NORTHBROOK, ILLINOIS 60062
AREA CODE 312
TELEPHONE 270-0000

October 30, 1968

Dr. E. E. Christofano
Medical Department
Hercules Incorporated
910 Market Street
Wilmington, Delaware 19899

Dear Chris:

Enclosed is the abstract of the paper to be submitted to SOT
for next year's meetings, March 9-12, 1969. The new title is "Influence
of Dioxin on Liver Function in the Rabbit."

Best regards.

Sincerely yours,



M. L. Keplinger, Ph.D.
Assistant Laboratory Director

MLK:phh
Enclosure

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101409

189283

(A'Z'0) 1-272134000

Dr. T. A. Loomis
 Director, Program Committee
 Society of Toxicology, Inc.
 Department of Pharmacology
 School of Medicine
 University of Washington
 Seattle, Washington 98105

Due to unforeseen difficulties, we will not be able to present the paper, "Influence of Diets on Liver Function in the Rabbit," an abstract of which was offered for the SOT Meeting March 9-12, 1960. Therefore it must be cancelled.

I am sorry we have to cancel the first paper, but hope that the substitutes will help you plan the final program.

M. L. Karpilov, Ph. D.
Assistant Laboratory Director

cc: Dr. O. E. Fischer
Mr. E. Christensen

ECREZ

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HERCULES POWDER COMPANY

cc: Mr. Paul Mayfield - Executive
Mr. Charles Maddock - Legal
Dr. Lemuel C. McGee - Medical
Mr. P. J. Reno - Synthetics
Mr. R. T. Yates - Synthetics
- Mr. C. L. Dunn - Synthetics
- Mr. J. M. Eagan - Synthetics
- Mr. H. E. Wilder - Jacksonville
Mr. A. D. Sidwell - Jacksonville
Mr. Ashworth Burslem - Advertising

Wilmington, Delaware
March 26, 1965

TO: Mr. John G. Copeland - Synthetics Department

FROM: John P. Frawley - Medical Department

Report of Meeting with Dow Chemical Company on the
Toxicity of Trichlorophenol Impurities

At the invitation of Mr. V. K. Rowe, Biochemical Research Department, Dow Chemical Company, Mr. C. L. Dunn and the writer (along with representatives of other TCP producers--see letter attached) met in Midland on March 24, 1965, to discuss impurities in TCP.

Mr. Rowe and Dr. Holder of Dow reported that 60 to 70 employees of Dow over the past two years have developed chloracne from exposures to materials in their TCP operation. Chloracne is a disfiguring disease involving blockage and inflammation of the sebaceous glands of the skin, particularly of the face. It is believed to be a systemic disease and requires several years after exposure for the condition to disappear.

Dow has conducted considerable research to identify the cause of this condition and has concluded that several impurities, sometimes present in TCP, are responsible. They have identified one of these impurities which they believe is the principal acnegen--2,3,7,8-tetrachlorodibenzo-p-dioxin. They have developed (and supplied to all attendees) a chemical method for the detection of this material which is sensitive to 1 ppm (gas chromatography and flame ionization).

There was considerable discussion of the clinical aspects of the disease and the toxicological research Dow has conducted. In brief, 2,3,7,8-TCDD has been shown to produce the disease in rabbits at a concentration of 40 ppm after one application of 0.1 ml to the ear, and at a concentration of 0.4 ppm after eight applications. No evidence of the disease has been produced by concentrations up to 20 ppm for a single application and up to 0.1 ppm for twenty-five applications to rabbit ears. The compound has also been demonstrated to be a potent liver toxicant by oral or skin exposure. As little as 0.017 mg/kg is lethal to rabbits by the oral route.

Dow has analyzed commercial samples of TCP of all producers and has found up to 20 ppm of 2,3,7,8-TCDD in some. In finished samples of 2,4,5-T-acid they have found up to 10 ppm. No Hercules sample analyzed contained any significant acnegen. Dow has reduced their TCP capacity and is checking all production to be certain that it contains less than 1 ppm 2,3,7,8-TCDD. Currently, Dow is burying all wastes and contaminated material from their TCP plant since they are

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Mr. John G. Copeland

Page 2

March 26, 1965

not positive that burning will completely destroy the acnegens. Dow's intention in requesting this meeting was to inform all TCP producers of this information so that they can take steps to control the quality of their TCP production. A sample of 2,3,7,8-TCDF for analytical control was supplied to each company.

The Michigan State Department of Health has been consulted on this problem because of labor relations problems. Dow suspects that the Federal Government has become aware of the problem.

I recommend that Hercules take immediate steps to determine whether any acnegens are formed in our TCP process. This should be determined by chemical analyses and biological assays. If any such materials are formed, we should determine the fate of these materials in our plant--whether they are chemically destroyed, burned, or discharged in the waste stream, etc. We should also consider the desirability of constant monitoring of our TCP or 2,4,5-T-acid production by chemical methods to protect against illegitimate claims of acne from users of our 2,4,5-T products.

JPF/ezv

John D. F. ...



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P-24 1d

2/8/54 JL

7/28/66

- Ries Dielsman - The Hague
- E. C. Phillips - International
- E. S. Christoforo - Medical
- M. A. Taves - Syn. Div. R.C.
- E. B. Scott - Synthetics
- A. E. Canner - Anal. Div. R.C.
- F. J. J. Ford - Anal. Div. R.C.



INCORPORATED

1 DEPARTMENT
WILMINGTON, DELAWARE 19800 - (302) 456-0011
17 28, 1966

Pharmkol. Inst. der BASF A.G.
Schwanthaler Allee 20
67 Ludwigshafen
Rhein, Deutschland

Dear Professor Ostal:

Last September (1965), during my visit to your laboratory, we discussed the hazards associated with the production of trichlorophenol. I reviewed with you the recent cases of chloracne in the United States and you reviewed the precautions taken by you to assure against a repetition of a similar epidemic experienced by BASF. One of your most helpful comments was that you analyze all shipments of incoming trichlorophenol for chloracnogens by an oral rat biological assay procedure which you have developed. You also offered to assay some of our samples according to this procedure.

In my letter of December 28, 1965, I indicated that we would send these samples in the near future. For a combination of reasons, it has taken us until now to assemble the samples which we consider most appropriate. We sincerely hope that your offer is still available to us.

On the assumption that you will still be able to perform these assays, we have shipped 18 samples (10-grams each) of phenoxy herbicide finished products and intermediates encountered in their manufacture to Mr. Ries Dielsman of our Hague Office. We have asked Mr. Dielsman to contact you to arrange a suitable time for personal delivery of these samples to you. In addition, he will have a small sample of 2,3,7,8-tetrachlorodibenzo-p-dioxin, which can be used as a standard.

Wherever possible, these samples have been analyzed for "dioxin" content by gas chromatography, and we will be very glad to exchange this information with you in an effort to determine the reliability of the chromatographic procedure. However, you should assume that some of the samples contain no detectable "dioxin"; others contain from 1 to 25 ppm added "dioxin" and others contain known concentrations of "dioxin" which developed in manufacture.

The samples are labeled and identified as follows:

Sample K14567-41-1	Standard 2,4,5,-T Acid with added Dioxin
41.2	:
41.3	:
41.4	:
41.5	:

H01450

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Professor H. Ottel

Page 2

July 28, 1966

Samples K15280-56-8

Plant Grade 2,4,5-F Acid with Known Dioxin

Samples K15280-55-1

Plant Grade Sodium Trichlorophosphate with
Added Dioxin

-2
-3
-4
-5

•
•
•
•

Samples K15280-56-1

2 Ethyl hexyl ester of 2,4,5,-F with
Added Dioxin

-2
-3
-4
-5

•
•
•
•

Sample K15280-56-7

Nonseparable fraction from plant process

Sample K15280-56-10

Pure 2,3,7,8-tetrachlorodibenz-p-dioxin

The samples of sodium trichlorophosphate (K15280-55-1 to -5) can be more easily handled if liquified by heating to 65°C. The sample of nonseparable fraction can be liquified at 50°C.

I am certain that there is no need for me to caution you to handle these materials with appropriate care. It is because of the hazard of handling these materials that we are arranging for personal delivery to you by Mr. Holzman.

We also plan to attempt a biological assay by dermal administration to rabbits with some of these samples. We will be glad to compare these results with yours, when they are available.

At the time of my visit to your laboratory, you indicated that you would try to locate a copy of your complete report on the chloracne epidemic which occurred at MGP in 1953. Since Hercules has never experienced a case of chloracne, we would appreciate receiving a copy of that report, with photographs, so that our people might better appreciate the potential effects of chloracne.

If you have any questions about these samples, please contact us. Let us hope that through this cooperative endeavor, we can both provide better protection to the employees of both of our companies.

Best personal regards.

Sincerely,

JH
John H. Fowler, Ph.D.
Chief Toxicologist

JH/ew

HQ:451

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discuss
- - -
didn't

July 28, 1956

PERSONAL AND CONFIDENTIAL

Mr. Men Medema
E. V. Kureles Paper Company
Cincinnati 12
P. O. Box 619
T. S. Rogers, Netherlands

Dear Men:

During my visit to Europe last September, I spent a half day with Dr. H. Oetzel at MSY. Most of our time was spent discussing the hazards associated with the manufacture of trichlorophenol.

During the year preceding this discussion, one of the U.S. producers of trichlorophenol had a serious epidemic of chloracne among their plant workmen. All other U.S. producers have had difficulty from time to time and MSY had not a serious episode in 1953 that they decided to discuss their own manufacture of trichlorophenol and to purchase it only from other manufacturers.

I am enclosing several confidential memoranda which describe the technical aspects of this problem and the serious health hazards involved with the "disin" impurity which sometimes occurs in trichlorophenol.

Trichlorophenol is used for the manufacture of 2,4,5-T and its esters which are, of course, used as herbicides. Fortunately, Kureles has never had a case of chloracne develop in any of its employees. This may be due to plain dumb luck, but we think it is due to the fact that our process is under more adequate temperature and pressure control to minimize the "disin" impurity level. After the most recent U.S. outbreak, we have instituted more rigid control of our plant production, and hope to be able to prevent any outbreaks in the future.

This letter and the attachments provide you with background that will be necessary to understand the attached letter to Professor Oetzel. You will note from this letter that we are sending to you a series of samples containing "disin" for you to deliver to Professor Oetzel personally. I state in the letter that you are delivering them personally because of the hazard associated with handling these materials. This is not the only reason. In delivering them yourself, you will have an opportunity to meet Professor Oetzel and in addition, we may be able to encourage him to give you a copy of the report referred to in my letter. Professor Oetzel promised to send me a copy of the report on their epidemic, but has never followed through on his promise.

J. J. Egan

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B 189320

Mr. Lisa Melman

Page 2

July 27, 1966

We will have someone from Villages carry these samples to you in the future. There is no need for you to upgrade them and there is no harm associated with handling the materials by the old, actual, police captain himself. However, you should appreciate that the past samples of 'Glands' is very crude and these materials should be kept away from anyone who does not appreciate the potential hazard of the samples.

I hope the enclosed information gives you sufficient background to be able to discuss this matter briefly with Professor Gittel. Obviously we do not wish to reveal any manufacturing know-how and the cooperation between Hercules and BASF is strictly in the interest of health protection of employees. It is not our wish to enter into a technical discussion with Professor Gittel, but I will leave that to your own discretion.

For official records, I suggest that you discuss this matter only with those people in the Bayer office who may know about it. We prefer that you discuss it with no one but you and find it necessary to inform V. C. Marshall and J. V. W. Jacobs.

I will have many questions to ask about this whole problem which cannot be answered in correspondence. I will be very happy to discuss it in a short time we meet in company's detail. In the meantime, I hope you will suggest Professor Gittel not attempt to take these samples to him at your next conference. Thanks very much.

Sincerely,

John F. Penning, Ph.D.
Chief Development

JFP/ent
cc: Mr. Herman C. Phillips - International

18933

h0144-

919-928-5142

Jim Morton
Rt 2 Box 243
Pittsboro, NC 27312

The Cancer Epidemic: Part 1

by James Morton

IN THE UNITED STATES the most profound consequence of the environmental crisis is the epidemic rise in the incidence of cancer. This epidemic indicates more than an ever increasing occurrence of a fatal disease; it indicates that the body chemistry is being so disrupted by environmental toxins that our abilities to resist disease and reproduce healthy children are also failing. Cancer is for us what hunger is for the people of El Salvador, the cutting edge of the survival issue. It is our revolutionary issue.

If our children are to survive we must have a comprehensive analysis of the epidemic. First, we must understand and be able to articulate in common English the empirical data that define the parameters of the epidemic and their full range of implications. The debate on cancer cannot continue to be confined to the world of the epidemiologist and oncologist. Second, we must understand the social forces that propel the epidemic and the implications for political action. To fail to understand either the physical or social nature of the epidemic will be suicidal.

It is significant that you are likely to be first reading about the epidemic of cancer in a small journal of the revolutionary left. The National Cancer Institute and the American Cancer Society, the primary state and private institutions responsible for representing the interest of the public in these matters, contend that the disease is only rising in response to cigarette smoking. The bourgeois press follows the official line. Even the liberal and left press has been unable to confront this issue.

While the failure of the left to confront the epidemic of cancer is more problematic and will be discussed in a subsequent article, it is obvious why the institutions of the right must deny the epidemic of cancer. Capital, or at the least its leading sector, can only stop the cancer epidemic by committing suicide as a class. This is because the aetiology (cause and origin—ed.) of the epidemic is found in the petrochemical transformation of the postwar economy.

The use of these synthetic, chemical poisons plays an irreplaceable role in the process by which capital extracts surplus value and maintains control over the process of production. That they can be manufactured, employed and disposed of with little or no concern for the toxic consequences to the environment is an essential condition for the use of petrochemicals in the capitalist world system.

Consequently, when intrepid academics, bureaucrats, and journalists begin to sense that they are pursuing an issue which is in fundamental conflict with the

James Morton is 44, a resident of the countryside near Chapel Hill, North Carolina, and in the process of finishing a book on political economy of species extinction. He gratefully acknowledges the assistance of Bart Jordan in preparing this article.

interest of the most powerful men in the world—they would be better off avoiding the epidemic of cancer. Their investigative exploits in this area are not likely to be rewarded.

There are three reasons why the cancer epidemic represents the single greatest threat to our lives. First is simple arithmetic: Humanity cannot continue to endure an ever increasing incidence of a fatal disease. For instance the most conservative estimate has cancer incidence increasing at .9% annually, with approximately 965,000 new cases reported in 1987. With this rate of increase that within 400 years over 10% of the U.S. population would be contracting cancer each year.

The second reason is that any compound that is capable of promoting an epidemic of cancer is also likely to disrupt the entire process of cellular reproduction. Thus arithmetic alone is too vulgar a tool to measure the impact of cancer. At the current rate of increase we could as species essentially be dead—that is, unable to reproduce—very soon, even within decades.

Cancer is a disorder in the process of cellular reproduction, propelled to epidemic rates by the introduction into the environment of new agents which disrupt that process. Cellular reproduction is the signature process of a living creature. In a human it is the reproduction of arterial walls, blood, nerve cells, organ tissue, skin, sperm or ova, and the genetic material that will determine the physical evolution of humanity. It is also the reproduction of the body's defense against "foreign" invaders: the immune system, that "complex network of specialized organs and cells...which equals in complexity the intricacies of the brain and nervous system" and whose success depends on an "incredibly elaborate and dynamic regulatory-communications network. Millions and millions of cells, organized into sets and subsets, pass information back and forth like clouds of bees swarming around a hive." (*Understanding The Immune System*, National Institute of Health, 1)

The success of the immune system or the reproduction of organ tissue relies on chemical messages which originate within the nucleus of each cell. Petrochemicals are capable of penetrating the protective membrane of the cell wall and causing a rewrite of the message by which the twin strands of DNA (basic genetic material) coiled within the cell direct its reproduction.

A petrochemical that is capable of scrambling the cellular message to cause some of the cells that reproduce the tissue of the liver, testes or ovaries to run amok and produce a cancerous tumor can also damage the genetic material that was being passed to future generations, cause sterility, miscarriages, birth defects and a weakened immune system which can itself lead to cancer. This same chemical may also influence the biochemical mechanisms that are part of thinking, making love and feeling good. An epidemic of cancer is indicative of a failure in the life process.

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The third reason why the cancer epidemic is our greatest threat is the pervasiveness and durability of petrochemicals. In the forty years since they have come into common use our lives have been saturated in petrochemicals. Every day every person in the United States breathes, eats, drinks, and absorbs petrochemicals through the skin.

Residents of industrial cities "live under a bubble of toxic gasses." Those who enjoy a more bucolic existence inhale a wide range of dioxin compounds via the incineration of municipal garbage. Even arctic wildlife is contaminated by air-born petrochemicals. A single carrot may have five different pesticide residues on it, a tomato three and a meal of a salad, baked potato, green-beans and meat will contain a hundred or more different petrochemicals and synthetic hormones, most of which were introduced to nature the last twenty years.

The typical American city's water supply is contaminated by a thousand or more organic compounds. When you bathe you breathe chemicals in the water vapor and absorb them through your skin. Hundreds of billions of pounds of these chemicals are dumped into our environment each year and one way or another they move into the sea, the source of all terrestrial life.

Petrochemical compounds also accumulate throughout the human body. They can do this because they are produced from oil and thus have a carbon base and the ability to bond with other carbon-based compounds. The cellular structure of any life form has a carbon base, but because these compounds are oil soluble they have a particular affinity for an oily substance such as human fat. The highest concentrations are found in fat tissue or the part of breast milk that is richest in fat. As the National Adipose Tissue Survey shows, you can determine a person's approximate age and geographic residence by the range and volume of contaminants found in fat tissue. They are also routinely found in blood, urine and semen.

The cancer epidemic then is not a discrete process, simply one of many fatal diseases, but an unequivocal signal that the life process of humanity is failing. Every aspect of our environment becomes each day more saturated with the agents of our extinction. What we see is an unsustainable accumulation of quantitative change: too many poisons in the environment, too much poison in our flesh, too much cancer. We can anticipate a qualitative change long before simple quantity overwhelms us. The evidence and the political imperative is clear.

Arsenic, asbestos, radiation and various heavy metals have all been causing cancer since at least the turn of the century and today they are killing a lot of people. But there is only one event, one aspect of the modern environment that is capable of propelling an epidemic of cancer: the *petrochemical transformation of the world economy* began after the Second World War.

Chemicals that were byproducts of petroleum refining began to be substituted for fertility, genetic resistance and labor in agriculture and forestry; and for wood, steel, hemp, rubber, cotton, glass, wool, natural oils and labor in manufacturing. In 1940 annual produc-

tion of petrochemicals in the United States was 1 billion pounds, by the 1950s the figure was 30 billion, by 1960 it was 100 billion and today over 400 billion pounds are produced each year.

Cancer really occurs as a series of small epidemics, most often bound in place and time to the production and use of petrochemicals. While everyone in the United States is more likely to contract cancer at a variety of sites than they were ten years ago, the working class bears the brunt of the cancer epidemic. The highest rates occur among folk who live around the places where organic compounds are manufactured, dumped or applied and among the workers who make them or employ them and their children.

There is a dose relationship: the workers who use the chemicals the most or the people who live closest to the dump suffer the very worst. New Jersey, capital's environment of the future, sports the nation's highest cancer mortality rates, ranging from 50% above normal to 150% in the counties with densest concentration of petrochemical waste. Another geographic analysis finds excess of all sorts but particularly of the bladder, liver, and lung in the 139 counties where the chemical industry is most concentrated.

The epidemic of Non-Hodgkins Lymphoma, which is showing striking increases among the general population, is 60% more likely to occur among Kansas farmers who use the dioxin tainted phenoxy herbicides. If the farmers use it for more than twenty days per year, there is a 600% excess cancer rate. And if they mix and apply it—as well as frequently use it—they suffer an 800% excess of lymphoma.

Children have their own type of occupational exposure, as their parents bring the chemicals the workplace home on their clothes, skin, and in their breath. The risk of leukemia, which provides almost a third of the cancer aggregate for white children, is 3-1/2 times the national average for children whose fathers worked with chlorinated solvents, 4-1/2 times if the fathers worked with dyes or pigments and twice as high for those whose fathers worked with spray paints while their mother was pregnant with them. In each instance the risk grew with duration and intensity of exposure to the organic compounds.

To understand the relationship in time between petrochemicals and cancer, one must bear in mind that cancer is a disease which typically has a 15-30 year gestation period. Today's cancer rates are primarily responding to the conditions of the 1960s and early 1970s. Consequently cancer among the working class today gives an indication of what will follow in the general population as the overall chemical contamination of the environment continues to accelerate. (See sidebar to the right for some details.)

As would be expected with a petrochemical propelled epidemic, cancer incidence rises at most body sites (18 out of 25), attacks the immune system (Non-Hodgkin's Lymphoma up 41.8%), the renal system (bladder up 9.3%, kidney up 17.5%), and the nervous system (up 17.5%). But the best evidence for the epi-

Tracking the Rise of an Epidemic

CANCER INCIDENCE BEGAN a serious rise sometime between the Second National Cancer Survey (SNCS 1947-50) and the Third National Cancer Survey (TNCS 1969-71). Mortality statistics collected annually indicate an almost flat response between 1950 and 1965, and then begin a continual and accelerating rise.

By 1965 Samuel Epstein, a physician specializing in occupational medicine, began to see evidence that a general cancer epidemic was building, propelled by the petrochemicals ravaging workers in petroleum refineries and in chemical and rubber manufacture. By 1979 Epstein had enough data to publish the seminal work in cancer analysis, *The Politics of Cancer* (Anchor Press/ Doubleday). We now have far better data proving that Epstein was correct.

The most reliable data we have for the overall increase of cancer incidence begins in 1973 with the initiation of the U.S. cancer registry, the Surveillance, Epidemiology, and End Results (SEER) Program of the National Cancer Institute.

The construction of the SEER registry avoids many of the inconsistencies of time, diagnostic technique, and geographic area which made it difficult to compare the data from previous national cancer surveys. SEER collects data on cancer incidence and survival rates twice a year from the same hospitals in four urban areas and five states, representing 12% of the U.S. population.

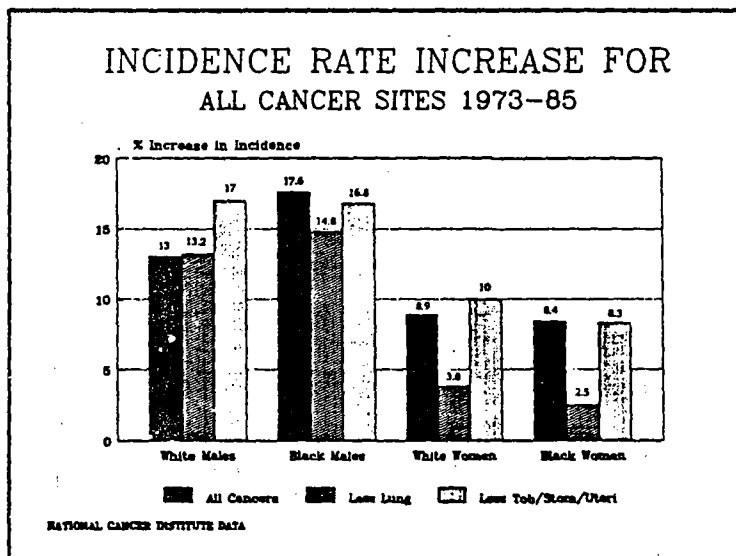
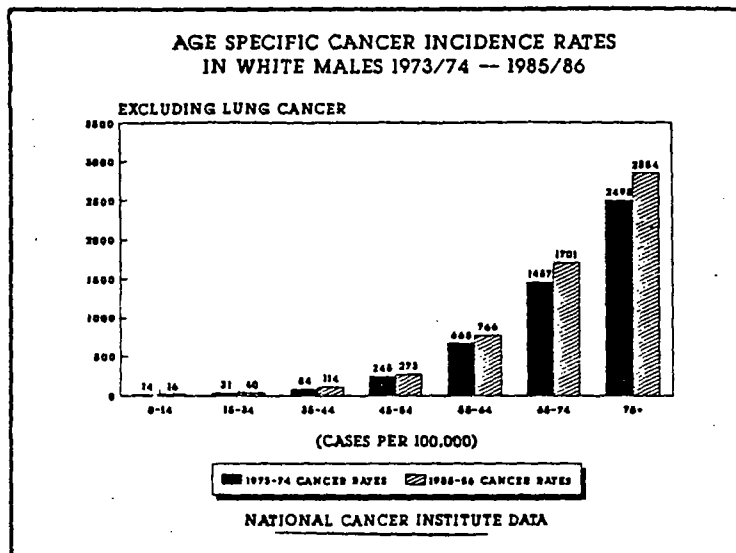
One of the most common apologies for the epidemic is that incidence is rising mostly because people are not dying as frequently of heart or infectious diseases, thus living long enough to die of cancer.

SEER disposes of this argument in two ways. First the information has been "age adjusted" to the 1970 population distribution so that in 1985 the percentage of elderly sampled is the same as in the 1970 population. Second, SEER gives age-specific incidence rates. Hence in the table "Age-Specific Cancer Incidence Rates in White Males," which excludes lung cancer, the incidence of cancer for white males rises significantly in seven out of eight age categories.

SEER presents cancer incidence as all-site composite figures and by site alone. The more these figures are refined, the more they tell us. For example, SEER withdraws lung cancer from the statistics to give us the second line in the table "Incidence Rate Increase For All Cancer Sites." Since the working class are the heaviest tobacco users and have the most intense contact with petrochemicals, cigarette smoking tends to obscure a number of petrocancers. There are other stu-

dies which suggest that from 33-47% of all lung cancer has an occupational aetiology. Nor does cigarette smoking explain why people living in cities like

exposed to far more organic compounds. Therefore it is useful for those obscuring the extent and origin of the epidemic to combine male and female rates.



Detroit and Atlanta have a 50% excess of lung cancer over rural areas.

Epstein provides the model for the far more pertinent data in the last line of the same table, which I have adjusted. First all body sites which come in contact with tobacco smoke or juice are removed.

Cervical and uterine cancers are removed because the use of pap smears is detecting abnormalities of the cervix in a precancerous state, and the high rate of hysterectomies means that there are less uteri to become cancerous.

The incidence of cancer is accelerating among men at almost twice the rate that it is among women; the only significant difference in their environments is found in the workplace, where men are

Lung cancer serves ruling-class purpose in the same manner. The standard ploy of the National Cancer Institute and the American Cancer Society has been to publish a combined incidence figure for the first line, then follow with a combination of the second line to say that it's just people killing themselves with cigarettes. These days that second line shows a grossly understated, but nonetheless alarming 7.9% increase.

