

CODING FORMS FOR SRC INDEXING

Microfiche No.	OTS0546325		
New Doc ID	88-920008775	Old Doc ID	8EHQ-0492-10481
Date Produced	04/27/92	Date Received	07/28/92
		TSCA Section	8ECP
Submitting Organization	CITGO PETRO CORP		
Contractor			
Document Title	INITIAL SUBMISSION: LETTER FROM CITGO PETRO CORP TO USEPA REGARDING STUDIES WITH PETROLIUM PRODUCTS WITH ATTACHMENTS AND COVER LETTER DATED 042792		
Chemical Category	PETROLIUM PRODUCTS		

8(e)

# CAP

(COMPLIANCE AUDIT PROGRAM)

## TSCA CONFIDENTIAL BUSINESS INFORMATION

ORIGINAL - TDAS (BLAKE)  
COPY # 1 - CBIC (Vera)  
COPY # 2 - SCOTT SHERLOCK  
(Box in CBIC)

10481

## COMPANY SANITIZED

ORIGINAL PUBLIC FILE  
COPY # 1 PUBLIC FILE  
COPY # 2 JIM DARR/Vivian

### CONTAINS NO CBI

ORIGINAL - PUBLIC FILE  
COPY # 1 - PUBLIC FILE  
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NOTE: Peter provides data entry in CBITS for the 8(e) CAP Documents.

8EHQ-0492-10481



CONTAINS NO CB

CITGO Petroleum Corporation 92 APR 28 AM 9:30

P.O. Box 3758  
Tulsa, Oklahoma 74102

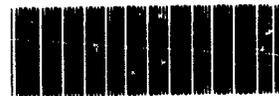
April 27, 1992

- VIA OVERNIGHT COURIER -

Document Processing Center (TS-790)  
Office of Toxic Substances  
Environmental Protection Agency  
401 M Street, S.W.  
Washington, DC 20460  
Attention: Section 8 (e) Coordinator  
(CAP Agreement)



8EHQ-92-10401  
INIT 07/28/92



88928888775

Re: Final Report  
ID #8ECAP-0104

Gentlemen:

In accordance with the terms of the signed Registration and Agreement for TSCA Section 8(e) Compliance Audit Program, CITGO Petroleum Corporation ("CITGO") is submitting its Final Report on the completion of the audit. The Final Report complies with the requirements of Unit II.C.4. of the CAP Agreement. Listed below are the studies or reports listed or submitted to EPA by CITGO under the terms of the CAP Agreement:

<u>Report Title</u>	<u>Date</u>	<u>CAP Category (Potential Penalty)</u>
CITGO's Submission No. 1 - Turbine Fuel (Botero Accident)	4/27/92	II.B.2.a. (\$15,000)
CITGO's Submission No. 2 - Cutting Oils 205 & 220	4/27/92	II.B.2.b. (\$12,000)
CITGO's Submission No. 3 - Lube Refinery Streams	4/27/92	II.B.2.b. (\$6,000)
CITGO's Submission No. 4 - Solvent 26	4/27/92	II.B.2.b. (\$6,000)
CITGO's Submission No. 5 Crude Oil (Rider Accident)	4/27/92	II.B.2.a. (\$15,000)

April 27, 1992  
Page 2

I would like to explain briefly why many of the submissions deal with studies or information connected to Cities Service Company. CITGO did not operate or exist as a company prior to March 18, 1983. Before then, CITGO was principally a trade name utilized in connection with the refining, marketing, and pipeline operations of Cities Service Company ("Cities"). Effective March 18, 1983, Cities assigned and transferred its refining, marketing, and pipeline assets to its wholly owned subsidiary, CITGO Petroleum Corporation. CITGO has had no corporate relationship to Cities since August 31, 1983 when CITGO was sold by Cities. It is CITGO's understanding that Canadian OXY Offshore Production Company ("CandianOXY") is now the successor-in-interest to Cities Service Company. While CITGO has no corporate relationship to Cities since August 31, 1983, many of Cities' files are in CITGO's possession and many former Cities employees work for CITGO. These files were reviewed and these employees interviewed in connection with CITGO's 8e) Compliance Audit.

Attached is the required certification from a corporate official certifying that CITGO's TSCA section 8(e) Compliance Audit is complete. If you have any further questions, please do not hesitate to contact me at (918) 495-5548.

Sincerely,

  
Dana A. Burch  
Senior Counsel

DAB/gmb  
Attachments

cc: Ira Dassa, Esq. - Perkins Coie

TSCA 8e) Compliance Audit Program

I certify that the information contained in or accompanying this Final Report is true, accurate, and complete. As to any identified portion(s) of this Final Report for which I cannot personally verify its truth and accuracy, I certify as the company official having supervisory responsibility for the person(s) who, acting under my direct instructions, made the verification, that this information is true, accurate, and complete.

Date: \_\_\_\_\_

4/27/92

  
\_\_\_\_\_  
Antonio S. Tepedino  
Vice President of Resource  
Protection & Risk Management

CITGO Petroleum Corporation



P.O. Box 3758  
Tulsa, Oklahoma 74102

April 27, 1992

- VIA OVERNIGHT MAIL -

Document Processing Center (TS-790)  
Office of Toxic Substances  
Environmental Protection Agency  
401 M Street, S.W.  
Washington, DC 20460  
Attention: Section 8(e) Coordinator  
(CAP Agreement)

RE: TSCA 8(e) CAP Submission  
CITGO Submission No. 1 -  
Turbine Fuel

Gentlemen:

CITGO Petroleum Corporation ("CITGO") is submitting this information pursuant to Section 8(e) of the Toxic Substances Control Act (TSCA) as part of the TSCA Compliance Audit Program (CAP). CITGO's CAP identification number is 8ECAP-0104. This information is not confidential.

This submittal relates to CITGO Turbine Fuel. The product is a mixture similar to kerosene which consists of hydrocarbons with carbon numbers predominantly in the range of C<sub>9</sub> to C<sub>16</sub> and which boil in the range of approximately 150 to 290°C. The product also contains small amounts of additives.

The enclosed information indicates that on September 24, 1989, a CITGO employee, [REDACTED] who was employed as a refueler at CITGO's Miami Aviation Terminal accidentally had turbine fuel sprayed into his eyes. The employee subsequently underwent surgery to correct tear duct and gland problems in both eyes. The incident is described in the attached information.

If you need additional information or have any questions, please contact me at 918/495-5548.

Sincerely,

*Dana A. Burch*  
Dana A. Burch  
Senior Counsel

DAB/gmb  
Enclosures

0 0 0 6

Report of Accident.

ACC : Rich Ramp  
A/C : DC 3 MIA Air Lease  
TIME : 2:15 PM Sunday 9/24/89  
Injury: Eyes

---

The copilot of the DC 3 got on top of the DC-3 and I handle him the hose from the ground while he picks the nose grave it from the gun and squish it pumping gasoline on my eyes. ~~He~~ right away I flush my eyes with the bottle and my contacts fell out but hurt when I wash'm with the Eye & Skin solution and put'm back on. It is 5 PM now and my eyes are very irritated.

---



# injury

DEPARTMENT OF LABOR AND EMPLOYMENT SECURITY  
 Division of Workers' Compensation  
 1321 Executive Center Drive, East  
 Tallahassee, Florida 32301

ATTENTION: W.C. CLAIMS OFFICE  
 Phone: 1-800-342-1741

Reports by telephone or telegram within 24 hours.

EMPLOYER INFORMATION		EMPLOYEE INFORMATION	
NAME <b>GO PETROLEUM CORP.</b>	NAME (Last, Middle, Initial) [REDACTED]	SOCIAL SECURITY NUMBER [REDACTED]	
MAILING ADDRESS (Include Zip Code) <b>PO BOX 3758 1st Floor OMP 3A, OK. 74102</b>	HOME ADDRESS (Include Zip Code) [REDACTED]	OCCUPATION <b>REFUELER</b>	SUPERVISOR'S NAME <b>GEORGE SESSURS</b>
PHONE [REDACTED] Number: [REDACTED] [REDACTED] Number: [REDACTED] <input type="checkbox"/> Same as Mailing	TELEPHONE Area Code: [REDACTED] Number: [REDACTED]	DEPARTMENT NAME <b>MIAMI AVIATION FUEL</b>	
DATE OF ACCIDENT <b>09-24-89</b>	DATE AND TIME FIRST REPORTED <b>09-24-89 2:30 P.M.</b>	DATE OF BIRTH <b>01-14-48</b>	SEX <input checked="" type="checkbox"/> M <input type="checkbox"/> F
NAME OF BUSINESS <b>MIAMI INTERNATIONAL AIRPORT</b>	How long employed? <b>1 yr &amp; 1 month</b>	Number of hours worked <b>40</b>	Number of days worked per week <b>5</b>
TYPE OF BUSINESS <b>CRAFT REFUELER</b>	Rate of Pay <input checked="" type="checkbox"/> Per Hour <input type="checkbox"/> Per Day <input type="checkbox"/> Per Week	If piece work or commission, enter average weekly amount	
EMPLOYER I.D. NUMBER [REDACTED]	If board, lodging or other advantages furnished, enter weekly amount		
WORKER'S COMPENSATION COVERAGE BY <input checked="" type="checkbox"/> Insurance Company <input type="checkbox"/> Self-Insured GIVE NAME, ADDRESS AND POLICY NUMBER OF INSURANCE COMPANY OR SELF-INSURED SERVICE COMPANY. <b>CIGNA INSURANCE CO. PROPERTY &amp; CASUALTY          P.O. BOX 8187          JACKSONVILLE, FL. 32239 (1-800-342-8615)</b>			

ACCIDENT INFORMATION		
DATE AND TIME OF ACCIDENT <b>09-24-89 2:15 P.M.</b>	DATE AND TIME FIRST REPORTED <b>09-24-89 2:30 P.M.</b>	NAME, ADDRESS AND PHONE NUMBER OF PHYSICIAN <b>SOUTHEAST EYE ASSC. (305) 578-2020</b>
LOCATION OF ACCIDENT (Street, City, County, State) <b>MIAMI INTERNATIONAL AIRPORT</b>	LAST DATE EMPLOYEE WORKED <b>09-24-89</b>	DR. HENRY TRATTLER <b>6600 SW 92nd ST. Suite 204 MIAMI, FL. 33156</b>
EMPLOYEE MISSED ONE SHIFT, ONE DAY OR MORE? <input checked="" type="checkbox"/> Yes <input type="checkbox"/> No	RETURNED TO WORK <input type="checkbox"/> Yes <input checked="" type="checkbox"/> No	PHYSICIAN AUTHORIZED BY EMPLOYER <input checked="" type="checkbox"/> Yes <input type="checkbox"/> No
WAS INJURY FATAL? <input type="checkbox"/> Yes <input checked="" type="checkbox"/> No If Yes, Date of Death	IF YES, DATE Employee Paid for Date of Injury <input checked="" type="checkbox"/> Yes <input type="checkbox"/> No	NAME, ADDRESS AND PHONE OF HOSPITAL <b>BAPTIST HOSPITAL 8900 KENDAL DR. MIAMI, FL.</b>
EMPLOYEE'S DESCRIPTION OF ACCIDENT (Give details such as, fell, was struck, etc.) <b>TURBINE FUEL IN THE EYES. EYES HURT AND WERE IRRITATED.</b>		DESCRIBE INJURY OR DISEASE AND INDICATE PART OF BODY AFFECTED (e.g. Amputation of right index finger at second joint, Fractured ribs, Lead Poisoning, etc.) <b>CHEMICAL INJURY. CHEMICAL KERATITIS BOTH EYES, BUT MOST IN THE RIGHT EYE.</b>
EMPLOYEE: I agree with this description? <input checked="" type="checkbox"/> Yes <input type="checkbox"/> No If no, explain in comments.		

*Asst. Mgr. 7068*

any person who, knowingly and with intent to injure, defraud or deceive any employer or employee, insurance company, or self-insured person, files a statement of claim containing any false or misleading information is guilty of a felony of the third degree.

EMPLOYER (Read and Sign) \_\_\_\_\_ SIGNATURE \_\_\_\_\_ DATE \_\_\_\_\_

EMPLOYEE (Read and Sign) \_\_\_\_\_ SIGNATURE \_\_\_\_\_ DATE \_\_\_\_\_

CITIES SERVICE  
INTEROFFICE LETTER

Tulsa, Oklahoma  
December 11, 1980

TO: Mr. A.W. Clinger - 2135 FNT  
FROM: H.N. Finkbone - 806 PPL *AF*  
SUBJECT: Results of 1980 Toxicity Testing Program

Attached is a table summarizing the results of the toxicity tests performed on twelve Company materials. For your record keeping, I have also attached individual test results for each material. These summary pages are extracted directly from the final reports as supplied by Cosmopolitan Safety Evaluation, Inc.

\* \* \* \* \*

Materials one through eleven present no substantial acute toxicity hazards. That is, all of these have Oral LD<sub>50</sub> values greater than 15g/Kg body weight; roughly equivalent to ingestion of more than two pounds or 35 ounces of the test material by a "typical healthy 150 pound male adult." The lethal concentration for 50 percent of the rats (LC<sub>50</sub>) exposed to an aerosol for four hours is greater than 5 mg/L (5g/M<sup>3</sup>) for nine of these and greater than 3 mg/L for two (highest concentrations possible). None of these eleven materials exhibited more than minimal irritancy to either skin or eyes.

Thus, none of these eleven materials would require cautionary labeling under current federal guidelines. [This is based on bulk packaging that would not require a consumer product classification by CPSC.]

Solvent 26

Solvent 26 did exhibit significant toxicity. Following is my interpretation of the various test results for Solvent 26:

Acute Oral Toxicity

With an Oral LD<sub>50</sub> in rats of 1.59g/Kg, Solvent 26 should be considered a moderately toxic material. The lethal dose for one percent of the exposed rats (LD<sub>1</sub>) is calculated to be 0.59 and the LD<sub>99</sub> is only 4.3g/Kg.

CITGO Petroleum Corporation



CONTAINS NO CBI

P.O. Box 3758  
Tulsa, Oklahoma 74102

April 27, 1992

- VIA OVERNIGHT MAIL -

Document Processing Center (TS-790)  
Office of Toxic Substances  
Environmental Protection Agency  
401 M Street, S.W.  
Washington, DC 20460  
Attention: Section 8(e) Coordinator  
(CAP Agreement)

RE: TSCA 8(e) CAP Submission  
CITGO Submission No. 4 -  
Solvent 26

Gentlemen:

CITGO Petroleum Corporation ("CITGO") is submitting this information pursuant to Section 8(e) of the Toxic Substances Control Act (TSCA) as part of the TSCA Compliance Audit Program (CAP). CITGO's CAP identification number is 8ECAP-0104. This information is not confidential.

This submittal relates to CITGO Solvent 26, a product not manufactured since 1982. The product is a mixture composed of the following components.

<u>Component</u>	<u>CAS Number</u>	<u>% Composition</u>
Ortho-Dichlorobenzene	95-50-1	20 - 50
Butyl Cellosolve	111-76-2	10 - 20
Kerosene	8008-20-6	10 - 20
Monoethanolamine	14-143-5	1 - 20
Fatty Acid	112-80-1	1 - 10
Mineral Oil	64742-36-5	< 5

An interoffice letter from H. N. Finkbone (dated December 11, 1980) reported the results of a series of toxicity tests performed in 1980 and identified that Solvent 26 exhibited toxicity. Three copies of this letter are enclosed.

April 27, 1992

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If you need additional information or have any questions,  
please contact me at 918/495-5548.

Sincerely,

*Dana A. Burch*

Dana A. Burch  
Senior Counsel

DAB/gmb  
Enclosures

In animals which died within 72 hours following dosing, autopsy indicated severe damage to kidneys, liver, adrenal glands, stomach and intestines. Damage to the stomach and intestines is most likely due to the corrosive nature of S26 while damage to the other organs is apparently due to the toxic effects of either O-dichlorobenzene or Butyl Cellosolve or both. Further, these findings are consistent with destruction of red blood cells (hemolysis), a known effect of Butyl Cellosolve. This later point would, however, require further biological analysis for its proof.

All animals showed evidence of central nervous system (CNS) depression during the first 24 hours as well as generalized stress and unwholesome condition.

Rats which survived til sacrifice 14 days after dosing showed no gross evidence of permanent damage.

#### Primary Eye Irritation

Solvent 26 is extremely irritating to the eyes, causing serious permanent damage. Most significantly, this test indicates that flushing the eyes with water after contact will have little or no effect in preventing permanent injury. This finding is consistent with the known effects of monoethanolamine on the eye. In "The Alkanolamines Handbook," Dow Chemical Company states that even with prompt thorough washing and proper medical care, eye contact with monoethanolamine may result in serious injury.

#### Primary Dermal Irritation

Solvent 26 causes severe irritation and destruction of rabbit skin under the conditions of this test. Though the primary irritation score is 4.38 out of 8, a score that would normally classify it as moderately irritating, the observed destruction of skin warrants the extremely irritating classification.

The conditions of this test were more severe than those prescribed by DOT for definition of a corrosive liquid. However, based on the skin reactions of the rabbits as tested and of guinea pigs during the sensitization study, I believe that if the skin irritation were conducted according to DOT criteria, it would rank as corrosive. Thus, Solvent 26 should be labeled as a corrosive liquid for transportation purposes.

#### Acute Inhalation Toxicity

Test results in this category would tend to minimize concern over acute aerosol exposure to S26. However, during the evaluation of test results, it became apparent that the aerosol generation system and other factors may have favored

December 11, 1980

differential vapor formation instead of aerosolization. Thus, the test results may more accurately reflect the toxicities of the more volatile components; e.g., dichlorobenzene and kerosine, rather than the composite S26.

#### Acute Dermal Toxicity

Toxic constituents of S26 are absorbed through rabbit skin in quantities sufficient to cause death. The LD<sub>50</sub> in rabbits by skin absorption is 2.5g/Kg. The computed lethal dose to one percent (LD<sub>1</sub>) is 0.92g/Kg. This later figure would compare roughly with spreading 64.4 grams or two ounces of S26 over the torso of a 150 pound adult male and holding it in contact for 24 hours. One should note that at a level that would be lethal to one percent of population, a much higher proportion of the exposed population, would experience significant illness. The calculated LD<sub>99</sub> by this route is 6g/Kg.

