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INFORMATION PROFILES ON POTENTIAL OCCUPATIONAL HAZARDS

VOLUME III. INDUSTRIAL PROCESSES

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INTRODUCTION

An information profile is a working paper used by the National Institute for Occupational Safety and Health (NIOSH) to assist in establishing Institute priorities. It is an initial step in determining the need to develop comprehensive documents or to initiate research. Each profile summarizes data on known and suspected health effects, the extent of worker exposure, physical and chemical properties, and the industrial importance of individual chemicals and classes of chemicals. The profile may also be used by industry, labor, and the occupational health community as a synopsis of information on each subject and to identify possible health hazards associated with their workplaces.

Although detailed literature searches are conducted using computerized and manual searching techniques to identify pertinent and recent information, not all the literature obtained is incorporated in the report due to the summary nature of the profiles. Further, literature published after 1978 may not be included in these profiles because it was generally unavailable at the time the search was completed.

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THE PETROCHEMICAL INDUSTRY

I. SCOPE OF PROFILE

The major processes used to manufacture petrochemicals have been reviewed for the purpose of identifying the potential occupational health hazards associated with the industry.

Important products of these processes, and the types of establishments primarily engaged in their manufacture, are defined by the Standard Industrial Classification Manual (SIC). Noncyclic intermediate petrochemical products are included under SIC Industry Code No. 2869, and aromatic or cyclic products are included as part of the petroleum refinery operation under SIC 2911. Full descriptions of these SIC categories are provided in Appendices A and B.

SIC 2869 applies to establishments primarily engaged in manufacturing industrial organic chemicals. The 170 listed products include, in addition to the 74 acyclic intermediate organic chemicals, other products such as synthetic perfumes and flavors, rubber additives, tanning agents, etc. Industries engaged in manufacturing plastics, synthetic rubber and fibers, wood distillation products, and urea are included in other classifications.

SIC 2911 applies to primary products made from crude petroleum. Although these are principally gasoline, distillate fuels oils and lubricants, the major primary aromatic and cyclic petrochemicals are also included in SIC 2911, as specifically explained in SIC 2865 (Appendix C).

II. SUMMARY

Each of fourteen processes by which the major petrochemicals are manufactured have been reviewed. The four processes that have inherently the highest potential for adverse health effects are judged to be:

The Dehydrogenation Process - Acyclic (Process No. 2)
The Dehydrogenation Process - Cyclic (Process No. 3)
The Halogenation Process - Acyclic (Process No. 6)
The Halogenation Process - Cyclic (Process No. 7)

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Process No. 2, used to dehydrogenate acyclic hydrocarbons, produces ethylene and propylene from crude petroleum refinery feed stock. These olefins, of all petrochemicals, have the highest total production and the greatest use as feeds for other petrochemical processes. Approximately 10,000 production workers are engaged in this process, in about 60 plants operated by over 40 companies; this is one of the larger groups in the petrochemical industry.

Process No. 3, used to dehydrogenate cyclic hydrocarbons, produces benzene, toluene, and the xylenes, which are the principal feed materials for the other cyclic petrochemical processes. This process produces the second largest quantity of petrochemicals. Approximately 8000 production workers are engaged in the process in nearly 50 plants operated by about 30 companies.

Process No. 6 is used in the halogenation of acyclic hydrocarbons, especially ethylene and methane, and in the production of chlorofluoro hydrocarbons. There are nearly 100 plants that halogenate acyclic hydrocarbons. These plants employ approximately 15,000 production workers, the largest number of workers employed in any of the several petrochemical processes.

Process No. 7 is used to halogenate cyclic products, especially benzene. This process is used in about 15 locations, and employs fewer than 2000 workers.

The dehydrogenation processes have a high potential for occupational hazard because of the large number of production workers exposed, the complexity of the operations, and the relatively severe, high operating temperatures and pressures required. In addition, the tendency to form coke and scale in the equipment and the toxicity, corrosion, and scaling effects from sulfides and other impurities contribute significantly to the potential hazards. The toxicity of benzene further adds to the potential hazards of Process No. 3.

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The Halogenation Processes, especially the chlorination processes, have a high health hazard potential because of the large number of workers exposed, the complexity of the related unit operations, the generally severe corrosive conditions arising from chlorine and byproduct hydrochloric acid, and the high toxicity of aromatic feed compounds (particularly benzene) in Process No. 7. Also, a number of the halogenated products are highly toxic.

Petrochemical workers are exposed to a myriad of specific chemical agents, each of which has characteristic toxic properties. Epidemiologic surveys have indicated that (1) workers in the petroleum refining and coal products industry have an increased risk of mortality from lung and digestive system cancer, and (2) cancer of the lung, nasal cavities and sinuses, and skin in counties with petroleum industries is increased.