Look how dramatically the appearance of the epidemic changes among women when only smoking is withdrawn—not too alarming—then pull the sites where there should be a decline and the rates become terrifying. Again, the general lack of decline indicates a crisis.

demc and the most alarming implications for our species comes from two sites associated with reproduction. While both testicular and breast cancers can now be diagnosed earlier, the ability of the physician to ultimately diagnose them correctly has not changed since 1950. *The incidence of cancer at these sites, both of which show heavy petrochemical accumulation, has increased dramatically and in step with the production of petrochemicals.*

Testicular cancer has risen by 27% over the last decade and by 90% since 1950. The rate of increase and the current incidence rate of 4.4 per hundred thousand per year are an average for the entire white male population, but testicular cancer only begins to be a major problem at the age of 15 and by age 44 it is well into a steep decline. However, within the 15-44 year old age span it is the most common malignancy.

In the peak years of 25-34 the incidence rate rose from 3.8 in 1947-48 to 11.6 per hundred thousand in 1979-80, approximately a 300% jump among the population most severely affected. Among 55 and older males the incidence rate has remained stable since 1950.

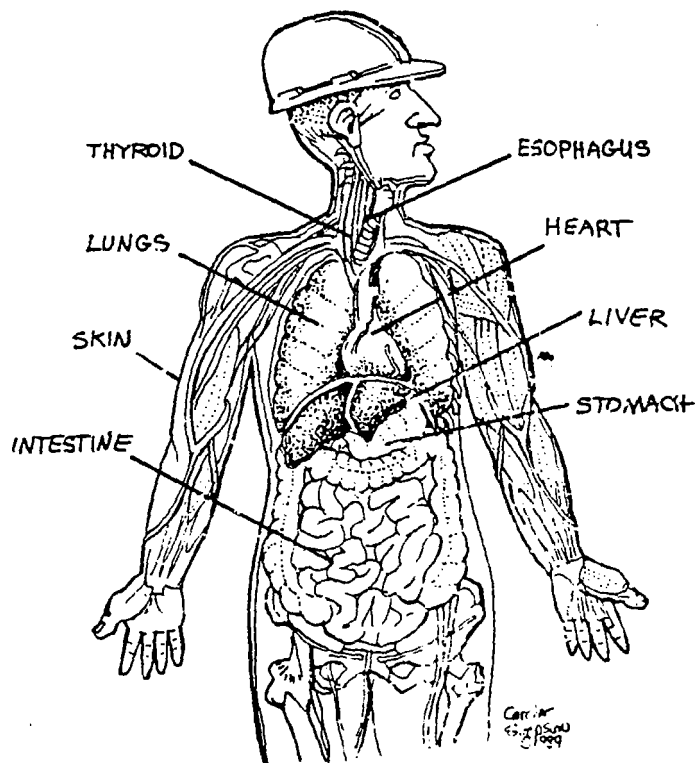
While the Black incidence rate is a fraction of that of white males, Blacks show an identical pattern of age distribution indicating that something new is happening to young Black men; either it happens less or it doesn't affect them as much. Similar rates of testicular cancer among U.S. whites and French, Germans and Swiss reinforce the validity of U.S. data, as do similarly low rates among U.S. Blacks and Africans, Japanese and Puerto Ricans.

Testicular cancer is associated with occupational hazards, the incompetence of the medical/pharmaceutical industries, and the chemical residues that typify the environment of the cancer epidemic. Working around the crude petroleum, or natural gas extraction industries, or the production of crops and livestock significantly increases a man's risk of testicular cancer. A finding consistent with the severe reproductive problems experienced by men working in the production of the pesticides Kepone and DBCP.

PCBs, phenoxy herbicides, fire retardants and other assorted carcinogens, mutagen and terratogens accumulate in seminal fluid and possibly in sperm cells. All of these industrial, weed, insect and fungus poisons are becoming part of the biochemistry that recreates the genetic material of the species as they freely intermix in this process of ultra rapid cellular division and reproduction where millions of spermatozoa are being produced each day, a thousand each second — each reproduction governed by a chemical message. The weight of evidence on reproductive disorders does not approach the unequivocal nature of the SEER data. However what data we have does suggest that the types of problems in the reproductive system we would expect to encounter with an epidemic of cancer are becoming more common.

From 1938 (when it was first possible to do accurate

Where employers like to store their most dangerous chemicals.



sperm counts) until about 1960, .05% of the male population was functionally sterile and the average sperm count was about 100 million to a milliliter of semen. Today there is evidence to suggest that throughout the industrialized world 20% of men are sterile and the average sperm count is around 60 million to the milliliter of semen.

Today, no one is threatened by cancer more than women are by breast cancer. Even though the incidence rate for lung cancer among women has climbed by over 50% in ten years, it has done so on an incidence base that is one-third that of breast cancer.

As bad as the 13.3% increase over the thirteen years of SEER is, we know that we have been witnessing a horrifying 3.8% annual surge in breast cancer for women above and below the age of 50 since 1980. Among the young women of the Seattle-Puget Sound area there has been a 22% increase over the ten year period and among Swedish women 30-39 there has been a 27% increase between 1972-1981.

An analysis of incidence data for white women collected from areas common to the Second and Third National Cancer Surveys and SEER show a 6% rise between 1950 and 1971, and a 23% rise between 1971 and 1984. Now breast cancer strikes one out of every eleven

American women.

Millions upon millions of dollars of grant money have been funneled into attempts to prove that women are contracting more breast cancer because they are eating too much fat. The bulk of the fat theories rely on geographic comparisons that purport to show a high correlation between nations with high fat consumption and breast cancer, which then ignore data that shows extremely high fat consumption among Inuit (Eskimo), Spanish and Italian women but a low incidence of breast cancer. The Inuit women and the Mediterranean women consume fat, blubber and olive oil respectively, that is extremely low in petrochemical contaminants.

The animal data that the fat theorist concocts is based on stuffing a mouse with massive amounts of cotton, corn or safflower oil, which bears a considerable burden of carcinogens. The proposition is never considered that those sad rodents possibly suffer more cancer not because their diet is 40% corn oil as against 10% but because they receive four times the dose of carbaryl, methomyl, permethrin, methyl parathion, carbofuran, captan, diazinon, lindane, alachlor, and atrazine. Moreover, best evidence suggest a substantial reduction in fat intake for everyone since at least 1960.

Chemical reactions are not confined to the laboratory. They occur as organic compounds mix in water systems, fields, salad bowls, smokestacks and bodies. No one understands very much about the content or consequences of these interactions—particularly when they occur within the confines of our flesh. Cancer is also a poorly understood process. However, we know that it is a complex event often involving a combination of agents over a period of time. In humanity cancer occurs within a very diverse genetic pool and among a population that is consuming a wide variety of cancer-causing agents. Thus it is difficult to pinpoint a specific agent as causing a cancer at a certain body part in the general population.

The female breast is essentially fat tissue and milk glands. In the fat of everyone in the United States can be found at the very least PCBs, DDT, Chlordane, Heptachlor, Aldrin, DDE, BHC, Pentachlorophenol, and many of the compounds of the ultra toxic dioxins including PCDFs and the most toxic of all, TCDD.

The presence of the PCBs and dioxin compounds is particularly frightening. In a survey of human milk, blood and fat in Europe and the United States, Alan Jensen found that dozens of variations of these chemicals contaminated almost everyone, but TCDD had a preference for women. The residues were unbelievably small, about 2 parts per trillion (ppt); a ppt on a plane of 183 square miles would cover the area of a quarter. However, when given to a pregnant mouse at 10 ppt, TCDD damages the fetus; rats develop excess cancers at 5 ppt and toxic affects are seen in the offspring of pregnant monkeys at 2.5 ppt.

In any part of our body fat there are a continuing series of biochemical reactions, but unlike other sites where there are heavy accumulations of fat (such as the buttocks or upper thigh) the fat of the female breast sur-

rounds the chemically complex milk producing organs. Thus, within the breast there are the uncontrolled chemical reactions of what easily could be hundreds of organic compounds, the most toxic known to science, many mimicking or enhancing the effects of estrogen and interacting with the normal cellular reproduction of the milk glands. The potential extent of this interaction can be measured by the list of synthetic chemical poisons in the mother's milk.

"In an overall assessment it may be wrong to look at one contaminant at a time, because these organohalogenes have similar targets in the body, indicating a potential for toxicological interactions" (Alan Jensen, *The Science of the Total Environment*, 1986).

Women who breast feed have, by a factor of about one-half, a lower incidence of breast cancer, with longer and more frequent the periods of lactation making it less likely they will have that cancer. We know that when the mother lactates she expels many of the petrochemical poisons in her system at a higher rate than the rate at which she absorbs them from the environment. In one study the levels of PCBs and DDEs (a byproduct of DDT) in breast milk dropped by 20% over six months and by 40% over 18 months.

Could women who breastfeed be less likely to develop cancer because they are expelling carcinogens from their systems into the rapidly developing nervous, immune and reproductive systems of their infants? The class structure of breast cancer rates in the Seattle-Puget Sound area reinforces that contention. There is a 53% rise among low income women, (those least likely to breast feed), a 27% rise among middle-income women and no rise among upper-income women, (the most frequent breastfeeders). Also the lower the income group the more likely the individual is to work around chemical poisons, live near where they are produced and to drink contaminated water.

Among dioxins, insect poisons, fungus poisons, high-temperature lubricants, weed killers mixing and reacting, who can say which carcinogen in what combination triggers this terrible reaction in women's flesh. But suddenly more women in the industrialized world begin to develop cancer of the breast, and in their breasts we find chemicals introduced over the last forty years which are known to cause cancer in monkeys, rats, mice, gerbils, hamsters, dogs, fish and humans.

What an analysis of testicular and breast cancer shows is an unequivocal epidemic rise that marches in lockstep with the introduction of petrochemicals. The reproductive cycle is in imminent danger of becoming irreparably harmed, with sperm too heavily contaminated to create a fetus and women's breasts so toxic that babies cannot survive. The poisons in the mother's womb and milk—made worse by a contaminated food and water supply—endanger our survival as a species.

If we do not stop this process that moment will come. The cancer epidemic is the most important single issue for the First World; it represents the most pressing danger in our lives and the lives of our children, a crisis with revolutionary implications to be discussed in the second part of this essay.

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The Cancer Epidemic: Part 2

by James Morton

THE CANCER EPIDEMIC is the most important single issue confronting the left in the first (industrial, capitalist) world because it represents the most pressing danger in our lives and in the lives of our children. While the epidemic of cancer and environmental collapse in the Third World has at least as devastating an impact as it does in the first, there starvation is the survival issue.

Environmental crisis and the epidemic of cancer can only be successfully challenged through a *revolutionary transformation of the global economy*. Most people do not make revolution to secure civil rights; in solidarity with another people's oppression, however severe; or in response to forced overtime. They only seem to be willing to endure the extreme personal sacrifice that revolution demands when their lives and their children's lives are at stake. The epidemic of cancer is the revolutionary issue that is most relevant in the lives of first world people, and it presents a logical strategic focus for a mass movement.

We will show here that the epidemic of cancer is an issue that capitalism cannot co-opt. Nor is the epidemic amenable to social democratic solutions. The struggle for a non-carcinogenic process of production generates day-to-day antisystemic resistance.

Why then does the left seem to ignore this issue? We cannot discount the personal terror that cancer inspires: that we might contract it, and that our children might, that the only real solution is revolution — which seems so far away.

Moreover, the left does not have good information. The epidemic was only becoming evident by the late 1970s, and since then the public agencies and the bourgeois press have relentlessly suppressed the evidence and denied its existence. Discussion has been limited to the small world of oncologists and epidemiologists, few of whom are active in left politics. Also, that school of thought which once held women's and racial issues to be subordinate to and separate from working-class issues still holds true when it comes to the environment. For them the environment is an "extra economic good," a hippie issue, somehow separate from the struggle of the working class, the most cancer-ridden folk in bourgeois society.

An examination of the political economy of the cancer epidemic first establishes that it is *the consequence of practices that are essential for maintaining the power of the capitalist class*. Though it is most likely structurally impossible for capital to make meaningful reforms in its use of petrochemicals, what's certain is that the sacrifices

James Morton is 44, a resident of the countryside near Chapel Hill, North Carolina, and in the process of finishing a book on the political economy of species extinction. He gratefully acknowledges the assistance of Bart Jordan in preparing this article. The first part of this article appeared in ATC 27.

would be so immense that it is inconceivable that capitalists would ever make them anyway. This, then, is an issue that they will not be able to co-opt.

"Without chemicals, life itself would be impossible" — the Monsanto corporate slogan. Except in its most literal sense this chemical company slogan is self-serving drivel. The new products of petrochemistry are mostly toxic substitutes for natural products that usually served our purposes better. If, conversely, the Monsanto public relations department had offered "without petrochemicals late capitalism would be impossible," it would have presented us with a profound insight into the circumstances of today's world.

To understand the value of petrochemicals to capital, one must first observe who composes the most powerful segment of the ruling class. At the very top of the capitalist hierarchy, there are oil merchants integrated into vast networks of banks, chemical companies, pharmaceutical firms and various types of manufacturing and service enterprises. Thus every barrel of oil that is sold feeds dollars straight into the maw of the beast.

Consequently, when it became possible to make shirts, bottles, tires, shoes, furniture and so on from oil, it was an immensely profitable transformation for the most powerful sector of the capitalist class, allowing it to consolidate control of capitalist production.

The Indian economist Narindar Singh has observed that ecological crisis under capitalism is inevitable given capital's insatiable demand for growth, but that the crisis we endure has its particular features because the leading sector of the capitalist class are oil merchants.

Capitalism is — must be — a system designed to reward the largest concentrations of capital. Petrochemical production is the most capital-intensive form of manufacture; hence, the centering of the world economy on petrochemicals that has occurred since World War II. This process has favored capital over workers, large capital over small capital and the capital of the major industrial powers over that of the Third World.

Organic compounds are great labor-saving devices, replacing human labor in agriculture, manufacture and forestry. This allows capital to perform a highly skilled, labor-intensive task such as farming, replacing the mental and physical labor involved in this process with chemicals. Farmers, forestry and factory workers replaced by chemicals join the army of the unemployed or re-enter the labor force at semi-skilled positions where they are cheap to hire and easy to replace.

Within the capitalist class, the war for control is fought on multiple levels. The immense resources that are required to establish a petrochemical refinery mean that at the primary level only the largest blocs of capital will be able to compete in chemical manufacture, in effect eliminating competition from small family-owned firms. This also favors the much richer capitalists of the

first world over those of the Third, particularly in the very expensive process of continually advancing the technology of production. Technical complexity acts as a type of first world patent while the power of the product is its market justification.

Venezuelan capital, for instance, is quite competitive in the production of the more conventional organochlorines or phosphates such as malathion and DDT, but does not have the technical expertise to compete with first world firms in the production of the small, fast molecular chemistry that provides the phenoxy acids. The much more sophisticated chemistry of the pharmaceutical firms, still a monopoly of the first world, is far better suited for turning out the dioxin-producing poisons of the agent-orange genre, which are today the world's best selling pesticides.

The immensely carcinogenic phenoxy acids are at the cutting edge of maintaining the first world's markets for commodities and loans in the Third World. About half of Brazil's foreign debt is for agricultural development. Petrochemistry is also a device for maintaining Third World dependency on foreign technology and finance, which translates into an opportunity to dominate their state systems.

But nowhere do we see the irreplaceable role that petrochemicals play in maintaining the world order more clearly than with modern agriculture. The chemical transformation of global food production was not prompted by its intrinsic superiority as a system for producing food. Traditional agriculture has fed our species for 10,000 years without a single application of chemical fertilizers or pesticides and, along with its contemporary variations, can produce far more calories per acre and per calories of energy invested than its carcinogen-shrouded modern counterpart.

This transformation, which began with the introduction of hybrid breeding, created a mass market in agricultural commodities. As R.C. Lewontin and Jean-Pierre Berlan explained in their article, "Technology, Research and the Penetration of Capital" (*Monthly Review*, vol. 38, no. 3, July 1986), this was not a transformation of an existing market, but the creation of a totally new market, without which it would be difficult to imagine the post-war boom that the capitalists of the first world have enjoyed.

The transfer of wealth and power is astounding. Before World War II, almost all of the world's food was produced by farmers who generated about 90 percent or more of their own inputs — seeds, fertilizer, pest control, labor etc. Then, beginning a few years after the war, all the food in the United States — and now in virtually all the rest of the world — was produced with petro products. The seeds come from the store and require the farmer to buy chemical fertilizer, insect poison, weed poison, fungus poison and gasoline to run the irrigation equipment, tractors, combines and threshers. All the wealth that had been created by small capitalist or non-capitalist farmers now flows into the center of the capitalist class — a series of families owning conglomerates that are oil / chemical / seedbreeding / equipment manufacturing / financial corporations.

Needless to say, when one can sell food and virtually everything needed to produce it to a substantial proportion of humanity, large profits can be made. And it does not hurt to be able to do it from a flexible position. If the price of oil is low — as it has been for the last few years — Exxon, Arco, Shell and their colleagues simply reap their profits through their chemical products divisions instead.

To understand the implications of modern agriculture it is necessary to look at the fathers of the "green revolution." By the late 1940s, the Rockefeller Foundation (Exxon) had begun to confront the specter of land reform during the Cardenas presidency in Mexico with a system that would use chemicals to make it possible for major landowners to enclose the lands of tenants and small farmers. Then, in the mid-1950s, as agricultural equipment and truck sales began to slump in the United States, the Ford Foundation turned its attention to world hunger.

In the early 1960s, when the Kellogg corporation discovered a method for cutting the cost of fertilizer production in half while doubling the output, it decided to join its corporate brothers in helping their Third World brethren struggle against starvation while coincidentally eliminating a ferocious glut in the fertilizer market. Nor should it be overlooked that Rockefeller *et al.* created immense profits for their banks by selling the financing to underwrite this "modernization" of Third World agriculture.

The "green revolution" not only meant that the capitalists of the center had made agriculture in the Third World dependent on their financing and technology, but also that they had gained a large measure of control over workers all over the world. Chemical — capital-intensive — agriculture meant that droves of peasants and farmers would be driven from the land and into urban labor markets. This huge army of unemployed allows capital to control their work conditions and lower their wages.

We can't survive consuming pesticides, but capitalism cannot survive without our doing so. Even the safe employment of petrochemicals, when possible, is circumstantially if not structurally against the interest of capital. Any number of chemicals can be manufactured, used and have their waste destroyed in perfect safety, if enough capital is invested in protective systems. However, to do this would push the price of many petrochemical products past the point where they would be competitive with the conventional products or processes they were designed to replace.

Even when safety precautions wouldn't price a commodity out of its market, the money would earn the capitalist no return. It makes by far the best sense to screw the workers, dump the chemicals into the river or turn them over to the Mafia.

These are some of the reforms capital must make if the cancer epidemic is to be stopped: its mass market for agricultural inputs, disposable plastic and aluminum, must be drastically curtailed or eliminated; production must be retooled to eliminate carcinogenic processes

and the systematic dumping of poisonous waste in the environment. All of the waste in the old dumps must be retrieved and if possible destroyed, or at least stored in secure, above-ground, earthquake-proof vaults. In each instance the reforms will cost capital billions — in lost markets, in retooling, and in recovery of waste. Each reform will tend to increase the value of labor.

We should hope that capital will make these reforms — no one wants to be poisoned to maintain a revolutionary issue. However, it does not seem likely that capitalists will address the epidemic or the environmental crisis with anything other than rhetoric.

Consequently, no coherent analysis or strategy to confront the epidemic is likely to emerge from the social democrats. Three formations prominent on the left or in the environmental movement are the Rainbow Coalition, the "post-Marxists" as represented by Michael Al-

bert and the staff of *Zeta Magazine*, and Earth First. These are all populated with deeply committed, politically valuable people, but because they do not grasp the role of capitalism in the environment, their analysis is incoherent and their strategic response can result in either a waste of scarce time and resources or in a dangerously racist, anti-labor and misanthropic response.

The Rainbow Coalition has been unable to design a meaningful program for a sustainable environment and has given no evidence that it would be able to implement such a program in the Democratic Party if it had one. All the energy of the Jackson campaign seemed to coalesce at the 1988 Democratic Convention in Atlanta around a series of compromises in which the Rainbow forces would refrain from demanding open debate on a reduction in defense spending, a no-first-strike nuclear policy, an independent Palestinian state and an end to

The Cancer Epidemic: Fiction or Reality?

SCIENCE FOR THE PEOPLE re-examined their stance on the question of the cancer epidemic in their January / February 1990 issue and reached a conclusion that was neither scientific nor in the interest of the people. This error was made possible by a failure to engage in principled debate.

The proper procedure for criticizing claims of a cancer epidemic is first to take the principal work on that issue, Samuel Epstein's *The Politics of Cancer* (Anchor / Doubleday, 1979), compare it with the latest and most pertinent data and show where he is in error. The primary writers in *SfP*, "Rick Hester," a public health official who used a pseudonym, and Howard Frumkin, a physician on the faculty of the University of Pennsylvania, dismiss Epstein with a couple of sentences as being wrong, without a clue as to why he is so.

The single, absolutely indispensable body of data for addressing the cancer epidemic, the Surveillance, Epidemiology and End Results (SEER) statistics on cancer incidence and mortality 1973 to 1985, is ignored. This report was released in January 1988. (Its significance and findings are discussed in the first part of this essay, ATC 27.) For "Hester" and Frumkin to overlook it is entirely analogous to looking for a crime wave and using arrest and conviction statistics four years out of date.

Perhaps "Hester" and Frumkin ignore the current edition of SEER because it consistently reinforces Epstein's position and shows unequivocally epidemic* or virtually epidemic increases in

cancer for a number of sectors, but most seriously for breast cancer incidence among white women in 1983, 1984 and 1985.

Frumkin attempts to buttress their arguments by misusing a study by John Bailar and Elaine Smith published in 1986 and relying on 1981 incidence and mortality data. Bailar and Smith do not attempt to address the question of a cancer epidemic but rather effectively destroy the National Institute of Cancer's claim that we are winning the war on cancer. If Frumkin had used the latest version of the SEER data that Bailar and Smith employed, increases that he dismissed as slight become — in the space of four years — classically epidemic.

Hester's argument relies on the primary apologists for the epidemic, Sir Richard Doll and his protege Richard Peto. According to Hester they are "among the world's foremost experts" and "the dominant explainers of the pattern of cancer in the United States." He even places Doll on the left, "politically courageous in the early part of his research career, and reportedly denied entry into the United States at one point because of his politics."

What "Hester" does not mention is that Doll is director and warden of Green College, Oxford, an industrially financed institution that, in the words of a founding fellow, is designed to be "a special point of entry for industrial interests wishing to collaborate with university departments in research." Nor does it impress "Hester" that Doll is an enthusiastic supporter of industry efforts to deny the carcinogenicity of the Dioxin-laden herbicides, 2,4-D and 2,4,5-T — an act that puts Doll squarely in the camp of the most depraved chemical-industry hacks. But then SEER puts Doll

and Peto in that camp, just as Epstein has for the last ten years. If I were "Hester," I wouldn't sign my real name either!

Stephanie Pollack's introductory article poses this question: "Let us assume ... that there is no massive cancer epidemic associated with occupational and environmental exposure to industrial chemicals ... what are the implications?" For Frumkin they include some acquiescence in our poisoning; we need to be "open minded" on thresholds — the idea that it is possible to determine a safe, long-term, low-level dose of a carcinogen (we are a lot closer to figuring out the technology for nuclear fusion).

Frumkin feels that "tradeoffs are inevitable ... some cancer may be justified by economic benefits ... and that it is not inherently evil or exploitative that people would voluntarily assume some cancer risk in return for other benefits."

But in a world with a cancer epidemic propelled by poisons that more thoroughly contaminate the environment daily, it is insane to be concerned about "thresholds" you cross, not just in those entirely unnecessary "tradeoffs" you are forced to accept to earn a living, but also when you drink, bathe, breathe and eat. An epidemic of cancer implies revolutionary change. —J.M.

(Readers interested in pursuing the cancer epidemic debate, including a trenchant critique of "the cancer establishment" and especially the claims of Doll and Peto, are encouraged to consult Dr. Samuel Epstein's congressional testimony, *Losing the War Against Cancer: Who's to Blame and What to Do About It*, presented to the House Subcommittee on Health and the Environment. It appears in the Congressional Record, September 9, 1987, pages E3449-E3454, and can be obtained from your congressperson's office — ed.)

*Epidemiologists define an epidemic as a 5 percent or more annual increase in incidence of mortality. But cancer is different from an infectious disease such as smallpox. It is almost always fatal and, as a disorder of cellular reproduction, it points to problems in every aspect of survival. Even a very small, continual increase in cancer is of the gravest consequence.

U.S. support for the oligarchy of El Salvador, in return for Jackson and his colleagues receiving seats on party policy-making boards.

The Jackson campaign moved the wretched Dukakis campaign to address key left issues in no discernible way. Will Jackson now be telling Robert Strauss, Lloyd Bentsen [both of whom are oil-linked Texas Democrats — ed.] and their clients that they must cut their own throats? If he does, are they likely to do so?

Post-Marxism attempts to construct a left analytical framework that removes class from the center of political life and, by necessity, anticapitalist struggle from the center of political activity. Albert suggests that social life is propelled by four categories of equal impact: culture, economics, politics and kinship. Depending on the circumstances, other spheres of influence — such as race, gender, and authoritarianism — emerge from these divisions as the primary actors in social events.

In South Africa, for instance, Albert would have racism rising to the fore as the motivating force that shapes the apartheid regime. Thus the white folk of South Africa are so repelled by black skin, woolly hair and superb music that they choose to rob the people of Southern Africa of their resources, labor and liberty, feeding it all into the maw of the voracious capitalist world economy.

A post-Marxist analysis would not give a clue as to what the forces are that propel the cancer epidemic. At no point in this brief analysis of the cancer epidemic does the evidence ever suggest that these chemicals are employed to bash a gay or lesbian, dominate a woman, oppress a racial group, or reinforce a state bureaucracy.