In rabbits which succumbed, findings at autopsy were consistent with liver and kidney damage and possibly destruction of red blood cells (hemolysis). Also, many animals had ulceration and bleeding of the stomach and intestines. This effect is ascribed to ingestion of residual S26 on the skin, and while this ingestion may have contributed to the overall toxicity, skin absorption was mainly responsible.

By skin absorption, S26 is moderately toxic.

#### Skin Sensitization

This test provided no evidence of allergy production by topical application to guinea pigs. This is implicit evidence that S26 presents no undue risk to humans in this category.

#### Comments and Recommendations

While none of the first eleven listed materials can be considered hazardous on the basis of acute toxicity, it must be borne in mind that these tests do not accurately reflect potential harmful effects of long-term low-level exposure. For those materials which are also either part of the Cit-Con Mouse Study or similar in nature to them, final evaluation should await the results of that study.

For Solvent 26, the overall assessment would require that it be categorized as a moderately toxic hazardous material on the basis of acute toxicity. Its potential for severe eye and skin irritation should be made clear to all those who handle it. Under no circumstances should anyone use S26 without wearing chemical splash goggles or full-face shielding. Also, gloves and aprons resistant to

solvent penetration and alkali attack should be worn at all times. Further, local ventilation should be provided to maintain the concentrations of components at or below recommended Threshold Limit Values (American Conference of Governmental Industrial Hygienists). These values as published in 1980 are:

Kerosine	- No TLV; generally accepted to be 500 ppm as total hydrocarbons.
Mineral Oil	- 5mg/M <sup>3</sup> as oil mist.
Water	- N/A
Monoethanolamine	- 3 ppm; 8 mg/M <sup>3</sup>
Ortho-dichlorobenzene	- 50 ppm; 300 mg/M <sup>3</sup>
Oleic Acid	- N/A
Butyl Cellosolve*	- 50 ppm; 250 mg/M <sup>3</sup>

\*Butyl Cellosolve has appeared in the 1979 and 1980 issues as intended for change to 25 ppm or 120 mg/M<sup>3</sup>. It is expected that these lower values will be adopted in 1981.

It is significant that the oral and dermal LD<sub>50</sub>'s of S26 are within the same order of magnitude; they differ by less than a factor of two. This indicates that the toxic constituent(s) is/are absorbed equally well by each route. Further, since the slopes of the lethality plots are similar, it is reasonable to speculate that the mode of action is the same following exposure by either route.

As with most mixtures, the acute toxicity of Solvent 26 appears to be the sum of the acute toxicities of its components. Thus, new information which comes available about the constituents should be readily translatable to the composite product. This may also apply to chronic toxicity.

I recommend the following as pertains to Solvent 26:

- Continued production and use should be accompanied by a 90-day subchronic dermal toxicity test. This test would be conducted using diluted material and would serve to better assess the potential long-term hazard of skin contamination with S26.
- If Solvent 26 were to be withdrawn from the market, a formulation research effort might be conducted using constituents with lower

December 11, 1980

risk potential. For example, could p-dichlorobenzene be substituted? Even through this is a solid, perhaps adequate amounts could be dissolved in the matrix. This compound appears to be less toxic than Ortho and has one fourth the vapor pressure. A variety of higher homologs of Butyl Cellosolve; e.g., Diethylene Glycol Monomethyl Ether and Dipropylene Glycol Monomethyl Ether, etc. appear less toxic, less readily absorbed through skin, and have much lower vapor pressures. Triethanolamine and triisopropanolamine are much less irritating to skin and eyes and are not likely to be absorbed through skin in toxic amounts.

- ° Appropriate changes in the wording of our Material Safety Data Sheet for S26 should be made to reflect new data. These changes would affect the Health Hazard Section, including First Aid.
- ° Appropriate changes in product labeling should be made to emphasize eye and skin contact hazards, use of protective equipment and first aid measures.

HNF:get

Attachments

cc: G.R. Tovey - CSTC - w/Table Only  
J.W. Swanson - 806 PPL - w/Table Only  
Dr. V.K. Yates - 1606 CSB - w/Table Only  
J.L. Boucher - 806 PPL - w/Table Only

TOX002/V

0 0 1 5

Toxicity Test Type and Scores

Cities Service Product (Test Code No.)	Muta Oral Toxicity (rats)	Eye Irritation (rabbits) Maximum Score: 110	Skin Irritation (rabbits) Maximum Score: 8	Acute Inhalation Toxicity (rats)	Acute Dermal Toxicity (rabbits)	Skin Sensitization (guinea pigs)
100 Neutral (1-2204-44-4P)	Practically Non-Toxic LD <sub>50</sub> >15 g/Kg	Practically Non-Irritating 0.7/110	Non-Irritating 0/7	LC <sub>50</sub> /4H >5mg/L	—	—
200 Neutral (2-2204-44-4P)	Practically Non-Toxic LD <sub>50</sub> >15 g/Kg	Practically Non-Irritating 0.7/110	Non-Irritating 0/8	LC <sub>50</sub> /4H >5mg/L	—	—
350 Neutral (3-2204-44-4P)	Practically Non-Toxic LD <sub>50</sub> >15 g/Kg	Practically Non-Irritating 1.0/110	Non-Irritating 0/8	LC <sub>50</sub> /4H >5mg/L	—	—
650 Neutral (4-2204-44-4P)	Practically Non-Toxic LD <sub>50</sub> >15 g/Kg	Practically Non-Irritating 1.3/110	Practically Non-Irritating 0.2/8	LC <sub>50</sub> /4H >5mg/L	—	—
150 Bright Stock (5-2204-44-4P)	Practically Non-Toxic LD <sub>50</sub> >15 g/Kg	Practically Non-Irritating 1.0/110	Non-Irritating 0/8	*LC <sub>50</sub> /4H >3.31mg/L	—	—
150 Cycle Oil (6-2-04-44-4P)	Practically Non-Toxic LD <sub>50</sub> >15g/Kg	Practically Non-Irritating 1.7/110	Non-Irritating <0.3/8	LC <sub>50</sub> /4H >5mg/L	—	—
700 Cycle Oil (7-2204-44-4P)	Practically Non-Toxic LD <sub>50</sub> >15g/Kg	Practically Non-Irritating 1.3/110	Practically Non-Irritating 0.6/8	*LC <sub>50</sub> /4H >3.54mg/L	—	—
Cutting Oil 150 (8-2204-44-4P)	Practically Non-Toxic LD <sub>50</sub> >15g/Kg	Practically Non-Irritating 1.3/110	Practically Non-Irritating 0.9/8	LC <sub>50</sub> /4H >5mg/L	—	—
Cutting Oil 400 (9-2204-44-4P)	Practically Non-Toxic LD <sub>50</sub> >15g/Kg	Practically Non-Irritating 0.7/110	Practically Non-Irritating 0.8/8	LC <sub>50</sub> /4H >5mg/L	—	—
Extra Range Two Cycle Oil (10-2204-44-4P)	Practically Non-Toxic LD <sub>50</sub> >15g/Kg	Practically Non-Irritating 0.7/110	Practically Non-Irritating 0.3/8	LC <sub>50</sub> /4H >5mg/L	—	—
Glycol FR-40 XD (11-24404-44-4P)	Practically Non-Toxic LD <sub>50</sub> >15g/Kg	Practically Non-Irritating 0.7/110	Practically Non-Irritating 0.3/8	LC <sub>50</sub> /4H >5mg/L	—	—
Solvent 26 (12-2204-44-4P/SA)	Moderately Toxic LD <sub>50</sub> 1.59g/Kg	Extremely Irritating 91/110	Extremely Irritating 6.38/8	LC <sub>50</sub> /4H >5mg/L	Moderately Toxic LD <sub>50</sub> 3.5 g/Kg	Non Sensitizing

\* Highest concentration possible with heating to +40°C as noted on viscosity chart.

CONTAINS NO CBI



CITGO Petroleum Corporation

P.O. Box 3758  
Tulsa, Oklahoma 74102

April 27, 1992

- VIA OVERNIGHT MAIL -

Document Processing Center (TS-790)  
Office of Toxic Substances  
Environmental Protection Agency  
401 M Street, S.W.  
Washington, DC 20460  
Attention: Section 8(e) Coordinator  
(CAP Agreement)

RE: TSCA 8(e) CAP Submission  
CITGO Submission No. 5 -  
Crude Oil

Gentlemen:

CITGO Petroleum Corporation ("CITGO") is submitting this information pursuant to Section 8(e) of the Toxic Substances Control Act (TSCA) as part of the TSCA Compliance Audit Program (CAP). CITGO's CAP identification number is 8ECAP-0104. This information is not confidential.

This submittal relates to crude oil. The product is characterized as a light, sweet crude oil, CAS Number 8002-05-9.

The enclosed information indicates that on October 19, 1983, a trespasser collapsed and died after sniffing fumes from a crude oil storage tank located at CITGO's Kernan Pumping station in Lake Charles, Louisiana.

If you need additional information or have any questions, please contact me at 918/495-5548.

Sincerely,

*Dana A. Burch*  
Dana A. Burch  
Senior Counsel

DAB/gmb  
Enclosures

REN S. RANIER, M.D.  
LEHRUE STEVENS, M.D.  
CHARLES SMITH, M.D.  
LIVIA UV, M.D.

**THE PATHOLOGY LABORATORY**

RANIER, STEVENS & SMITH  
(A PROFESSIONAL MEDICAL CORPORATION)  
830 BAYOU PINES DRIVE P. O. BOX UU  
LAKE CHARLES, LOUISIANA 70001

TELEPHONE  
(504) 438-8887

**DO NOT COPY**  
CONFIDENTIAL MEDICAL INFORMATION

DECEDENT: [REDACTED] AC83-157  
AUTOPSY PERFORMED: 10-20-83, 9:00 AM  
AUTOPSY PERFORMED BY: Lehrue Stevens, Jr., M.D.; assisted by  
Jack Stroh  
AUTOPSY PERFORMED AT: St. Patrick Hospital Morgue  
AUTOPSY REQUESTED BY: Charles Smith, M.D., Coroner, Calcasieu  
Parish, Louisiana

**FINAL ANATOMIC DIAGNOSES:**

1. INHALATION OF PETROLEUM DERIVATIVE PRODUCTS.
  - A. CEREBRAL EDEMA AND CONGESTION.
  - B. LARYNGEAL EDEMA.
  - C. BILATERAL PULMONARY CONGESTION AND FOCAL PERIBRONCHIAL HEMORRHAGE.
  - D. HEPATIC AND RENAL CONGESTION.

COMMENT: Drug studies are negative. The blood alcohol is 22 mg%. Information obtained subsequent to the autopsy revealed that the deceased apparently was inhaling fumes at a petroleum products storage tank when he collapsed and died.

  
Lehrue Stevens, Jr., M.D.  
Pathologist

LSim

DU NOT COPY  
CONFIDENTIAL MEDICAL INFORMATION

16 y/o white male pronounced dead on arrival at Emergency Hospital last night. The body was transported to the morgue at St. Patrick for autopsy. Autopsy performed by Dr. Stevens assisted by Jack Stroh 10-20-83 commencing at 9 AM.

**INFORMATION AVAILABLE:** Not detailed but apparently the deceased was partying with a group of friends in an automobile and they stopped the car at the railroad tracks near the hospital so the deceased could go to the restroom and he apparently slumped on the ground outside the car and apparently was dead almost instantaneously. No other information available.

**GENERAL DESCRIPTION:** The body is that of a well-developed, well-nourished young white male. He is of rather large physical stature. The extremities are symmetrical. There is moderate cyanosis in the nail beds. There are no vena puncture marks identified on the extremities. There are no abrasions and there is no evidence of trauma. The trunk and abdomen are essentially unremarkable. The abdomen is not distended. The neck is supple. There are no marks on the neck. There is noted a significant degree of postmortem dependent lividity in the back and posterior legs. Rigor mortis is rather pronounced. The head and neck area is examined. There is no evidence of trauma. Bloody sputum and bloody material exudes from the nares. Pupils are dilated and equal. There is no scleral icterus.

**BRAIN:** The scalp is reflected. The calvarium is removed. There is no evidence of epidural, subdural or subarachnoid hemorrhage. The brain appears somewhat edematous. It is removed intact. The vessels at the base of the brain are unremarkable. The brain weighs 1200 grams, and is placed in formalin for fixation and later dissection.

**THORACIC CAVITY:** Sternal plate is removed. Lungs expanded grossly appear congested. No pleural effusions. Ribs unremarkable. Trachea opened. Laryngeal edema is rather pronounced. A small finger can barely be pushed through the larynx. No food product obstructs the larynx. The trachea is edematous and focally hemorrhagic. The lungs are removed. The right lung weighs 600 grams. The left lung weighs 550 grams. There appears to be a tracheobronchitis with mucopurulent thick tenaceous mucin present within the bronchi and bronchioles. The lungs are transected and demonstrate extensive bilateral congestion. No active inflammatory changes are apparent.

**HEART:** Pericardium incised. No significant pericardial effusion. The heart is not remarkable in size. It weighs 385 grams. Focal agonal hemorrhages are noted on the epicardium. The right and left ventricles are opened and are unremarkable. The valves and valve leaflets are unremarkable. The coronary artery circulation is normal. The myocardium is unremarkable. The aorta is opened. There is no evidence of aneurysm.

**ABDOMINAL CAVITY:** The stomach is opened and contains approximately 200 cc's of watery brownish-yellow fluid which has a distinct but unrecognizable odor. This material is saved for the Sheriff's Department and Pathology Lab for toxicology. The small and large

bowels are unremarkable. The pancreas is soft and demonstrates early autolytic changes.

**LIVER:** It weighs 2400 grams. It is enlarged somewhat and appears slightly congested. The extrahepatic biliary system is normal. The bile is light green and unremarkable. Spleen is enlarged weighing 350 grams. The parenchyma is firm and reddish-tan. The adrenal glands are normal. The kidneys are removed and are normal other than demonstrating congestion. The urinary bladder contains approximately 40 cc's of clear urine which is obtained for toxicology.

Samples of liver, lung, spleen and stomach are reserved for toxicology.

**PROVISIONAL GROSS DIAGNOSIS:**

**TRACHEOBRONCHITIS: LARYNGEAL EDEMA.  
BILATERAL PULMONARY CONGESTION AND FOCAL EDEMA.**

**RULE OUT OVERDOSE - ETHANOL, METHANOL?**

**CONGESTIVE HEPATOMEGALY AND SPLENOMEGALY, ETIOLOGY UNDETERMINED, MODERATE.**

**CEREBRAL EDEMA.**

LS/lp

**BLOOD ALCOHOL: 22 mgs %  
DRUG SCREEN (GASTRIC): NONE DETECTED**

**BRAIN:** Following adequate fixation, brain, cerebellum and brain stem are dissected. Multiple transverse sections through the cerebral hemispheres demonstrate narrowed sulci. Some degree of vascular congestion is noted. No areas of infarction are encountered. No areas of hemorrhage. The ventricles are unremarkable. The cerebellum is unremarkable. There is no evidence of subarachnoid hemorrhage.

**MICROSCOPIC:**

**BRAIN:** Sections of brain reveal vascular congestion and those changes consistent with cerebral edema.

**LUNGS:** Sections of both lungs demonstrate marked pulmonary congestion with focal areas of peribronchial hemorrhage. No inflammatory changes.

**HEART:** Sections of myocardium are unremarkable.

**LIVER:** Sections of liver demonstrate dilatation of sinusoids. No other significant changes.

**SPLEEN:** Sections are unremarkable.

**KIDNEYS:** Sections demonstrate congestion but are otherwise unremarkable.

**PANCREAS:** Sections of pancreas demonstrate autolysis.

**FINAL ANATOMIC DIAGNOSES:**

- 1). **INHALATION OF PETROLEUM DERIVATIVE PRODUCTS.**
  - A). **CEREBRAL EDEMA AND CONGESTION.**
  - B). **LARYNGEAL EDEMA.**
  - C). **BILATERAL PULMONARY CONGESTION AND FOCAL PERIBRONCHIAL HEMORRHAGE.**
  - D). **HEPATIC AND RENAL CONGESTION.**

**COMMENT:** Drug studies are negative. The blood alcohol is 22 mg.%. Information obtained subsequent to the autopsy revealed that the deceased apparently was inhaling fumes at a petroleum products storage tank when he collapsed and died.

LSgb/dp

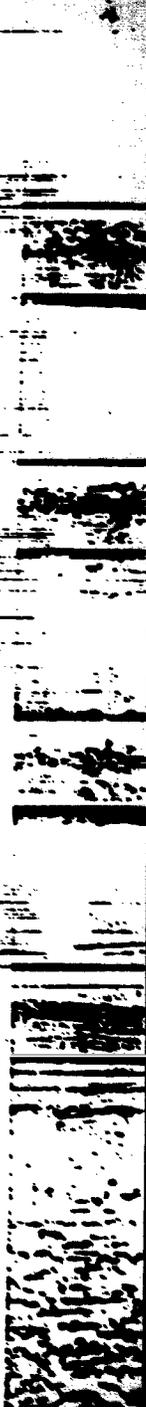
STATE OF LOUISIANA  
**CERTIFICATE OF DEATH**

STATE FILE NO. 119

IMPORTANT:  
 Check ink or Typewriter Ribbon Mandatory by State Law.