In conclusion, this profile indicates that, of the fourteen processes reviewed, processes No. 2, 3, 6, and 7 appear to have the highest potential risks of occupational hazards. In the other processes, the high risk potential is not consistent, although several individual processes may have higher risks than are indicated for the entire classification. An exception to this conclusion may be made regarding Process No. 4, Oxidation Processes for Acyclic Products. Although the operations in this classification are generally simple, with few steps and involving products of relatively low toxicity, the fact that approximately 10,000 workers are exposed during production would suggest that further consideration may be warranted.

III. STATISTICAL INFORMATION

The latest Annual Survey of Manufacturers published by the Bureau of Census (Anon., 1978e) gives the total employment of production workers in 1976 for SIC 2869 to be 68,700. On the basis that 55 percent of the products listed in SIC 2869

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are petrochemical based, the number of production workers employed in 1976 on noncyclic petrochemical intermediate products would be approximately 40,000. The number of operating installations producing these chemicals was about 500, as listed in the 1977 U.S. Trade Commission report with additions from the SRI 1978 Directory of Chemical Producers; this corresponds to about 50 percent of all petrochemical operations as detailed in the following section (Production and Trends). The total number of production workers employed in the petrochemical industry may be prorated, therefore, to be about 80,000. Based on a similar derivation, the 50 major petrochemical companies employed approximately 60,000 production workers in 1976. A breakdown on the estimated number of workers employed in each of the 14 major production processes is presented in Characterization of Processes (Table 6).

Incidence rates for occupational injury and illness are presented in Table 1. It should be noted that, compared to that of the total manufacturing industry, the rates for the petrochemical industry are generally better-than-average.

IV. PRODUCTION AND TRENDS

The petrochemical industry has been engaged in producing industrial organic chemicals at rapidly growing rates since World War I. The annual U.S. production of the fifty primary and intermediate petrochemical products for 1972 and 1977, with annual growth rates for each, are listed in Table 2. These and other petrochemical products account for about 70 percent of the 150 listed in Table 3 as the most significant organic chemicals. All petrochemical products (including names of manufacturers) are fully listed in the U.S. International Trade Association report "Synthetic Organic Chemicals, U.S. Production and

Table 1. Occupational Injury and Illness Incidence Rates - 1977*

	Incidence Rates per 100 full time employees			
	Total cases	Lost work-day cases	Non fatal without lost workdays	Lost workdays
		Industrial Organic Chemical SIC 2869		
Injuries	4.8	1.9	2.9	31.0
Illnesses	0.7	0.3	0.4	3.1
Total	5.5	2.2	3.3	34.1
		Petrochemical Refining SIC 291		
Injuries	5.5	2.5	3.0	44.3
Illnesses	0.3	0.1	0.2	1.1
Total	5.8	2.6	3.2	45.4
		Average for all manufacuturing (non durable goods)		
Injuries	11.3	4.5	6.8	73.5
Illnesses	0.5	0.2	0.3	2.8
Total	11.8	4.7	7.1	76.3
		API average for 13 companies (1977)**		
Injury and Illness	4.3	1.5	2.8	24.9
		API averages for 4 best and 4 worst plants		
Injury and Illness (best 4)	3.0	1.2	1.8	21.5
Injury and Illness (worst 4)	11.5	2.4	9.1	50

*Anon., 1978a, 1979

**Anon., 1978b

Table 2. Principal Petrochemicals (Production and Other Data)

Production	Production[a] 10^9 lb. 1972	1977	Change %	No. of Plants[b]	Process No.	NIOSH Criteria Document Status	CAS Number
Ethylene	20.85	25.43	4	37	2	0	74-85-1
Propylene	8.47	13.33	11	30	2	0	115-07-1
Ethylene dichloride	7.81	11.00	8	18	6	C	156-59-2
Benzene	8.65	10.04	3	46	3	C	71-43-2
Styrene	5.94	8.87	9	14	8	I	100-42-5
Ethylbenzene	5.68	8.31	9	18	8	0	100-41-4
Toluene	6.55	7.30	2	38	3	C	108-88-3
Methanol (Synthetic)	6.47	6.45	0	12	1	C	67-56-1
p-Xylene	5.31	6.15	3	25	3	C	106-42-5
Formaldehyde	5.65	6.05	2	48	4	C	50-00-0
Vinyl chloride	5.09	5.99	3	14	6	C	75-01-4
Terephthalic acid	4.10	5.41	6	6	5	0	100-21-0
Ethylene oxide	3.96	4.36	2	16	4	C	75-21-8
Ethylene glycol	3.76	3.68	0	17	10	D	107-21-1
Butadiene	3.53	3.26	-2	20	2	0	106-99-0
Cyclohexane	2.30	3.02	6	11	8	0	110-82-7
Cumene	2.29	2.64	3	14	8	0	98-82-8
Acetic Acid (Synthetic)	2.23	2.37	1	8	4	0	64-19-7
Acetone	1.82	2.22	2	21	4	0	67-64-1
Phenol	2.05	2.13	1	16	5+	C	108-95-2
Isopropyl alcohol	1.79	1.89	1	5	11 & 10	C	67-63-0
Propylene oxide	1.52	1.87	5	6	9 - 4	0	75-56-9
Acrylonitrile	1.11	1.65	10	6	12	C	107-13-1
Vinyl acetate	1.21	1.59	6	7	11	C	108-05-4
Adipic acid	1.49	1.54	1	5	5	0	124-04-9