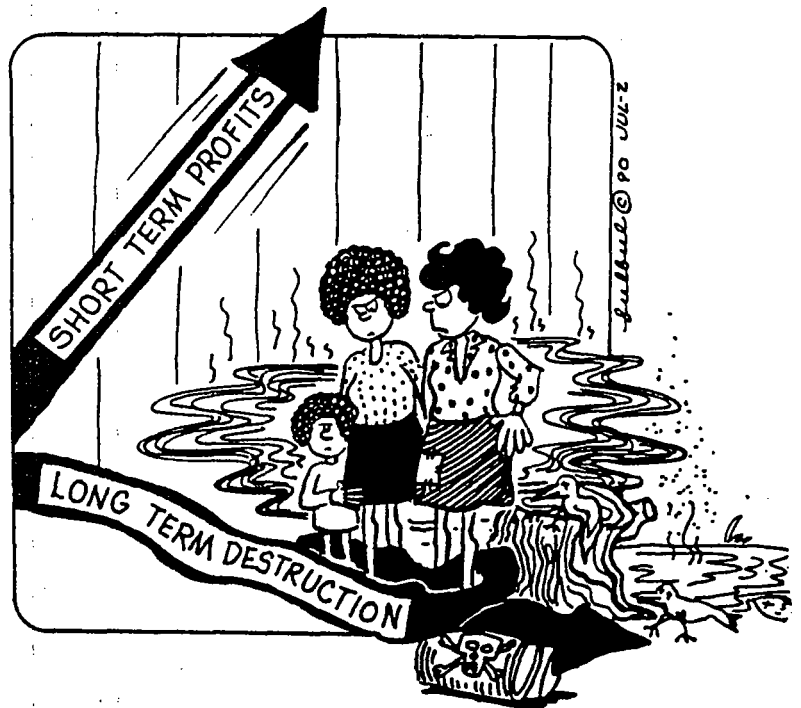
Nor does the concept of "economy" really explain this phenomenon. In the economic lives of the American people, the cost of medical treatment for cancer and birth defects, the loss of productive labor, and the squandering of natural resources far outweigh any savings that come from dumping numerous poisons into the environment. Even with all questions of the social cost of pollution put aside, corporations will use chemicals when it would be much cheaper in the short term to employ labor.

The forces that propel the epidemic of cancer only become clearly visible when viewed in Marxist terms, as a process by which a ruling class maintains control of the process of production and accumulates profits. The bourgeois state refuses to design and implement laws that will protect the public interest, not because the issue is unpopular with the electorate — environmental protection enjoys overwhelming support — but because it is not in the interest of the capitalist class.

Capitalism could be absolutely race and gender blind, indifferent to sexual preference, run by a state system free of bureaucratic Napoleons, and there would still be a cancer epidemic and an environmental crisis.

Capitalism propels the cancer epidemic and destroys the environment because it is what it is. Homophobia, misogyny and racism are tools that it employs in its struggle for profit and control of the process of production. It has lent those tools a dynamism: that no previous regime of accumulation was capable of giving them.

While the "monkey wrench" tactics of Earth First are right on target, their focus on "technology" and overpopulation is elitist, racist, misanthropic and dead wrong. Technology is a creature of the system that employs it; when it oppresses, it does so by choice. Nontoxic alternatives exist for modern manufacture. Technology is not carcinogenic; capitalism is.



Technology represents an immense source of wealth. Most of the people in this world need more — not less — access to the benefits of technology. Babble about the evils of modern technology is usually followed by calls for sacrifice. Working people around the world need have no doubt as to who will be called upon to make the most sacrifice and remain forever in poverty. Not only does placing blame for the epidemic on technology mask the real source of environmental crisis, but calls for sacrifice make a lousy recruitment line as well.

Overpopulation only exacerbates the ills of capitalism. The poisoning of the environment, the destruction of the tropical forest and the extinction of the seeds of traditional agriculture are propelled by the logic of the market and class rule rather than by numbers of people. If the world's population were halved, the forest would still be cut, the poisons would still flow, and the ozone layer would shrink while greenhouse gasses accumulated. Extinction would just advance at a slower pace.

Overpopulation is a real problem, but it is a consequence of the distribution of resources and the oppression of women. There are now enough agricultural

resources to feed everyone. Population control is a problem when a high percentage of children die before the age of five, child labor is an important component of family income, parents are dependent on children to care for them in their old age and women do not have control over their bodies — problems for the most part caused by the same people who are responsible for environmental crises. An obsession with overpopulation is a great misanthropic whine that the problem is "there are too many of us," which actually means there are too many of *them*, the poor and the brown.

An inability to critique capital leads to a capitalist analysis of the problem — that it is the responsibility of the most victimized — while a class analysis shows why there is an epidemic of cancer and that a strategy to combat the epidemic is entirely consistent with a left program. What follows is not an attempt to design a left program but to show that an ecological socialism is entirely consistent with the methodology and goals of left struggle for democratic socialism, where control of the process of production is centered on the factory floor and in the communities.

The working class occupies the physical center of the solution to the epidemic of cancer. If a worker is not poisoned at the factory or in the field, or if a working-class family (the ones most likely to live closest to the factory, dump or farm) is not poisoned by the air and water, then no one will be. Workers stand at the front line of each location in the process of production where physical injury to the society can occur. Workers must have the responsibility and power to make sure that commodities are produced, employed and destroyed safely. The rest of society has the right to demand that workers produce commodities with greater caution.

There must be a system of elected community and national committees regulating the production and disposal of hazardous materials. The composition of these committees should reflect the geographic movement of major air currents and watersheds. This type of organization will insure that no institution within a community, nor any community (at the head of a watershed for example), will be able to compromise the safety of other members of the society. All the information that these committees would employ to regulate the compounds and processes used in the production of a commodity — as well as the methods of disposal and records of their regulatory activities — should be available to the general public.

A democratic environmental movement must by definition be anti-imperialist. The commodities of nations that were produced so that the workers and the environment were poisoned must be barred from the U.S. market, as must commodities produced by labor that did not have the right to freely organize. Nor can the Third World continue to be a dumping zone for first world poisons. Not only is this practice morally despicable, but it only delays the impact of these poisons in our lives. Environmental crisis is a social disease propelled by undemocratic regimes; only militant support for socialist democracy around the world can insure the

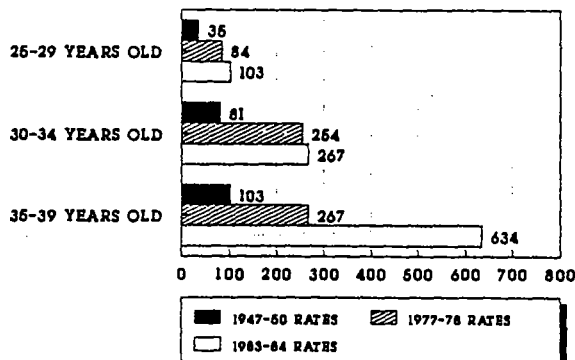
safety of the global environment.

Worker democracy and a safe environment are absolutely dependent on the return of women to the center of political economy. The most important task of the working class and of humanity is the reproduction of the species. The left must create structures to insure that the labor of bearing and raising children receives the economic and political power that it deserves.

Women, and particularly pregnant women, have always and will likely continue to most powerfully represent the interests of children, and thus must at least have an equal role in deciding what can be produced, as well as in what fashion it can be produced. The right to refuse a burden of fungicides and high temperature lubricants — hence insuring a degree of safety for children — and to be both free from threats of physical violence and terminate a pregnancy at will are inseparable parts of a woman's right to control her body.

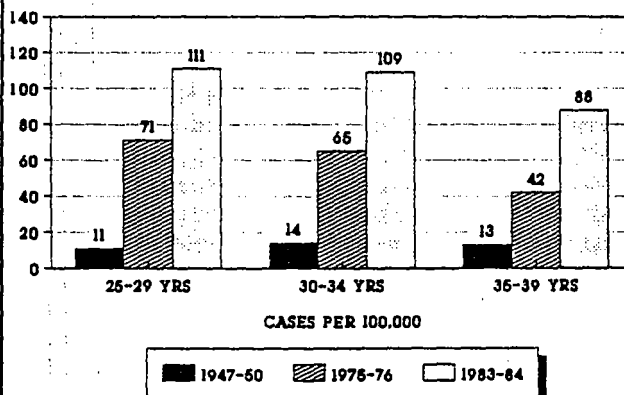
INCREASES IN BREAST CANCER INCIDENCE
RATES FOR WOMEN 1947/50-77/78-83/84

(CASES PER 100,000)



NATIONAL CANCER INSTITUTE DATA

TESTICULAR CANCER RATES IN
WHITE MALES (NEW CASES PER 100,000)



SEER/NTL CANCER INSTITUTE DATA

The frightening rise in breast and testicular cancer highlights the threat to both genders — and to the reproductive process.

18943

It will most likely be impossible to establish a sustainable, non-carcinogenic agriculture in the first world without the genetic material and technology of traditional agriculture in the Third World. Women typically are responsible for most of the labor — and particularly the seed breeding — in traditional agriculture. Their highly skilled labor and complex science are absolutely essential in maintaining the genetic base of world food production. We can only have such assurance if Third World women have control over their land, just as we can only finally be sure that Third World manufacture is not slowly poisoning the globe when Third World women have the same control over the process of production that first world women must have. A successful strategy to confront the cancer epidemic is fundamentally a struggle for women's rights all over the world.

If the revolutionary left confronts the cancer epidemic it has an issue that the right cannot co-opt — one demanding worker democracy, anti-imperialism and feminism, and responding on a personal level to the most pressing dangers in every first world person's life.

It is also a program for prosperity. A transition to a non-carcinogenic economy will not mean a loss of jobs, but full employment. Many workers would simply begin to use different processes and materials or begin to employ petrochemicals safely. New industries would also have to be created. The safe cleanup of dump sites and aquifers should provide high wages and long-term employment for any chemical-industry workers who would be laid off by the termination of unsafe production processes.

Rebuilding the nation's water systems, dramatically enlarging the rail lines and providing insulation and solar retrofits to buildings throughout the United States are new endeavors that would be constituent parts of a clean economy. The hundreds of thousands of jobs that would be provided would be a powerful stimulation to the general economy.

In agriculture and forestry the demand for labor, and particularly for skilled labor, would rise dramatically as natural products and labor replaced petrochemicals. The profits the oil merchant receive from the sale of pesticides would be transformed into agricultural wages spent in local communities, and a rise in agricultural employment would then reinforce the position of labor as it bargained for wages and control in manufacture. The specific varieties of a crop most suitable for chemical-free production would be least suited for the corporate marketing system. But such a program would be consistent with an entire system of food production from the farm to the marketplace that favored small local organizations over transnational corporations.

Environmental struggle must be equated with class struggle. Above all, the awful image of the neo-Malthusian elitist must be purged from the environmental movement. As Marx put it, Malthus provides an ideology for people who are unable to confront the control of property.

Inevitably there are going to be short-term contradictions between individual groups of workers and left groups about environmental issues as well as over

gender and race. Corporations will often threaten to shut down or move, and they will use environmental restrictions as an excuse to lay off workers. How effectively we are able to resolve those contradictions depends on the class content of our work. A group that militantly supports working-class struggle and actively seeks solutions for laid-off workers is far less vulnerable to a fascist response than an elite organization that focuses only on its own poisoning and ignores the consequence to workers who can lose everything for which they have been working.

The cancer epidemic is coming at us like a bat out of hell and there is nothing that capitalism can or will do about it. Obviously whatever we do about it is going to have to be quick and revolutionary. Because of the very general nature of the epidemic and its very specific cause and development, there is a wide potential base to organize that cuts across class, race and gender lines, and which clearly separates the interests of the ruling class from those serving the rest of humanity. The immediacy of the crisis and the breadth of the affected population does not call for a classic Leninist, vanguard party, but a looser affiliation of independently organized groups bound by common principles but responding primarily to whatever is most important to their particular constituency.

For most people in the United States there are crises more immediately important than the environment. It is hard to imagine a single mother, earning five dollars an hour and terrorized by some brute, then running from her trailer to support a group that does not actively address her oppression. A revolutionary organization that tried to help this woman organize daycare and defend her safety would find her quite willing to understand that capitalism exploits the material conditions in the natural world which support her life, just as they do her labor; and that the bourgeois state is no more willing to protect her from the physical attack of capitalism than it is from that of violent males.

Similarly, an organization that militantly supports Black liberation struggles can anticipate Black support on environmental issues. The failure to overcome racial and ethnic divisions has been the single most crippling event in the experience of the U.S. left. Single-issue politics can only ensure that the legacy of failure continues. Black and Latino support are essential to the success of any liberation movement in the United States. As Mike Davis notes, equal economic citizenship for them "would require levels of change dangerously close to the threshold of socialist transformation."

Nature is dying. Humanity is suffering a cancer epidemic. Two distinct groups have emerged, comprising those who profit directly from this process and those who do not. Capitalism can only confront the crisis of our impending extinction by laying the groundwork for its own destruction. The day-by-day attempt to respond to this crisis generates antisystemic elements of protest and demands political solidarity. The practice we evolve to survive the epidemic of cancer shall be determined by our analysis of these events. □

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STATE OF ARKANSAS
DEPARTMENT OF POLLUTION CONTROL AND ECOLOGY

8001 NATIONAL DRIVE P. O. BOX 9583
LITTLE ROCK, ARKANSAS 72219

501 371-1701 WATER
501 371-1701 GEN. OFF.
501 371-1136 AIR DIV.
501 371-2130 SOLID WASTE

MEMORANDUM

TO: Governor Clinton
FROM: Jarrell Southall *JSS*
DATE: November 26, 1979
SUBJECT: STATUS REPORT - VERTAC AT JACKSONVILLE

CSN: 600028 Permit No.
Media: Air, Water, Solid, Hazardous, *Superfund*
Sort: Permit, Compliance, Legal, *Misc.*

The Department is now in the process of attempting to bring together some "loose-ends" concerning dioxin (TCDD) contamination resulting from Vertac's operation. Some studies which have been conducted under EPA sponsorship have yet to be completed and reported. Some of the Department's monitoring efforts have been deferred in order that other federal commitments could be met. It is anticipated that monitoring/analytical activities can be resumed by late December.

A meeting has been scheduled for November 29, 1979 involving Vertac and the Department. Topics of the meeting are to include: (1) Status of 2,4,5-T start-up plans, (2) compliance with the Department's order, and (3) discussion of monitoring and analytical efforts of Vertac, EPA and DPC&E. I will update this report after the meeting on the 29th.

Jacksonville Sewage Treatment System

The oxidation ponds of the current wastewater plant are contaminated with TCDD. Jacksonville has completed initial plans for a new system which would by-pass defective collector lines and the old wastewater treatment plant. The plans were completed prior to the Vertac incident. However, the Air Force claims that it is unable to participate in the funding of the project and, as a consequence, EPA will not receive the plans for review and subsequent funding of a construction grant. (Typically, EPA pay 75% of the construction costs and the community pays 25%.)

Senator Bumpers earlier this year was talking about a special appropriation to the Air Force in order that we could get the project moving. It is highly desirable that we do so because we can then isolate a portion of the TCDD problem. Your assistance in getting the Air Force or Congress moving would be helpful. Alternatively, the Department could, according to EPA, sue the Air Force. We stand ready to discuss the issue with you.

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Meanwhile, Jacksonville is proceeding with the construction of an interceptor line that should eliminate the problem of overflowing manholes in the residential area just south of Vertac. This may, however, create problems at the city's existing wastewater plant and require that the plant be by-passed during high flow conditions. We will be watching the situation closely.

Ambient Monitoring

Earlier commitments to EPA necessitated suspension of much of the Department's monitoring of soils, sediments and waters for TCDD. We now have a backlog of soil samples taken from the residential area surrounding Vertac and hope to be in a position to start working on them the latter part of December.

The Department has conducted some rather crude air sampling on Vertac's property. The finding has been that TCDD adsorbed on particulate matter (dust) collected by our sampling device is in the same range as we have found in soil samples on Vertac's property. We are expecting a set of more sophisticated sampling equipment from EPA to install and operate both on Vertac's property and in the surrounding residential area. We hope that EPA's equipment will give some idea as to the size fraction of the contaminated particles. Such information will provide better insight as to the health hazards involved.

*ewr
analyzed*

Site Cleanup

Vertac appears to be reasonably on schedule with requirements of this Department. Paul Means has sent an inquiry to Vertac which, in effect, provides a vehicle for final determination/reconciliation of Vertac's compliance status. This will be discussed in detail with Vertac on the 29th and a report submitted to you.

I am very interested in establishing a erosion control program on Vertac's property. Such a program will reduce wind blown dust (contaminated with TCDD) as well as reduce the continued contamination of Rocky Creek and Bayou Meto. Before finalizing the elements of the program, I would like to have benefit of EPA's recently completed soils and geology study. The report of the study is now in preparation.

Analytical Questions

Our contacts within EPA continue to alert us concerning analytical questions. These questions impact current understandings of the biological half-life of TCDD and the potential for TCDD to be degraded under varying environmental conditions. At issue is the extent to which TCDD is bound to soil particles, the stereochemistry of the TCDD molecule and "active sites" on the molecule.

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If you desire, I will provide a detailed explanation of the issue. For purposes of this report, however, I am merely alerting you to the possibility that greater TCDD concentrations exist in soils and sediments than previously reported and that the TCDD half-life is longer than previously estimated.

Resumption of 2,4,5-T Production

Vertac continues to hold production of trichlorophenol and 2,4,5-T in abeyance until such time that the state and EPA approve proposed plans for containment and destruction of TCDD.

In a confidential report dated November 5, 1979, Vertac summarized the results of various laboratory scale experiments for clean-up and destruction of TCDD. The report also contained flow charts depicting how TCDD containment, cleanup and destruction would be accomplished, using the process described in Vertac's patent application. It is unlikely, however, that the depicted process will be placed into operation because the report alludes to an alternative/modified process which Vertac has developed which achieves a hundred-fold improvement in TCDD destruction efficiency (to 99.999%). Presumably, plans and drawings of the improved process will be submitted to the Department and EPA after Vertac completes amendments to its earlier patent application.

I have not received comments from EPA concerning Vertac's November 5 report. Delays are expected because EPA's principal coordinator, Bruce Elliot, has been stricken with ulcer problems.

EPA and the Department monitored some of Vertac's laboratory-scale TCDD destruction runs. Samples were split between the Department and at least two EPA-sponsored labs. Although the outside labs have not formally reported their results, preliminary information suggests there is substantial agreement with DPC&E's data. Based upon the foregoing and based upon the Department's analysis of Vertac's more recent destruction efforts, I am convinced that there are chemical means of destroying TCDD in Vertac's waste through a dechlorination/extraction process to a level less than 10 parts per trillion. The Department has not confirmed the identity of the products of the destruction process. The identification may be accomplished by EPA-sponsored labs.

Vertac maintains that it is capable of installing and safely operating the equipment necessary to contain and destroy TCDD resulting from the production of trichlorophenol and 2,4,5-T. Vertac officials have discussed the possibility of securing an EPA grant to assist in the processing of stored waste products and contaminated soils and sediments. EPA appears to be favorably impressed with the idea

and would, in my opinion, fund such a program provided that it was satisfied with the chemical destruction process and provided that you fully supported the project. It is anticipated that the project would include, in addition to the chemical destruction for materials containing high TCDD concentrations, physical separations and biological degradation of less concentrated materials. Please note, however, that biological degradation has not yet been proven.

Vertac maintains that it will not be able to afford the installation of process equipment for the chemical destruction of TCDD unless it is permitted to resume production of trichlorophenol and 2,4,5-T. I am not sure that Vertac will be able to afford the safeguards that will be imposed if production is allowed. Unfortunately, that will remain an open question until such time that the engineering progresses beyond the conceptual stage.

I continue to recommend that Vertac not be allowed to resume production of trichlorophenol or 2,4,5-T unless (a) the destruction of TCDD-containing waste can be assured, (b) both the production and destruction processes can be adequately safeguarded, and (c) Vertac commits to a phased program for the destruction of stored waste products, including highly contaminated soils and sediments. The dimensions of the phased program would necessarily be dependent upon the degree of federal support obtained.

While the conditions described in the above paragraph are necessary, I am not sure that they are sufficient. Broader questions concerning worker safety and environmental impacts relative to the use of 2,4,5-T must also be factored into the equation. Studies being conducted outside of Arkansas may eventually provide guidance. Recognizing that the fate of 2,4,5-T rests primarily in EPA's hands and recognizing the federal resources and responsibilities in the field, I would be hesitant in attempting a ban, at the state level, on the manufacture and use of 2,4,5-T. Until Vertac forces the issue by finally submitting detailed plans and specifications for the containment and destruction of TCDD wastes, I do not feel that the state is obligated to take a stand. By then, better data could be available.

Water-

Water-

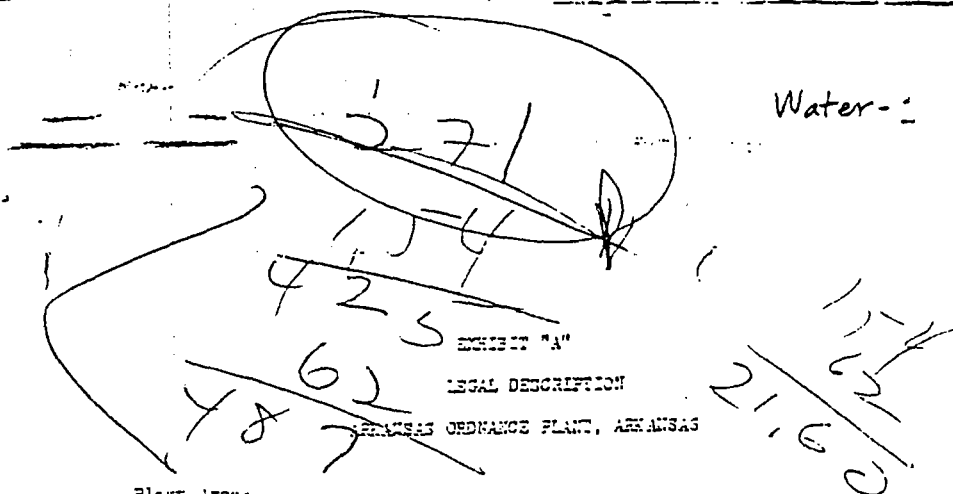


EXHIBIT "A"

LEGAL DESCRIPTION

ARKANSAS ORDNANCE PLANT, ARKANSAS

Plant Area:

A tract of land situated in the County of Pulaski, State of Arkansas, being part of Fractional Sections 6, 7, 18, 19, and 30, Township 5 North, Range 10 West, all of Fractional Sections 1 and 2, and Sections 11, 12, 13, 14, 23, and 24, and part of Sections 25 and 26, Township 5 North, Range 11 West of the 5th Principal Meridian, and being more particularly described as follows:

Beginning at the northwest corner of said Fractional Section 2; thence east along the north line of said Fractional Section 2, the north line of said Fractional Section 1, and the north line of said Fractional Section 6 to the north quarter corner of said Fractional Section 6; thence south along the north and south quarter line of said Fractional Section 6, the north and south quarter line of said Fractional Section 7, the north and south quarter line of said Fractional Section 18, the north and south quarter line of said Fractional Section 19, and the north and south quarter line of said Fractional Section 30 to the corner of said Fractional Section 30; thence east along the east and west quarter line of said Fractional Section 30 to a point on the southwesterly right-of-way line of Arkansas State Highway No. US 67; thence in a southeasterly direction along said southwesterly right-of-way line to a point on the northwesterly line of the Missouri Pacific Railroad Company's right-of-way; thence in a southwesterly direction along said northwesterly right-of-way line to a point on the south line of said Fractional Section 30; thence west along the south line of said Fractional Section 30 to the southwest corner thereof; thence north along the west line of said Fractional Section 30 to the southeast corner of the NE $\frac{1}{4}$ SE $\frac{1}{4}$ of said Section 25; thence west along the south line of the NE $\frac{1}{4}$ SE $\frac{1}{4}$ of said Section 25 and the south line of the NE $\frac{1}{4}$ SW $\frac{1}{4}$ of said Section 25 to the southwest corner of said NE $\frac{1}{4}$ SW $\frac{1}{4}$ of Section 25; thence north along the west line of said NE $\frac{1}{4}$ SW $\frac{1}{4}$ of Section 25 to the southeast corner of the SW $\frac{1}{4}$ NW $\frac{1}{4}$ of said Section 25; thence west along the east and west quarter line of said Section 25 and the east and west quarter line of said Section 26 to the west quarter

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Plant Area, (cont'd)

corner of said Section 26; thence north along the west line of said Section 26, the west line of said Section 25, the west line of said Section 11, the west line of said Section 11, and the west line of said Fractional Section 2 to the point of beginning, containing 7,251.11 acres, more or less.

Water Pipe Line Easement:

A tract of land situated in the County of Pulaski, State of Arkansas, being part of the NW¹/₄ of Fractional Section 31, Township 3 North, Range 10 West and part of the SE¹/₄ NE¹/₄ of Section 36, Township 3 North, Range 11 West of the 5th Principal Meridian and being more particularly described as follows:

Part 1: (J-212, J-213, J-214, & J-215)

Beginning on the east line of said SE¹/₄ NE¹/₄ of Section 36 at a point which is S. 01° 03' E., 398.6 feet from the northeast corner of said SE¹/₄ NE¹/₄ of Section 36; thence N. 45° 03' E., 607.0 feet to a point; thence N. 23° 46' E., 574.0 feet to a point; thence N. 26° 21' E., 141.2 feet to a point on the southeasterly line of the Missouri Pacific Railroad Company's right-of-way; thence N. 54° 09' E., 30.4 feet along said southeasterly right-of-way line to a point; thence S. 26° 21' E., 160.2 feet to a point; thence S. 23° 46' E., 511.0 feet to a point; thence S. 46° 03' E., 621.5 feet to a point; thence S. 31° 03' E., 77.6 feet to a point on the northeasterly right-of-way line of the Arkansas Ordnance Plant Water Pipe Line Easement; thence N. 43° 57' E., 42.4 feet along said northeasterly right-of-way line to a point; thence N. 01° 03' E., 60.0 feet to a point; thence N. 46° 03' E., 21.2 feet to the point of beginning, containing 0.94 acres, more or less.

Part 2: (J-214)

Beginning on the north line of said Fractional Section 31 at a point which is S. 87° 45' E., 99.3 feet from the northwest corner of said Fractional Section 31; thence S. 87° 45' E., 34.2 feet along said north line of Fractional Section 31 to a point; thence S. 26° 21' E., 795.2 feet to a point on the northwesterly line of the Missouri Pacific Railroad Company's right-of-way; thence S. 54° 09' E., 30.4 feet along said northwesterly right-of-way line to a point; thence N. 26° 21' E., 816.6 feet to the point of beginning, containing 0.55 acres, more or less.

Permit for Water Pipe Line Crossing: (J-204-A)

A tract of land situated in the County of Pulaski, State of Arkansas, being part of the SE¹/₄ NE¹/₄ of Section 36, Township 3 North, Range 11 West of the 5th Principal Meridian, and being more particularly described as follows:

Beginning on the southeasterly line of the Missouri Pacific Railroad Company's right-of-way at a point which is N. 69° 09' E., 393.5 feet from the northeast corner of the SE¹/₄ NE¹/₄ of said Section 36; thence S. 56° 09' E., 30.0 feet along said southeasterly right-of-way line to a point; thence N. 33° 21' E., 100.0 feet to a point on the northwesterly line of said Missouri Pacific Railroad Company's right-of-way; thence S. 56° 09' E., 30.0 feet along said northwesterly right-of-way line to the point of beginning, containing 0.11 acres, more or less.

Pacific Railroad Company's right-of-way; thence N. 86° 09' E., 304.3 feet
along said northwesterly right-of-way line to a point; thence S. 55° 21' E.,
100.3 feet to the point of beginning, containing 0.37 acres, more or less.