1A. LAST NAME OF DECEASED [REDACTED]		1C. SUFFIX None		1D. DATE OF BIRTH Oct. 19, 1983		1E. SEX Male		1F. RACE White		1G. MARRIAGE STATUS Single		1H. CITIZENSHIP USA	
1I. TIME OF DEATH 9:40 P		1J. PLACE OF DEATH Dequincy		1K. CITY, TOWNSHIP, PARISH, OR LOCATION OF DEATH Dequincy		1L. COUNTY OR PARISH OF DEATH Dequincy Memorial Hospital		1M. OCCUPATION Student		1N. PLACE OF BIRTH Lake Charles, La.		1O. STATE OF BIRTH Louisiana	
1P. USUAL RESIDENCE OF DECEASED [REDACTED]		1Q. USUAL RESIDENCE OF DECEASED [REDACTED]		1R. USUAL RESIDENCE OF DECEASED [REDACTED]		1S. USUAL RESIDENCE OF DECEASED [REDACTED]		1T. USUAL RESIDENCE OF DECEASED [REDACTED]		1U. USUAL RESIDENCE OF DECEASED [REDACTED]		1V. USUAL RESIDENCE OF DECEASED [REDACTED]	
1W. PARENTS [REDACTED]		1X. PARENTS [REDACTED]		1Y. PARENTS [REDACTED]		1Z. PARENTS [REDACTED]		1AA. PARENTS [REDACTED]		1AB. PARENTS [REDACTED]		1AC. PARENTS [REDACTED]	
1AD. INFORMANT'S CERTIFICATION [REDACTED]		1AE. INFORMANT'S CERTIFICATION [REDACTED]		1AF. INFORMANT'S CERTIFICATION [REDACTED]		1AG. INFORMANT'S CERTIFICATION [REDACTED]		1AH. INFORMANT'S CERTIFICATION [REDACTED]		1AI. INFORMANT'S CERTIFICATION [REDACTED]		1AJ. INFORMANT'S CERTIFICATION [REDACTED]	
1AK. CAUSE OF DEATH [REDACTED]		1AL. CAUSE OF DEATH [REDACTED]		1AM. CAUSE OF DEATH [REDACTED]		1AN. CAUSE OF DEATH [REDACTED]		1AO. CAUSE OF DEATH [REDACTED]		1AP. CAUSE OF DEATH [REDACTED]		1AQ. CAUSE OF DEATH [REDACTED]	
1AR. DEATH DUE TO EXTERNAL VIOLENCE Approx: 9P Oct. 19, 1983		1AS. DEATH DUE TO EXTERNAL VIOLENCE Approx: 9P Oct. 19, 1983		1AT. DEATH DUE TO EXTERNAL VIOLENCE Approx: 9P Oct. 19, 1983		1AU. DEATH DUE TO EXTERNAL VIOLENCE Approx: 9P Oct. 19, 1983		1AV. DEATH DUE TO EXTERNAL VIOLENCE Approx: 9P Oct. 19, 1983		1AW. DEATH DUE TO EXTERNAL VIOLENCE Approx: 9P Oct. 19, 1983		1AX. DEATH DUE TO EXTERNAL VIOLENCE Approx: 9P Oct. 19, 1983	
1AY. PHYSICIAN'S CERTIFICATION [REDACTED]		1AZ. PHYSICIAN'S CERTIFICATION [REDACTED]		1BA. PHYSICIAN'S CERTIFICATION [REDACTED]		1BB. PHYSICIAN'S CERTIFICATION [REDACTED]		1BC. PHYSICIAN'S CERTIFICATION [REDACTED]		1BD. PHYSICIAN'S CERTIFICATION [REDACTED]		1BE. PHYSICIAN'S CERTIFICATION [REDACTED]	
1BF. FUNERAL DIRECTOR'S CERTIFICATION #911		1BG. FUNERAL DIRECTOR'S CERTIFICATION #911		1BH. FUNERAL DIRECTOR'S CERTIFICATION #911		1BI. FUNERAL DIRECTOR'S CERTIFICATION #911		1BJ. FUNERAL DIRECTOR'S CERTIFICATION #911		1BK. FUNERAL DIRECTOR'S CERTIFICATION #911		1BL. FUNERAL DIRECTOR'S CERTIFICATION #911	
1BM. BURIAL PERMIT [REDACTED]		1BN. BURIAL PERMIT [REDACTED]		1BO. BURIAL PERMIT [REDACTED]		1BP. BURIAL PERMIT [REDACTED]		1BQ. BURIAL PERMIT [REDACTED]		1BR. BURIAL PERMIT [REDACTED]		1BS. BURIAL PERMIT [REDACTED]	

PHS 36 - (REV. 3/80)  
 DMMR, OFFICE OF HEALTH SERVICES AND ENVIRONMENTAL QUALITY, VITAL RECORDS REGISTRY



**OFFICE OF THE CORONER**

**CALCASIEU PARISH COURTHOUSE  
LAKE CHARLES, LOUISIANA 70601**

CONFIDENTIAL MEDICAL INFORMATION

SMITH, M. D.

**PROCES VERBAL**

**NAME:** [REDACTED] **AGE:** 15  
**ADDRESS:** [REDACTED] **SEX:** Male  
**RACE:** Caucasian

**DATE & TIME OF DEATH:** October 19, 1983  
Approximately 9:40 P.M.

**PLACE OF DEATH:** DeQuincy Memorial Hospital  
DeQuincy, La.

**PLACE OF ACCIDENT:** Rural Tank Farm, Old Boise Sawmill Entrance, on Hwy. 12,  
1/2 mile East of 24 mile marker, Calcasieu Parish

**CAUSE OF DEATH:** Inhalation of petroleum derivative products

I, Charles M. Smith, M.D., Coroner of the Parish of Calcasieu, having been notified of the death of [REDACTED], and having made inquiries respecting this death, did authorize Lehrue Stevens, M.D., a board certified pathologist as well as a Deputy Coroner, to perform a post-mortem examination.

From reports received, [REDACTED] allegedly sniffed fumes from a large tank which contained a hydrocarbon. This occurred at approximately 9:00 P.M. on October 19, 1983. He was allegedly with two companions who drove him to DeQuincy Memorial Hospital after his collapse.

A Blood Alcohol Determination was performed and found to be 22 mgs. %. Levels of 100 mgs. % and above are considered evidence of intoxication.

A Drug Screen was performed and found to be negative.

*Charles M. Smith*  
Charles M. Smith, M.D.  
Coroner of Calcasieu parish

~~CONFIDENTIAL~~

**CONTAINS NO CBI**

A  
FINAL REPORT  
on the  
RESULTS OF THE 1981 TOXICITY SCREENING PROGRAM  
for the  
LUBRICANTS AND SPECIALTY PRODUCTS DIVISION  
of  
CITIES SERVICE COMPANY

Submitted by  
THE TOXICOLOGY DEPARTMENT  
of  
SAFETY AND ENVIRONMENTAL SERVICES  
December, 1981

  
Harry N. Finkbone  
Toxicologist

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<b>SECTION TWO - Tabular Summary of Results</b>	
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OFFICE DOCUMENT RECEIPT



CONTAINS NO CBI

CITGO Petroleum Corporation

92 APR 28 AM 9:30

P.O. Box 3758  
Tulsa, Oklahoma 74102

April 27, 1992

**- VIA OVERNIGHT MAIL -**

Document Processing Center (TS-790)  
Office of Toxic Substances  
Environmental Protection Agency  
401 M Street, S.W.  
Washington, DC 20460  
**Attention:** Section 8(e) Coordinator  
(CAP Agreement)

RE: TSCA 8(e) CAP Submission  
CITGO Submission No. 2 -  
Cutting Oils 205 & 220

Gentlemen:

CITGO Petroleum Corporation ("CITGO") is submitting this information pursuant to Section 8(e) of the Toxic Substances Control Act (TSCA) as part of the TSCA Compliance Audit Program (CAP). CITGO's CAP identification number is 8ECAP-0104. This information is not confidential.

This submittal relates to CITGO Cutting Oils 205 and 220. The composition of the oils investigated are listed below.

<u>Component</u>	<u>CAS No.</u>	<u>% Composition</u>
<u>CITGO Cutting Oil 205</u>		
Refined Petroleum Oil(s)	64741-89-5	85-90
	64742-65-0	
	64742-52-5	
Petroleum Sulfonates	Mixture	10-15
<u>CITGO Cutting Oil 220</u>		
Refined Petroleum Oil(s)	64741-89-5	72-80
	64742-52-5	
Petroleum Sulfonates	Mixture	18-25
Chlorinated Paraffins	Mixture	4-8

• April 27, 1992  
Page 2

Note: The composition shown above is reflective of the current compositions of the products and is the only information readily available.

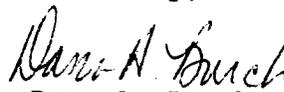
The results of a toxicity screening program conducted in 1981 for the Lubricants and Specialty Products Division of Cities Service Company indicated that repeated or prolonged exposure may pose skin irritation problems and toxicity may result via inhalation of the aerosols.

A follow-up study of Cutting Oil 205, completed in 1982, indicated no health risks associated with routine inhalation of its aerosol. This study is summarized in an interoffice letter from Harry N. Finkbone (dated August 25, 1982) to Mr. J. I. Boucher.

Three copies of each report are enclosed.

If you need additional information or have any questions, please contact me at 918/495-5548.

Sincerely,



Dana A. Burch  
Senior Counsel

DAB/gmb  
Enclosures

THIS DOCUMENT RECEIPT OFF

CITGO Petroleum Corporation <sup>82 APR 28</sup> AM 9: 30



CONTAINS NO CBI

P.O. Box 3758  
Tulsa, Oklahoma 74102

April 27, 1992

- VIA OVERNIGHT MAIL -

Document Processing Center (TS-790)  
Office of Toxic Substances  
Environmental Protection Agency  
401 M Street, S.W.  
Washington, DC 20460  
Attention: Section 8(e) Coordinator  
(CAP Agreement)

RE: TSCA 8(e) CAP Submission  
CITGO Submission No. 3 -  
Lube Refinery Streams

Gentlemen:

CITGO Petroleum Corporation ("CITGO") is submitting this information pursuant to Section 8(e) of the Toxic Substances Control Act (TSCA) as part of the TSCA Compliance Audit Program (CAP). CITGO's CAP identification number is 8ECAP-0104. This information is not confidential.

This submittal relates to lube oil refinery stream samples collected at the CIT-CON facility in Lake Charles, Louisiana which was operated in 1982 by Cities Service Company. A list of the relevant streams and CAS numbers are attached (Table 1).

The results of carcinogenicity testing conducted for Cities Service Company published in 1982 for these streams indicated that they were either carcinogenic or marginally tumorigenic following dermal application to C<sub>3</sub>H mice during a 24-month investigation. Three copies of this report are enclosed.

If you need additional information or have any questions, please contact me at 918/495-5548.

Sincerely,

*Dana A. Burch*  
Dana A. Burch  
Senior Counsel

DAB/gmb  
Enclosures

TOXICITY TESTING RESULTS - 1981

Lubricants and Specialty Products Screening Program

I. Abstract

The following fifteen CITGO Lubricants and Specialty products were submitted for acute toxicity assessments.

Mileage Plus, SAE 10W-40	Pacemaker GEO 800
All Season Multigrade 10W-40 (SF)	Pacemaker 100
ATF Dexron® II	EP Compound 68
ATF Type F	Open Gear Compound 4A
Cutting Oil 140	Concrete Form Oil
Cutting Oil 425	Extra Range Grease
Cutting Oil 205	Antifreeze and Coolant
Cutting Oil 220	

All of these were tested for acute oral toxicity and eye and skin irritation. Only thirteen were tested for acute aerosol inhalation toxicity, due to limitations imposed by the physical properties of two products.

All of the products had acute oral LD<sub>50</sub>'s of greater than 15g/kg except CITGO Antifreeze and Coolant. The observed toxicity of Antifreeze and Coolant has been ascribed to its ethylene glycol content, however, it was not possible to ascertain the influence of the additives in the

overall toxicity of this product. Recommendations for assessing this are provided.

Each of the fifteen products ranked as either non-irritating or practically non-irritating to the eye.

Except for Cutting Oil 220, all fifteen samples scored as either non-irritating or practically non-irritating to skin. Cutting Oil 220 ranked as mildly irritating. The implications of this finding with respect to occupational exposure during machining operations are discussed.

It was not possible to generate an aerosol concentration of  $>5\text{mg/L}$  for three of the thirteen samples submitted for assessment of inhalation toxicity. However, at the concentrations attained, no undue toxicity was observed. Seven of the products for which suitable aerosol concentrations were obtained showed no untoward toxicity at the tested concentrations. Three products, Cutting Oils 205 and 220 and Antifreeze and Coolant, produced lethality. This is not considered a problem for Antifreeze and Coolant. Concerns regarding these findings for the Cutting Oils are discussed as well as recommendations for further study.

## II. Results

### Acute Oral Toxicity

All of the tested products except CITGO Antifreeze and Coolant present no substantial acute toxicity hazards when administered orally. That is, all of these have oral LD<sub>50</sub> values greater than 15g/kg body weight. This is roughly equivalent to ingestion of more than two pounds or 35 ounces of the test material by a "typical healthy 150-pound male adult human." Diarrhea, nasal discharge, tearing and generally unhealthy condition were common clinical signs observed for this group of products. These findings are typical when large doses of oily materials are administered and are not signs of substantial toxicity.

CITGO Antifreeze and Coolant has an oral LD<sub>50</sub> value of <15g/kg. At this dose, eighty percent of the rats died within 48 hours. Toxic signs included loss of coordinated muscular movement (ataxia), tearing, irregular breathing and prostration. Autopsy revealed no outstanding findings. Thus, it is not possible to determine from this test whether the additives in this product modify its toxicity. To determine this would require additional testing.

Eye and Skin Irritation

All fifteen samples exhibited only minimal eye irritancy. The highest eye irritation score observed was 2.0/110 for Cutting Oil 220. This score was observed at 24 hours post administration in the group of rabbits which did not have test article washed from their eyes. The score decreased to 1.0, 0.7 and 0.0 at 48 hours, 72 hours and day four, respectively, and remained at zero for the remainder of the test period. This illustrates that the slight irritation is readily reversible. The score for the "washed" group was zero throughout the test, indicating that immediate washing of the eyes with water is an effective means to reduce eye irritancy resulting from both Cutting Oils 205 and 220 following a splash.

Of the fifteen products tested for skin irritation, nine are ranked as non-irritating ( $<0.1/8$ ) and five are practically non-irritating (0.1-0.9). Cutting Oil 220, with a score of 2.04/8, ranks as mildly irritating (1.0-2.4/8). This score is a composite average of all scores at 24 hours. One animal scored as low as 0.63, but three of the six rabbits had scores above 2.5 (2.88 highest) which would indicate a moderately irritating agent. Significantly, each of the highest scoring rabbits was observed to have blanching or desquamation (scaling or peeling off of the upper layers of skin) at the site of application. However, no permanent

damage occurred and all animals had scores of 0.0/8 within six days, illustrating the reversibility of these lesions.

#### Inhalation Toxicity

The inhalation toxicity assays provided mixed results. All samples were warmed to between 70°C and 100°C to facilitate aerosolization. Even under these conditions, the target aerosol concentration of  $\geq 5\text{mg/L}$  was not achievable for three of the products (Mileage Plus, All Season Multigrade, and Dexron II). However, no lethality or serious toxicity was observed at the maximum concentrations obtained. Of the ten products for which the target concentration was achieved, no significant toxicity or lethality was observed for seven. Three products, Cutting Oil 205, Cutting Oil 220 and Antifreeze and Coolant, did exhibit lethality at the tested concentrations.

Cutting Oils 205 and 220. The  $LC_{50}$  values for Cutting Oils 205 and 220 were  $\sim 5.92\text{mg/L}$  and  $\sim 7.31\text{mg/L}$ , respectively. This is contrasted with our other oils which have never produced lethality when tested in similar fashion.

Rats generally died between two and four days after exposure. One rat was found dead on day one (24 hours) and one was found dead on day seven. There were no specific signs or symptoms preceding death nor were there any out-

standing findings at necropsy. Thus, unfortunately, it was not possible to identify a specific target organ or cause of death. It is clear, however, based on gross observations, that the cause was not due to irritation of the respiratory system and that the products do have the capacity to cause generalized systemic toxicity.

This generalized toxic response was also evident in survivors. The males exposed to both 205 and 220 and females, only, exposed to 205 exhibited significant ( $P < 0.05$ ) weight gain deficits ( $> 30\%$ ) as compared to controls. This is an indication of substantial stress, the magnitude of which is not routinely observed in our studies.

The factor that appears to confer toxicity to these products is the sulfonate base. Inexplicably, Cutting Oil 220 which contains nearly twice as much of this agent as Cutting Oil 205, was responsible for fewer deaths, at a higher concentration. I suspect that this is an anomaly caused by the relative insensitivity of acute toxicity assays. However, without further study, one cannot reject the hypothesis that the chlorinated paraffin in 220 confers some protection or that it is the ratio of base oil to sulfonate and/or chloroparaffin that is the important factor in toxicity.

Antifreeze and Coolant. Of the ten rats exposed to CITGO Antifreeze and Coolant at a concentration of 5.49mg/L, two died during the test period. Therefore, the LC<sub>50</sub> for this product is substantially greater than 5.49mg/L. No data was found reporting inhalation toxicity for ethylene glycol under similar exposure conditions. However, our data would appear to be consistent with previous reports that no lethality was observed when rats were exposed for twenty eight hours over five days to saturated vapors (~0.5mg/L).

### III. Discussion and Recommendations

#### Cutting Oils 205 and 220.

The fact that Cutting Oils 205 and 220 produced irritation to eyes and skin is not surprising. However, the fact that in the skin irritation test, three out of six rabbits had scores of moderately irritating and the overall score was mildly irritating from an acute exposure, does raise some concerns. First, the range of scores indicates that wide variability may be expected in human responses. Consequently, some occupationally exposed individuals may experience substantial reactions. Secondly, if these scores are obtained acutely, repeated or prolonged exposure as occurs during machining operations may pose substantial skin irritation problems, especially to those that may be most susceptible or who do not practice careful personal hygiene. The importance of preventing repeated and/or prolonged contact with these products and of careful and thorough hygienic practices during their use should continue to be emphasized to our customers.

The inhalation results with Cutting Oils 205 and 220 are of special concern. While the exposure concentrations are tremendously above the recommended human exposure levels (5.9-7.37mg/L versus 2mg/m<sup>3</sup>) and the normal use pattern for these products is as dilute solutions in water,

the finding of lethality with these products is in stark contrast to our findings with other oils at similar concentrations.

Lethality by any exposure route is not a desirable end point for considering potential human health effects. It is used in acute studies in conjunction with observations of pharmacotoxic signs as a convenient and indisputable index of relative toxicity. When considering potential human health impacts from continued, relatively low level exposure we must be concerned about more subtle effects. This is particularly true when the material in question has demonstrable toxicity.

These products obviously have the capacity to cause significant toxicity via inhalation of their aerosols, albeit at very high levels. Thus, we should ask what non-lethal but potentially serious health effects might be associated with lower level exposures and what are the target tissue(s) and mode of action.

These study results warrant our consideration of additional studies aimed at establishing a no observable effect level, target tissue(s) and mechanism of action. A reasonable next step would be to conduct a full LC<sub>50</sub> determination combined with microscopic evaluation of selected tissues. This would allow an estimation of a no acute

effect level and provide a better chance of identifying the source of toxicity. In addition, it may be necessary and desirable to conduct subacute studies. Such studies would include longer exposures to lower concentrations of active product with more sophisticated attention to biological indicators of damage. Since these studies would be significantly more costly than previous studies and take substantially longer to conduct and interpret, we are willing to discuss the issues with you at your convenience and/or prepare a formal proposal for your consideration.

Antifreeze and Coolant.

The results obtained in both the acute oral and inhalation assays with CITGO Antifreeze and Coolant are not sufficiently outstanding to warrant undue concern. It is unfortunate that the data do not allow an estimate of the oral LD<sub>50</sub> or the influence of additives on overall toxicity. In the interest of economy, we could simply apply data for ethylene glycol to this product, assuming nominal effects from additives. Alternatively, we could conduct another "single dose" study at or near the LD<sub>50</sub> value for ethylene glycol, for comparative purposes. The optimum approach would be to conduct a full LD<sub>50</sub> determination for our blended product.

TOX005/X

**TOXICITY TESTING RESULTS - 1981**  
**Lubricants and Specialty Products Screening Program**  
**Conducted at ToxiGenics, Inc., Decatur, IL**

Cities Service  
 Product

(Test Code No.)

	Acute Oral Toxicity (rats)	Eye Irritation (rabbits) Maximum Score: 110	Skin Irritation (rabbits) Maximum Score: 8	Acute Inhalation Toxicity (rats)
CITGO Mileage Plus, SAE 10W-40 (1-2174-01-4P)	Practically Non-Toxic LD <sub>50</sub> >15g/kg	Practically Non-Irritating 1.7/110	Non-Irritating 0/8	LC <sub>50</sub> /4H <sup>c</sup> >0.82mg/L
CITGO All Season Multigrade 10W-40(SF) (2-2174-01-4P)	Practically Non-Toxic LD <sub>50</sub> >15g/kg	Practically Non-Irritating 1.3/110	Non-Irritating 0/8	LC <sub>50</sub> /4H <sup>c</sup> >0.81mg/L
CITGO ATF Dexron® II (3-2174-01-4P)	Practically Non-Toxic LD <sub>50</sub> >15g/kg	Non-Irritating 0/110	Practically Non-Irritating 0.38/8	LC <sub>50</sub> /4H <sup>c</sup> >3.97mg/L
CITGO ATF Type F (4-2174-01-4P)	Practically Non-Toxic LD <sub>50</sub> >15g/kg	Practically Non-Irritating 0.7/110	Non-Irritating 0/8	LC <sub>50</sub> /4H >5.61mg/L

Cities Service  
Product  
(Test Code No.)

	Acute Oral Toxicity (rats)	Eye Irritation (rabbits) Maximum Score: 110	Skin Irritation (rabbits) Maximum Score: 8	Acute Inhalation Toxicity (rats)
CIT60 Cutting Oil 140 (5-2174-01-6P)	Practically Non-Toxic LD <sub>50</sub> >15g/kg	Practically Non-Irritating 0.7/110	Non-Irritating 0.02/8	LC <sub>50</sub> /4H >5.82mg/L
CIT60 Cutting Oil 425 (6-2174-01-6P)	Practically Non-Toxic LD <sub>50</sub> >15g/kg	Non-Irritating 0.3/110	Non-Irritating 0.04/8	LC <sub>50</sub> /4H >6.87mg/L
CIT60 Cutting Oil 205 (7-2174-01-6P)	Practically Non-Toxic LD <sub>50</sub> >15g/kg	Non-Irritating 0.3/110	Practically Non-Irritating 0.42/8	LC <sub>50</sub> /4H ~5.92mg/L
CIT60 Cutting Oil 220 (8-2174-01-6P)	Practically Non-Toxic LD <sub>50</sub> >15g/kg	Practically Non-Irritating 2.0/110	Mildly Irritating 2.04/8	LC <sub>50</sub> /4H ~7.31mg/L
CIT60 Pacemaker Oil 800 (9-2174-01-6P)	Practically Non-Toxic LD <sub>50</sub> >15g/kg	Non-Irritating 0.3/110	Non-Irritating 0/8	LC <sub>50</sub> /4H >5.48mg/L

Cities Service Product (Test Code No.)	Acute Oral Toxicity (rats)	Eye Irritation (rabbits) Maximum Score: 110	Skin Irritation (rabbits) Maximum Score: 8	Acute Inhalation Toxicity (rats)
CITGO Pacemaker 100 (10-2174-01-4P)	Practically Non-Toxic LD <sub>50</sub> >15g/kg	Non-Irritating 0/110	Non-Irritating 0.02/8	LC <sub>50</sub> /4H >6.03mg/L
CITGO EP Compound 68 (11-2174-01-4P)	Practically Non-Toxic LD <sub>50</sub> >15g/kg	Non-Irritating 0/110	Non-Irritating 0.06/8	LC <sub>50</sub> /4H >5.24mg/L
CITGO Open Gear Compound 4A (12-2174-01-4P)	Practically Non-Toxic LD <sub>50</sub> >15g/kg	Practically Non-Irritating 1.3/110	Non-Irritating 0/8	_____ d
CITGO Concrete Form Oil (13-2174-01-4P)	Practically Non-Toxic LD <sub>50</sub> >15g/kg	Non-Irritating 0/110	Practically Non-Irritating 0.73/8	LC <sub>50</sub> /4H >6.07mg/L
CITGO Extra Range Grease (14-2174-01-3P)	Practically Non-Toxic LD <sub>50</sub> >15g/kg	Non-Irritating 0.3/110	Practically Non-Irritating 0.65/8	_____ d
CITGO Antifreeze & Coolant (15-2174-01-4P)	LD <sub>80</sub> ~15g/kg <sup>a</sup>	Non-Irritating 0/110	Practically Non-Irritating 0.15/8	LC <sub>50</sub> /4H <sup>e</sup> >5.49mg/L

<sup>a</sup>Since only a single dose test was done and 8 out of 10 animals died, a determination of LD<sub>50</sub> is not possible. See text of report for details.

<sup>b</sup>All test articles were warmed to between 70 and 100°C to facilitate aerosolization.

<sup>c</sup>Highest concentrations attainable even with heating up to 100°C.

<sup>d</sup>Due to physical properties of these products, no inhalation testing was possible.

<sup>e</sup>While the LC<sub>50</sub> is greater than 5mg/L, two of the ten exposed animals did die during the test; thus, the LC<sub>20</sub> is ~5.49mg/L.

TOX005/DB

Harry N. Finkbone  
Consultant Toxicologist  
1620 Parkers Mill Road  
Lexington, KY 40504  
August 25, 1982

Mr. J.L. Boucher  
Manager of Toxicology  
Cities Service Co.  
P.O. Box 300  
Tulsa, OK 74102

Dear John:

All final reports from contract laboratories have now been received and reviewed. In summary, the results of this year's testing are as follows:

- CITGO Cutting Oil 205, (C.O. 205) poses no unusual health risks associated with routine inhalation of its aerosol. This finding is based on the comparative testing conducted this year in which it was shown that both C.O. 205 and its base oil 100 Neutral elicited the same toxic responses in rats following aerosol inhalation exposures at  $> 5$  mg/L for four hours. The four hour LC50's for these materials were found to be  $> 5.18$  mg/L and  $> 5.54$  mg/L for C.O. 205 and 100 Neutral, respectively.

- CITGO Glycol FR-40 XD was assessed for potential toxic impact to aquatic life by a combination of static and dynamic bioassays and by investigating its effects on representative activated sludge microorganisms. The 48 hr static and dynamic LC50's for Daphnia magna (water flea) were greater than 1000 mg/L and the static and dynamic LC50's for Pimephales promelas (fathead minnow) were also greater than 1000 mg/L.

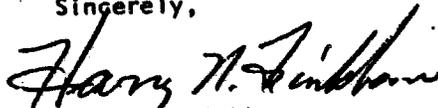
After 16 days of continuous exposure of activated sludge microorganisms to concentrations of this product of up to 150 mg/L (ppm), no significant adverse effects were detected with respect to the efficiency of removal of dissolved organic carbon or to the population of sludge microorganisms.

These data for toxicity to aquatic macroorganisms and to sludge microorganisms indicate that CITGO Glycol FR-40 XD is essentially non-toxic to aquatic life. Thus, it should have no adverse effects upon fresh water biology or activated sludge waste treatment during normal use.

I have attached, as appendices, more detailed reports for each of the two aspects of the 1982 toxicity testing program. Upon your acceptance of this report, I will return to you the copies of the reports that I have. Further, I would be glad to assist you in incorporating this data into MSDS's or other Company literature.

If you have any questions regarding these tests or reports, please feel free to call on me.

Sincerely,

  
Harry N. Finkbone  
Consultant Toxicologist

HNF:crb

Appendix I  
Inhalation Toxicity of  
CITGO Cutting Oil 205  
August, 1982

Background

In 1981, as a part of a routine acute toxicity screening program, CITGO Cutting Oils 205 and 220 were examined for acute aerosol inhalation toxicity in rats. These products were found to have 4 hr LC50's of approximately 5.9 mg/L and 7.3 mg/L, respectively. This finding appeared to be in stark contrast to previous test results with other lubricant products which had always had 4 hr LC50 values > 5 mg/L and had produced no deaths. This previous testing had included 100 Neutral oil, the base oil for the 200 series soluble cutting oils. The gross observations during exposure and at necropsy in 1981 for C.O. 205 & 220 showed nothing remarkable to suggest a mechanism of toxic response.

Based on these findings, additional testing was recommended that would better delineate the inhalation toxicity profile of the 200 series soluble Cutting Oils and thus provide better guidance in assessing the realistic hazard associated with aerosol inhalations of these products.

Study Design - 1982

In early 1982, a final testing protocol was approved that would meet the above objective. This protocol can be summarized as follows:

- 1) Initially, groups of 10 rats (5 male, 5 female) each would be exposed to an aerosol concentration of 5.0-5.5 mg/L for four hours to Cutting Oil 205 or 100 Neutral (vehicle control). In addition a similar group would be exposed to air only as an untreated control.

- 2) Depending upon the results of phase one, which would serve as a confirmation of the 1981 test results, additional parallel exposure levels to Cutting Oil 205 and 100 Neutral would be used until enough data was collected

to construct a meaningful dose-response curve and quantitate the LC50 of C.O. 205.

In each phase, lungs, liver, trachea, kidney and any abnormal tissues were to be preserved for further studies if necessary. Lung, liver and kidney weights were recorded.

Cutting Oil 205 was selected for this study because it had previously given the greater toxic response and it did not contain a chlorinated paraffin constituent found in C.O. 220. This was believed to be important since it was felt that the probable factor in toxicity would be the sulfonate base contained in the 200 series oils.

Further, 100 Neutral was used as a parallel "vehicle control" so that the toxicity of the Cutting Oil could be reliably compared with its major constituent. This was especially important since the previous testing with 100 Neutral had been conducted at another laboratory using entirely different equipment to generate the aerosol and different methodology to assess aerosol concentration and particulate size. It was postulated that the apparent difference in toxicity of the Cutting Oils versus 100 Neutral could be attributable to the quality and quantity of oil particulate in the exposure chambers and subsequent deposition in rat lungs.

#### Findings and Conclusions.

Following the initial exposures at 5.0-5.5 mg/L for C.O. 205 and 100 Neutral, the contract laboratory reported, by phone, that in both exposure groups, two animals had died between 2 and 5 days post exposure. Examination of the carcasses of the animals revealed no remarkable pathology. However, virtually all animals in both groups did exhibit irregular breathing during and/or the following exposure. Further testing was terminated at this point, pending review of the final results since the data indicated no substantive difference in toxicity.

Based on the testing conducted to date, it would appear that the original apparent discrepancy in toxicity for the 200 Series Cutting Oils can be accounted

for on the basis of the differences in the methods used in aerosol generation. I believe that the test system used by Toxi-Genics in 1981 for the Cutting Oils and in 1982 for C.O. 205 and 100 Neutral were more effective in creating high levels of respirable aerosols and provided more accurate quantitation of exposure levels. This resulted in greater deposition of the oily material into the lungs with subsequent greater toxic response. The most likely explanation of the observed toxicity is impaired lung function attributable to the spreading of a thin oily film over the gas exchange surfaces of the lungs.

These data in no way detract from the validity or reliability of previously collected inhalation data. In fact, they support a conclusion of the overall safety of these materials. The four hour LC50's are still in excess of 5 mg/L, a very stringent cut off value for safety assessment. Thus, there is now no reason to believe that the very low levels of human exposure to aerosols of the tested CITGO soluble cutting oils would pose any greater risk of injury than exposure to 100 Neutral, the current ACGIH TLV for which is 5 mg/M<sup>3</sup>.

  
Harry N. Pinkbone  
Consultant Toxicologist

## Appendix II

### Aquatic Toxicity of CITGO Glycol FR-40 XD

August, 1982

#### Background

In September of 1981, it was brought to the attention of the Toxicology Department of Cities Service Company that certain potential customers appeared hesitant to purchase glycol-based fire resistant hydraulic fluids. This resistance stemmed from concerns over potential aquatic impacts and effects on waste treatment systems. Subsequently the Toxicology Department proposed a testing program that would adequately assess the magnitude of toxicity, if any, to aquatic species and waste treatment biota.

#### Study Design

Based on the above mentioned proposal, a study program was initiated in the Spring of 1980 consisting of the following five assays:

- 1) Static Acute Toxicity to Daphnia magna (water flea), 48 hr.
- 2) Dynamic (Flow Through) Acute Toxicity to Daphnia magna, 48 hr.
- 3) Static Acute Toxicity to Pimephales promelas (Fathead Minnow), 96 hr.
- 4) Dynamic Acute Toxicity to Pimephales promelas, 96 hr.
- 5) Activated Sludge Biodegradation

The justification of test organisms and protocol designs are discussed in the original proposal (dated December 1981). All assays were conducted in accordance with the intent of Good Laboratory Practice Regulations and each has a basis in regulations and recommendations either proposed or issued by the U.S. E.P.A., American Public Health Assoc. or the American Society for Testing and Materials.

Findings and Conclusions

Static/Daphnia: The 48 hr LC50 and the 48 hr no observed effect levels were both > 1,000 mg/L.

Dynamic/Daphnia: The 48 hr LC50 was > 1,000 mg/L. The 48 hr no observed effect level was 500 mg/L. (One of ten daphnia was found dead @ 48 hrs.

This is statistically of no consequence).

Static/Minnow: The 96 hr LC50 and no observed effect levels were > 1,000 µl/L (ppm).

Dynamic/Minnow: The 96 hr LC50 and no observed effect levels were > 1,000 µl/L (ppm).

Activated Sludge Biodegradation:

Dissolved Organic Carbon (DOC) removal efficiencies were:

<u>Day</u>	<u>Control</u>	<u>FR-40 XD</u>
7	77.6%	92.5%
14	67.8%	59.7%
16	55.0%	56.6%

Thus, even though efficiencies decreased with time (attributable to "aging" of the sludge), the FR-40 XD treatment group was essentially unaffected as compared to the control. This shows that concentrations of up to 150 mg/L (ppm) of CITGO Glycol FR-40 XD have no adverse effect on secondary waste treatment activated sludge with respect to its capacity to remove dissolved organic carbon.

Over the duration of the study, the microbial populations in control and treatment reactors averaged  $4.2 \times 10^6$  and  $4.4 \times 10^6$  organisms/ml of reaction mixture, respectively. In addition, the populations at points approximately halfway through the study and at termination were quite comparable.

<u>Day</u>	<u>Control</u>	<u>FR-40 XD</u>
9	$4.3 \times 10^6$ /ml	$4.6 \times 10^6$ /ml
16	$4.2 \times 10^6$ /ml	$6.0 \times 10^6$ /ml

This data indicates that upto a concentration of 150 mg/L (ppm) CITGO Glycol FR-40 XD exhibits no toxic effect on activated sludge microflora.

Taken together, the DOC removal efficiency and microbial toxicity data show that users of CITGO Glycol FR-40 XD should experience no adverse impacts on their waste treatment systems during normal operations. Further, municipal waste treatment plants employing activated sludge secondary treatment should have no undue concern over traces of this material being in their influent.



Harry N. Finkbone

Consultant Toxicologist

CITIES SERVICE  
INTEROFFICE LETTER

May 12, 1982

TO: Dr. P. V. Roling  
FROM: H. N. Finkbone, Toxicologist *HF*  
SUBJECT: Final Report -  
B5 Toxicity Testing

Acute Toxicity/Mammalian

No significant toxic responses were observed during the course of testing. The following specific results were obtained:

<u>Test</u>	<u>Test Article ID Number</u>	<u>Result</u>
Acute Oral Toxicity (rats)	80-66-27-A	LD50 >5g/Kg Essentially Non-Toxic
Eye Irritation (rabbits)	80-66-27-A	2.0/100 (Draize) Practically Non-Irritating
Skin Irritation (rabbits)	80-66-27-A	0.5/8 (Draize) Practically Non-Irritating
Acute Inhalation Toxicity (rats)	80-66-27-B*	LC50 >5.95 mg/L (5.95 g/M <sup>3</sup> ) Essentially Non-Toxic

These data indicate that normal safe chemical handling procedures would be adequate to ensure the protection of workers from the acute exposure effects of this material.

\*The reason that the inhalation study was conducted using a test article with a different identification number is that it was anticipated that there would be insufficient material available from the original lot (80-66-27-A) to complete

Dr. P. V. Roling  
Page Two  
May 12, 1982

the study. Therefore, a second batch (80-66-27-B) of the same material was used and was essentially identical in every physicochemical respect to the original lot.

In Vitro Assays

Test article 80-66-27-A was evaluated for genetic toxicity potential using the Salmonella Mutagenicity Assay (Ames Test) and the Bacterial DNA Repair Assay. Both assays were conducted using initial liquid suspension/preincubation to maximize the probability of detecting effects.