Tator Mill Site:

Part 1:

A tract of land situated in the County of Pulaski, State of Arkansas, being the south 100 feet of Fractional Section 31, Township 3 North, Range 10 West of the 5th Principal Meridian, containing 9.39 acres, more or less.

Part 2:

A tract of land situated in the County of Pulaski, State of Arkansas, being part of the SW $\frac{1}{4}$ SW $\frac{1}{4}$ of Section 32, Township 3 North, Range 10 West of the 5th Principal Meridian, and being more particularly described as follows:

Beginning at the southwest corner of said Section 32; thence north along the west line of said Section 32, 100.0 feet to a point; thence east and parallel to the south line of said Section 32, 451.0 feet to a point; thence south 100.0 feet to a point on the south line of said Section 32; thence west along said south line to the point of beginning, containing 1.21 acres, more or less.

Part 3:

A tract of land situated in the County of Pulaski, State of Arkansas, being part of the NW $\frac{1}{4}$ NW $\frac{1}{4}$ of Fractional Section 5, Township 2 North, Range 10 West of the 5th Principal Meridian and being more particularly described as follows:

Beginning at the northwest corner of said Fractional Section 5; thence east along the north line of said Fractional Section 5, 700.0 feet to a point; thence south 100.0 feet to a point; thence west and parallel to the north line of said Fractional Section 5, 700.0 feet to a point on the west line of said Fractional Section 5; thence north along said west line to the point of beginning, containing 1.60 acres, more or less.

Permanent Easement for Access Road: (J-207)

A tract of land situated in the County of Pulaski, State of Arkansas, being part of the NW $\frac{1}{4}$ of Fractional Section 30, Township 3 North, Range 10 West of the 5th Principal Meridian, in Duprou's Addition to the town of Jacksonville, Arkansas, and being more particularly described as follows:

Parcel A: - Beginning on the north and south quarter line of said Section 30 at a point which is N. 02° 00' E., 518.0 feet from the center of said Fractional Section 30; thence N. 02° 00' E., 116.5 feet along said north and south quarter line to a point; thence S. 41° 04' E., 289.1 feet to a point; thence S. 48° 36' E., 251.2 feet to a point; thence S. 56° 57' E., 172.7 feet to a point on the westerly right-of-way line of U.S. Highway No. 67; thence

Permanent Easement for Access Road: (J-207) cont'd.

in a southeasterly direction 17.3 feet along said right-of-way line to a point on the east and west quarter line of said Fractional Section 30; thence N. 83° 14' W., 177.3 feet along said east and west quarter line to a point; thence N. 86° 57' W., 43.2 feet to a point; thence N. 12° 54' W., 242.1 feet to a point; thence N. 41° 04' W., 183.3 feet to the point of beginning, containing 1.40 acres, more or less.

Parcel 5.—Beginning on the north and south quarter line of said Fractional Section 30 at a point which is N. 02° 00' E., 516.9 feet from the center of said Fractional Section 30; thence N. 02° 00' E., 181.1 feet along said north and south quarter line to a point; thence N. 82° 38' E., 549.5 feet to a point on the westerly right-of-way line of U.S. Highway No. 67; thence in a southeasterly direction along the arc of a curve 121.7 feet to a point; thence S. 82° 38' W., 492.1 feet to the point of beginning, containing 1.20 acres, more or less.

NOTE: In addition to the land acquired in fee and the easements acquired as described above, permits were obtained from the Missouri Pacific Railroad Company and the Arkansas Highway Commission for pipe line crossings which involve no acreage.

FORM OF TRANSFER

KNOW ALL MEN BY THESE PRESENTS, That the War Department (Transferor), acting through the Commanding Officer, Arkansas Ordnance Plant, Little Rock, Arkansas, by these presents does transfer custody, control, and accountability unto the War Assets Administration (Transferee), the following land and improvements thereon, to wit:

The Arkansas Ordnance Plant located in Pulaski County, Arkansas and containing a total of seven thousand two hundred fifty two and ninety-six one hundredths acres (7,252.96) the legal description of which is attached hereto as Exhibit "A" which is made a part hereof:

All buildings, utilities and improvements which are presently located on the land embracing the Arkansas Ordnance Plant, the description of which is attached hereto as Exhibit "B" which is made a part hereof:

All "installed real property" which is presently located in the above-described buildings or located on the above-described premises the description of which is attached hereto as Exhibit "C" which is made a part hereof:

All of the personal property located at the Arkansas Ordnance Plant as described on Forms SPS-1 or SPS-1.1, ORD 05-011-46-1 through 465 inclusive. This transfer is intended to cover and embrace all U. S. Government personal property except metal components and packaging material for which the Transferor is accountable. Said metal components and packaging material will be removed from the premises by the Transferor within 30 days after the effective date hereof.

The Transferee will proceed to make such inventory checks as he deems necessary prior to 1 July 1946 of the personal property described in above-mentioned Forms SPS-1. Any discrepancies disclosed as a result of such checks will be reported by the Transferee to the Transferor for necessary adjustment by 1 July 1946.

The entire facility (including real and personal property) has been decontaminated and is satisfactory for idle stand-by condition for use in its original purpose. The facility has been reviewed by a board of consultants and it has been recommended that seventy-three (73) buildings (listed on Page 1 Exhibit C) which cannot be economically decontaminated should be destroyed in the event the facility is disposed of for other than its original purpose.

The undersigned Transferee hereby acknowledges that delivery of the said land and improvements was made by the Transferor and receipt of said property is hereby acknowledged.

The undersigned Transferee hereby agrees that on 1 July 1946 full accountability will be assumed by said Transferee for all personal property listed on Forms SPS-1, ORD 05-011-46-1 thru ORD 05-011-46-465 and no further requests for adjustment will be made to the Transferor.

IN WITNESS WHEREOF, the War Department acting through the Commanding Officer, Arkansas Ordnance Plant, Arkansas, and War Assets Administration, have hereunto set their hands this 11th day of June 1946.

WAR DEPARTMENT (Transferor)

BY: [Signature]
 Edwin Johnson
 Capt., Ord./Dep.,
 Commanding Officer
 Arkansas Ordnance Plant, Arkansas

WAR ASSETS ADMINISTRATION (Transferee)

BY: [Signature]
 G. S. CHRISTIAN
 Regional Director

18955

HERCULES INCORPORATED

C. F. Silwell

Wilmington, Delaware
September 11, 1967

TO: Messrs. J. G. Copeland, Jr.
E. Turk
J. M. Eagan
J. Z. Miller
K. T. Givens -
G. A. Seely - Engineering
A. L. Larson - Engineering
B. W. Dickerson - Engineering
H. F. Heckroth - Engineering
H. H. McCrea - Engineering
H. E. Wilder - Jacksonville

FROM: A. L. Treisback - Synthetics Department

C. F. Silwell

DEFOLIANT ORANGE

8.0 Million Gallons/Year Mixed Butyl D and Butyl T Esters

Weldon Spring, Missouri

Orange - 8 Million Gallons/Year

Criteria

The attached is a basic process criteria for an Orange plant calculated to produce 8.0 million gallons of Orange per year. The liberty was taken to use the data and calculations and assumptions made in March 1967 as a base line which was calculated to produce Orange at 6.0 million gallons per year. It is realized that several major decisions must be made, namely:

1. Continuous versus batch MCA process
2. Clean up process and quality required
3. Waste treatment and disposal specifications

The following is intended as a preliminary criteria from which the final guide lines, project estimate, and the formal proposal will be made.

Comments, changes and criticisms are solicited.

The following assumptions have been made:

1. The quantities of D and T acid are based on the Government specification as 50/50 Butyl D and T Esters by volume.
2. Production of MCA is based on the present batch system used at Jacksonville.
3. Both D and T acid will be dried and handled to Esterification with Tote Bins.
4. The acid reactors will be 3,000 gallons maximum working capacity to avoid unknown agitation scale-up problems especially on T acid.
5. The glass lined vessels will be 2,000 and 4,000 gallon standard reactors and Chemstor type storage tanks to minimize delivery time.
6. Dechlorinators will be nickel clad 750 gallon capacity reactors built for shell operation at 350 psig. and jacket operation at 150 psig.
7. Solvent clean up is based on the present multi-stage batch process currently being used at Jacksonville.
8. An entirely new and complete waste disposal system must be designed and installed.
9. Approximately seven-day capacity has been used for raw materials and in-process storage.

18957

Calculations Basis 100% Acid & Ester

Orange - 8 Million Gallons/Year

	<u>Wgt./Wgt.</u> (Hercules)	<u>Vol./Vol.</u> (Gov't.)
Assume average wt./gal.	42.8 MM Lbs.	4 MM Gal. Butyl-D
10.70 lbs.	42.8 MM Lbs.	4 MM Gal. Butyl-T
	<u>85.6 MM Lbs.</u>	<u>8 MM Gal.</u>

Assume sp. gr. Butyl-D - 1.245 10.35 lb./gal.
" " " Butyl-T - 1.325 11.02 Lb./gal.

$$\begin{aligned} 1.245 \times 8.33 \times 4 \text{ MM} &= 41.48 \text{ MM lbs. Butyl-D} \\ 1.325 \times 8.33 \times 4 \text{ MM} &= 44.15 \text{ MM lbs. Butyl-T} \end{aligned}$$

	<u>Difference</u> <u>Lbs. Ester</u>	<u>Lbs. Acid</u> <u>Represented</u>	<u>Difference</u>
. D Required	1.32 MM	34.24 MM	33.18 MM = -1.06 MM D Acid
Lbs. T Required	1.35 MM	35.10 MM	36.20 MM = +1.10 MM T Acid

Have built into estimate sufficient capacity to go either way.

By A. E. Sidwell
8/25/67

POWDER COMPANY

cc: J. M. Egan - Syn.
M. A. Torres - R. C.
J. J. Ford - R. C.
A. Z. Conner - R. C.
A. D. Sidwell - Jacksonville

Wilmington, Delaware
November 18, 1965

TO: C. L. Dunn - Synthetics Department
FROM: E. E. Christofano - Medical Department

The following comments will summarize the investigations we contemplate on chloracne possibly associated with 2,4,5-T esters.

1. Badische uses a bioassay technique to check each batch of TCP purchased. Their test consists of feeding each of three rabbits with 1 gm./kg. of TCP, with a determination of bromsulphalein retention after 5 days. More than 5% of BSP retention is cause for rejection of the batch. Sensitivity is claimed at 3 ppm.

2. Dow bioassays by a rabbit ear painting technique. The internal surface of one rabbit ear is painted daily with 0.1 ml. of a chloroform solution of test material (10 or 50%) of an extract of TCP in chloroform. Unless severe irritation is noted 10 doses are applied. The ears are observed for two additional weeks for the appearance of folliculitis and cyst formation. They have noted fatalities from a single application and liver damage has accompanied the chloracne reactions. Sensitivity is claimed at about 1 ppm.

While the Dow testing may be more sensitive, the Badische method is faster and less expensive. In order to evaluate both methods we recommend that Hercules supply material to Badische for their testing and simultaneously begin gathering confirming data in a commercial laboratory. Because of a lack of information on the toxicity of in-process materials, these latter studies should begin only after oral toxicity has been determined. For this first stage the acute oral LD₅₀ studies would cost approximately \$300. Subsequent adnexa studies on these materials are expected to cost about \$6,000, however, an accurate estimate is not possible until Stage 1 is complete. Preparation of the samples and subsequent analysis is estimated to cost \$500.

Hercules

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C. L. Dunn - Synthetics

- 2 -

November 18, 1965

Dr. Ottel of Radische has agreed to bioassay several spiked samples to permit comparison of results with the gas chromatographic determination of dioxin and with the Dow ear painting procedure. To permit this study we request that 25 g. of each of the following spiked samples be prepared:

- a. Standard 2,4,5-T acid spiked with 0, 2, 5, 10, 20 ppm dioxin.
- b. Plant grade 2,4,5-T acid with a known dioxin content. - *high level - 400*
- c. Plant grade sodium trichlorophenate spiked with 0, 1, 3, 5, 10 ppm dioxin (based on TCP equivalent).
- d. Dioxin standard approximately 2 mg. - *in oil. Hest*
- e. Plant grade ~~propyl~~ ester of 2,4,5-T acid as 6 lbs/gal. (Crushed. *High level*) solution in xylene spiked with 0, 2, 5, 10, 20 ppm dioxin.

Approximately 10 gms. of each sample should be prepared for shipment to Dr. Ottel and the remainder retained for future confirming tests conducted by Bio-Test. Chemical analysis of the spiked samples would be required after the biological testing demonstrates physiological activity.

Acute oral toxicity data on sodium trichlorophenate, 2,4,5-T acid and finished propyl ester formulation should be begun promptly. Approximately 50 gms. of each material should be sent to Dr. Joseph C. Calandra, Industrial Bio-Test Laboratories, 1810 Frontage Road, Northbrook, Illinois. Dr. Calandra has a supply of dioxin.

After these preliminary tests are conducted we will establish a more comprehensive program for the evaluation of hazard during manufacture and in the product as it would be used by the customer. Without these preliminary data a test program would be unnecessarily expensive.

E. Christofano

6/1/66

*Side stream sample was to be analyzed Feb. 66
L being act acid, a has been*

EEC:wh



H03893

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After investigating that a serious problem existed, BAF started a thorough investigation which centered on identity in RZ as the sensitive agent.

Although BAF indicated the identity they did not identify its structure as completely as they. The indicated identity was located to rubric as an oral name of C-1114/24. The compound appears to be the same as that indicated by BAF and identified to be 2,3,5-trichlorobenzene-1,4-diol.

Because of the financial entry for composition claims, BAF classified materials of RZ and Dr. Gertel noted BAF isn't large enough to afford another such episode. They are persons all under RZ from BAF, was reported. They had only a few cases of evidence.

In order to insure that all personnel RZ is free of the economy, BAF holds all materials until they have been biologically analyzed. If they have any detectable anomaly, the materials are refused. The sensitivity of their entry is 3 ppm. BAF has had no further trouble since launching this operation.

Dr. Gertel provided us with the details of their laboratory. The BAF entry procedure is more rigid than the BAF procedure and much less expensive. To our knowledge, no one in the United States has tried the BAF procedure. I asked Dr. Gertel if he could identify several "spiked" samples for us by this procedure to assist us to compare results with the standard biographic procedure and the Dr. Gertel's procedure. He agreed. He also agreed to send us a copy of an unpublished report on the chemical aspects of the BAF episode and their biological research.

HC 1413

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A&G

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A&G 201789

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h014.5

CONFIDENTIAL

John Capeland

c d o

October 11, 1964

As soon as the new process is operational at Jacksonville, I recommend that we submit several production samples and "spiked" samples to Dr. Ortolani at the Research Center for comparative analysis. This will help confirm whether our analytical procedure detects the major enzymes and whether the R2P laboratory will be useful to Bureau.

JTC/asm



DOW CHEMICAL U.S.A.

11-3-78

November 1, 1978

BENNETT BUILDING
2030 DOW CENTER
MIDLAND, MICHIGAN 48640

Mr. John Calloway
Vertac Consolidated
Suite 2414
5100 Poplar Avenue
Memphis, TN 38137

Dear John:

Re: 2,4,5-T ACID - YOUR LETTER OF OCT. 24, 1978

John, we are issuing the purchase order this date to cover the movement of 500,000 lbs. of 2,4,5-T Acid in accordance with my letter of October 9, 1978, subject to the following addendums as noted and accepted in your letter of October 24, 1978:

- 1) Will agree to accept your clause stating that Dow will purchase any product that you have in inventory for Dow at the time of any government action that bans the sale, manufacture or importation of 2,4,5-T Acid.
- 2) Trip leases of Dow cars will be 15 days for 10,000 gallon tank cars and 21 days for a 20,000 gallon tank car. Detention charges shall be as per my letter for days beyond this.
- 3) There shall be no imbalances in raw materials input and materials supplied to Dow. Vertac will supply materials to Dow to balance out any excess in trichlorophenol supplied by Dow.
- 4) Specifications: We will temporarily suspend the 2,4-D Acid specification subject to further discussion.

John, as I pointed out on the telephone, I feel that there should be no problem on the movements for the majority of this product; however, there are some small applications for which we may have to have a much tighter 2,4-D Acid specification. However, to allow us to begin to move product to areas that will require it in December and January, I think we must proceed leaving this one particular ambiguity.

Appreciate your cooperation in this matter.

Sincerely,

E. R. Russell

E. R. Russell
Supply Manager

U.S.A. Purchasing OPERATING UNIT OF THE DOW CHEMICAL COMPANY

18983



Industrial BIO-TEST Laboratories, Inc.

810 FRONTAGE ROAD
NORTHMOORE, ILLINOIS 60062

AREA CODE 312
TELEPHONE 979-1000

October 30, 1968

Dr. E. E. Christofano
Medical Department
Hercules Incorporated
910 Market Street
Wilmington, Delaware 19899

Dear Chris:

Enclosed is the abstract of the paper to be submitted to SOT for next year's meetings, March 9-12, 1969. The new title is "Influence of Dioxin on Liver Function in the Rabbit."

Best regards.

Sincerely yours,



M. L. Kaplinger, Ph.D.
Assistant Laboratory Director

MLK:ph
Enclosure

100-4508

101459

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18905
H238003

Dr. C. E. Frazier
Mr. E. C. Frazier

Mr. Frazier

M. L. Kephart, Ph.D.
Assistant Laboratory Director

Sincerely yours,

I am sorry we have to cancel the first paper, but hope that the
abstracts will help you plan the final program.

As you will recall, we submitted an abstract of another paper,
"Reproduction Studies in Rats and Rabbits with Cyclophosphamide Salts,"
which arrived too late to be included in the program. If possible, could
our "Reproduction" paper be substituted for the "Diarrhea" paper which
has to be cancelled.

Due to unforeseen difficulties, we will not be able to present the
paper, "Influence of Diets on Liver Function in the Rabbit," an abstract
of which was allowed for the SOT Meeting March 9-12, 1969. Therefore
it must be cancelled.

Dear Ted:

C. F. A. Loomis
Program Committee
Faculty of Toxicology, Inc.
Department of Pharmacology
School of Medicine
University of Washington
Seattle, Washington 98105

January 3, 1969

02011

0000343

October 16, 1968

[Handwritten signature/initials]
10M-

Mr. V. K. Rowe
Biochemical Research Laboratory
The Dow Chemical Company
1701 Building
Midland, Michigan

[Handwritten signature]

Dear Mr. Rowe:

As you may recall, Hercules has been attempting to develop a bioassay technique to simplify detection of dioxin in herbicide formulations. Based principally upon work initiated by Dr. Oettel at BASF, the tests measured liver function changes which result from feeding rabbits with herbicide. We feel such a technique offers several advantages over rabbit ear painting tests.

Unfortunately, we have been unsuccessful. But to state it so bluntly is really unfair. First, we attempted to determine the sensitivity of liver change by feeding test materials with known additions of dioxin. The toxicity of test materials prevented use of liver function change as a bioassay for dioxin even at 10 ppm. We then dosed animals with 0.01 & 0.1 mg/kg of dioxin suspended in corn oil. Carbon tetrachloride was administered as a positive control at 100, 250 and 500 mg/kg. Clinical determinations including SGOT, SGPT and BSP retention were conducted prior to administration and every two to three days thereafter for at least 14 days.

Significant elevations in one or more of the clinical determinations were found in some but not all dioxin animals. The changes were not well correlated with dose nor were they consistent with regard to onset or duration. Animals on the positive control test responded as would be expected with significant blood chemistry changes only two days after dosing with 100 mg/kg.

Although positive results were obtained with dioxin, the usefulness of this technique as a bioassay for the presence of dioxin is questionable.

At the Toxicology Roundtable I mentioned these results to Ken Olsen who suggested that you might comment upon them. But the other reason for writing is to solicit your opinion on the usefulness of presenting our data at the Society of Toxicology meeting next spring. Certainly such a presentation would raise questions as to the reason for conducting an unsuccessful study.



18986

Mr. V. K. Rove

-2-

October 16, 1968

On the other hand, someone might be spared useless effort if such negative information were offered to the scientific community.

I'd like to have your comments before we proceed.

Sincerely,

Emil E. Christofano
Industrial Hygienist

EEC:rbm

18967

WINDMILL POWDER COMPANY

DELICIOUS

cc: Dr. E. B. Scott - Genetics
Mr. E. C. Phillips - Inter.
Mr. Nils Holman - T. & R. Co.
Dr. H. A. Taves - S. & S. R. Co.
Mr. J. J. Ford - Anal. Div. R. Co.

October 19, 1956

P-2542
2/8/84 JL

Professor E. Ottel
Pharmakol. Inst. Ger. USP A.G.
6 Bismarck Allee 20
67 Ludwigshafen
Rhein, Deutschland

Dear Professor Ottel:

Mr. Nils Holman of our Rags office has sent me a report on his interesting and informative visit with you and Dr. Rothman on the 28th of August. I sincerely appreciate the courtesy you showed to Mr. Holman during this visit to your laboratory. He has referred several questions to me which I will attempt to answer.

In our process for the manufacture of 2,4,5-T acid, we do not isolate trichlorophenol. It is for this reason that we did not send any trichlorophenol. It was our hope, however, that you would be able to administer the samples of crude trichlorophenol, 2,4,5-T acid, and ethyl hexyl ester. We realize that because of the greater toxicity of the acid, the sensitivity of your biological assay for "dioxin" may not be as great.

Mr. Holman stated that the original samples of 10 grams would not be adequate for your assays. Accordingly, we have shipped directly to your laboratory approximately 100 grams additional of samples:

11570-56-1	Ethyl hexyl ester of 2,4,5-T acid
11570-55-1	sodium 2,4,5-trichlorophenolate
11570-56-7	non-saponifiable fraction from plant process

We have also shipped 100 grams of a sample identified as:

11570-56-11 2,4,5-T acid

which is the same as previous sample 11570-1-1, but from a different production batch. None of these samples contained any detectable dioxin. If you wish to add dioxin, the previous sample 11570-56-17 of pure dioxin may be used.

Since you expressed an interest in receiving a sample of the trichlorophenol, although we do not customarily isolate this material, we have prepared a sample of crude TC from our process especially for your test purposes. This sample (100 grams) has also been shipped and is identified as 11570-15.

You inquired about the nature of the non-saponifiable fraction previously delivered by Mr. Holman. This consists of the non-saponifiable

WINDMILL
HENDON

ENCLOSURE

H03002

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HERCULES FOREIGN COMPANY

Reference is called

Page :

October 19, 1961

Material which is removed from our FD process and if not acceptable, return of which is turned to our process, the subject should appear in this non-acceptable process.

11 *

The also required through Mr. DeLeon, whether we intended to try a new method for the discovery of Alaska. In the end, however, we are unable to establish detailed determinations by the above-mentioned with the result our discovery method of Dey and with the result our discovery with you have developed. Obviously, if the above-mentioned is a reliable method it can be used more easily as a pilot method before than a discovery method.

The Discovery procedure requires placing a discovery contract on the part of the reliable and willing for development of hydrocarbons in about 14 to 15. Our report, positive results with samples of 1,4,5,6 and 6,7,8,9,10,11,12,13,14,15,16,17,18,19,20,21,22,23,24,25,26,27,28,29,30,31,32,33,34,35,36,37,38,39,40,41,42,43,44,45,46,47,48,49,50,51,52,53,54,55,56,57,58,59,60,61,62,63,64,65,66,67,68,69,70,71,72,73,74,75,76,77,78,79,80,81,82,83,84,85,86,87,88,89,90,91,92,93,94,95,96,97,98,99,100,101,102,103,104,105,106,107,108,109,110,111,112,113,114,115,116,117,118,119,120,121,122,123,124,125,126,127,128,129,130,131,132,133,134,135,136,137,138,139,140,141,142,143,144,145,146,147,148,149,150,151,152,153,154,155,156,157,158,159,160,161,162,163,164,165,166,167,168,169,170,171,172,173,174,175,176,177,178,179,180,181,182,183,184,185,186,187,188,189,190,191,192,193,194,195,196,197,198,199,200,201,202,203,204,205,206,207,208,209,210,211,212,213,214,215,216,217,218,219,220,221,222,223,224,225,226,227,228,229,230,231,232,233,234,235,236,237,238,239,240,241,242,243,244,245,246,247,248,249,250,251,252,253,254,255,256,257,258,259,260,261,262,263,264,265,266,267,268,269,270,271,272,273,274,275,276,277,278,279,280,281,282,283,284,285,286,287,288,289,290,291,292,293,294,295,296,297,298,299,300,301,302,303,304,305,306,307,308,309,310,311,312,313,314,315,316,317,318,319,320,321,322,323,324,325,326,327,328,329,330,331,332,333,334,335,336,337,338,339,340,341,342,343,344,345,346,347,348,349,350,351,352,353,354,355,356,357,358,359,360,361,362,363,364,365,366,367,368,369,370,371,372,373,374,375,376,377,378,379,380,381,382,383,384,385,386,387,388,389,390,391,392,393,394,395,396,397,398,399,400,401,402,403,404,405,406,407,408,409,410,411,412,413,414,415,416,417,418,419,420,421,422,423,424,425,426,427,428,429,430,431,432,433,434,435,436,437,438,439,440,441,442,443,444,445,446,447,448,449,450,451,452,453,454,455,456,457,458,459,460,461,462,463,464,465,466,467,468,469,470,471,472,473,474,475,476,477,478,479,480,481,482,483,484,485,486,487,488,489,490,491,492,493,494,495,496,497,498,499,500,501,502,503,504,505,506,507,508,509,510,511,512,513,514,515,516,517,518,519,520,521,522,523,524,525,526,527,528,529,530,531,532,533,534,535,536,537,538,539,540,541,542,543,544,545,546,547,548,549,550,551,552,553,554,555,556,557,558,559,560,561,562,563,564,565,566,567,568,569,570,571,572,573,574,575,576,577,578,579,580,581,582,583,584,585,586,587,588,589,590,591,592,593,594,595,596,597,598,599,600,601,602,603,604,605,606,607,608,609,610,611,612,613,614,615,616,617,618,619,620,621,622,623,624,625,626,627,628,629,630,631,632,633,634,635,636,637,638,639,640,641,642,643,644,645,646,647,648,649,650,651,652,653,654,655,656,657,658,659,660,661,662,663,664,665,666,667,668,669,670,671,672,673,674,675,676,677,678,679,680,681,682,683,684,685,686,687,688,689,690,691,692,693,694,695,696,697,698,699,700,701,702,703,704,705,706,707,708,709,710,711,712,713,714,715,716,717,718,719,720,721,722,723,724,725,726,727,728,729,730,731,732,733,734,735,736,737,738,739,740,741,742,743,744,745,746,747,748,749,750,751,752,753,754,755,756,757,758,759,760,761,762,763,764,765,766,767,768,769,770,771,772,773,774,775,776,777,778,779,780,781,782,783,784,785,786,787,788,789,790,791,792,793,794,795,796,797,798,799,800,801,802,803,804,805,806,807,808,809,810,811,812,813,814,815,816,817,818,819,820,821,822,823,824,825,826,827,828,829,830,831,832,833,834,835,836,837,838,839,840,841,842,843,844,845,846,847,848,849,850,851,852,853,854,855,856,857,858,859,860,861,862,863,864,865,866,867,868,869,870,871,872,873,874,875,876,877,878,879,880,881,882,883,884,885,886,887,888,889,890,891,892,893,894,895,896,897,898,899,900,901,902,903,904,905,906,907,908,909,910,911,912,913,914,915,916,917,918,919,920,921,922,923,924,925,926,927,928,929,930,931,932,933,934,935,936,937,938,939,940,941,942,943,944,945,946,947,948,949,950,951,952,953,954,955,956,957,958,959,960,961,962,963,964,965,966,967,968,969,970,971,972,973,974,975,976,977,978,979,980,981,982,983,984,985,986,987,988,989,990,991,992,993,994,995,996,997,998,999,1000,1001,1002,1003,1004,1005,1006,1007,1008,1009,1010,1011,1012,1013,1014,1015,1016,1017,1018,1019,1020,1021,1022,1023,1024,1025,1026,1027,1028,1029,1030,1031,1032,1033,1034,1035,1036,1037,1038,1039,1040,1041,1042,1043,1044,1045,1046,1047,1048,1049,1050,1051,1052,1053,1054,1055,1056,1057,1058,1059,1060,1061,1062,1063,1064,1065,1066,1067,1068,1069,1070,1071,1072,1073,1074,1075,1076,1077,1078,1079,1080,1081,1082,1083,1084,1085,1086,1087,1088,1089,1090,1091,1092,1093,1094,1095,1096,1097,1098,1099,1100,1101,1102,1103,1104,1105,1106,1107,1108,1109,1110,1111,1112,1113,1114,1115,1116,1117,1118,1119,1120,1121,1122,1123,1124,1125,1126,1127,1128,1129,1130,1131,1132,1133,1134,1135,1136,1137,1138,1139,1140,1141,1142,1143,1144,1145,1146,1147,1148,1149,1150,1151,1152,1153,1154,1155,1156,1157,1158,1159,1160,1161,1162,1163,1164,1165,1166,1167,1168,1169,1170,1171,1172,1173,1174,1175,1176,1177,1178,1179,1180,1181,1182,1183,1184,1185,1186,1187,1188,1189,1190,1191,1192,1193,1194,1195,1196,1197,1198,1199,1200,1201,1202,1203,1204,1205,1206,1207,1208,1209,1210,1211,1212,1213,1214,1215,1216,1217,1218,1219,1220,1221,1222,1223,12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June 26, 1947

Professor H. G. Cottel
Pharmaceutical Inst. der Kaiser A. G.
Schweizerstrasse 11
67 Ludwigshafen
Main, Germany

Dear Professor Cottel:

5100 (R) 4

that you very much for callir. to my attention the article on
exceptional case which was published in Paulo Lourenco, Medicina Unica 3, 225-27
(1966). Mr. Stelerman forwarded a copy to me and we have translated it into English.
I am enclosing a copy of the English translation for your files.