Both assays provided negative results. As a matter of protocol, the testing laboratory reported the results of the Bacterial DNA Repair Assay as a "No Test". However, it is my judgement and considered opinion that this test was performed adequately and in such manner that the observed lack of toxic response is, in fact, a finding of no effect on DNA repair competency.

Based on these tests, there is no reason to expect that this test article is capable of inducing significant genetic lesions. Therefore, there is essentially no likelihood that exposure to this material will result in genetically related medical maladies such as cancer, birth defects or reproductive deficits.

---

You have previously received copies of the mammalian acute toxicity testing reports; thus, I am attaching to this report only your copies of the in vitro assays final reports. If you have any questions, feel free to call. We have sincerely appreciated your interest and support.

HNF:sdh  
Attachments  
cc Mr. J. L. Boucher  
Dr. G. A. Mortimer ✓

CONTAINS NO CBI

**FINAL REPORT**

**Investigation**

of the

**Tumor Producing Potential on Mice**

of

**Eighteen Lube Oil Refinery Streams**

for

**CIT-CON OIL CORPORATION**

Submitted By

The Industrial Hygiene and Toxicology Departments  
of

**CITIES SERVICE COMPANY**

March 1982

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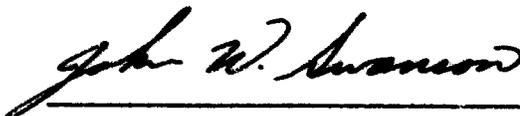
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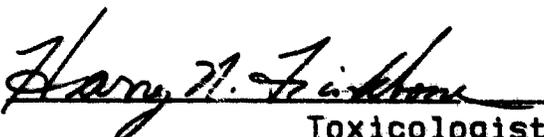
# FINAL REPORT

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March 1982

  
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Manager, Industrial Hygiene

  
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Toxicologist

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**TABLE 1**

<u>Test Substance</u>	<u>CAS No.</u>
Gas Oil	64741-49-7
100 Distillate	64741-50-0
200 Distillate	64741-51-1
Light Intermediate Distillate	64741-51-1
100 Extract	64742-11-6
200 Extract	64742-11-6
Light Intermediate Extract	64741-11-6
Heavy Intermediate Extract	64742-11-6
Light Intermediate Cycle Oil Extract	64742-11-6
Heavy Intermediate Distillate	64741-51-1
Short Residuum	64741-56-6

Abstract

Eighteen lube oil refinery stream samples from the CIT-CON facility were tested for tumorigenicity by dermal application to C<sub>3</sub>H mice three times per week for twenty-four months.

The following CIT-CON samples were demonstrated to be carcinogenic to mouse skin:

Gas Oil	200 Extract
100 Distillate	Light Intermediate Extract
200 Distillate	Heavy Intermediate Extract
Light Intermediate Distillate	Light Intermediate Cycle
100 Extract	Oil Extract

The following materials, as tested, were not carcinogenic to mouse skin:

Bright Stock Extract	Finished Heavy Intermediate
Finished 100 Neutral	Neutral
Finished 200 Neutral	Finished Bright Stock
Finished Light Intermediate	Finished Light Intermediate
Neutral	Cycle Oil

Two samples were marginally active tumorigens:

Heavy Intermediate Distillate  
Short Residuum

### Introduction

Concern with skin effects of oils began with the observed cancers among cotton textile workers (mule spinners) in England during the late nineteenth and early twentieth centuries. These workers used Scottish shale oil as lubricants and practiced minimal or no personal hygiene. In 1922, the first skin cancer was produced on experimental animals using Scottish shale oil. The next three decades were dedicated to finding a suitable substitute lubricant. Petroleum oils were found to be less active than shale or coal derived oils. Refining with acid and other methods produced lubricating oils that were not active in animal tests.

During the next several decades, research was conducted to investigate the reasons why some oils were active tumorigens and others were not. Some active components were isolated and identified. In addition, other materials that initiate, promote or inhibit activity were identified. The roll of sulfur and nitrogen compounds began to be investigated.

Our current state of knowledge about skin activity for petroleum hydrocarbons has improved but there are many unknown factors remaining. Although we know some polynuclear aromatic compounds (PNA's) are active while others

are not and some sulfur species contribute to the activity, there are still no identified physical and chemical parameters that can be reliably used to predict activity on animal skin. The only way to determine skin activity for any hydrocarbon mixture is to test it on the animal. In order to assure handling procedures are appropriate for operations and maintenance during the manufacture and use of stock oils and to adequately inform customers of the potential biological activity of lubricants, rubber extender oils and other marketable products, CIT-CON chose to test several streams from its facility.

The primary factors used to select streams for study were throughput volume, probability of exposure, and a preliminary qualitative assessment of potential carcinogenicity. This latter parameter was based on historical observations that highly refined finished lubricant stocks are not carcinogenic whereas more highly aromatic fractions and "bottoms" frequently are. Distillates were relatively unstudied but were expected to have intermediate biological activity. Thus, if representative samples from each of these categories were studied, the results should allow for reasonable extrapolations of potential activity to other fractions similarly derived and blends of each. On these predicates, the following CIT-CON streams were selected for study:

	<u>Abbreviation</u>	<u>Sample Code No.</u>
Gas Oil	GasO	T9156
100 Distillate	CD	T9157
200 Distillate	CCD	T9158
Light Intermediate Distillate	LID	T9159
Heavy Intermediate Distillate	HID	T9160
Short Residuum	RESID	T9161
100 Extract	CX	T9162
200 Extract	CCX	T9163
Light Intermediate Extract	LIX	T9164
Heavy Intermediate Extract	HIX	T9165
Bright Stock Extract	BSX	T9166
Finished 100 Neutral	FCN	T9167
Finished 200 Neutral	FCCN	T9168
Finished Light Intermediate Neutral	FLIN	T6169
Finished Heavy Intermediate Neutral	FHIN	T9170
Finished Bright Stock	FBS	T9171
Light Intermediate Cycle Oil Extract	LICyX	T9172
Finished Light Intermediate Cycle Oil	FLICy	T9173

For comparative purposes, a negative (sham) control substance (Squibb® white mineral oil) and a positive control substance (cat cracker bottoms, Sample Code No. T9174)) were also tested. As well, an untreated control group was maintained.

Since the primary route of potential employee exposure was believed to be via skin contact, the streams were tested by dermal application. Additional details of protocol are given under Materials and Methods.

This project was initiated in February 1977, under contract with Cannon Laboratories, Inc., Reading, PA. The original contract called for Cannon to conduct the entire study, including application, observation, gross pathology

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and microscopic pathology. Cannon completed the assigned project up to and including final sacrifice and tissue collection. Some histopathology was done, however it was incomplete.

In April of 1981, prepared histology slides, fixed tissues, paraffin blocked tissues and associated laboratory data and records pertaining to this study were retrieved from Cannon Laboratories and placed in secure custody. On October 2, 1981, the previously prepared slides and fixed and embedded tissues were delivered to Microbiological Associates. Under contract dated October 14, 1981, Microbiological Associates completely re-evaluated all available slides for brain and skin tissues and prepared and evaluated slides for brain and skin tissues that had not previously been evaluated. On January 20, 1982, final copies of the histopathology report prepared by Micro, based on their work, were received.

This report summarizes and integrates the data generated by each of the two prime data sources. Only gross and histopathologic findings for skin and brain are discussed in this report since this information for other organs is incomplete. No assessment has been made of the credibility of the data collected or the methods used by Cannon Laboratories, Inc. except to ascertain that the data collection and reporting track for individual animals is

reasonably complete. The original study design and conduct were in conformance with practices common at that time but were not necessarily consistent with standards developed and published subsequent to the initiation of this study, such as the Food and Drug Administration's Good Laboratory Practice Regulations promulgated in 1978.

#### Methods and Materials

The original protocol and the partial draft final report from Cannon Laboratories, Inc.\* and the final report from Microbiological Associates are attached as Appendices II, III, and IV, respectively. These provide the details of protocols, therefore only a summary is presented here.

#### Animals

Twelve hundred male weanling C<sub>3</sub>H mice were originally started on test divided into groups as . . . 100 each in the untreated, negative and positive control groups and 50 each in the eighteen test groups. C<sub>3</sub>H mice were selected, in part, because they have a low incidence of

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\*Only that portion of the Cannon Laboratories' draft final report concerning experimental procedures and gross observations is attached. Some additional data is on file.

spontaneous skin tumors, they were the historical animal of choice for this type of study and there was a large body of comparative data available in the scientific literature concerning this mouse strain.

Mice were housed in groups of five in closed bottom plastic cages. Corn cob bedding was provided and changed three times per week. Food (Purina® Rat Chow) and water were available ad lib. The mice were maintained in environmentally controlled rooms with a 12-hour light/dark cycle. Individual identification of mice was by ear punch codes.

#### Test Article Application

Test article was applied three times per week for 24 months to the shaved backs of the mice. Shaving was done initially 72 hours prior to the first application and as needed thereafter, always on a non-application day. Test article was applied undiluted from a syringe. The volume applied was "one or two drops." This amount corresponded to approximately 20 mg/mouse/application.

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Observations, Pathology and Tissue Collection

All mice were observed daily for signs of toxicity. In addition, each was evaluated for appearance and progress of observable masses.\* Time of appearance of masses, number of animals with masses, mortality, toxic signs and condition of carcasses were recorded.

All mice were necropsied either at the time of spontaneous death or when sacrificed. Moribund animals were sacrificed, as were survivors at 24 months. Gross pathological observations were recorded with particular emphasis given to tumors.

Tissue samples from the organs listed in Table 1 were collected from all mice which died or were sacrificed in extremis (unless autolysis was excessive). Tissues were fixed in buffered formalin.

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\*No definition of "observable mass" was given in the original study protocol. In this report, it is assumed that observable mass is synonymous with tumor or neoplasm since these words are more common and both apply equally well to both benign and malignant tissues. "Observable mass" also includes non-neoplastic proliferative epidermal lesions such as epidermal hyperplasia, although such lesions constituted a relatively small proportion of the total "observable masses". The words tumorigen and tumorigenicity may be used to describe "observable masses" regardless of their final histological definition. The word cancer, carcinogen and carcinogenicity will be reserved for discussions of malignant neoplasms only, such as squamous cell carcinoma.

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Table 1: Tissues Taken and Fixed at Necropsy

Skin	Skeletal Muscle
Heart	Trachea
Lung	Spinal Cord
Liver	Eye
Testes	Intestine
Bone Marrow	Stomach
Kidney	Adrenal Gland
Salivary Gland	Thyroid
Brain	Parathyroid
Spleen	Peripheral Nerve
Urinary Bladder	Optic Nerve
Prostate	Lymph Node
Pituitary	

Results and Discussion

Brain

No treatment related lesions were noted in brain tissues.

Skin

There are few subtleties to the interpretation of these test results. First, the test system was sensitive to the induction of skin tumors by the types of agents tested. This is evidenced by the positive results obtained from the positive control, cat cracker bottoms (T9174). Further, the system was not prone to false positives, as evidenced by the low spontaneous tumor rate in both the untreated control and the sham control (Squibb white mineral oil).

Under the conditions of test, the following CIT-CON samples were unequivocally carcinogenic to mouse skin following prolonged and repeated contact:

Gas Oil  
100 Distillate  
200 Distillate  
Light Intermediate Distillate  
100 Extract  
200 Extract  
Light Intermediate Extract  
Heavy Intermediate Extract  
Light Intermediate Cycle Oil Extract

All of these materials caused high incidences of tumors and large proportions of these tumors were squamous cell carcinoma, a highly invasive malignant cancer.

The following materials, as tested, were not carcinogenic to mouse skin:

Bright Stock Extract  
Finished 100 Neutral  
Finished 200 Neutral  
Finished Light Intermediate Neutral

Finished Heavy Intermediate Neutral  
Finished Bright Stock  
Finished Light Intermediate Cycle Oil

Two test articles were of marginal biological activity:

Heavy Intermediate Distillate  
Short Residuuum

Neither of these marginally active materials produced statistically significant excess numbers of squamous cell carcinomas (SCC) in this study. However, both did produce such tumors, as contrasted to no production of SCC in either of the control groups or any of the non-carcinogenic test groups mentioned above. In addition, Heavy Intermediate Distillate produced four times the incidence of observable masses as compared to the sham control. Thus, these materials probably do have some marginal or minimal inherent capacity to produce both benign and malignant tumors but these capacities are quite weak compared to the nine carcinogenic streams given above.

#### Additional Observations

Tables 1 through 21 in Appendix I list pertinent data elements for each of the materials in this study.

Figures 1 through 13 graphically illustrate trends and correlations.

Total Percent of Mice Developing Observable Masses and Percent of Mice with Squamous Cell Carcinoma. As shown in Figures 1 and 2, there is a strong positive correlation between the total percent of mice in each group that developed tumors and the percent incidence of histologically confirmed squamous cell carcinoma. The strength of this correlation is further demonstrated by the fact that in no case was there a low incidence of total observable masses associated with a high incidence of SCC nor were there any cases of a high incidence of total observable masses associated with a low incidence of SCC.\* That is, as the total incidence of observable masses increases, so does the fraction of those masses that are malignant tumors.

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\*The correlated incidence of SCC is actually the calculated minimum percent incidence of this tumor. This minimum value is taken to be the ratio of the number of histologically confirmed SCC to the total number of mice started on test. This statistic was necessary because skin tissue was not available for all mice. The ratio of histologically confirmed SCC to the number of tissues examined is generally higher. If this ratio held when distributed over the number of animals having observable masses, then the total incidence would also be higher. However, since it is not known whether the unexamined animals bore SCC tumors, we cannot make such an extrapolation with much confidence. What is known is that the total incidence of SCC was not any lower than the calculated value, but it could have been higher.

FIGURE 1  
COMPARATIVE INCIDENCE OF OM & SCC

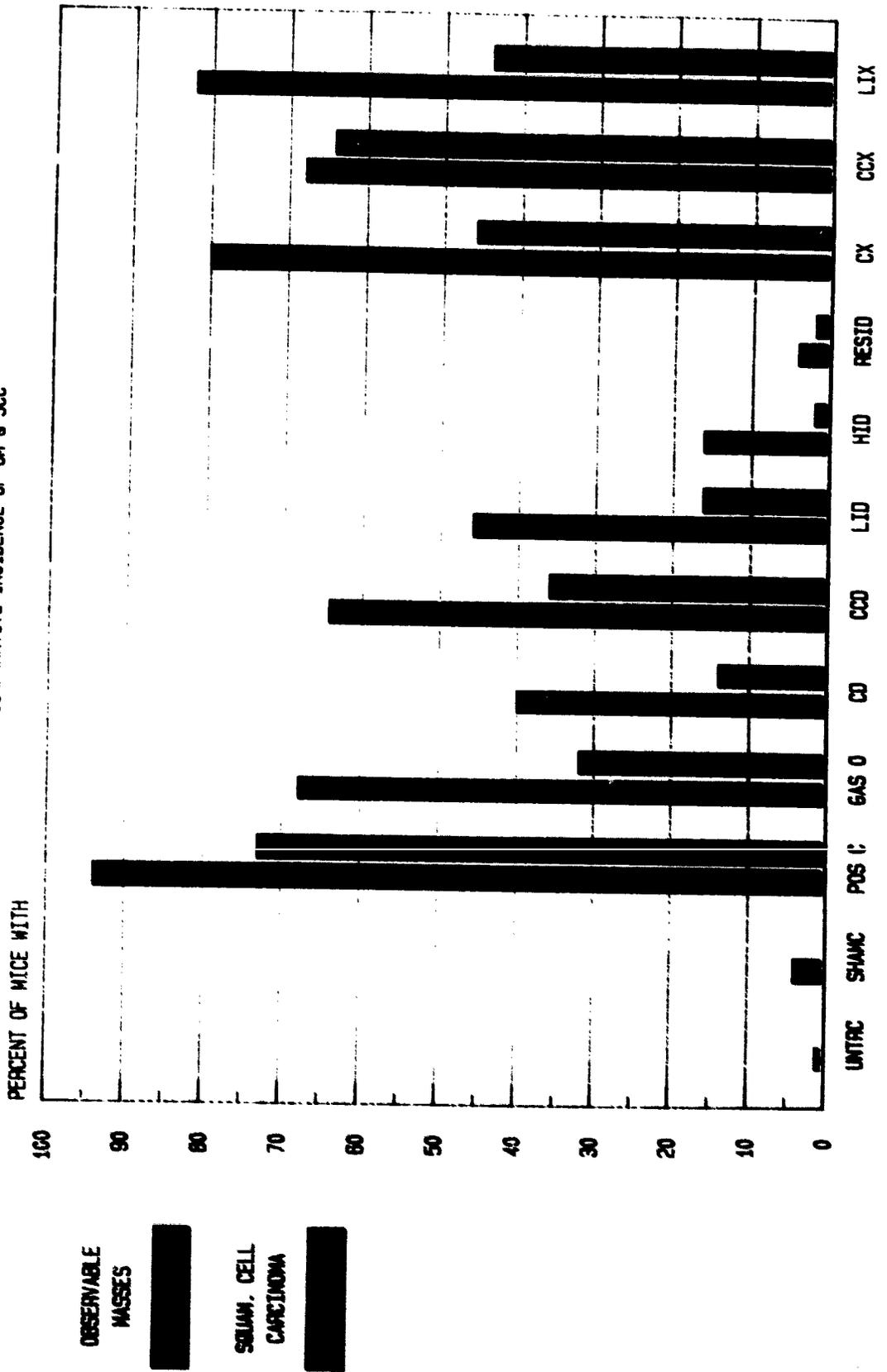
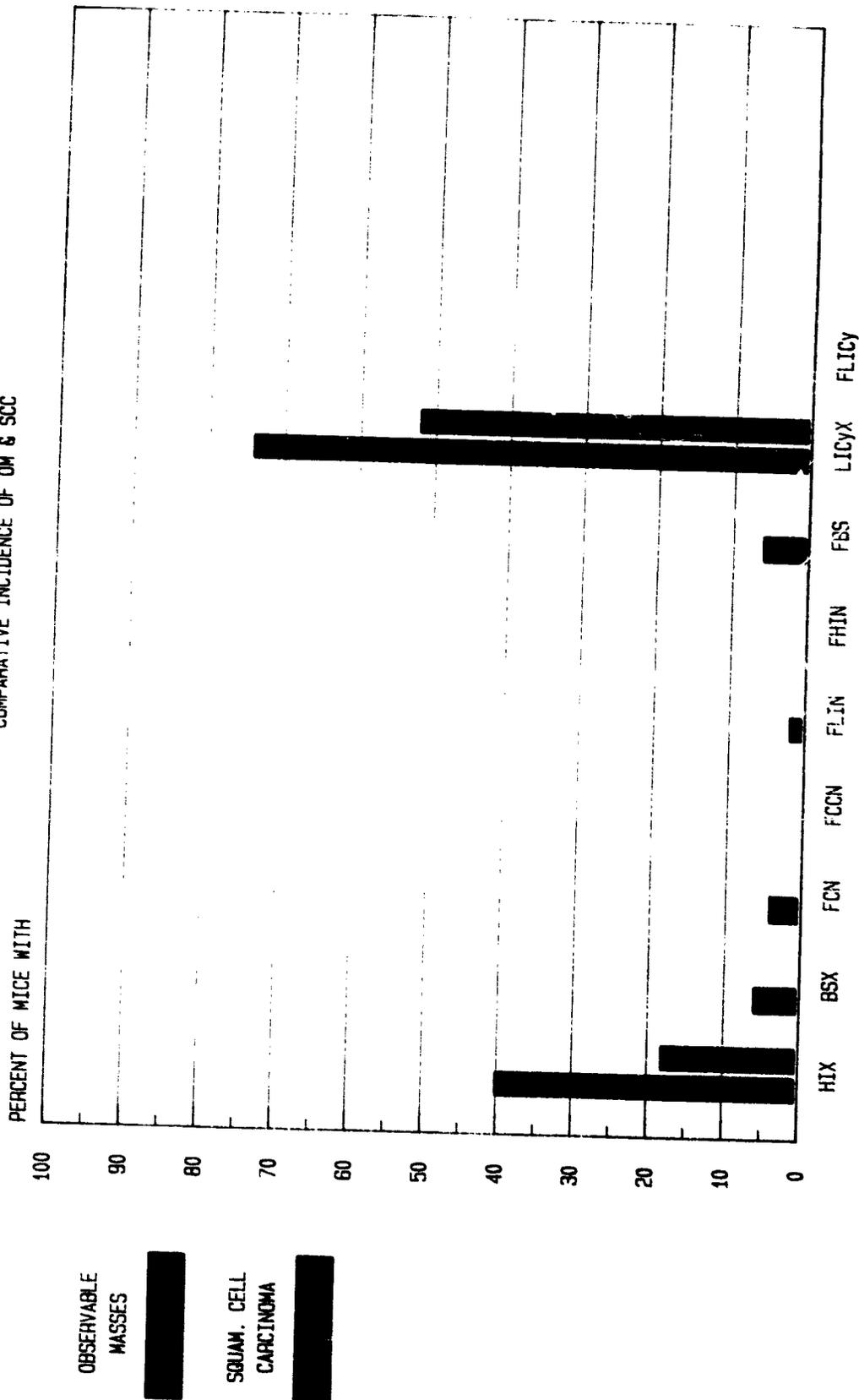
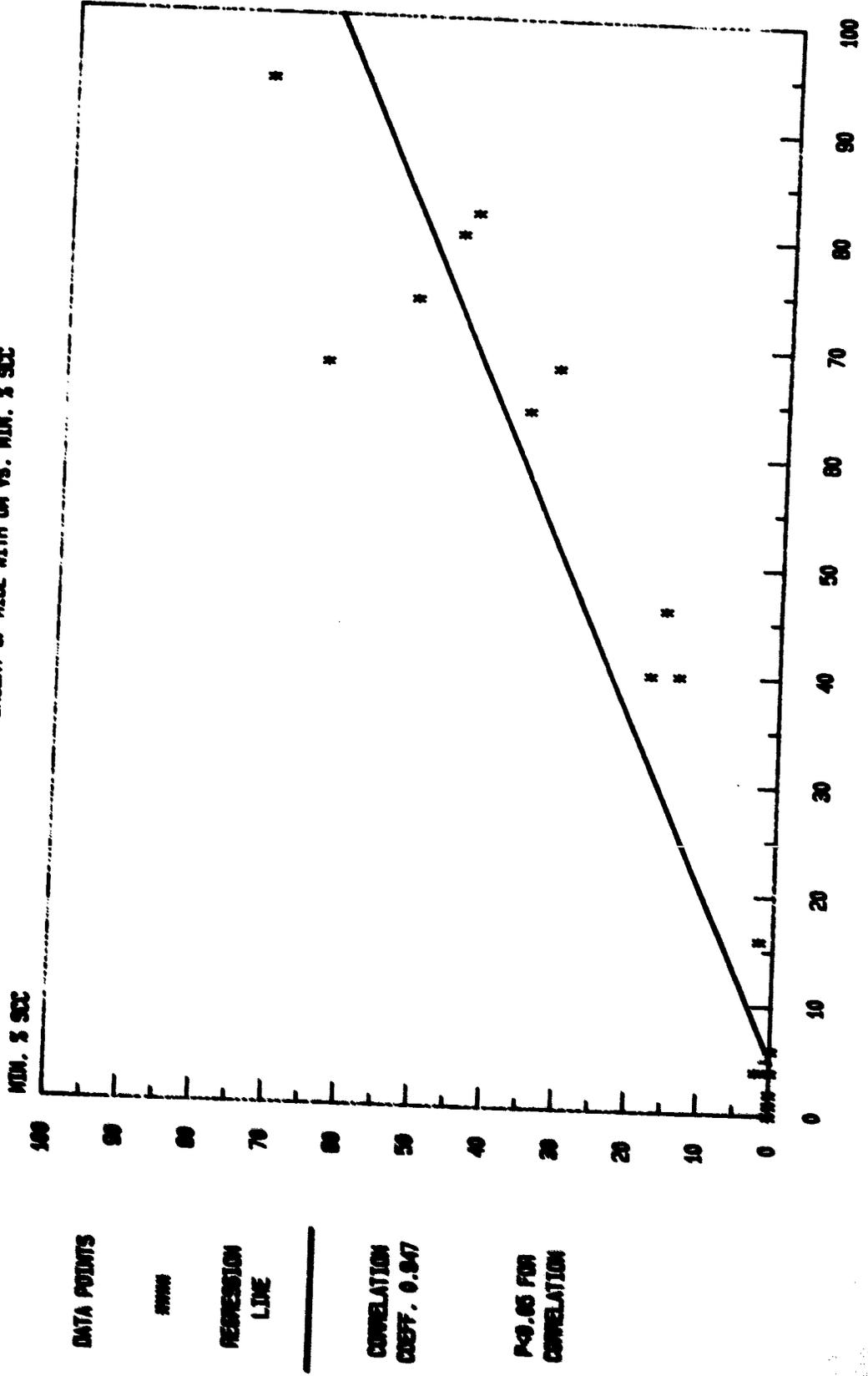


FIGURE 1 (CONT'D)  
COMPARATIVE INCIDENCE OF OM & SCC



**FIGURE 2**  
**PERCENT OF MICE WITH ON VS. MIN. % SCC**

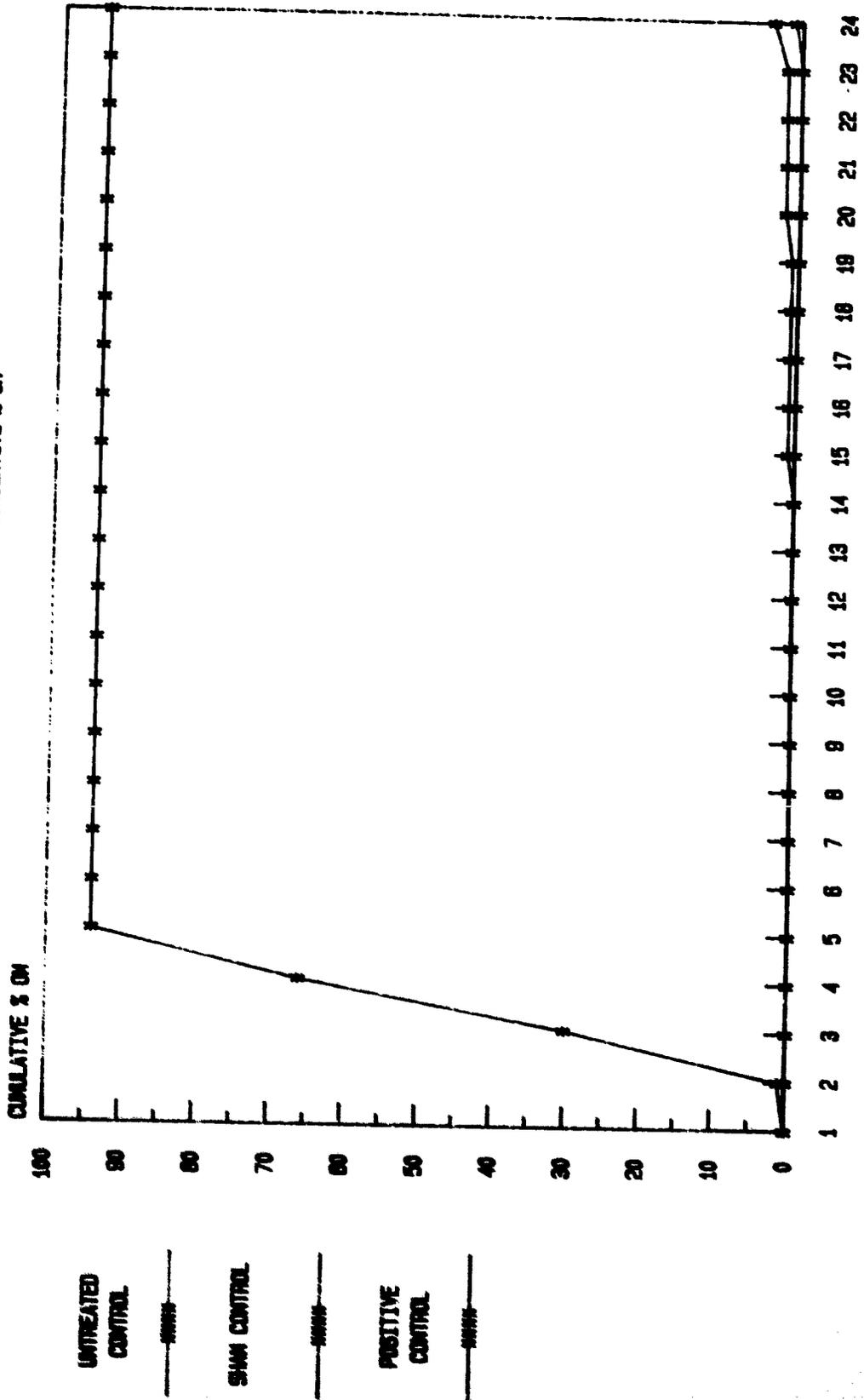


STATISTICAL ANALYSIS SYSTEM

Note that this correlation means that for those streams that were demonstrated to produce high tumor yields, it was also shown that they are generally potent as carcinogens. This does not mean that there is a "cause and effect" relationship between the capacity to cause tumors and the capacity to produce cancer or that benign tumors progress to malignant tumors. It has only been shown, in this study, that where one capacity is associated with a material, the other capacity is found as well. Their causes may or may not be totally independent.

Time to Tumor Data. Figures 3 through 7 show the rate and extent of development of observable masses for all test materials. The tumor incidence is shown for each study month from 1 to 24 as the cumulative percent of tumor bearing mice. No adjustments have been made to account for early mortality (i.e., prior to final sacrifice at 24 months). Also, even when all animals had died early, the final maximum tumor incidence has been plotted for the duration of the study. For clarity and convenience, the test materials have been grouped as controls, distillates (excluding gas oil), extracts, finished oils (excluding cycle oil), and gas oil and cycle oils. In addition, Figure 8 shows the rate and extent of tumor development for the Light Intermediate Stream, including distillate, extracts, finished oil and cycle oil.

FIGURE 3  
MONTHS ON STUDY VS. CUMULATIVE % ON



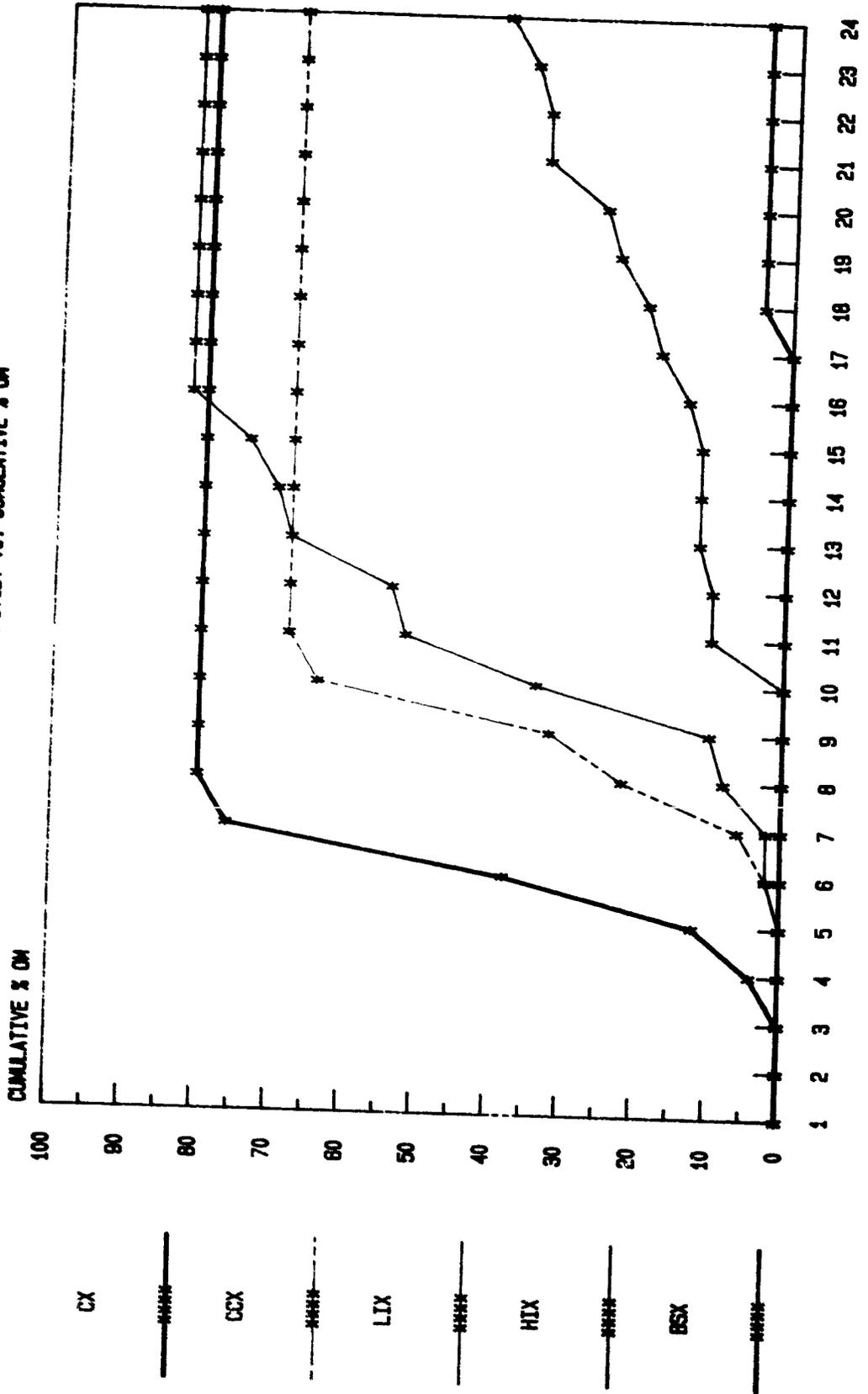


These data show that the choices for control groups were very appropriate. The positive control was a very potent tumorigen and carcinogen, with development of tumors as early as the second month. Death of all animals exposed to this material occurred by the fifth month. The incidence of tumors in the untreated control was negligible and development occurred near the termination of the study. The sham treated control group did show slightly more tumors than the untreated group and at an earlier time, but this is insignificant.

All distillates were active tumorigens though Short Residuum was only weakly so. These materials could be classed as moderately active based on the length of time necessary to produce tumors.

Figure 5 clearly illustrates that, as a class, the extracts are the most potent and rapid acting tumorigens tested in this study. One of these, however, Bright Stock Extract, is relatively weak. In this class, tumor development began as early as four months, only two months later than the positive control. In addition, mortality was high in these groups, with 100% mortality occurring as early as 8 months. The rate of tumor development was also generally high.

FIGURE 5  
MONTHS ON STUDY vs. CUMULATIVE % ON



CUMULATIVE % ON STUDY

Figure 6 shows that finished stock streams are essentially non-active.