I agree with you that this report is very disturbing. These products
are mentioned in the report: Liller, Laterose and Small Seed Killers. Liller is
manufactured by Green Cross Products (of Canada), a division of The Sherwin-Williams
Company of Canada, Limited. Currently Liller contains 2,4-D and Menthyl but in
1962 it may have contained 2,4,5-T instead of Menthyl. Liller is 3,6-dichloro-2-
methylphenolic acid. Since this compound was not manufactured 2,4,5-T, they could
have purchased it from any one of four several different manufacturers.

Laterose is a name used by some United States firms to describe a variety
of phenylacetic acid formulations. Some of which contain 2,4,5-T. The "Small Seed
Killers" also could describe any herbicide formulation. It is not of the same origin
2,4,5-T. In our literature mail does not manufacture 2,4,5-T as their seed killers
contain, 2,4,5-T could have been purchased from any of the basic producers.

Consequently, the source of the 2,4,5-T which presumably was involved
in these exposures cannot be identified. I have sent a copy of the same article to
W. A. Stone of Ohio, but I have not received any comments from him.

As I have mentioned, we are relying on an extraordinary to assure
ourselves that our 2,4,5-T production is free of dieldrin. We have made some
attempt to bypass the analysis of the intermediate sent to you but are unable to
achieve desired sensitivity, partially because the 2,4,5-trichlorophenylacetic
acid and the ester are significantly more toxic than trichlorophenol. We are
continuing our effort to to confirm the concentration of dieldrin necessary to each to
elicit a positive skin reaction. After a while to show if you have had any success
with these samples.

100-100000-1000

100-100000-1000

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100-100000-1000

HERCULES INCORPORATED

Professor F. Wetzel

- 2 -

Jan 2, 1957

Also, we would still appreciate receiving copies of the photo, rays
which accompanied your trip in the "Lorain" at June 1956.

As soon as we have something more definite to report, we will contact
you. Thanks again for your continued interest in Urania, an interesting matter
of great importance to both companies.

Sincerely,

John P. Bradley, Inc.
Chief Scientist

JPI/c>

100305

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HERCULES 2 (b) (7)

TO: Mr. J. H. Dunn - Syracuse
Mr. A. D. Silver - Jacksonville

Villages, Delaware
April 10 1967

TO: Mr. C. L. Dunn - Syracuse Department
FROM: John J. Dunbar - Medical Department

I have obtained the attached information from Bureau regarding the problems my and Beltsch have had in relation.

Aside from providing additional information concerning the high degree of reliability of the information, the report the background information on why both comparative experimental problems and point out that Beltsch has always been in touch of TCP with their purchase from Buyer. Beltsch has more confidence in the BP robot; Liver function test than in the robot our last value for was. The sensitivity of this assay is not stated, but from the data provided, a sample which contained 5 ppm of the eluate would be several' value. Whether this refers to blood or Liver damage is not clear.

BT/om
Attachments

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HERCULES 4 (K) 0480

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October 16, 1968

Mr. V. K. Rowe
Biochemical Research Laboratory
The Dow Chemical Company
1701 Building
Midland, Michigan

Chlorine

Dear Mr. Rowe:

As you may recall, Hercules has been attempting to develop a bioassay technique to simplify detection of dioxin in herbicide formulations. Based principally upon work initiated by Dr. Oettel at BASF, the tests measured liver function changes which result from feeding rabbits with herbicide. We feel such a technique offers several advantages over rabbit ear painting tests.

Unfortunately, we have been unsuccessful. But to state it so bluntly is really unfair. First, we attempted to determine the sensitivity of liver change by feeding test materials with known additions of dioxin. The toxicity of test materials prevented use of liver function change as a bioassay for dioxin even at 10 ppm. We then dosed animals with 0.01 & 0.1 mg/kg of dioxin suspended in corn oil. Carbon tetrachloride was administered as a positive control at 100, 250 and 500 mg/kg. Clinical determinations including SGOT, SGPT and ESP retention were conducted prior to administration and every two to three days thereafter for at least 14 days.

Significant elevations in one or more of the clinical determinations were found in some but not all dioxin animals. The changes were not well correlated with dose nor were they consistent with regard to onset or duration. Animals on the positive control test responded as would be expected with significant blood chemistry changes only two days after dosing with 100 mg/kg.

Although positive results were obtained with dioxin, the usefulness of this technique as a bioassay for the presence of dioxin is questionable.

At the Toxicology Roundtable I mentioned these results to Ken Olsen who suggested that you might comment upon them. But the other reason for writing is to solicit your opinion on the usefulness of presenting our data at the Society of Toxicology meeting next spring. Certainly such a presentation would raise questions as to the reason for conducting an unsuccessful study.



18973

Mr. V. K. Rowe

-2-

October 16, 1968

On the other hand, someone might be spared useless effort if such negative information were offered to the scientific community.

I'd like to have your comments before we proceed.

Sincerely,

Emil E. Christofano
Industrial Hygienist

EEC:rbm

18974

HERCULES POWDER COMPANY

cc: Dr. R. S. George
Dr. R. B. Scott
Mr. E. S. P. Bellinger
Mr. J. M. Egan
Mr. R. T. Yates
Mr. J. H. Neal
Dr. J. P. Frawley - Medical
Mr. J. G. Kuniheim - Legal
Miss Jan Hunter

Wilmington, Delaware
March 26, 1965

TO: Mr. J. G. Copeland, Jr.

FROM: C. L. Dunn

Highly Toxic Impurities in 2,4,5-Trichlorophenol

On March 24 Dr. J. P. Frawley and I attended a meeting at the Dow Chemical Company Biochemical Research Laboratory at the invitation of Mr. V. K. Rowe, Assistant Director of the laboratory. At that meeting we were informed of Dow's findings relating to highly toxic impurities that may occur in 2,4,5-trichlorophenol. Methods for detecting these impurities in 2,4,5-trichlorophenol and products such as 2,4,5-T were also given.

Dow discovered that a change in their manufacturing process caused the appearance of chloracne in their trichlorophenol. Plant personnel have shown mild to severe cases of chloracne as a consequence of exposure to small amounts of tars from the process. Recovery from chloracne may require several years; there is no effective therapy. Since diagnosing the cause, Dow has modified its process and has been operating without incident for the past five months.

Dow says that their examination of their own and competitors 2,4,5-T products shows that some may contain what they term "surprisingly high" amounts of the toxic impurities. Their analysis of Hercules 2,4,5-T has given a low value for these toxic impurities. In view of the serious problems that can arise from the presence of even minute quantities of such impurities, I recommend that a program designed to examine and test current production of trichlorophenol and TCP process waste be started, and that a system of sample retention and periodic testing of TCP and/or 2,4,5-T be set up for future production.


HERCULES

H01327

18975

A&G

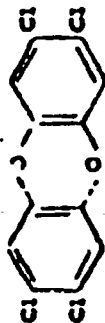
201

Mr. J. G. Copeland, Jr.

- 2 -

March 26, 1948

The chief toxic impurity identified by Dow is 2,3,7,8-tetrachlorodibenz-p-dioxin:



Acute oral LD₅₀ in rabbits:
17 micrograms/Kg body wt.
(extremely toxic)

0 5 9 0 (11) 000000

There is evidence that the 1,3,7,8 isomer and other closely related toxic compounds may also be present, although in smaller quantities. As little as four micrograms applied in 0.1 ml benzene to the ear of a test rabbit will give a characteristic skin response (folliculitis). Multiple applications (up to 25) at daily intervals show a no-folliculitis-effect level of 100 parts per billion. In addition to the skin effect, liver damage is severe, and a no-effect level based on liver response has not yet been established. Even vigorous washing of the skin fifteen minutes after application will not prevent damage, and may possibly enhance absorption of the material. There is some evidence that it is systemic.

Analytical method for the detection of the impurities is based on gas chromatography. Using a flame ionization detector, Dow has established lower detection limits of 10 p.p.m. in the unseparable oils from 2,4,5-TCP, and 1 p.p.m. in 2,4,5-TCP, 2,4,5-T acid, or 2,4,5-TP acid. It is likely that the method can be further refined to give even lower limits of detection. Upon our request, an analytical reference sample of 2,3,7,8-tetrachlorodibenzo-p-dioxin was furnished by Dow.

Plant waste from the TCP process in the Dow operation is now being encapsulated and buried.

I would like to discuss this matter with you at an early time.

CLD:40
Amach.

h01325

18978

A&G

201743

CONFIDENTIAL

Mr. Jack Copeland - Synthetics
John Egan - Synthetics
C. L. Dunn - Synthetics
H. E. Waller - Jacksonville, Ark.
Attn: Mr. A. C. Strwell
J. G. Kurikala - Local
L. C. McGee - Medical

NOTE TO JACKSONVILLE ARKANSAS PLANT FILE, Re: 2,4,5-T

On July 9, 1968, Mr. Earl Parnham of Dow Chemical Company telephoned me stating that he was calling at the request of Mr. Donald Baldwin, Vice-President of Dow to inquire how serious I considered the chloracne problem in relation to the consumer use of 2,4,5-T. When I suggested that he should discuss this with Hercules management rather than with me, he stated that on the advice of their toxicologist Dow has gone to great expense to alter their manufacturing conditions in order to produce 2,4,5-T acid which has less than 1 ppm acnege.

Since several months ago Dow had made available to all other producers the same data which convinced their toxicologists to set an internal specification of 1 ppm on the acid, they had assumed that the other producers would take similar action. On the basis of their chemical analyses, they are convinced that no one else has done anything to remove the acnege from their 2,4,5-T and consequently, they wanted my opinion whether they had been mis-advised by their own toxicologists.

I advised Mr. Parnham that I did not think this was a proper question for me and that he should seek outside advice from a private consultant if he doubted the advice of his own toxicologists. I pointed out that considerable individual professional judgment would be involved in establishing a specification of this type because all of the important facts are not known.

He then stated that Dow was extremely frightened that this situation might explode. They are aware that their competitors are marketing 2,4,5-T which contains "alarming amounts" of acnege and if the government learns of this the whole industry will suffer. They are particularly fearful of a Congressional investigation and excessive restrictive legislation on manufacture of pesticides which might result.

I advised Mr. Parnham that we shared his fear but were not aware of his allegation that the competitors' products were hazardous. He asked if Hercules had established an internal specification. I stated that he should discuss this with someone in our management and referred him to Mr. Copeland. I reminded him that we had experienced great difficulty in conducting the analyses for the acnege by the Dow procedure, and that only within the past few weeks, following a visit of our chemists to Midland, have we been able to obtain any useful information. I suggested that if he wanted any additional information on this problem he should talk to Mr. Copeland. He asked that he be transferred to Mr. Copeland.

(After the call was transferred I learned that Mr. Copeland was out of town and Mr. Parnham left word that he would call on Monday, July 15).

JFF/mav
July 14, 1968
Medical Department



101504

18977

HERCULES INCORPORATED

C. F. Silwell

Wilmington, Delaware
September 11, 1967

TO: Messrs. J. G. Copeland, Jr.
E. Turk
J. M. Eagan
J. Z. Miller
K. T. Givens
G. A. Seely - Engineering
A. L. Larson - Engineering
B. W. Dickerson - Engineering
H. F. Heckroth - Engineering
H. H. McCrea - Engineering
H. E. Wilder - Jacksonville

FROM: A. L. Treisback - Synthetics Department

(i) Treisback

DEFOLIANT ORANGE

8.0 Million Gallons/Year Mixed Butyl D and Butyl T Esters

Weldon Spring, Missouri

18978

Orange - 8 Million Gallons/Year

Criteria

The attached is a basic process criteria for an Orange plant calculated to produce 8.0 million gallons of Orange per year. The liberty was taken to use the data and calculations and assumptions made in March 1967 as a base line which was calculated to produce Orange at 6.0 million gallons per year. It is realized that several major decisions must be made, namely:

1. Continuous versus batch MCA process
2. Clean up process and quality required
3. Waste treatment and disposal specifications

The following is intended as a preliminary criteria from which the final guide lines, project estimate, and the formal proposal will be made.

Comments, changes and criticisms are solicited.

The following assumptions have been made:

1. The quantities of D and T acid are based on the Government specification as 50/50 Butyl D and T Esters by volume.
2. Production of MCA is based on the present batch system used at Jacksonville.
3. Both D and T acid will be dried and handled to Esterification with Tote Bins.
4. The acid reactors will be 3,000 gallons maximum working capacity to avoid unknown agitation scale-up problems especially on T acid.
5. The glass lined vessels will be 2,000 and 4,000 gallon standard reactors and Chemstor type storage tanks to minimize delivery time.
6. Dechlorinators will be nickel clad 750 gallon capacity reactors built for shell operation at 350 psig. and jacket operation at 150 psig.
7. Solvent clean up is based on the present multi-stage batch process currently being used at Jacksonville.
8. An entirely new and complete waste disposal system must be designed and installed.
9. Approximately seven-day capacity has been used for raw materials and in-process storage.

18979

Calculations Basis 100% Acid & Ester

Orange - 8 Million Gallons/Year

	<u>Wgt./Wgt.</u> (Hercules)	<u>Vol./Vol.</u> (Gov't.)
Assume average wt./gal. 10.70 lbs.	42.8 MM Lbs. <u>42.8 MM Lbs.</u> 85.6 MM Lbs.	4 MM Gal. Butyl-D <u>4 MM Gal. Butyl-T</u> 8 MM Gal.

Assume sp. gr. Butyl-D - 1.245 10.35 lb./gal.
" " " Butyl-T - 1.325 11.02 Lb./gal.

$$\begin{aligned} 1.245 \times 8.33 \times 4 \text{ MM} &= 41.48 \text{ MM lbs. Butyl-D} \\ 1.325 \times 8.33 \times 4 \text{ MM} &= 44.15 \text{ MM lbs. Butyl-T} \end{aligned}$$

	<u>Difference</u> <u>Lbs. Ester</u>	<u>Lbs. Acid</u> <u>Represented</u>	<u>Difference</u>
. D Required	1.32 MM	34.24 MM	33.18 MM = -1.06 MM D Acid
Lbs. T Required	1.35 MM	35.10 MM	36.20 MM = +1.10 MM T Acid

Have built into estimate sufficient capacity to go either way.

By A. E. Sidwell
8/25/67

12-2-F2

NO

ATTACHMENT Y

DOW

THE DOW CHEMICAL COMPANY

September 26, 1967

Colonel C. C. Shand (SAD)
 Directorate of Air Force Aerospace Fuels
 Kelly Air Force Base, Texas 78241

Dear Colonel Shand:

We have been asked to bid on the design, conversion and operation of an 8,000,000 gallon per year "Orange" plant at the Government owned chemical plant at Weldon Spring, Missouri.

This is to inform you that we have advised W. G. Kratz, Colonel, Corps of Engineers in Kansas City, Missouri, that we do not intend to bid on their solicitation No. DAAG1-68-R-0001, dated September 7, 1967.

The basic reason for our decision is due to critical factors outlined below:

The time allotted for submission of bids, September 8, 1967 to October 12, 1967, is not ample for preparation of bids on a project of this magnitude.

The presentation of alternative design at locations other than Weldon Spring were precluded because of the time allowed for preparation of a responsive bid in answer to your solicitation.

We would like to sum up some other reasons for not presenting a bid at this time, as follows:

1. The Weldon Spring site, located as it is between the University of Missouri Experimental Farm and the August Busch Reserve, presents too much of a hazard to the plant life in these areas, in case of an accidental release of products from the Orange Plant.
2. The requirement of 13 months start up and full operation in 18 months on the Weldon Spring site appears almost impossible to meet without excessive overtime.
3. The labor situation in the St. Louis area would present too many problems.
4. It would be almost impossible to solve the pollution problems in the area.

18981

BATCH 513 15A JUS 0063

ORANGE - 8 Million Gallons/Year
 (Basis: 6.0 million gallons/year estimate dated March 17, 1967)

27,600,000 #/yr. =	2,300,000 #/mo.	(2,000 gal.)	17,000 #/batch
21,000,000 #/yr. =	1,750,000 #/mo.	(2,000 gal.)	20,000 #/batch
20,200,000 #/yr. =	1,685,000 #/mo.	(750 gal.)	2,000 #/batch
26,400,000 #/yr. =	2,200,000 #/mo.	(3,000 gal.)	4,600 #/batch
27,600,000 #/yr. =	2,300,000 #/mo.	(3,000 gal.)	4,600 #/batch
64,500,000 #/yr. =	5,370,000 #/mo.	(4,000 gal.)	16,500 #/batch

ors for 8 million gallons Orange:

Basis: Government Specifications - by volume
 4 million gals. Bu-D @ 1.245 sp. gr. = 10.35#/gal.
 4 million gals. Bu-T @ 1.325 sp. gr. = 11.02#/gal.

$$\begin{aligned} D &= 1.245 \times 8.33 \times 4,000,000 = 41,500,000 \text{ #/year Butyl "D" Ester} \\ T &= 1.325 \times 8.33 \times 4,000,000 = 44,200,000 \text{ #/year Butyl "T" Ester} \\ &\quad \underline{85,700,000 \text{ #/year Total Mixed Ester}} \end{aligned}$$

	<u>6MM</u>		<u>8MM</u>
Ester	64,500,000 # mixed	$\times 1.328 \longrightarrow$	85,700,000 # mixed
"D" Acid	26,400,000 # (2.44)	$= \frac{85,700,000}{2.44}$	$= 35,100,000 \text{ #/yr.}$

"T" Acid	27,600,000 # (2.34)	$= \frac{85,700,000}{2.34}$	$= 36,600,000 \text{ #/yr.}$
----------	---------------------	-----------------------------	------------------------------

$$\underline{54,000,000 \text{ #}}$$

$$\underline{71,700,000 \text{ #/yr.}}$$

Total "D" and "T" Acid

Ester 85,700,000 #/year mixed 50/50 by weight.
 Acid 71,700,000 #/year mixed "D" and "T".
 D 35,100,000 #/year
 T 36,600,000 #/year

$$\text{TCP} = 20,200,000 \text{ #} \times \frac{36,600,000 \text{ # T @ } 8 \text{ M}^2}{27,600,000 \text{ # T @ } 6 \text{ M}^2} = \underline{\underline{26,700,000 \text{ #/year TCP}}}$$

$$\text{DCP} = 21,200,000 \text{ #} \times \frac{35,100,000 \text{ # D @ } 8 \text{ M}^2}{26,400,000 \text{ # D @ } 6 \text{ M}^2} = \underline{\underline{28,200,000 \text{ #/year DCP}}}$$

$$\text{MCA} = 27,600,000 \text{ #} \times \frac{71,700,000 \text{ # Total Acid (8M}^2\text{)}}{54,000,000 \text{ # Total (6M}^2\text{)}} = \underline{\underline{36,600,000 \text{ #/year MCA}}}$$

Orange - MCA

$$36,600,000 \text{ \#/yr.} = 3,050,000 \text{ \#/mo.} = 102,000 \text{ \#/day} = 4,250 \text{ \#/hr.}$$

$$\frac{3,050,000 \text{ \#MCA/mo.}}{17,000 \text{ \# MCA/batch}} = 180 \text{ Batches/month}$$

$$\frac{720 \text{ hrs./mo.}}{65 \text{ hrs./batch/unit}} = 11 \text{ Batches/Unit/Month}$$

Chlorinators:	$\frac{180 \text{ Batches/Month}}{11 \text{ Batch/Unit/Month}}$	=	16.4 Units on MCA
@ 2,000 gallons			
(@ 4,000 gallons		=	8 Units?)

- 2 - Rows of 8-2,000 gallon glass-lined, jacketed agitated reactors.
- 7 - Chlorinating each bank - 1 prechlorinating.
- 2 - Weigh tanks - acetic acid with plate coils, glass-lined.
- 16 - Primary condensers.
- 16 - Secondary condensers.
- 2 - Weigh tanks - phosphorous trichloride - stainless.
- 2 - Chillers - one for each chlorinator bank.
- 8 - Pumps - 1 for each 2 chlorinators.
- 2 - Absorbers - 1 for each 8 chlorinator row.

Orange - DCP

$$28,200,000 \text{ \#/yr.} = 2,350,000 \text{ \#/mo.} = 78,200 \text{ \#/day} = 3,260 \text{ \#/hr.}$$

$$\frac{2,350,000 \text{ \# DCP/mo.}}{20,000 \text{ \# DCP/batch}} = 117 \text{ Batches/month.}$$

$$\frac{720 \text{ Hrs./mo.}}{60 \text{ Hrs./Batch/Unit}} = 12 \text{ Batches/Unit/Month}$$

$$\frac{117 \text{ Batches/Month}}{12 \text{ Batches/Unit/Month}} = 9.8 \text{ -- Say } 10 \text{ Units on DCP @ } 2,000 \text{ gal.}$$

- 2 - Rows of 5-2,000 gal. glass-lined, jacketed, agitated reactors.
- 2 - Absorbers - 1 for each bank of 5 chlorinators with temperature controls on makeup water.
- 5 - Pumps - 1 for each 2 chlorinators.
- 2 - Chillers - for chilled tempered jacket water, 1 for each 5 units.
Also chilled tempered water on absorber condensers (2).
- 2 - Weigh tanks - 2,000 gals. glass-lined with plate coil vent tied into absorbers.

Orange - Chlorination - Outside Tanks

Chlorine: 58,500,000 #Cl₂/yr. = 4,880,000 #/mo. = 162,000 #/day = 6,800 #/hr.

$$\frac{162,000}{2,000} = 81 \text{ tons/day} = \frac{81}{55} = 1.5 \text{ cars/day} \quad (55 \text{ tons/car})$$

Use railcars to store chlorine

Vaporizers: 8 - 2 for each of 4 chlorinator banks

Phenol: 1,500,000 #/mo. = 17.3 cars/mo. @ 10,000 gal. each
4 - 12,500 gal.-glass Chemstor storage tanks - (50,000 gal.)

Acetic: 1,700,000 to 2,000,000 #/mo. = 25.3 cars/mo. @ 10,000 gal. each
(Mix) 6 - 12,500 gal. - (75,000 gal.)

DCP: 28,200,000 #/yr. = 2,350,000 #/mo. = 78,200 #/day = 3,260 #/hr.
(11.6 #/gal.) 2,430,000 gal./yr. = 202,500 gal./mo. = 6,750 gal./day = 280 gal./hr.
4 - 12,500 gal.-glass lined tanks (50,000 gal. = 7.4 days)

MCA: 36,600,000 #/yr. = 3,050,000 #/mo. = 102,000 #/day = 4,250 #/hr.
(11.5 #/gal.) 3,180,000 gal./yr. = 265,000 gal./mo. = 8,800 gal./day = 366 gal./hr.
4 - 12,500 gal.-glass lined tanks (50,000 gal. = 5.7 days)

HCl: 20° (32%) - Average from MCA = 122,000 #/day
" " DCP = 105,000 #/day
 $\frac{227,000 \text{ #/day}}{9.7} = 23,500 \text{ gal./day}$ containing phenolics, etc.

240,000 gal. (6 - 40,000 gal) Rubber Lined Tanks
125,000 gal. (10 - 12,500 gal.) Glass Lined Tanks
32% HCl purchased = 415,000 gals./yr. = 415 T/C's = 1.1 T/C per day

Acetic Anhydride:

Phosphorus Trichloride:

Brine: For Secondary MCA condensers
2 - 4,000 gal. wood (1 - for each chiller)

Orange - Chlorination - Outside Tanks (Cont'd.)