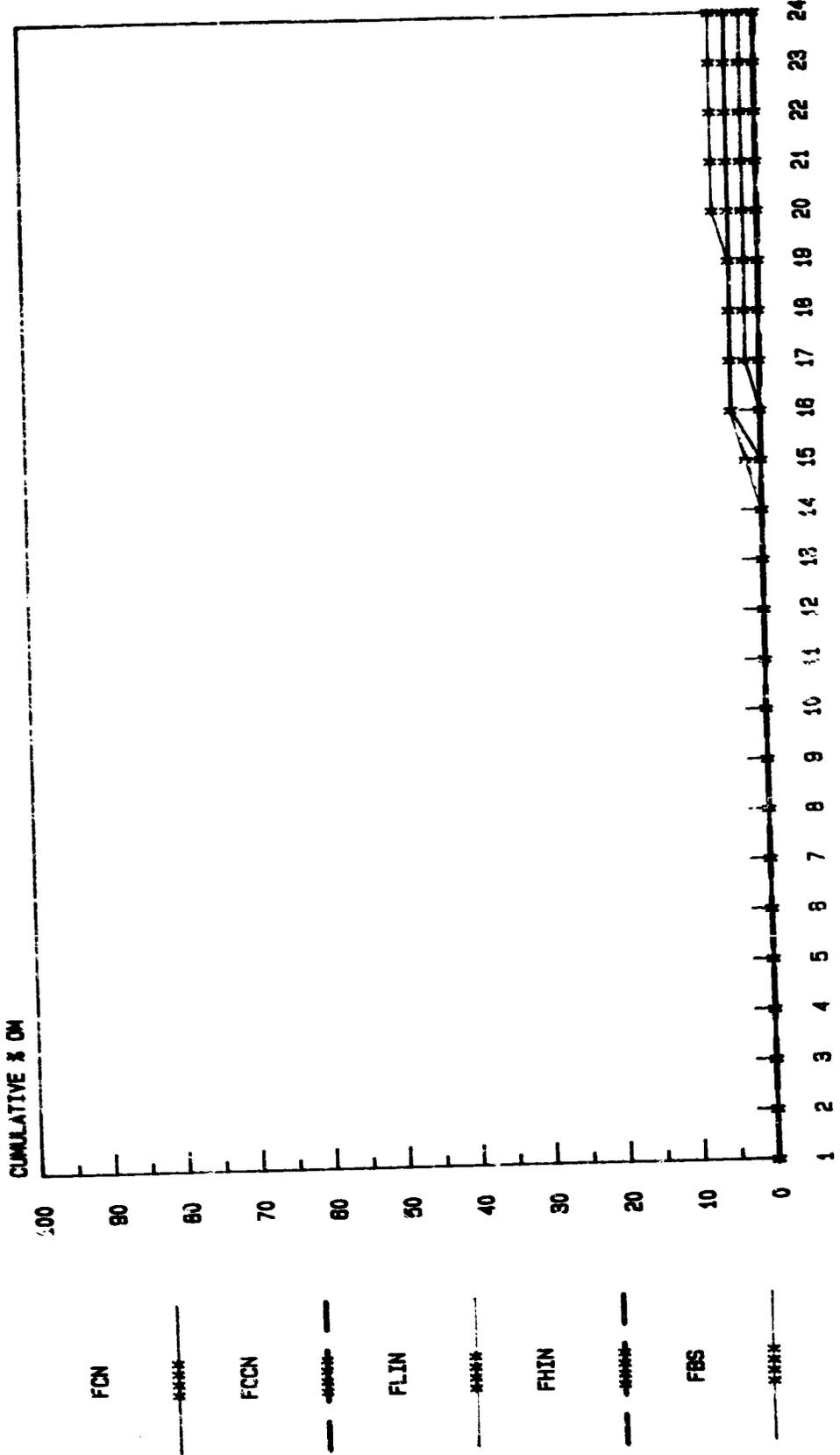
Figure 7 again demonstrates the high activity of distillates and extracts and the essentially non-tumorigenic nature of finished oils.

Figure 8 is an excellent example of the classes of activity seen in this study. There is essentially no difference between the rate and extent of tumorigenic activity for Light Intermediate Extract and Light Intermediate Cycle Oil Extract. The distillate stream is moderately active and the finished oils are both essentially non-active.

The finding that materials within classes of refinery streams share biological properties is not surprising. Also, the type and extent of biological activity demonstrated here is generally congruent with the basic physicochemical properties that should be associated with each stream class.

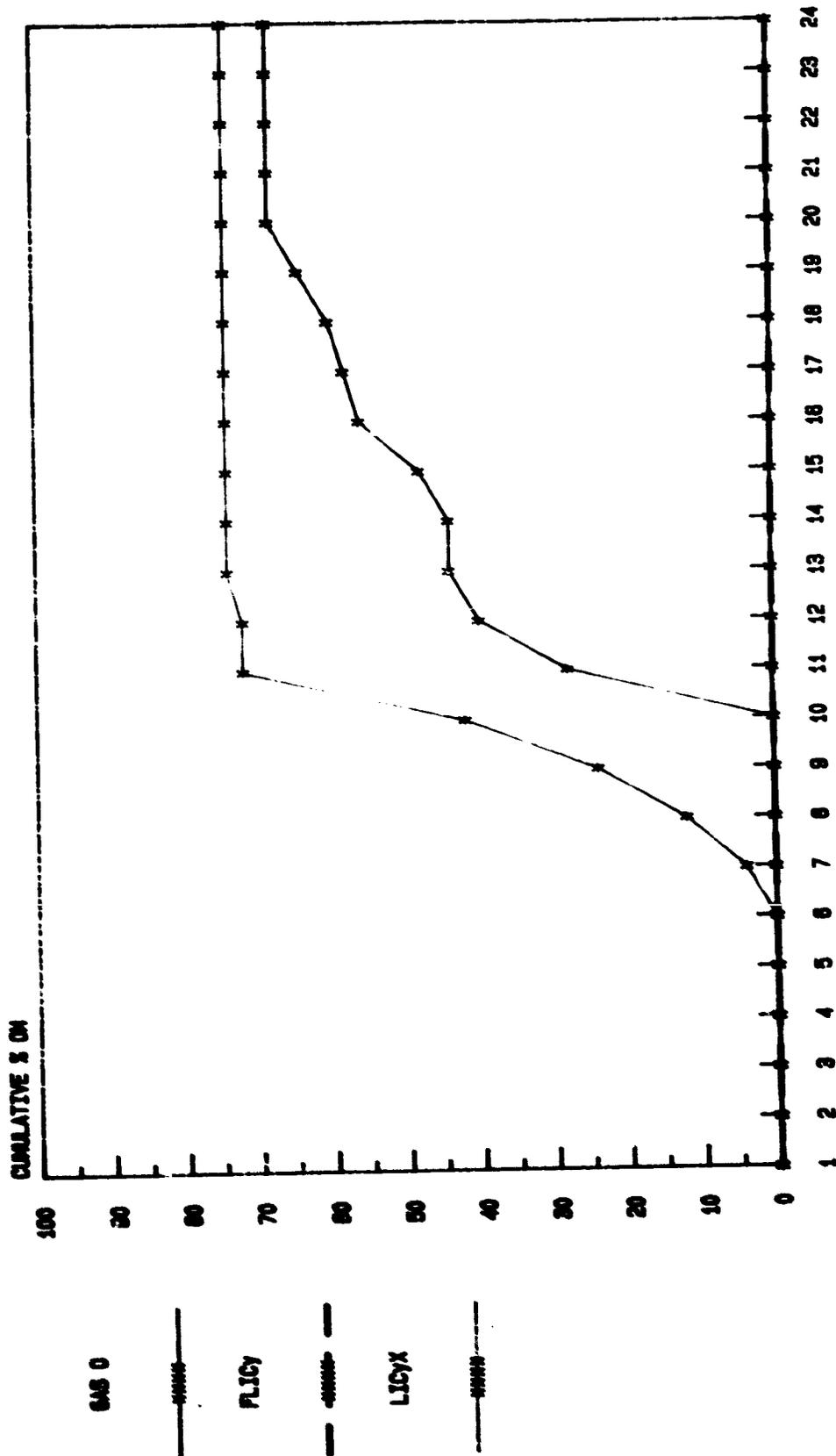
Distillates are the "first cuts" of the incoming crudes and are relatively unrefined. That is, they still contain a broad spectrum of chemical types including those with known tumorigenic activity, such as polynuclear aromatics (PNA's), heterocyclic nitrogen and sulfur

FIGURE 6  
MONTHS ON STUDY vs. CUMULATIVE % ON



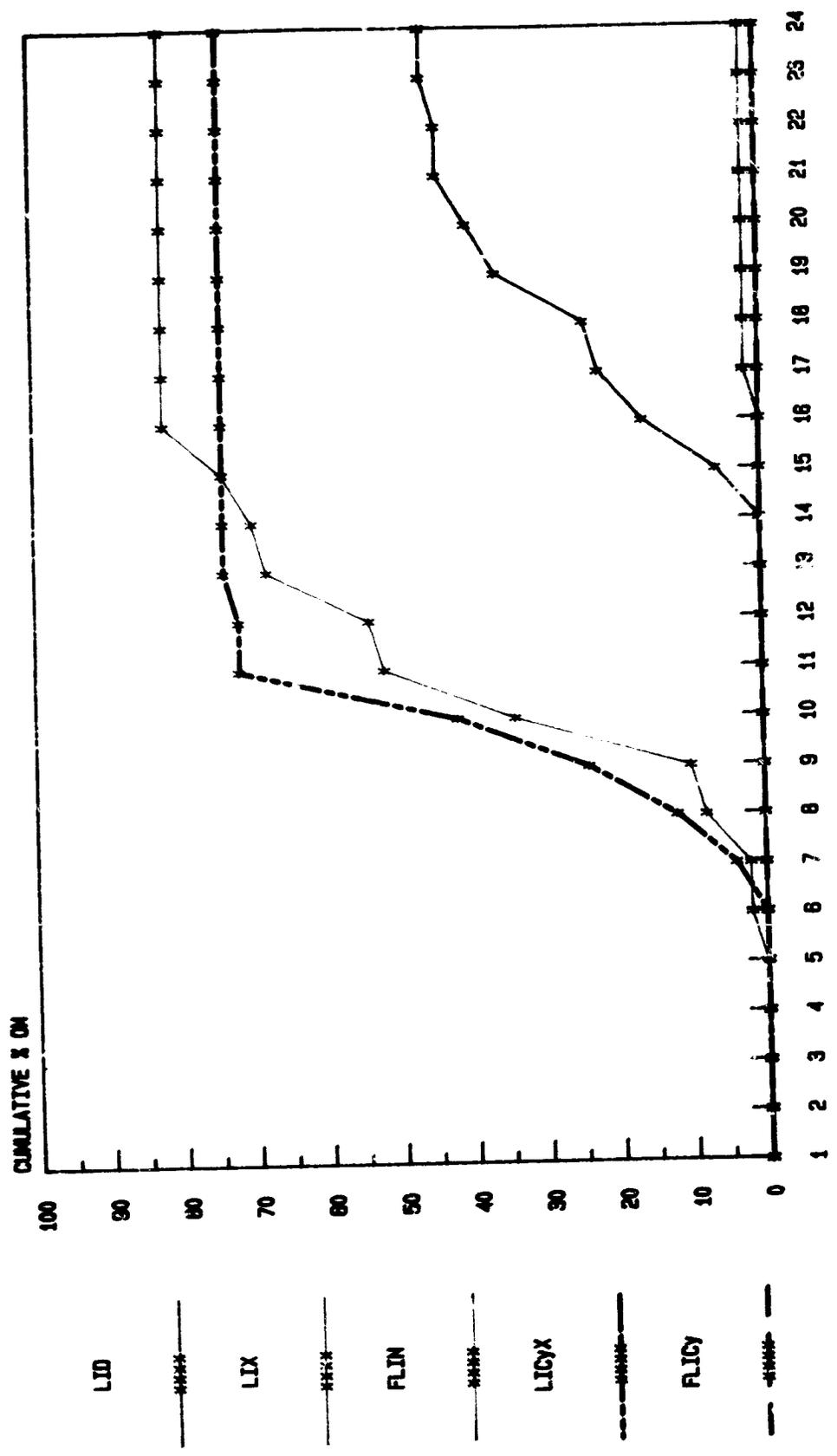
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FIGURE 7  
MONTHS ON STUDY VS. CUMULATIVE % ON



STATISTICS BY MONTH

FIGURE 8  
MONTHS ON STUDY VS. CUMULATIVE % ON



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compounds, and ring-substituted nitrogen and sulfur chemicals. Further, they contain these chemicals in proportions and types that would be expected for the boiling range and molecular weight distribution associated with each stream. Thus, it is logical that these streams would have some tumorigenic activity and that such activity would be intermediate to that found with finished oils and extracts.

The solvent extraction/refining process is designed to separate aromatics, polynuclear aromatics and relatively polar ring-substituted chemicals from the distillate feed. In so doing, essentially two streams are created, the finished highly paraffinic oils and an extractate stream enriched in the PNA's and polars. This process should produce products at the extremes of tumorigenic activity, from the essentially non-active paraffinic finished oil to the highly active aromatic extract stream. This is precisely what was demonstrated in the study.

Further, it has long been known that while certain PNA's are highly carcinogenic, eg. dimethylbenzanthracene and benzo(a)pyrene, others are non-active or only weakly so. Generally, carcinogenic PNA's contain 4 to 6 rings. Fewer or greater numbers of rings are progressively non-active. Further, the presence of 4 to 6 ring PNA's in refinery streams is roughly correlated with boiling point such that both very high boiling and very low boiling streams are

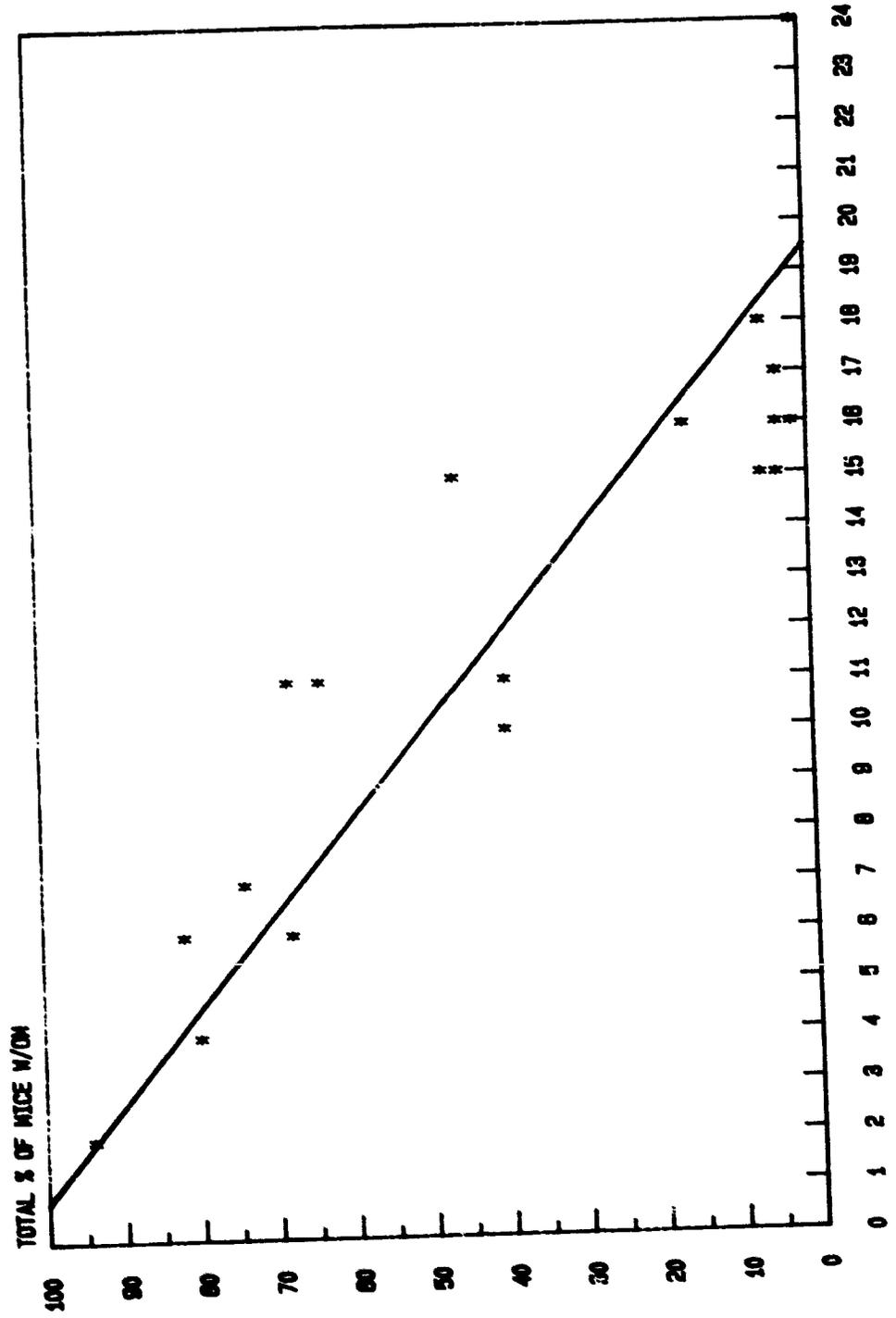
generally deficient in these, with a continuum between. In this study we see that tumorigenic activity is highest in the 200 vis stream, while above and below this stream activity begins to decline.

Figures 9 through 12 demonstrate the correlation between the time of appearance of tumors and the total final incidence of tumors associated with the test materials. Historically, two time parameters have been shown to be correlated with tumorigenic activity, the lag time from start of testing to the first appearance of tumors and the group mean or average time from start of testing to development of tumors. Figures 9 and 10 show the correlations for the time to first tumor and mean time to tumor versus the total percent incidence of tumors. In Figure 9 only 18 data points are plotted since three test materials failed to induce any tumors and in Figure 10 only eleven points are apparent since nine materials produced too few tumors to calculate the mean and one of the plotted points actually represents two different test materials with identical data.

Figures 11 and 12 are plots of time to first tumor and mean time to tumor versus the calculated minimum percent incidence of squamous cell carcinoma.