Tempered water: For phenol condensers

2 - 4,000 gal. wood (1 - for each tempered system)

Unloading Stations - Chlorination

3 - Chlorine - Tank car
1 - Acetic - Tank car
1 - Phenol - Tank car
1 - HCl - Tank Car
1 - Acetic anhydride tank truck

18908

Orange - TCP

$$26,700,000\#/yr. = 2,250,000\#/mo. = 74,500\#/day = 3,100\#/hr.$$

$$\frac{2,250,000\#/mo.}{2,000\#/batch} = 1,110 \text{ Batches/month} = \underline{37.2 \text{ batches/day}}$$

$$\frac{720 \text{ Hrs./Mo.}}{8 \text{ Hrs./batch/unit}} = 90 \text{ batches/unit/Mo.}$$

$$\text{Dechlorinators: } \frac{1,110 \text{ batches/Mo.}}{90 \text{ batches/unit/Mo.}} = 12.4 \text{ units on TCP}$$

14 - Dechlorinators @ 750 Gal.-nickel clad, jacketed, agitated
Shell: 350 psig. oper. press; Jacket: 150 psig. oper. press.
3 Rows - 4 dechlorinators - barricaded with rupture disc vent liner
TCB (Ground) = 88,000#/day = 440 Drums @ 200# = 147/shift

$$\text{NaOH (Flake)} = 53,000\#/day = 110 \text{ drums @ } 400\# \\ 110 \text{ drums @ } 100\#$$

MeOH (fresh make-up) = 5,400 Gal./day

2-25,000 Gal. Alcohol Storage -

Drum handling facilities for dechlorinator charging.

3 - 10,000 Gal. NaTCP (dirty) Storage -304 S/S, agitated w/coil.

2 Hold Tanks - 6,000 Gals. with vent condensers

2 Stills - 3,000 Gal. Monel clad, agitated, jacketed (150 psig)
still pots - 316 S/S column

2 Still condensers

1 Alcohol Hold Tank - 304 S/S

18907

Orange - Acid

2,4-D

35,100,000 #/yr.
2,930,000 #/mo.
97,500 #/day
32,500 #/shift
4,050 #/hr.

2,4,5-T

36,600,000 #/yr.
3,050,000 #/mo.
102,000 #/day
33,800 #/shift
4,230 #/hr.

- 10 - 3,000 Gal. brick lined, agitated (Titanium) Reactors
5 Units on D and 5 Units on T - normally
Weigh tank and piping arranged for flexibility
for ratio of units on D and T.
Basis : Approx. 95% operating time.
- 8 - 4,000 Gal. Glass Lined, agitated, jacketed crystallizers
2 - Refrigeration units -
2 - 10,000 Gal. Slurry Hold Tanks - heavy duty - agitated
5 - 6,000 Gal. Slurry Feed Tanks - heavy duty - agitated - jacketed
4 - Brine Extraction Column (1 for D and 1 for T) Haveg
4 - Brine Storage Tanks - 10,000 Gal. Haveg
Independent weigh tanks for each reactor
- 10 - NaTCP weigh tanks - 304 S/S
10 - DCP weigh tanks - glass lined - jacketed
10 - MCA weigh tanks - glass lined - jacketed
10 - caustic weigh tanks - steel
6 - recycle liquor measuring tanks - glass lined 2,000 gal.
6 - HCL measuring tanks - Haveg
2 - brine solvent separators - 1,000 Gal. - glass lined
10 - Centrifuges 48 in. - 316L S/S , Kynar Coated
5 - Blenders
4 - Conveyor/Dryers (for flexibility between D&T
316 SS/ 2,000 - 2,500#/hour
5 - Filtrate Tanks (1 for each 2 centrifuges)
- 400 - Tote Bins (97,500#/day x 7 = 682,000#/Wk. 195 Tote Bins @ 3,500#)
(102,000 #/day x 7 = 714,000#/Wk. = 204 Tote Bins @ 3,500#)
Aluminum - 90 cu. ft. capacity

18008

Orange - Ester

85,700,000 #/yr. $\neq$ 7,140,000 #/mo. $\neq$ 238,000 #/day $\neq$ 9,900 #/hr.
@330 days/yr. 265,000 #/day $\neq$ 11,000 #/hr.

- 10 - 4,000 gal. 316 L S/S, agitated, jacketed, vacuum esterifiers
- 5 - 4,000 gal. 316 L S/S " " preesterifiers
- 2 - 4,000 gal. Glassed lined agitated, jacketed recovered acid esterifiers
- 2 - Vacuum systems (for each 5 esterifiers)
- 10 - Karbate esterifier condensers
- 2 - 30,000 gal. Butanol storage tank
- 265,000 #/day BuE-Mixed
- 132,500 #/day Bu-T ester = 35,400
- 132,500 #/day Bu-D ester = 35,000
- 70,400 #n-Butanol/day

$$\frac{70,400}{6.76} = 10,500 \text{ gals. n-Butanol/day}$$

- 5 - 10,000 gal. Spent Butanol Storage - Steel (1 for each 2 esterifiers)
- 4 - 20,000 gal. - Butyl D Ester Storage - steel w/coil
- 4 - 20,000 gal. - Butyl T Ester Storage - steel w/coil

18909

Orange - Solvent Clean Up

NaTCP clean up 4 - 6,000 Gal. agitated tanks
NaTCP clean 6- 10,000 Gal. agitated w/plate coils

2 - D - Clean Solvent	15,000 Gal.-
2 - D - Spent Solvent	15,000 Gal.-
2 - T - Clean Solvent	15,000 Gal.-
2 - T - Spent Solvent	15,000 Gal.-
4 - Separator - Decanters	6,000 Gal.-
4 - Clean Up Tanks	6,000 Gal. agitated - heavy duty

Unloading Stations

1 - Toluene
1 - Methanol
1 - Butanol

18990

Orange - Waste

Basis: 85,700,000 # mixed D and T Butyl ester/year
61,000,000 # NaOH (100%)/yr.
NaCl - 90,000,000 # NaCl/yr.
7,500,000 # NaCl/mo.
250,000 # NaCl/day
10,400 # NaCl/hr (5.4 tons/hr.)

Glycollic Acid

5,500,000 #/yr. = 458,000 #/mo. = 15,300 #/day = 638 #/hr.

Oxalic Acid

129,000 #/yr. = 10,800 #/mo. = 360 #/day = 15 #/hr.

Acetic Acid

1,100,000 #/yr. = 91,800 #/mo. = 3,050 #/day = 137 #/hr.
plus all acetyls carried from plant generated HCl.

Still Bottoms - Toluene Recovery Still

1,530,000 #/yr. = 128,000 #/mo. = 4,250 #/day = 177 #/hr.

Still Bottoms - Methanol Still

990,000 #/yr. = 82,500 #/mo. = 2,750 #/day = 115 #/hr.

Combined Bottoms: 7,000 #/day = 292 #/hr.

Approximate composition

35% Toluene
32.5% TCP Anisole
13.0% Trichlorobenzene
19.5% Tetrachlorobenzene

This would generate about 3,200 #/day HCl.

Orange - Utilities

	<u>Required for Orange - 8.0</u>	<u>Available at Weldon Spring</u>
Steam (Salt evaporation not included)	200,000 lb./hr.	216,000 lb./hr. (240,000 lb./hr max.)
Air	1,500 CFM	2,000 CFM
Water - make up	10,000,000 Gal./Mo.	10,000,000 Gal./day (wells-treated)
Water - Cooling tower	20,000 GPM	
Electric	9,000 KVA	
Gas		Liquid Propane
Inert Gas	20,000 CFH	Not Available

18932

Orange - Services (Existing at Weldon Spring, Missouri)

Railroads - existing, may need minor additions

Roads - adequate

Office - adequate

Cafeteria - adequate

Shop - adequate

Storeroom - adequate

Warehouse - existing, may be too small and not convenient to process.

Laboratory - existing but not available for Orange

Locker - Change Facility - adequate

ROBIN COMPANY

cc: J. M. Duga - Byn.
M. A. Dyes - N. C.
J. J. Ford - N. C.
A. Z. Conner - N. C.
A. D. Sidwell - Jacksonville

Wilmington, Delaware
November 16, 1965

To: C. L. Dunn - Synthesis Department
FROM: E. Z. Cristofano - Medical Department

The following comments will summarize the investigations we
contemplate on chloromane possibly associated with 2,4,5-T ester.

1. Badische uses a bioassay technique to check each batch of TCP
purchased. Their test consists of feeding each of three rabbits with
1 g./kg. of TCP with a determination of bromobiphenyl retention after
5 days. More than 5% of BCP retention is cause for rejection of the batch.
Sensitivity is claimed at 3 ppm.

2. Dry bioassays by a rabbit ear painting technique. The internal
surface of one rabbit ear is painted daily with 0.1 ml. of a chloroform
solution of test material (10 or 50%) of an extract of TCP in chloroform.
Unless severe irritation is noted 10 doses are applied. The ears are
observed for two additional weeks for the appearance of folliculitis and
cyst formation. They have noted fatalities from a single application and
liver damage has accompanied the chloromane reactions. Sensitivity is
claimed at 3 ppm.

While the Dow testing may be more sensitive, the Badische method
is faster and less expensive. In order to evaluate both methods we recommend
that Hercules supply material to Badische for their testing and simultaneously
begin gathering continuing data in a commercial laboratory. Because of a
lack of information on the toxicity of in-process materials, these latter
studies should begin daily after oral toxicity has been determined. For this
first stage the acute oral LD50 studies would cost approximately \$300.
Subsequent adjuvant studies on these materials are expected to cost about
\$6,000, however, an accurate estimate is not possible until Stage 1 is
complete. Preparation of the samples and subsequent analysis is estimated
to cost \$300.

HERCULES 2 (b) (v)

18964

C. L. Dunn - Synthetics

- 2 -

November 18, 1965

Dr. Ottel of Badische has agreed to bioassay several spiked samples to permit comparison of results with the gas chromatographic determination of dioxin and with the Dow ear painting procedure. To permit this study we request that 25 g. of each of the following spiked samples be prepared:

- a. Standard 2,4,5-T acid spiked with 0, 2, 5, 10, 20 ppm dioxin.
- b. Plant grade 2,4,5-T acid with a known dioxin content. - *high level - 400*
- c. Plant grade sodium trichlorophenate spiked with 0, 1, 3, 5, 10 ppm dioxin (based on TCP equivalent).
- d. Dioxin standard approximately 2 mg. - *known in prod. House*
- e. Plant grade ~~propyl~~ ester of 2,4,5-T acid as 6 lbs/gal. (Biosch. Rep. 1000) solution in xylene spiked with 0, 2, 5, 10, 20 ppm dioxin.

Approximately 10 gms. of each sample should be prepared for shipment to Dr. Ottel and the remainder retained for future confirming tests conducted by Bio-Test. Chemical analysis of the spiked samples would be required after the biological testing demonstrates physiological activity.

Acute oral toxicity data on sodium trichlorophenate, 2,4,5-T acid and finished propyl ester formulation should be begun promptly. Approximately 50 gms. of each material should be sent to Dr. Joseph C. Calandra, Industrial Bio-Test Laboratories, 1810 Frontage Road, Northbrook, Illinois. Dr. Calandra has a supply of dioxin.

After these preliminary tests are conducted we will establish a more comprehensive program for the evaluation of hazard during manufacture and in the product as it would be used by the customer. Without these preliminary data a test program would be unnecessarily expensive.

E. Christofano

6/1/66

*Side stream sample was to be analyzed Feb. 66
Is being act. still, a line been*

REC:vrh

H03893

18995

Dr. Ortel outlined that in 1971, after producing a batch of R2 from various collections, the process seemed usual procedure and unimportant. Although no injuries resulted at the time, subsequent events started to develop about a week later in employees who worked in this process area and other areas connected to working. Although the plant for the most part is safe, approximately 10 cases were identified with some cases developing in relatives of employees who worked the station of the workers. Many of these individuals were personally identified.

After recognizing that a serious problem existed, R2 started a thorough investigation which uncovered an impurity in R2 at the chemical agent. Although R2 had indicated the impurity they did not identify the structure as completely as they. The indicated impurity was listed as rubidium or an oral dose of 100 mg/kg. The compound appears to be the same as that indicated by R2 and identified to be 2,3,7,8-tetrachlorodibenzo-p-dioxin.

Because of the financial policy for compensation claims, R2 discontinued manufacture of R2 and Dr. Ortel stated that that's large enough to affect the other work schedule. They now purchase all under R2 from R2, no report, but not only a few cases of children.

In order to insure that all personnel R2 is free of the concern, R2 holds all employees until they have been biologically analyzed. If they have any detectable concern, the employees are refused. The sensitivity of their assay is 1 ppm. R2 has had no further trouble since launching this operation.

Dr. Ortel provided an idea the details of their laboratory. The R2 assay procedure is more rigid than the R2 procedure and more than expansion. To use knowledge, no one in the R2 plant has tried the R2 procedure. I asked Dr. Ortel if he would personally report. He replied, "I would like to see the procedure to work" as a company results with the use of chromatographic procedure and the R2 laboratory procedure. He agreed. He also agreed to send me a copy of an unpublished report on the chemical aspects of the R2 plant and their laboratory procedure.

H01413

A&G

201788

18806

CONFIDENTIAL

TO: Dr. J. H. Campbell - Agriculture Department
FROM: John P. Kennedy - National Department

cc: Dr. E. G. Sargent - Agriculture
Dr. John D. Smith - Agriculture
Dr. C. L. Smith - Agriculture
Dr. E. L. Vetter - Agriculture
Attn: Dr. A. L. Smith
Dr. L. C. Smith

Washington, D.C.
January 11, 1953

Belgium (1953) - Agriculture via Orléans

John has been able to bring in other matters, I had occasion to visit several people at Belvoir Hotel - 5 days - April 10 in Washington. There was not an epidemic of diseases with widespread production about twelve years ago, I had advantage of the opportunity to discuss "diseases" with Dr. B. G. Smith, Director of Industrial Hygiene and Pharmacology for DAF. I had not Dr. Smith on several other occasions so there was no difficulty in discussing the industrial problem with him directly.

HERCULES 4 (H)

0 5 5 6

CONFIDENTIAL

Just Copeland

• 4 •

October 24, 1963

As soon as the new process is operational at Jacksonville, I recommend that to select several production samples and "spiked" samples to be tested and to the Research Center for comparative analysis. This will help confirm whether our analytical procedure detects the major defects and whether the R&D laboratory will be useful to the Bureau.

WJ/ear

h0:4.-

A&G 201789

7 5 8 0 (K) MERCURIES

18907



STATE OF ARKANSAS
DEPARTMENT OF POLLUTION CONTROL AND ECOLOGY

8001 NATIONAL DRIVE P. O. BOX 9583
LITTLE ROCK, ARKANSAS 72219

501 371-1701 WATER
501 371-1701 GEN. OFF.
501 371-1136 AIR DIV.
501 371-2130 SOLID WASTE

MEMORANDUM

TO: Governor Clinton
FROM: Jarrell Southall *JSS*
DATE: November 26, 1979
SUBJECT: STATUS REPORT - VERTAC AT JACKSONVILLE

CSN: 600023 Permit No.
Media: Air, Water, Solid, Hazardous, *Superfund*
Sort: Permit, Compliance, Legal, *Misc*

The Department is now in the process of attempting to bring together some "loose-ends" concerning dioxin (TCDD) contamination resulting from Vertac's operation. Some studies which have been conducted under EPA sponsorship have yet to be completed and reported. Some of the Department's monitoring efforts have been deferred in order that other federal commitments could be met. It is anticipated that monitoring/analytical activities can be resumed by late December.

A meeting has been scheduled for November 29, 1979 involving Vertac and the Department. Topics of the meeting are to include: (1) Status of 2,4,5-T start-up plans, (2) compliance with the Department's order, and (3) discussion of monitoring and analytical efforts of Vertac, EPA and DPC&E. I will update this report after the meeting on the 29th.

Jacksonville Sewage Treatment System

The oxidation ponds of the current wastewater plant are contaminated with TCDD. Jacksonville has completed initial plans for a new system which would by-pass defective collector lines and the old wastewater treatment plant. The plans were completed prior to the Vertac incident. However, the Air Force claims that it is unable to participate in the funding of the project and, as a consequence, EPA will not receive the plans for review and subsequent funding of a construction grant. (Typically, EPA pay 75% of the construction costs and the community pays 25%.)

Senator Bumpers earlier this year was talking about a special appropriation to the Air Force in order that we could get the project moving. It is highly desirable that we do so because we can then isolate a portion of the TCDD problem. Your assistance in getting the Air Force or Congress moving would be helpful. Alternatively, the Department could, according to EPA, sue the Air Force. We stand ready to discuss the issue with you.

18908

Meanwhile, Jacksonville is proceeding with the construction of an interceptor line that should eliminate the problem of overflowing manholes in the residential area just south of Vertac. This may, however, create problems at the city's existing wastewater plant and require that the plant be by-passed during high flow conditions. We will be watching the situation closely.

Ambient Monitoring

Earlier commitments to EPA necessitated suspension of much of the Department's monitoring of soils, sediments and waters for TCDD. We now have a backlog of soil samples taken from the residential area surrounding Vertac and hope to be in a position to start working on them the latter part of December.

The Department has conducted some rather crude air sampling on Vertac's property. The finding has been that TCDD adsorbed on particulate matter (dust) collected by our sampling device is in the same range as we have found in soil samples on Vertac's property. We are expecting a set of more sophisticated sampling equipment from EPA to install and operate both on Vertac's property and in the surrounding residential area. We hope that EPA's equipment will give some idea as to the size fraction of the contaminated particles. Such information will provide better insight as to the health hazards involved.

ever analyzed?

Site Cleanup

Vertac appears to be reasonably on schedule with requirements of this Department. Paul Means has sent an inquiry to Vertac which, in effect, provides a vehicle for final determination/reconciliation of Vertac's compliance status. This will be discussed in detail with Vertac on the 29th and a report submitted to you.

I am very interested in establishing a erosion control program on Vertac's property. Such a program will reduce wind blown dust (contaminated with TCDD) as well as reduce the continued contamination of Rocky Creek and Bayou Meto. Before finalizing the elements of the program, I would like to have benefit of EPA's recently completed soils and geology study. The report of the study is now in preparation.

Analytical Questions

Our contacts within EPA continue to alert us concerning analytical questions. These questions impact current understandings of the biological half-life of TCDD and the potential for TCDD to be degraded under varying environmental conditions. At issue is the extent to which TCDD is bound to soil particles, the stereochemistry of the TCDD molecule and "active sites" on the molecule.

If you desire, I will provide a detailed explanation of the issue. For purposes of this report, however, I am merely alerting you to the possibility that greater TCDD concentrations exist in soils and sediments than previously reported and that the TCDD half-life is longer than previously estimated.

Resumption of 2,4,5-T Production

Vertac continues to hold production of trichlorophenol and 2,4,5-T in abeyance until such time that the state and EPA approve proposed plans for containment and destruction of TCDD.

In a confidential report dated November 5, 1979, Vertac summarized the results of various laboratory scale experiments for clean-up and destruction of TCDD. The report also contained flow charts depicting how TCDD containment, cleanup and destruction would be accomplished, using the process described in Vertac's patent application. It is unlikely, however, that the depicted process will be placed into operation because the report alludes to an alternative/modified process which Vertac has developed which achieves a hundred-fold improvement in TCDD destruction efficiency (to 99.999%). Presumably, plans and drawings of the improved process will be submitted to the Department and EPA after Vertac completes amendments to its earlier patent application.

I have not received comments from EPA concerning Vertac's November 5 report. Delays are expected because EPA's principal coordinator, Bruce Elliot, has been stricken with ulcer problems.

EPA and the Department monitored some of Vertac's laboratory-scale TCDD destruction runs. Samples were split between the Department and at least two EPA-sponsored labs. Although the outside labs have not formally reported their results, preliminary information suggests there is substantial agreement with DPC&E's data. Based upon the foregoing and based upon the Department's analysis of Vertac's more recent destruction efforts, I am convinced that there are chemical means of destroying TCDD in Vertac's waste through a dechlorination/extraction process to a level less than 10 parts per trillion. The Department has not confirmed the identity of the products of the destruction process. The identification may be accomplished by EPA-sponsored labs.

Vertac maintains that it is capable of installing and safely operating the equipment necessary to contain and destroy TCDD resulting from the production of trichlorophenol and 2,4,5-T. Vertac officials have discussed the possibility of securing an EPA grant to assist in the processing of stored waste products and contaminated soils and sediments. EPA appears to be favorably impressed with the idea

and would, in my opinion, fund such a program provided that it was satisfied with the chemical destruction process and provided that you fully supported the project. It is anticipated that the project would include, in addition to the chemical destruction for materials containing high TCDD concentrations, physical separations and biological degradation of less concentrated materials. Please note, however, that biological degradation has not yet been proven.

Vertac maintains that it will not be able to afford the installation of process equipment for the chemical destruction of TCDD unless it is permitted to resume production of trichlorophenol and 2,4,5-T. I am not sure that Vertac will be able to afford the safeguards that will be imposed if production is allowed. Unfortunately, that will remain an open question until such time that the engineering progresses beyond the conceptual stage.

I continue to recommend that Vertac not be allowed to resume production of trichlorophenol or 2,4,5-T unless (a) the destruction of TCDD-containing waste can be assured, (b) both the production and destruction processes can be adequately safeguarded, and (c) Vertac commits to a phased program for the destruction of stored waste products, including highly contaminated soils and sediments. The dimensions of the phased program would necessarily be dependent upon the degree of federal support obtained.

While the conditions described in the above paragraph are necessary, I am not sure that they are sufficient. Broader questions concerning worker safety and environmental impacts relative to the use of 2,4,5-T must also be factored into the equation. Studies being conducted outside of Arkansas may eventually provide guidance. Recognizing that the fate of 2,4,5-T rests primarily in EPA's hands and recognizing the federal resources and responsibilities in the field, I would be hesitant in attempting a ban, at the state level, on the manufacture and use of 2,4,5-T. Until Vertac forces the issue by finally submitting detailed plans and specifications for the containment and destruction of TCDD wastes, I do not feel that the state is obligated to take a stand. By then, better data could be available.



STATE OF ARKANSAS
OFFICE OF THE GOVERNOR
State Capitol
Little Rock 72201

January 10, 1980

JAN 1980
RECEIVED
Ark. Dept. of
Pollution Control
& Ecology

Southall
Vertac
Bill Clinton
Governor

Mr. Jarrell Southall, Director
Department of Pollution Control & Ecology
8001 National Drive
Little Rock, AR

Dear Jarrell:

On Monday, January 7, my office received a telephone communication from Ms. Adlene Harrison informing us that a letter was forthcoming with regard to the problems surrounding the cleanup operations at Vertac, Inc. in Jacksonville. It is very important that the contents of the letter not be discussed, at this time, with anyone other than members of our respective staffs and the staff of EPA.

Sincerely,

Bill
BILL CLINTON
Governor

BC/SS/hnj

19332



THE DOW CHEMICAL COMPANY

WILMINGTON, DELAWARE 19899

December 24, 1968

Emil E. Christofano
Industrial Hygienist
Hercules Incorporated
Hercules Tower
910 Market Street
Wilmington, Delaware 19899

Dear Chris:

This is a belated reply to your letter of October 16, 1968. A delay in replying is for two reasons. First, I wanted a chance to evaluate some of the information we had to see how it agreed with your conclusions and second, to consider further, the advisability of publication of such information at this time.

In regard to the first question I am not at all surprised at your conclusions with regard to the liver function tests for we have observed essentially the same inconsistency in responses. I do not believe this is unique for the acnagen you mentioned for I think it is true of many other hepatotoxic substances. I feel quite confident that if one wants to rely on such tests, then a good sized group of animals would have to be used at each dosage level. Individual variation is simply too great to permit using the data from small groups. On the other hand we have still found that the rabbit ear tests to be quite consistent and evaluation of perhaps three animals seems to give us very good assays.

In regard to publication I am not satisfied that we are ready to publish on the subject yet. I think this requires a considerable amount of thought and premeditation with regard to possible consequences. I feel that it would be a mistake to kick this in the public eye until such time as we have answers to obvious questions.

Best wishes for a Happy Holiday and a Prosperous New Year.

Sincerely yours,

VKR
V. K. Rowe
Biochemical Research Laboratory
1403 Building

VKR/cc

H0:504

19003

The changes were neither well correlated with dose nor consistent in onset and duration, even in animals showing apparently significant effects.

Although some positive results were obtained with dioxin itself, the usefulness of this technique as a bioassay for the presence of dioxin is questionable.

H01501

19004



HERCULES POWDER COMPANY

INCORPORATED

JACKSONVILLE, ARKANSAS

FIRST AID

FOR

CAUSTIC

"MONOCHLOR"

PHENOL

If splashed with any of these materials,

- 1.) Go as quickly as possible to a Safety Shower.
- 2.) Call for help on the way.
- 3.) Get under the shower.
- 4.) Wash repeatedly with water. Rub lightly over areas affected to hasten the removal of caustic or monochlor.
- 5.) While being rinsed with the water, have someone help remove clothing which may be contaminated with the splashed material.
- 6.) Wash for at least five (5) minutes. Continuous washing and rinsing with water is best for the removal of caustic or monochlor, or solutions of these.

For phenols or phenol solutions, after flushing with water and removal of affected clothing, pat dry the areas immediately affected -- do not rub -- and apply a generous layer of glycerin. Allow this to stay on for approximately one (1) minute and then flush off with water. Repeat this at least two (2) to three (3) times. Finally, pat dry and apply a layer of glycerin.

If any of the materials are accidentally splashed on the eye lids or into the eye, immediately flush with water, using an eye fountain. If splashed generally and incidentally in the eyes, rinse eyes while in the shower. Never rub an eye to help remove something, only flush it. Have a helper hold the eyes open if you find it impossible to force yourself to do this.

Report all accidents to supervisor or have someone do it.

Remember!

Prompt Flushing with Water,

Removal of Affected Clothing,

Care to be sure that all body areas are washed, otherwise an area may be overlooked which may cause more trouble than the area first noticed.

19005

0000342 KD

Return to
 Research Center
 CORRESPONDENCE
 Technical Information
 Wilmington, Delaware
 February 24, 1966

TO: H. E. Wilder - Jacksonville
 FROM: E. E. Christofano - Medical - Home Office

I'd like to express my appreciation to you and Dr. Sidwell for the time and effort you spent explaining the plant efforts in environmental control. There has been a marked improvement during the past year and if the program continues at this rate even minor problems will be under control. One potential hazard stems from the use of supplied air masks when cleaning the Sharples centrifuge. Under certain circumstances it is possible to generate carbon monoxide in oil lubricated air compressors. If men breathe this air for extended periods their acuity might be impaired, but the effects would not be pronounced if the breathing air contained less than 100 ppm of CO. Determination of the CO content of breathing air is justified, and the enclosed literature describes a system for monitoring breathing air.

Dr. Savon and Mr. Cholak (representing the NAC feasibility study team) appeared satisfied with the precautions taken to prevent occupational illness at Jacksonville. They noted a unique opportunity to study possible health implications because this plant is the only one entirely devoted to phenyl herbicides. They are not aware of occupational illness associated with the manufacture or use of these materials but they will probably recommend a more thorough study of exposure to raw materials, solvents intermediates and finished products. In addition they would like to see some medical data such as urine analysis. Their report will be sent to you when it is received.

Dr. Sidwell agreed to forward samples of 1,4,5,-T production streams and recycle or waste streams. One pound of each sample should be sent to J. J. Ford at the Research Center. These samples will then be used in preparing material for test by bioassay techniques for chlorine or BCP retention.

EEC:vvh
 Enclosure



19006

CONFIDENTIAL

Mr. Jack Copeland - Synthetics
John Egan - Synthetics
C. L. Dunn - Synthetics
H. E. Waller - Jacksonville, Ark.
Attn: Mr. A. L. Stowell
J. G. Kunkel - Local
L. C. McGee - Medical

NOTE TO JACKSONVILLE ARKANSAS PLANT FILE, Ref. 100-107

On July 9, 1965, Mr. Earl Farnham of Duv Chemical Company telephoned me stating that he was calling at the request of Mr. Donald Baldwin, Vice-President of Duv to inquire how serious I considered the chloracne problem in relation to the consumer use of 2,4,5-T. When I suggested that he should discuss this with Hercules management rather than with me, he stated that on the advice of their toxicologist Duv has gone to great expense to alter their manufacturing conditions in order to produce 2,4,5-T acid which has less than 1 ppm acnegen.

Since several months ago Duv had made available to all other producers the same data which convinced their toxicologists to set an internal specification of 1 ppm on the acid, they had assumed that the other producers would take similar action. On the basis of their chemical analyses, they are convinced that no one else has done anything to remove the acnegen from their 2,4,5-T and consequently, they wanted my opinion whether they had been mis-advised by their own toxicologists.

I advised Mr. Farnham that I did not think this was a proper question for me and that he should seek outside advice from a private consultant if he doubted the advice of his own toxicologists. I pointed out that considerable individual professional judgment would be involved in establishing a specification of this type because all of the important facts are not known.

He then stated that Duv was extremely frightened that this situation might explode. They are aware that their competitors are marketing 2,4,5-T which contains "alarming amounts" of acnegen and if the government learns of this the whole industry will suffer. They are particularly fearful of a Congressional investigation and excessive restrictive legislation on manufacture of pesticides which might result.

I advised Mr. Farnham that we shared his fear but were not aware of his allegation that the competitors' products were hazardous. He asked if Hercules had established an internal specification. I stated that he should discuss this with someone in our management and referred him to Mr. Copeland. I reminded him that we had experienced great difficulty in conducting the analyses for the acnegen by the Duv procedure, and that only within the past few weeks, following a visit of our chemists to Midland, have we been able to obtain any useful information. I suggested that if he wanted any additional information on this problem he should talk to Mr. Copeland. He asked that he be transferred to Mr. Copeland.

(After the call was transferred I learned that Mr. Copeland was out of town and Mr. Farnham left word that he would call on Monday, July 12).

JFF/mav
July 12, 1965
Medical Department



100-107

19007

Highly Toxic Impurities in 2,4,5-Trichlorophenol

On March 24 Dr. J. P. Frawley and I attended a meeting at the Dow Chemical Company Biochemical Research Laboratory at the invitation of Mr. V. K. Rowe, Assistant Director of the Laboratory. At that meeting we were informed of Dow's findings relating to highly toxic impurities that may occur in 2,4,5-trichlorophenol. Methods for detecting these impurities in 2,4,5-trichlorophenol and products such as 2,4,5-T were also given.

Dow discovered that a change in their manufacturing process caused the appearance of chloracene in their trichlorophenol. Plant personnel have shown mild to severe cases of chloracne as a consequence of exposure to small amounts of tars from the process. Recovery from chloracne may require several years, there is no effective therapy. Since diagnosing the cause, Dow has modified its process and has been operating without incident for the past five months.

Dow says that their examination of their own and competitors 2,4,5-T products shows that some may contain what they term "surprisingly high" amounts of the toxic impurities. Their analysis of Hercules 2,4,5-T has given a low value for these toxic impurities. In view of the serious problems that can arise from the presence of even minute quantities of such impurities, I recommend that a program designed to assume and test current production of trichlorophenol and TCP process waste be started, and that a system of sample retention and periodic testing of TCP and/or 2,4,5-T be set up for future production.

FBI
LABORATORY

HO 1327

19008

A86

20

MERCURY POWER COMPANY

TO: Mr. J. G. Copeland, Jr.

FROM: C. L. Dunn

cc:

Dr. R. S. George

Dr. R. B. Scott

Mr. E. S. P. Bellinger

Mr. J. M. Egan

Mr. R. T. Yates

Mr. J. H. Neal

Dr. J. P. Frawley - Medical

Mr. J. G. Kuebelin - Legal

Miss Jan Heffner

Wilmington, Delaware
March 26, 1965

MERCURY (R) 0 4 5 5

There is evidence that the 1,3,7,8 isomer and other closely related toxic compounds may also be present, although in smaller quantities. As little as four micrograms applied in 0.1 ml benzene to the ear of a test rabbit will give a characteristic skin response (folliculitis). Multiple applications (up to 25) at daily intervals show a no-folliculitis-effect level of 100 parts per billion. In addition to the skin effect, liver damage is severe, and a no-effect level based on liver response has not yet been established. Even vigorous washing of the skin 15-20 minutes after application will not prevent damage, and may possibly enhance absorption of the material. There is some evidence that it is systemic.

Analytical method for the detection of the impurities is based on gas chromatography. Using a flame ionization detector, Dow has established lower detection limits of 10 p.p.m. in the unseparable oils from 2,4,5-TCP, and 1 p.p.m. in 2,4,5-TCP, 2,4,5-T acid, or 2,4,5-TP acid. It is likely that the method can be further refined to give even lower limits of detection. Upon our request, an analytical reference sample of 2,3,7,8-tetrachlorodibenz-p-dioxin was furnished by Dow.

Plut waste from the TCP process in the Dow operation is now being encapsulated and buried.

I would like to discuss this matter with you at an early date.

EL Allen

CLD:ld
Atch.

HO1323

W. H. H. H.

19009

A&G

201743

Mr. J. G. Copeland, Jr.

- 2 -

March 26, 1965

The chief toxic impurity identified by Dow is 2,3,7,8-tetrachloro-
dibenz-p-dioxin:



Acute oral LD50 to rabbits:
17 micrograms/Kg body wt.
(extremely toxic)

MOLECULES (H) 0 4 5 0

HERCULES POWDER COMPANY

cc: Mr. Paul Mayfield - Executive
Mr. Charles Maddock - Legal
Dr. Lemuel C. McGee - Medical
Mr. P. J. Reno - Synthetics
Mr. R. T. Yates - Synthetics
— Mr. C. L. Dunn - Synthetics
— Mr. J. M. Eagan - Synthetics
— Mr. H. E. Wilder - Jacksonville
Mr. A. D. Sidwell - Jacksonville
Mr. Ashworth Burslem - Advertising

Wilmington, Delaware
March 26, 1965

TO: Mr. John G. Copeland - Synthetics Department

FROM: John P. Frawley - Medical Department

Report of Meeting with Dow Chemical Company on the
Toxicity of Trichlorophenol Impurities

At the invitation of Mr. V. K. Rowe, Biochemical Research Department, Dow Chemical Company, Mr. C. L. Dunn and the writer (along with representatives of other TCP producers--see letter attached) met in Midland on March 24, 1965, to discuss impurities in TCP.

Mr. Rowe and Dr. Holder of Dow reported that 60 to 70 employees of Dow over the past two years have developed chloracne from exposures to materials in their TCP operation. Chloracne is a disfiguring disease involving blockage and inflammation of the sebaceous glands of the skin, particularly of the face. It is believed to be a systemic disease and requires several years after exposure for the condition to disappear.

Dow has conducted considerable research to identify the cause of this condition and has concluded that several impurities, sometimes present in TCP, are responsible. They have identified one of these impurities which they believe is the principal acnegen--2,3,7,8-tetrachlorodibenzo-p-dioxin. They have developed (and supplied to all attendees) a chemical method for the detection of this material which is sensitive to 1 ppm (gas chromatography and flame ionization).

There was considerable discussion of the clinical aspects of the disease and the toxicological research Dow has conducted. In brief, 2,3,7,8-TCDED has been shown to produce the disease in rabbits at a concentration of 40 ppm after one application of 0.1 ml to the ear, and at a concentration of 0.4 ppm after eight applications. No evidence of the disease has been produced by concentrations up to 20 ppm for a single application and up to 0.1 ppm for twenty-five applications to rabbit ears. The compound has also been demonstrated to be a potent liver toxicant by oral or skin exposure. As little as 0.017 mg/kg is lethal to rabbits by the oral route.

Dow has analyzed commercial samples of TCP of all producers and has found up to 20 ppm of 2,3,7,8-TCDED in some. In finished samples of 2,4,5-T-acid they have found up to 10 ppm. No Hercules sample analyzed contained any significant acnegen. Dow has reduced their TCP capacity and is checking all production to be certain that it contains less than 1 ppm 2,3,7,8-TCDED. Currently, Dow is burying all wastes and contaminated material from their TCP plant since they are

19010

P-24 4d
215/54 JL

7/25/66



INCORPORATED

1 DEPARTMENT
WILMINGTON, DELAWARE 19800 • (302) 650-0011
LY 86, 1966

- Ries Dielmann - The Hague
- E. C. Phillips - International
- E. Z. Christofani - Medical
- M. A. Taves - Syn. Div. R.C.
- E. B. Scott - Synthetics
- A. Z. Canner - Anal. Div. R. C.
- J. J. Ford - Anal. Div. R.C.

Pharmkol. Inst. der BASF A.G.
Schwanthaler Allee 20
67 Ludwigshafen
Rhein, Deutschland

Dear Professor Ottal:

Last September (1965), during my visit to your laboratory, we discussed the hazards associated with the production of trichlorophenol. I reviewed with you the recent cases of chloracne in the United States and you reviewed the precautions taken by you to assure against a repetition of a similar epidemic experienced by BASF. One of your most helpful comments was that you analyze all shipments of incoming trichlorophenol for chloracnogens by an oral rat biological assay procedure which you have developed. You also offered to assay some of our samples according to this procedure.

In my letter of December 26, 1965, I indicated that we would send these samples in the near future. For a combination of reasons, it has taken us until now to assemble the samples which we consider most appropriate. We sincerely hope that your offer is still available to us.

On the assumption that you will still be able to perform these assays, we have shipped 15 samples (10-grams each) of phenoxy herbicide finished products and intermediates encountered in their manufacture to Mr. Ries Dielmann of our Hague Office. We have asked Mr. Dielmann to contact you to arrange a suitable time for personal delivery of these samples to you. In addition, he will have a small sample of 2,3,7,8-tetrachlorodibenzo-p-dioxin, which can be used as a standard.

Wherever possible, these samples have been analyzed for "dioxin" content by gas chromatography, and we will be very glad to exchange this information with you in an effort to determine the reliability of the chromatographic procedure. However, you should assume that some of the samples contain no detectable "dioxin"; others contain from 1 to 25 ppm added "dioxin" and others contain known concentrations of "dioxin" which developed in manufacture.

The samples are labeled and identified as follows:

Samples K14567-41-1	Standard 2,4,5,-T Acid with added Dioxin
2	:
3	:
4	:
5	:

h01450

19012

Professor H. Ottel

Page 2

July 28, 1966

Samples K15280-56-8

Plant Grade 2,4,5-T Acid with Known Dioxin

Samples K15280-55-1

Plant Grade Sodium Trichlorophenate with
Added Dioxin

Samples K15280-56-1

2 Ethyl hexyl ester of 2,4,5-T with
Added Dioxin

Sample K15280-56-7

Nonseparifiable fraction from plant process

Sample K15280-56-10

Pure 2,3,7,8-tetrachlorodibenzo-p-dioxin

The samples of sodium trichlorophenate (K15280-55-1 to -5) can be more easily handled if liquified by heating to 65°C. The sample of nonseparifiable fraction can be liquified at 50°C.

I am certain that there is no need for me to caution you to handle these materials with appropriate care. It is because of the hazard of handling these materials that we are arranging for personal delivery to you by Mr. Holman.

We also plan to attempt a biological assay by dermal administration to rabbits with some of these samples. We will be glad to compare these results with yours, when they are available.

At the time of my visit to your laboratory, you indicated that you would try to locate a copy of your complete report on the chloracne epidemic which occurred at BASF in 1953. Since Hercules has never experienced a case of chloracne, we would appreciate receiving a copy of that report, with photographs, so that our people might better appreciate the potential effects of carelessness.

If you have any questions about these samples, please contact us. Let us hope that through this cooperative endeavor, we can both provide better protection to the employees of both of our companies.

Best personal regards.

Sincerely,

John F. Frawley, Ph.D.
Chief Toxicologist

JFF/cav

H01451

19013

July 28, 1956

PERSONAL AND CONFIDENTIAL

Mr. Max Friedman
R. V. Eversole Paper Company
Chicago 11
P. O. Box 619
The Hague, Netherlands
Dear Max:

During my visit to Europe last September, I spent a half day with Dr. H. Oetzel at MIT. Most of our time was spent discussing the hazards associated with the manufacture of triethylphenol.

During the year preceding this discussion, one of the U.S. producers of triethylphenol had a serious episode of chloracne among their plant workers. All other U.S. producers have had difficulty from time to time and MIT had had a serious episode in 1953 that they decided to discuss in detail the manufacture of triethylphenol and to purchase it only from other manufacturers.

I am enclosing several confidential memoranda which describe the technical aspects of this problem and the serious health hazards involved with the "ETO" isomerization side-reaction which occurs in triethylphenol.

Triethylphenol is used for the manufacture of E.B.S.-F and its esters which are, of course, used as herbicides. Fortunately, Eversole has never had a case of chloracne developing in any of its employees. This may be due to plants such as MIT, but we could it is due to the fact that our process is safer than the one Eversole uses and pressure control to maintain the "ETO" isomer level. After the most recent U.S. outbreak, we have instituted more rigid control of our plant production, and hope to be able to prevent any outbreaks in the future.

This letter and the enclosures provide you with background that will be necessary to understand the attached letter to Professor Oetzel. You will note from this letter that we are sending to you a series of articles concerning "ETO" for you to deliver to Professor Oetzel personally. I state in the letter that you are forwarding them personally because of the hazard associated with handling these materials. This is not the only reason. In forwarding them to you, you will have an opportunity to meet Professor Oetzel and to tell him, as he is able to encourage him to give you a copy of the report referred to in my letter. Professor Oetzel promised to send me a copy of the report as their epidemic, but has never followed through on his promise.

John E. Eversole

h01448

19014

Mr. Lisa Melman

Page 2

July 27, 1966

We will have someone from Wilmington carry these samples to you in the Eagle. There is no need for you to unpack them and there is no hazard associated with handling the containers; they are adequately packed against breakage. However, you should appreciate that the pure sample of 'dioxin' is very toxic and these materials should be kept away from anyone who does not appreciate the potential hazard of the samples.

I hope the enclosed information gives you sufficient background to be able to discuss this matter briefly with Professor Cottel. Obviously we do not wish to reveal any manufacturing know-how and the cooperation between Hercules and BASF is strictly in the interest of health protection of employees. You do not wish to enter into a technical discussion with Professor Cottel, but I will leave that to your own discretion.

For obvious reasons, I suggest that you discuss this matter only with those people in the Eagle office who must know about it. We prefer that you discuss it with no one but you may find it necessary to inform W. C. Norwood and J. V. Weymiller.

You will have many questions to ask about this whole problem which cannot be answered in correspondence. I will be very happy to discuss it the next time we meet in complete detail. In the meantime, I hope we will contact Professor Cottel and arrange to take these samples to him at your earliest convenience. Thanks very much.

Sincerely,

John P. Hawley, Ph.D.
Chief Toxicologist

JPH/cav

cc: Mr. Herman C. Phillips - International

19015

h01445

HERCULES FERTILIZER COMPANY

RECEIVED

October 19, 1936

Dr. B. B. Smith - Entomologist
Dr. E. C. Phillips - Director
Mr. H. H. Williams - F. & M. Agent
Dr. H. A. Davis - Agr. Ext. Agent
Mr. J. J. Ford - Asst. Dir. Ent. ✓

Professor E. Correll
Memphis, Tenn. Oct. 15, 1936
6 Hamilton Allen St.
67 Levee, Memphis
Tenn., Tennessee

Dear Professor Correll:

Mr. H. H. Williams of our Region office has sent me a report on his interesting and informative visit with you and Dr. Williams on the 21st of August. I extremely appreciate the courtesy you showed to Mr. Williams during this visit to your laboratory. He has referred several questions to me which I will attempt to answer.

In our process for the manufacture of 7-3-5-2 acid, we do not isolate trichlorophenol. It is for this reason that we did not send any trichlorophenol. It was our hope, however, that you would be able to analyze the sample of solid trichlorophenol, 7-3-5-2 acid, and ethyl mercaptan. We realize that because of the greater variety of the acid, the sensitivity of your analytical assay for "acids" may not be as good.

Mr. Williams stated that the original sample of 10 grams would not be adequate for your assay. Accordingly, we have shipped directly to your laboratory approximately 100 grams additional of samples:

115-20-56-2	Cryst. merc. ester of 7-3-5-2 acid
115-20-56-3	solid 7-3-5-trichlorophenol
115-20-56-7	non-responsible fraction from plant process

We have also shipped 100 grams of a sample identified as:

115-20-56-11 7-3-5-2 acid

which is the same as previous sample 115-20-56-1, but from a different production batch. Some of these samples contained any other details. If you wish to add details, the previous sample 115-20-56-11 of pure acids may be used.

Please you expressed an interest in receiving a sample of the trichlorophenol, although we do not currently have this material, we have prepared a sample of crude T-1 from our process especially for your test purposes. This sample (100 grams) has also been shipped and is identified as 115-20-56-13.

The material above the nature of the non-responsible fraction previously delivered by Mr. Williams. The results of the non-responsible

The type your own work

RECEIVED

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HERCULES 2 (b) (v)

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HERCULES POWDER COMPANY

Reference Is Made:

Re: :

October 19, 1966

material which is removed from our R&D process and if any significant amount of disease is found in our process, the majority should appear in this non-comparable fraction.

You also inquired through Mr. Melamed whether we intended to try a new method for the bioassay of disease. We do not. However, we are anxious to correlate chemical determinations by gas chromatography with the rabbit ear bioassay method of Drs. and with the rabbit ear bioassay which you have developed. Obviously, if gas chromatography is a reliable method it can be used more easily as a direct control rather than a bioassay method.

The Doe bioassay procedure involves placing a chloroform extract on the ear of the rabbit and waiting for development of hyperemia which is about 14-16. The report positive results with samples of 1,000 mg each containing 1 ppm disease.

Thank you for the copy of your report on the 1973 episode of chloroform. Thanks to Mr. Melamed we have translated this report into English, a copy of this translation is enclosed. Mr. Melamed reported that you would be sending directly to us copies of the slides and photographs used during this lecture. It will look forward to receiving these because they will help illustrate the various steps of the disease to which you referred in this paper.

If you have any questions regarding these samples, or wish to discuss this project further, please feel free to contact Mr. Melamed or me. We look forward to being able to compare results on these samples in the near future. Thank you again for your cooperation.

Sincerely,

JAL

John J. Freuder, Ph.D.
Chief Microbiologist

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NOV 1966 140 1978

JB

100-1003

19017

MERCURY INCORPORATED

Mr. H. C. Phillips
Dr. R. B. Scott
Mr. C. L. Dunn
Mr. A. E. Sigball

June 29, 1967

Professor M. Guttel
Pharmakol. Inst. der BASF A. G.
Schweinstaler Allee 11
67 Ludwigshafen
Rhein, Westfalen

Dear Professor Guttel:

Thank you very much for calling to my attention the article on occupational acne which was published in *British Journal of Dermatology* 3, 225-27 (1966). Mr. Dieleman forwarded a copy to me and we have translated it into English. I am enclosing a copy of the English translation for your files.

I agree with you that this report is very disturbing. Three products are mentioned in the report: Aillex, Isterone and Shell Seed Killers. Aillex is manufactured by Green Cross Products (of Canada), a division of The Sherrin-Williams Company of Canada, Limited. Currently Aillex contains 2,4,5-T and Dieldrin but in 1963 it may have contained 2,4,5-T instead of Dieldrin. Isterone is 3,5-dichloro-4-methoxybenzoic acid. Since this company does not manufacture 2,4,5-T, they would have purchased it from any one of several different manufacturers.

Isterone is a herbicide used by some chemical companies to describe a variety of phenoxy herbicide formulations, some of which contain 2,4,5-T. The "Shell Seed Killers" also could describe any herbicide formulation which may or may not contain 2,4,5-T. In our knowledge Shell does not manufacture 2,4,5-T so their seed killers contain 2,4,5-T could have been purchased from any of the basic producers.

Consequently, the source of the 2,4,5-T which presumably was involved in these exposures cannot be identified. I have sent a copy of the same article to V. A. some of whom, but I have not received any comments from them.

As I have mentioned, we are relying on our chromatography to assure ourselves that our 2,4,5-T preparation is free of Dieldrin. We have made some attempt to bioassay the samples of the intermediate sent to you but are unable to achieve desired sensitivity, partially because the 2,4,5-trichlorophenoxyacetic acid and the ester are significantly more toxic than trichlorophenol. We are continuing our efforts to confirm the concentration of Dieldrin necessary in each to elicit a positive BS₁ reaction. We are anxious to know if you have had any success with these samples.

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MERCUDES INCORPORATED

Professor H. L. Lott

- 2 -

June 1, 1967

Also, we would still appreciate receiving copies of the photo, which accompanied your talk in the Journal in June 1966.

As soon as we have something more definite to report, we will contact you. Thanks again for your continued interest in us. We defer on a matter of Post assistance to both companies.

Sincerely,

John P. Bradley, Jr.
Chief Toxicologist

JPL/c>

MERCUDES 2 (b) (v)

100005

19020



STATE OF ARKANSAS
OFFICE OF THE GOVERNOR
State Capitol
Little Rock 72201

January 10, 1980

JAN 1980
RECEIVED
Ark. Dept. of
Pollution Control
& Ecology

Southall
Vertac
Bill Clinton
Governor

Mr. Jarrell Southall, Director
Department of Pollution Control & Ecology
8001 National Drive
Little Rock, AR

Dear Jarrell:

On Monday, January 7, my office received a telephone communication from Ms. Adlene Harrison informing us that a letter was forthcoming with regard to the problems surrounding the cleanup operations at Vertac, Inc. in Jacksonville. It is very important that the contents of the letter not be discussed, at this time, with anyone other than members of our respective staffs and the staff of EPA.

Sincerely,

Bill
BILL CLINTON
Governor

BC/SS/hnj

19021

Water-1

EXHIBIT "A"

LEGAL DESCRIPTION

ARKANSAS ORDINANCE PLANT, ARKANSAS

Plant Area:

A tract of land situated in the County of Pulaski, State of Arkansas, being part of Fractional Sections 6, 7, 18, 19, and 30, Township 3 North, Range 10 West, all of Fractional Sections 1 and 2, and Sections 11, 12, 13, 14, 23, and 24, and part of Sections 25 and 26, Township 3 North, Range 11 West of the 5th Principal Meridian, and being more particularly described as follows:

Beginning at the northwest corner of said Fractional Section 2; thence east along the north line of said Fractional Section 2, the north line of said Fractional Section 1, and the north line of said Fractional Section 6 to the north quarter corner of said Fractional Section 6; thence south along the north and south quarter line of said Fractional Section 6, the north and south quarter line of said Fractional Section 7, the north and south quarter line of said Fractional Section 18, the north and south quarter line of said Fractional Section 19, and the north and south quarter line of said Fractional Section 30 to the center of said Fractional Section 30; thence east along the east and west quarter line of said Fractional Section 30 to a point on the southwesterly right-of-way line of Arkansas State Highway No. US 67; thence in a southeasterly direction along said southwesterly right-of-way line to a point on the northwesterly line of the Missouri Pacific Railroad Company's right-of-way; thence in a southwesterly direction along said northwesterly right-of-way line to a point on the south line of said Fractional Section 30; thence west along the south line of said Fractional Section 30 to the southwest corner thereof; thence north along the west line of said Fractional Section 30 to the southeast corner of the NE $\frac{1}{4}$ SE $\frac{1}{4}$ of said Section 25; thence west along the south line of the NE $\frac{1}{4}$ SE $\frac{1}{4}$ of said Section 25 and the south line of the NE $\frac{1}{4}$ SW $\frac{1}{4}$ of said Section 25 to the southwest corner of said NE $\frac{1}{4}$ SW $\frac{1}{4}$ of Section 25; thence north along the west line of said NE $\frac{1}{4}$ SW $\frac{1}{4}$ of Section 25 to the southeast corner of the SW $\frac{1}{4}$ NE $\frac{1}{4}$ of said Section 25; thence west along the east and west quarter line of said Section 25 and the east and west quarter line of said Section 26 to the west quarter

19022

Flatt Area, (cont'd)

corner of said Section 26; thence north along the west line of said Section 26, the west line of said Section 25, the west line of said Section 14, the west line of said Section 11, and the west line of said Fractional Section 2 to the point of beginning, containing 7,251.14 acres, more or less.

Water Pipe Line Easement:

A tract of land situated in the County of Pulaski, State of Arkansas, being part of the NW¹/₄ of Fractional Section 31, Township 3 North, Range 10 West and part of the SE¹/₄ NE¹/₄ of Section 36, Township 3 North, Range 11 West of the 5th Principal Meridian and being more particularly described as follows:

Part 1: (J-212, J-213, J-214, & J-215)

Beginning on the east line of said SE¹/₄ NE¹/₄ of Section 36 at a point which is S. 01° 03' E., 398.6 feet from the northeast corner of said SE¹/₄ NE¹/₄ of Section 36; thence N. 45° 03' E., 607.0 feet to a point; thence N. 23° 46' E., 474.0 feet to a point; thence N. 26° 21' W., 111.2 feet to a point on the southeasterly line of the Missouri Pacific Railroad Company's right-of-way; thence N. 51° 09' E., 30.4 feet along said southeasterly right-of-way line to a point; thence S. 26° 21' E., 160.2 feet to a point; thence S. 23° 46' W., 714.0 feet to a point; thence S. 46° 03' W., 621.3 feet to a point; thence S. 01° 03' W., 77.6 feet to a point on the northwesterly right-of-way line of the Arkansas Ordnance Plant Water Pipe Line Easement; thence N. 43° 57' W., 42.4 feet along said northwesterly right-of-way line to a point; thence N. 01° 03' E., 60.0 feet to a point; thence N. 46° 03' E., 21.2 feet to the point of beginning, containing 0.94 acres, more or less.