All of these correlations are strong, and highly statistically significant. Thus, the shorter the period

FIGURE 9  
TIME TO 1ST ON VS. TOTAL % OF MICE W/ON



DATA POINTS

\*\*\*\*\*

REGRESSION  
LINE

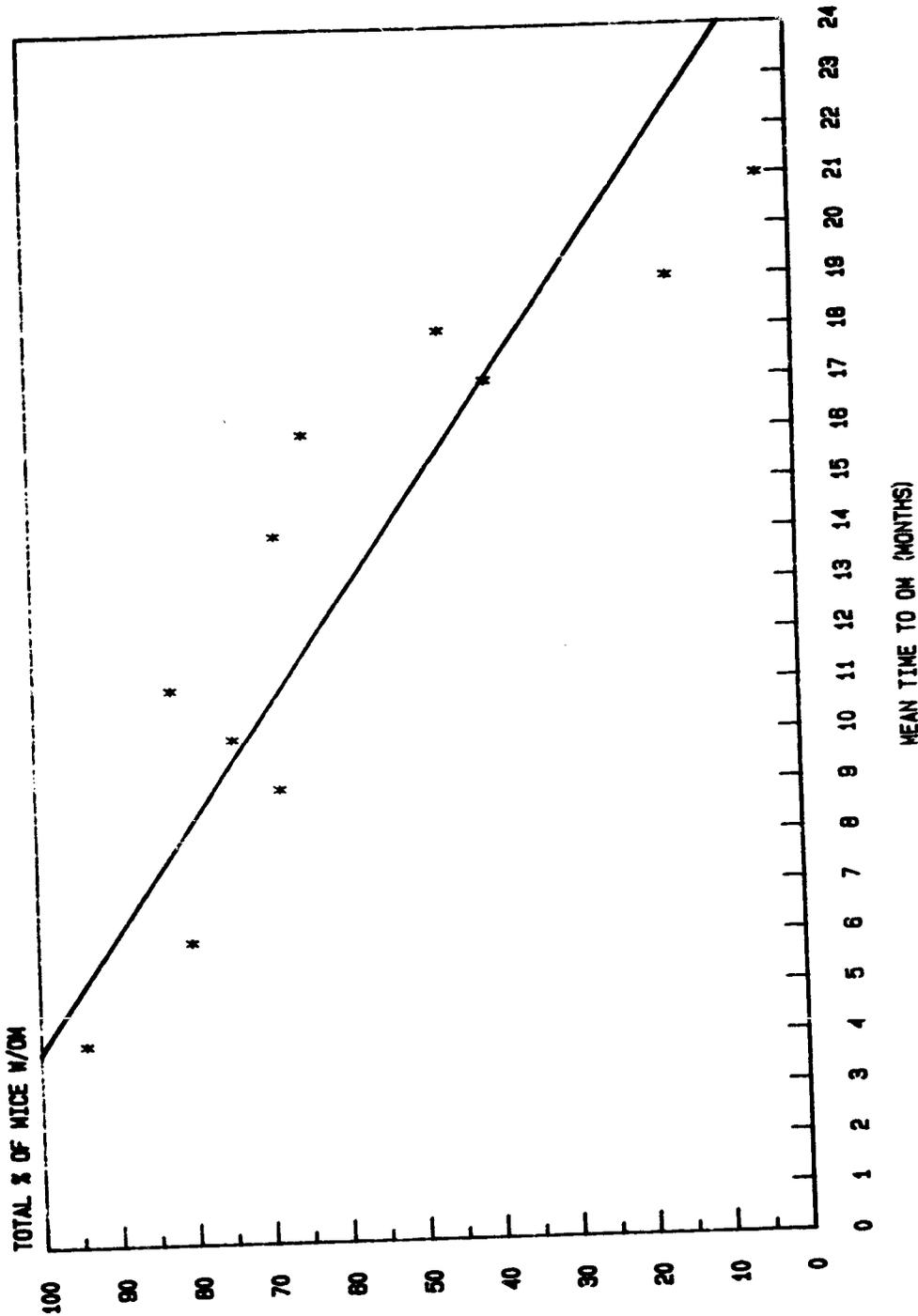
—————

CORRELATION  
COEFF. -0.802

P < 0.05 FOR  
CORRELATION

GRAPHED BY: [unreadable]

FIGURE 10  
MEAN TIME TO OM vs. TOTAL % OF NICE W/OM



DATA POINTS

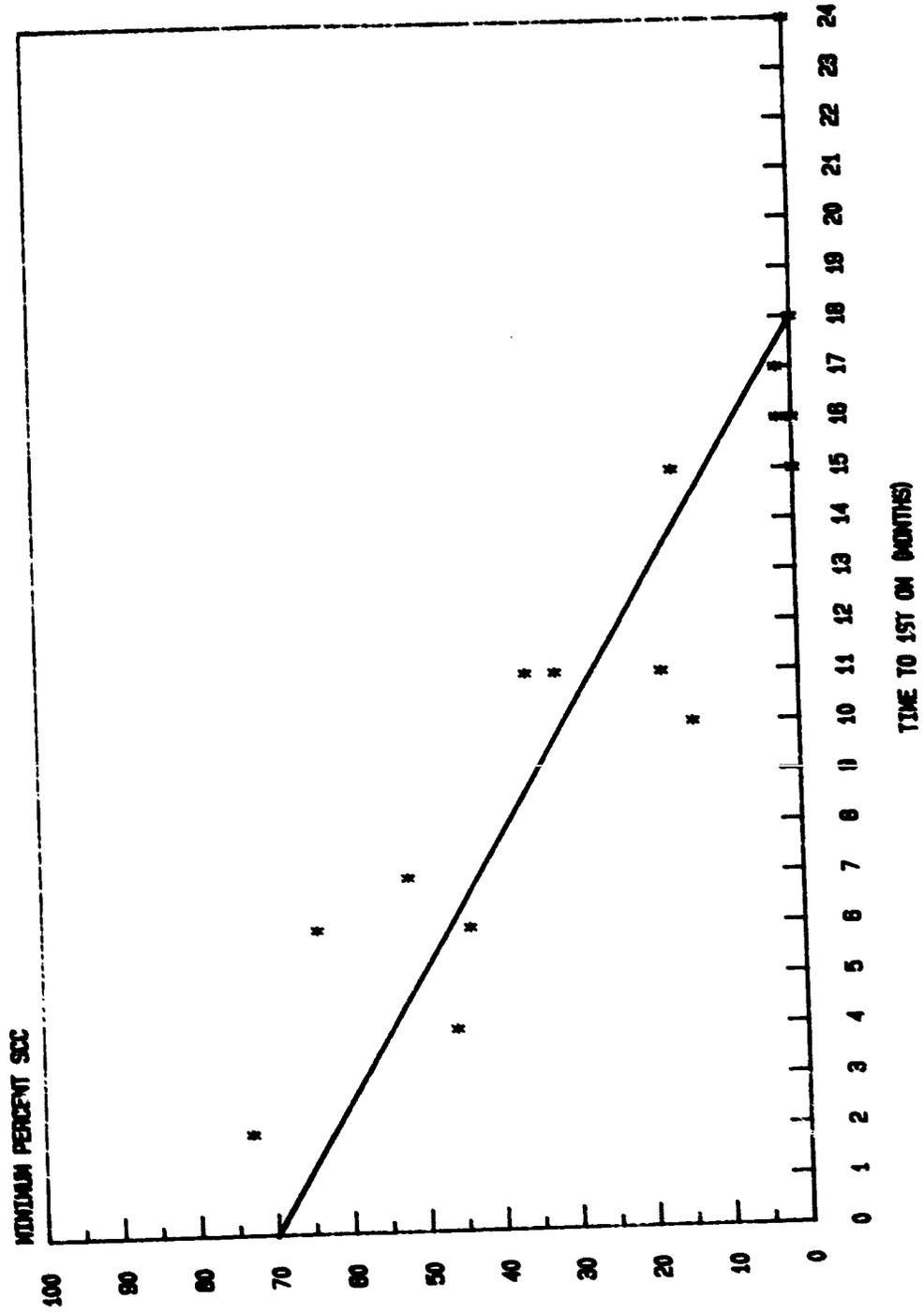
\*\*\*\*

REGRESSION  
LINE

CORRELATION  
COEFF. -0.885

P<0.05 FOR  
CORRELATION

FIGURE 11  
TIME TO 1ST ON VS. MINIMUM PERCENT SOC



DATA POINTS

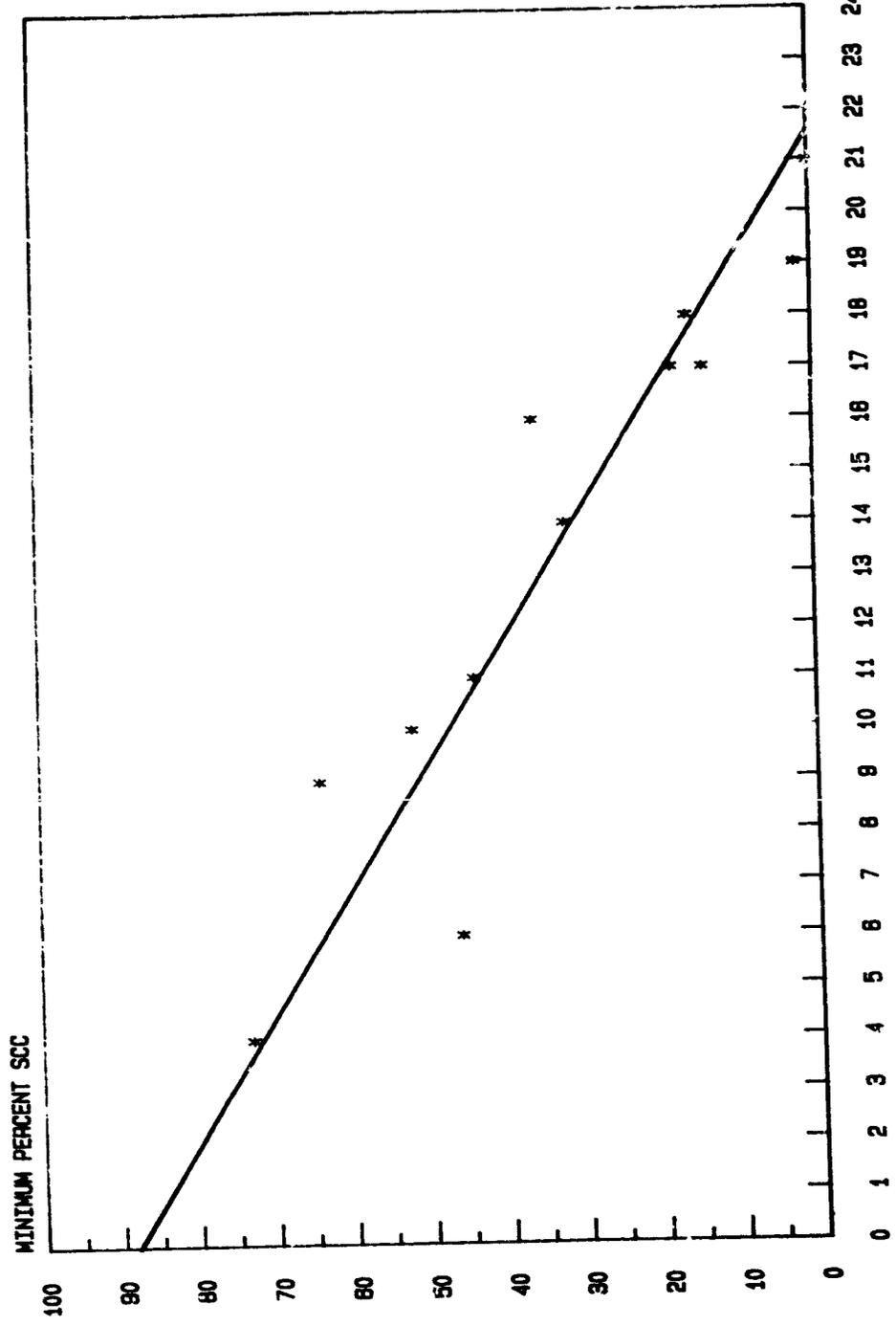
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REGRESSION  
LINE

CORRELATION  
COEFF. -0.987

P<0.05 FOR  
CORRELATION

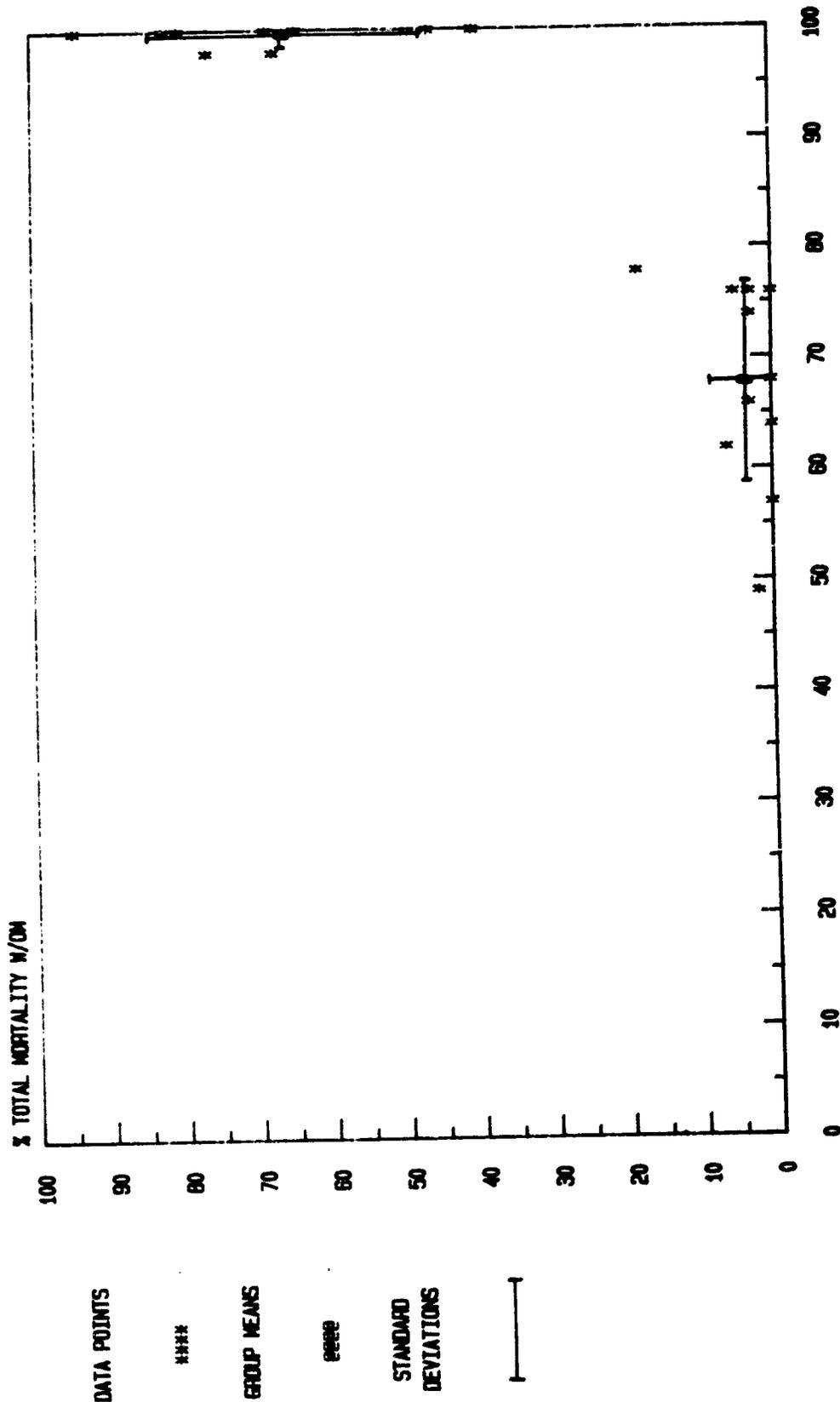
FIGURE 12  
MEAN TIME TO OM vs. MINIMUM PERCENT SCC



needed to produce tumors generally, or SCC specifically, the higher would be the expected final incidence of each. Or, in other words, potent tumorigens usually act rapidly (within a few months) while weak tumorigens take longer to express their inherent activity. This is one reason that studies of tumorigenic activity are usually conducted over the entire normal life span of the experimental animals.

Mortality. In reviewing the gross observations, it was evident that tumor production (regardless of type) had deleterious effects on the longevity of the test animals such that in groups where total tumor yield was high, so was mortality. Just how this was related was not clear. However, a regression of total percent mortality versus the fraction of mortality that was contributed by tumor bearing animals showed that the test groups were clustered in at least two major divisions, a "high mortality/high mortality with tumors group" and a "normal (or nearly so) mortality/low mortality with tumors group". This is shown in Figure 13. When the two dimensional means and standard deviations of the means were calculated, it was apparent that the data were actually composed of at least six separate subgroupings. The members of these apparent subgroups are:

FIGURE 13  
TOTAL % MORT. vs. % TOTAL MORT. W/DM



GRAPHIC PREPARED BY [unreadable]

<u>Subgroup</u>	<u>Member(s)</u>
i. Lowest Mortality/ Lowest Mortality w/OM	Untreated Control Sham Control
ii. Low Mortality/ Low Mortality w/OM	Finished 100 Neutral Finished 650 Neutral Short Residuum Finished 200 Neutral Finished Bright Stock Bright Stock Extract Finished 350 Neutral Finished 350 Cycle Oil
iii. Low Intermediate Mortality/ Low Intermediate Mortality w/OM	650 Distillate
iv. High Intermediate Mortality/ High Intermediate Mortality w/OM	100 Distillate 650 Extract 350 Distillate
v. High Mortality/High Mortality w/OM	Gas Oil 200 Distillate 100 Extract 200 Extract 350 Extract 350 Cycle Oil Extract
vi. Highest Mortality/Highest Mortality w/OM	Positive Control

Though not shown here, similar grouping results when total mortality is compared with mortality associated with squamous cell carcinoma. This is so because SCC is highly correlated with overall tumor incidence.

These data and groupings are consistent with the general tumorigenic activity of the materials tested and the general well established finding that tumors of any type have a negative effect on the general well-being and longevity of laboratory mice.

Actually, what we have here are probably "bits and pieces" of a larger single group in which the biological activity varies continuously and in a rather smooth logarithmic fashion over the range shown. Further, the differences in biological activity are probably a function of some physicochemical property(ies) that also change in similar fashion, such as PNA type/concentration versus boiling range or molecular weight distribution, etc. Additional chemical and physical data would be needed to test this hypothesis.

#### Conclusions

In summary, this study was well designed and accomplished its basic goal of separating a broad range of refinery stream types into two classes, those that are of concern with respect to carcinogenic potential and those that are not. In addition, this basic biological data can provide a foundation from which to build predictive models when correlations are developed with physicochemical parameters.

While certain administrative difficulties arose during the conduct of this study, none of these would appear to have substantial impact on the basic findings. There were few gray areas in the results. Where tumorigenic activity was found, it was strongly significant when

compared to untreated and sham controls. In addition, all of the data appear to be biologically, physically and chemically congruent. This adds to the weight of significance that can be given these findings.

The data presented in this report are believed to be accurate and reliable. No gross data for other than skin or brain tumors or histological data for other than skin or brain tissues is reported or discussed since such data were incomplete and the reliability of such data as was available is totally unknown. Therefore, no conclusions are drawn regarding the potential of the tested materials to produce either benign or malignant neoplasms in other tissues following dermal exposure.