Part 2: (J-214)

Beginning on the north line of said Fractional Section 31 at a point which is S. 87° 45' E., 99.3 feet from the northwest corner of said Fractional Section 31; thence S. 87° 45' E., 34.2 feet along said north line of Fractional Section 31 to a point; thence S. 26° 21' E., 795.2 feet to a point on the northwesterly line of the Missouri Pacific Railroad Company's right-of-way; thence S. 51° 09' W., 30.4 feet along said northwesterly right-of-way line to a point; thence N. 26° 21' W., 616.6 feet to the point of beginning, containing 0.55 acres, more or less.

Permit for Water Pipe Line Crossing: (J-204-A)

A tract of land situated in the County of Pulaski, State of Arkansas, being part of the SE¹/₄ NE¹/₄ of Section 36, Township 3 North, Range 11 West of the 5th Principal Meridian, and being more particularly described as follows:

Beginning on the southeasterly line of the Missouri Pacific Railroad Company's right-of-way at a point which is N. 89° 09' W., 393.5 feet from the northeast corner of the SE¹/₄ NE¹/₄ of said Section 36; thence S. 56° 09' W., 30.0 feet along said southeasterly right-of-way line to a point; thence N. 33° 21' W., 100.0 feet to a point on the northwesterly line of said Missouri

Pacific Railroad Company's right-of-way; thence N. 86° 09' E., 30.3 feet
along said northwesterly right-of-way line to a point; thence S. 33° 21' E.,
130.3 feet to the point of beginning, containing 0.37 acres, more or less.

Tater Jail Site:

Part 1:

A tract of land situated in the County of Pulaski, State of Arkansas, being the south 100 feet of Fractional Section 31, Township 3 North, Range 10 West of the 5th Principal Meridian, containing 9.09 acres, more or less.

Part 2:

A tract of land situated in the County of Pulaski, State of Arkansas, being part of the SW $\frac{1}{4}$ SW $\frac{1}{4}$ of Section 32, Township 3 North, Range 10 West of the 5th Principal Meridian, and being more particularly described as follows:

Beginning at the southwest corner of said Section 32; thence north along the west line of said Section 32, 100.0 feet to a point; thence east and parallel to the south line of said Section 32, 451.0 feet to a point; thence south 100.0 feet to a point on the south line of said Section 32; thence west along said south line to the point of beginning, containing 1.04 acres, more or less.

Part 3:

A tract of land situated in the County of Pulaski, State of Arkansas, being part of the NW $\frac{1}{4}$ NW $\frac{1}{4}$ of Fractional Section 5, Township 2 North, Range 10 West of the 5th Principal Meridian and being more particularly described as follows:

Beginning at the northwest corner of said Fractional Section 5; thence east along the north line of said Fractional Section 5, 700.0 feet to a point; thence south 100.0 feet to a point; thence west and parallel to the north line of said Fractional Section 5, 700.0 feet to a point on the west line of said Fractional Section 5; thence north along said west line to the point of beginning, containing 1.60 acres, more or less.

Permanent Easement for Access Road: (J-207)

A tract of land situated in the County of Pulaski, State of Arkansas, being part of the NW $\frac{1}{4}$ of Fractional Section 30, Township 3 North, Range 10 West of the 5th Principal Meridian, in Dupree's Addition to the town of Jacksonville, Arkansas, and being more particularly described as follows:

Parcel A: - Beginning on the north and south quarter line of said Section 30 at a point which is N. 02° 00' E., 318.0 feet from the center of said Fractional Section 30; thence N. 02° 00' E., 116.5 feet along said north and south quarter line to a point; thence S. 41° 04' E., 289.1 feet to a point; thence S. 48° 56' E., 234.2 feet to a point; thence S. 56° 57' E., 172.7 feet to a point on the westerly right-of-way line of U.S. Highway No. 67; thence

Permanent Easement for Access Road: (J-207) cont'd.

in a southeasterly direction 17.3 feet along said right-of-way line to a point on the east and west quarter line of said Fractional Section 30; thence N. 82° 14' W., 177.2 feet along said east and west quarter line to a point; thence N. 86° 57' W., 45.2 feet to a point; thence N. 48° 56' W., 243.1 feet to a point; thence N. 41° 04' W., 183.3 feet to the point of beginning, containing 1.40 acres, more or less.

Parcel B, Beginning on the north and south quarter line of said Fractional Section 30 at a point which is N. 81° 00' E., 518.9 feet from the center of said Fractional Section 30; thence E. 32° 30' N., 1014.1 feet along said north and south quarter line to a point; thence N. 82° 38' E., 549.5 feet to a point on the westerly right-of-way line of U.S. Highway No. 67; thence in a southeasterly direction along the arc of a curve 184.7 feet to a point; thence S. 22° 38' W., 492.1 feet to the point of beginning, containing 1.20 acres, more or less.

NOTE: In addition to the land acquired in fee and the easements acquired as described above, permits were obtained from the Missouri Pacific Railroad Company and the Arkansas Highway Commission for pipe line crossings which involve no acreage.

FORM OF TRANSFER

KNOW ALL MEN BY THESE PRESENTS, That the War Department (Transferor), acting through the Commanding Officer, Arkansas Ordnance Plant, Little Rock, Arkansas, by these presents does transfer custody, control, and accountability unto the War Assets Administration (Transferee), the following land and improvements thereon, to wit:

The Arkansas Ordnance Plant located in Pulaski County, Arkansas and containing a total of seven thousand two hundred fifty two and ninety-six one hundredths acres (7,252.96) the legal description of which is attached hereto as Exhibit "A" which is made a part hereof:

All buildings, utilities and improvements which are presently located on the land embracing the Arkansas Ordnance Plant, the description of which is attached hereto as Exhibit "B" which is made a part hereof:

All "installed real property" which is presently located in the above-described buildings or located on the above-described premises the description of which is attached hereto as Exhibit "C" which is made a part hereof:

All of the personal property located at the Arkansas Ordnance Plant as described on Forms SPB-1 or SPB-1.1, ORD 05-014-46-1 through 485 inclusive. This transfer is intended to cover and embrace all U. S. Government personal property except metal components and packaging material for which the Transferor is accountable. Said metal components and packaging material will be removed from the premises by the Transferee within 90 days after the effective date hereof.

The Transferee will proceed to make such inventory checks as he deems necessary prior to 1 July 1946 of the personal property described in above-mentioned Forms SPB-1. Any discrepancies disclosed as a result of such checks will be reported by the Transferee to the Transferor for necessary adjustment by 1 July 1946.

The entire facility (including real and personal property) has been decontaminated and is satisfactory for idle stand-by condition for use in its original purpose. The facility has been reviewed by a board of consultants and it has been recommended that seventy-three (73) buildings (listed on Page 1 Exhibit C) which cannot be economically decontaminated should be destroyed in the event the facility is disposed of for other than its original purpose.

The undersigned Transferee hereby acknowledges that delivery of the said land and improvements was made by the Transferor and receipt of said property is hereby acknowledged.

The undersigned Transferee hereby agrees that on 1 July 1946 full accountability will be assumed by said Transferee for all personal property listed on Forms SPB-1, ORD 05-014-46-1 thru ORD 05-014-46-485 and no further requests for adjustment will be made to the Transferor.

IN WITNESS WHEREOF, the War Department acting through the Commanding Officer, Arkansas Ordnance Plant, Arkansas, and War Assets Administration, have hereunto set their hands this 14th day of June 1946.

WAR DEPARTMENT (Transferor)

BY: [Signature]
 Edwin Johnson
 Capt., Ord. Dept.,
 Commanding Officer
 Arkansas Ordnance Plant, Arkansas

WAR ASSETS ADMINISTRATION (Transferee)

BY: [Signature]
 C. C. Christian
 Regional Director

TRANSVAAL, INC.

THE GAS CHROMATOGRAPHIC DETERMINATION
OF 2,3,7,8-TETRACHLORODIBENZO-P-DIOXIN
IN 2,4,5-TRICHLOROPHENOXYACETIC ACID (2,4,5-T),
2,4,5-T BUTYL ESTER, AND 2,4,5-T 2-ETHYLHEXYL ESTER

Edward M. Harris

August 13, 1974

19009

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DIGEST

Objective

This is the report of an investigation to determine the 2,3,7,8-Tetrachlorodibenzo-p-dioxin (TCDD) content of 2,4,5-T and 2,4,5-T butyl and 2-ethylhexyl esters manufactured by Transvaal, Inc. at Jacksonville, Arkansas.

The compound of interest, TCDD, may be produced as a by-product in the manufacture of 2,4,5-T, and is of significance due to its alleged high toxicity to humans.

The objective of this investigation was to determine the amount of TCDD produced in the 2,4,5-T and its butyl and 2-ethylhexyl esters manufactured by Transvaal, Inc.

Results and Conclusions

The analytical method developed in this investigation was based on methods by Dow Chemical Company, Hercules Incorporated, and D. A. Elvidge.¹

Samples of 2,4,5-T acid were dissolved in aqueous acetonitrile and extracted with hexane. The extracts were concentrated and then analyzed for TCDD by gas chromatography using a flame ionization detector.

Analysis of samples of esters involved a preliminary saponification procedure followed by extraction of TCDD from aqueous dimethylformamide

¹ Elvidge, D. A., Analyst, 96, 721-727 (1971).

with hexane. The concentrated hexane extracts of the esters were analyzed by gas chromatography using an electron capture detector.

None of the samples of 2,4,5-T acid and 2,4,5-T esters examined contained TCDD at a concentration greater than 0.1 ppm.

EXPERIMENTAL SECTION

Reagents

n-Hexane

Quality suitable for pesticide residue analyses. (Burdick and Jackson Laboratories, Muskegon, Michigan)

Acetonitrile

Quality suitable for pesticide residue analyses. (Matheson, Coleman, and Bell)

Aqueous Acetonitrile

Solution of 90% acetonitrile and 10% distilled water by volume.

Equilibrated n-Hexane

n-Hexane saturated with the aqueous acetonitrile solvent.

Diethyl Ether

Quality suitable for pesticide residue analyses. (Burdick and Jackson Laboratories, Muskegon, Michigan)

<u>Chloroform</u>	Quality suitable for pesticide residue analyses. (Matheson, Coleman, and Bell)
<u>Ethanol</u>	Reagent alcohol (Anderson Laboratories, Ft. Worth, Texas)
<u>Methanol</u>	Anhydrous, Reagent grade (Mallinckrodt)
<u>25% Ether-Hexane</u>	
<u>Chloroform-Ether, 1:1</u>	
<u>Double Distilled Water</u>	
<u>N,N-Dimethylformamide</u>	A. C. S. Reagent Grade (Baker and Adamson)
<u>Methylene Chloride</u>	Spectroquality Reagent (Matheson, Coleman, and Bell)
<u>Sodium Sulfate</u>	Anhydrous, Granular, A. C. S. Reagent Grade (Mallinckrodt)
<u>Potassium Hydroxide</u>	Reagent grade pellets (Mallinckrodt)
<u>Ammonium Hydroxide: Water Solutions</u>	1:1 and 1:2 by volume (using 25% NH_4OH and double distilled water)
<u>Aluminum Oxide</u>	Woelm, basic (cationotropic), Activity Grade I
<u>Florisil</u>	PR Grade, 60/100 mesh (Supelco, Inc.)

TCDD Reference Material - Obtained from D. Firestone, U. S. Food and Drug Administration.

TCDD Standard Solution: 2.5 milligrams of TCDD were dissolved, with warming, in 10 ml of diethyl ether contained in a 25 ml volumetric flask and adjusted to volume with ether. Dilutions were made, with

25% ether-hexane to yield solutions containing TCDD at concentrations of 20 ng per microliter and 0.2 ng per microliter.

Apparatus

All glassware was cleaned in chromic-sulfuric acid mixture, washed with water, dried and rinsed with hexane prior to use.

A Tracor MT-220 gas chromatograph, equipped with a flame ionization detector, an electron capture detector (with a 10 mCi ^{63}Ni source), a 1-mV Honeywell Elektronik 194 Recorder, and an Infotronics automatic digital integrator, was used.

Chromatographic Columns - Two six-foot glass columns of 2 mm i.d. were packed with 3 percent OV-17 (Pierce Chemical Company) on 80/100 mesh Chromosorb G (Johns-Manville Company) and conditioned at 250⁰ C. for 24 hours before use. One column was attached to the flame ionization detector and the other to the electron capture detector.

Operating Conditions

The following operating conditions were used:

(A) For 2,4,5-T:

Detector temperature - 260⁰ C.

Recorder chart speed - 12 inches per hour

Carrier gas - Nitrogen (Prepurified grade)

Column temperature - 200⁰ C.

Injection port temperature - 250⁰ C.

Carrier gas flow rate - 30 ml per minute

Hydrogen flow rate - 60 ml per minute

Air flow rate - 1.2 cu. ft. per minute

Attenuation settings were adjusted to give at least a 25 percent full-scale recorder deflection for an injection of 40 ng 2,3,7,8-TCDD.

(B) For the butyl and 2-ethylhexyl esters: (Electron capture detector):

Detector voltage - 12V

Detector temperature - 290⁰ C.

Chart speed - 12 inches per hour

Carrier gas and purge gas - Nitrogen (Prepurified Grade)

Column temperature - 200⁰ C.

Injection port temperature - 250⁰ C.

Carrier gas flow rate - 30 ml per minute

Purge flow - 20 ml per minute

Attenuation settings were adjusted to give at least a 25 percent full-scale recorder deflection for an injection of 0.4 ng 2,3,7,8-TCDD.

Methods and Procedures

Procedure for Preliminary Treatment of the Sample: (1) For 2,4,5-T:

Extraction: Twenty grams of sample were weighed in a 500 ml. separatory funnel and dissolved in 100 ml of warm aqueous acetonitrile. Then 100 ml of equilibrated hexane were added, and the funnel shaken vigorously for 30 seconds. After the phases separated, the lower phase

(Acetonitrile) was transferred to a second 500 ml funnel. The first 500 ml funnel was swirled to recover traces of acetonitrile adhering to the funnel walls, and these drainings were transferred to the acetonitrile phase. The hexane phase was added to a 1-liter funnel containing 500 ml of distilled water.

The partition step was repeated twice more, using 100 ml of n-hexane each time. The acetonitrile phase was transferred between the two 500 ml funnels and the hexane phase added to the 1-liter funnel after each partition. Following the third partition, the acetonitrile phase was discarded. The three combined hexane phases in the 1-liter funnel were then washed by shaking with distilled water for 30 seconds.

After the phases separated, the aqueous wash was drained off and discarded. The hexane phase was dried by passing it through a four-inch glass funnel containing a small cotton plug and 50 g of anhydrous Na_2SO_4 . The hexane was collected in a 400 ml beaker and the separator was rinsed with several 10 ml washes of hexane. The washes were passed through the funnel to wash the Na_2SO_4 and collected in the same beaker.

The hexane phase was evaporated just to dryness on a steam bath using a gentle stream of dry nitrogen to aid in the evaporation.

Alumina Column Chromatography - A column was prepared in a glass tube, 150 x 10 mm, having a porous glass plug, by filling the tube with ether and adding alumina while gently tapping the tube to release any air bubbles. The alumina was added until it reached a height of 8 cm. The column was then washed with 50 ml of ether, followed by 50 ml of n-hexane.

The residue from the evaporated hexane phase in the extraction step was dissolved in a small volume (about 1-2 ml) of diethyl ether and transferred to the alumina column. The beaker was rinsed with several additional ether washes, and these were added to the column. The column was then eluted with 50 ml of 25% ether-hexane solution.

The ether-hexane fraction was evaporated just to dryness on a steam bath under a gentle stream of dry nitrogen. The residue was quantitatively transferred to a 4 ml screw cap vial, using a mixture of 1:1 Chloroform-Ether to accomplish the transfer. The sample was evaporated just to dryness once more, and the final residue dissolved in 0.5 ml of 25% ether-hexane solution.

Procedure for Preliminary Treatment of the Sample: (2) For 2,4,5-T Esters:

Saponification: About 10 g of ester sample was accurately weighed in a 400 ml beaker and dissolved in 50 ml of ethanol. After the sample was dissolved, 10 g of potassium hydroxide dissolved in a few ml of water were added, followed by the addition of 50 ml of double distilled water. The solution was heated under reflux for three hours, shaking occasionally. The solution was then evaporated on a hot plate until no noticeable odor of butyl or 2-ethylhexyl alcohol was present. The residual solids were dissolved in 100 ml of N,N-dimethylformamide and 200 ml of double distilled water with slight warming and transferred to a 500 ml separatory funnel.

Extraction: The solution was then extracted with 5 x 50 ml portions of n-hexane, the combined extracts being collected in a 500 ml

separatory funnel. The combined hexane extracts were then washed with 60 ml of 1:1 NH_4OH and 30 ml of 1:2 NH_4OH in that order, and finally washed three to five times with 50 ml of double distilled water (until wash water was neutral). The extracts were dried by the addition of 30 g of sodium sulfate to the separatory funnel and the funnel contents swirled and allowed to remain in contact with the sodium sulfate for 30 minutes. The extracts were then filtered through a funnel containing a cotton plug and about 3 g of sodium sulfate into a 600 ml beaker, and evaporated to dryness on a steam bath under a gentle stream of dry nitrogen.

Florisisil Column Chromatography: A column was prepared by filling a glass tube, 150 x 10 mm, having a porous glass plug, with n-hexane and adding Florisisil while gently tapping to release any air bubbles. The Florisisil was added until it reached a height of 8 cm. The column was then washed with 50 ml of n-hexane, followed by 50 ml of 20% methylene chloride-hexane solution.

The residue from the evaporated hexane extracts was dissolved in a small volume (1-2 ml) of n-hexane and transferred to the Florisisil column. The beaker was rinsed with several additional hexane washes, and these were added to the column. The column was then eluted with 50 ml of 20% methylene chloride-hexane solution.

The methylene chloride-hexane fraction was evaporated just to dryness on a steam bath under a gentle stream of dry nitrogen. The residue was quantitatively transferred to a 10 ml volumetric flask using the 20% methylene chloride-hexane solution to accomplish the transfer, and the solution was diluted to volume.

Procedure for the Gas-Chromatographic Determination of 2,3,7,8-Tetrachlorodibenzo-p-dioxin:

Standard TCDD Solutions:

Solutions were prepared containing 20 ng of TCDD per μl in 25% ether-hexane and 0.2 ng of TCDD per μl in 25% ether-hexane. These solutions were used as standards for flame ionization detection and electron capture detection, respectively. The standard used in flame ionization detection corresponds to a TCDD content in 2,4,5-T of 0.5 ppm, and the standard for electron capture detection corresponds to a TCDD content in 2,4,5-T esters of 0.2 ppm.

Extract solutions of samples of 2,4,5-T and 2,4,5-T esters prepared as described were chromatographed under the conditions described. For 2,4,5-T samples, a 2 μl injection of standard TCDD was followed by injection of a 2 μl aliquot of sample solution. For the esters, the injection volume for standard and samples was 1 μl . The retention time for TCDD in 2,4,5-T samples was about ten minutes and in the ester samples about six minutes. The concentration of TCDD in the samples was calculated using the following formula:

$$C_u = \frac{A_u V_s C_s}{A_s V_u} \times f$$

where $f = \frac{10}{w}$ for esters, $f = \frac{0.5}{w}$ for 2,4,5-T,

and

C_u = concentration of TCDD in original sample, ppm

A_u = peak area of TCDD in aliquot of sample injected

A_s = peak area of TCDD in aliquot of standard injection

V_s = injection volume of standard, μl

V_u = injection volume of sample, μl

C_s = concentration of TCDD in standard, $\text{ng}/\mu\text{l}$

W = weight of sample taken, g

Results and Discussion:

A total of 15 samples of 2,4,5-T and 15 samples of 2,4,5-T esters were analyzed for 2,3,7,8-tetrachlorodibenzo-p-dioxin. The ester samples chosen for analysis were of esters manufactured from 2,4,5-T analyzed in this work, with the exception of one sample of agent orange herbicide. The date of manufacture of the samples ranges from 1966 to the present. Only four butyl esters were analyzed, whereas ten 2-ethylhexyl esters were analyzed. This is proportional to the quantity of manufacture and use of the two esters.

The esters required a more efficient clean-up procedure than did the 2,4,5-T samples, owing to the use of the electron-capture detector which has greater sensitivity, but is more easily contaminated than the flame ionization detector. Clean-up by Florisil column chromatography proved to be very satisfactory in removing interfering substances.

All of the samples contained less than 0.1 ppm of 2,3,7,8-tetrachlorodibenzo-p-dioxin, except the sample of agent orange herbicide, which contained 6.21 ppm. The agent orange was received from the Air Force and has been stored for about two years at this location.

Recovery of 2,3,7,8-Tetrachlorodibenzo-p-dioxin:

One ml of a solution containing 2 μ g of TCDD per ml was added to 20 g portions each of four samples of 2,4,5-T that were free from the impurity (less than 0.1 ppm), and the samples were analyzed by the method described. The addition produced the equivalent of 0.1 ppm TCDD in the 2,4,5-T, which was detected by the flame ionization detector.

A 0.5 ml aliquot of standard solution containing 0.7 μ g TCDD per ml was added to 10 g portions of each of two butyl and two 2-ethylhexyl esters that were free from the impurity (less than 0.1 ppm), dissolved in 50 ml ethanol, and the samples were analyzed by the method described. The spiked samples contained the equivalent of 0.35 ppm TCDD in the esters. Recoveries of 43 to 60 percent were obtained.

Recovery of 2,3,7,8-Tetrachlorodibenzo-p-dioxin from Florisil Column Chromatography:

A 2 μ l aliquot of standard solution containing 0.7 ng TCDD per μ l was spotted on a Florisil column prepared as described earlier. The sample was then eluted with 50 ml of 25% methylene chloride-hexane solution. After evaporation to near dryness and dissolving the residue with 0.5 ml of 25% methylene chloride-hexane solution, a 2 μ l aliquot was injected into the gas chromatograph. A recovery of 95% was obtained.

Linearity of Response of the Electron Capture Detector:

Portions of 0.4, 1.0, 1.2, 1.4, and 2.0 μ l of a standard solution containing 7.0 ng of TCDD per μ l were injected on to the OV-17 column connected to the electron capture detector. The attached graph of peak area versus nanograms of TCDD on column appears to be linear up to 8.4 ng TCDD over the range examined and passes through the origin.

Limits of Detection:

Under the conditions of the method the lowest level of TCDD detectable corresponded to a sample concentration of 0.1 ppm TCDD in 2,4,5-T and its esters.

Typical chromatograms are attached.

Linearity of Response of Electron Capture
Detector for 2,3,7,8-Tetrachlorodibenzo-
p-dioxin

Peak Area
 $\times 10^{-3}$

10 X 10 TO THE CENTIMETER 46 1515
18 X 25 CM. MADE IN U.S.A.
KEUFFEL & ESSER CO.

60

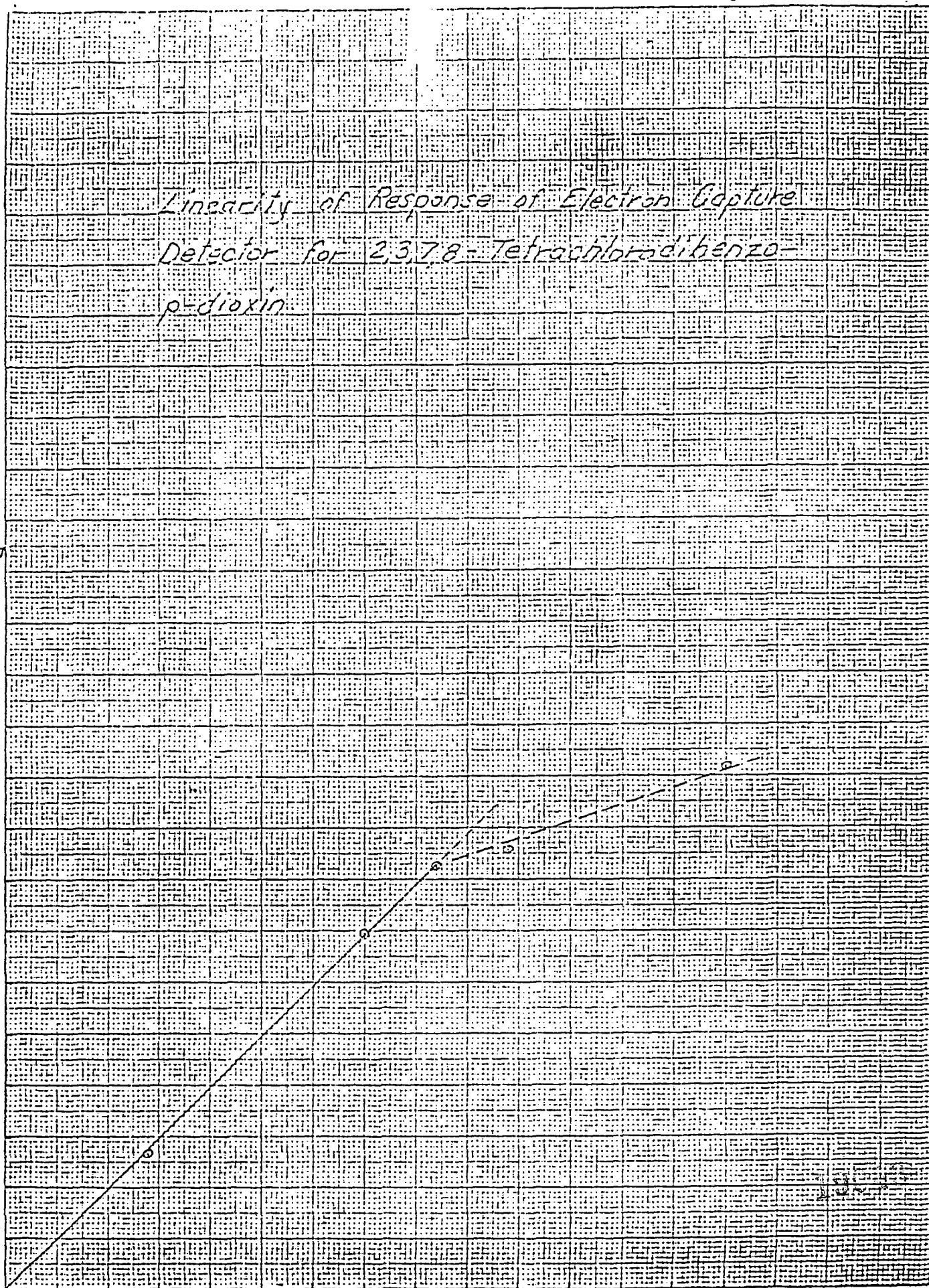
50

40

30

20

10



10 20 30 40 50 60 70 80 90 100 110 120 130 140 150

ng TCDD