[a] Anon., 1978c

[b] Anon., 1978e

Key = Criteria Document Status
C - Completed
D - Deferred
I - In process
0 - None available

Table 2. Principal Petrochemicals (Production and Other Data) (Cont'd)

Production	Production[a] 10^9 lb. 1972	1977	Change %	No. of Plants[b]	Process No.	NIOSH Criteria Document Status	CAS Number
Acetic anhydride	1.57			6	4	0	104-24-7
Ethanol (Synthetic)	1.85	1.34	-6	13	10	0	64-17-5
Chloromethanes							
Phthalic anhydride	0.93	0.93	0	10	5	I	85-44-9
Fluorinated hydrocarbons	0.74	0.92	5	13	6	I	
Hexamethylene diamine	0.85	0.88	1	3	13	0	124-09-4
Caprolactam	0.64	0.87	7	5	12	0	105-60-2
Carbon tetrachloride	1.00	0.81	-4	11	6	C	56-23-5
Cyclohexanone	0.78	0.74	0	8	5	0	108-94-1
Methyl methacrylate	0.60	0.74	5	7	-	0	80-62-6
Phosgene	0.64	0.67	1	17	5	C	75-44-5
Trichloroethane	0.44	0.63	9	3	6	C	71-55-6
Perchloroethylene	0.73	0.61	-3	11	6	0	127-18-4
Ethyl chloride	0.58	0.61	1	7	6	0	75-00-3
Toluene diisocyanate	0.42	0.58	8	10	6	0	584-84-9
Nitrobenzene	0.55	0.55	0	10	14	I	98-95-3
Alkyl benzenes	0.52	0.53	0	4	8	0	
Aniline	0.41	0.52	5	7	12	0	62-53-3
Ethyl hexanol	0.53	0.49	-2	7	1	0	104-76-7
Propylene glycol	0.56	0.49	-3	6	10	0	57-55-6
Chlorobenzenes	0.47	0.48	0	10	7	I	108-90-7
Bisphenol A	0.26	0.45	14	4	8	0	80-05-7
Diethylene glycol	0.25	0.33	5	18	4	0	111-46-6
Trichloroethylene	0.43	0.30	-6	5	6	C	79-01-6
Maleic anhydride	0.27	0.29	1	10	8	0	108-31-6

Table 3. The Most Significant Organic Chemicals by Quantity of Production (Austin, 1974)

Chemical	Production, 10^9 Lb/Yr
Ethylene dichloride	7.45
Urea	6.24
Methanol, synthetic	4.93
Ethyl benzene	4.83
Formaldehyde (37% solution)	4.43
Styrene	4.34
Vinyl chloride (monomer)	4.04
Ethylene oxide	3.86
Ethylene glycol	3.04
Cumene	1.98
Ethyl alcohol (synthetic)	1.96
Acetic acid (synthetic)	1.93
Isopropyl alcohol	1.92
Cyclohexane	1.84
Phenol	1.75
Acetone	1.62
Acetaldehyde	1.61
p-Xylene	1.59
Acetic anhydride	1.59
Dimethyl terephthalate	1.45
Terephthalic acid	1.33
Propylene oxide	1.18
Adipic acid	1.08
Acrylonitrile	1.04
Carbon tetrachloride	1.01
Potassium & sodium salts of rosin and tall oil acids	0.924
Cellulose acetate	0.820
Vinyl acetate	0.803
o-Xylene	0.799
Phthalic anhydride	0.734
Carbon disulfide	0.721
Cyclohexanone	0.714
Perchloroethylene	0.707
Ethyl chloride	0.678
Phosgene	0.617
Hexamethylene diamine	0.613
Trichloroethylene	0.610
Alkyl benzenes	0.553
Nitrobenzene	0.548
Sodium slats of tallow acids	0.505
Tetra (methyl -ethyl) leads	0.504
Chlorobenzene	0.485
Methyle ethyl ketone	0.480
n-Butanol	0.468
2-Ethyl-1-hexanol	0.457
Methyl methacrylate	0.445
Propylene glycol	0.428
Methyl chloride	0.423
Methylene chloride	0.402
Dodecylbenzene sulfonic acid, sodium salt	0.401
Aniline	0.398
Dichlorodifluoromethane	0.375
1,1,1-Trichloroethane	0.366
Di(2-ethylhexyl) phthalate	0.350
Diethylene glycol	0.341
Tetraethyl lead	0.325
Lignin sulfonic acid, calcium salt	0.310
Toluene 2,4- and 2,6-diisocyanate (80/20 misture)	0.305
Ethylene dibromide	0.297
2,4- and 2,6-Dinitrotoluene	0.297
Trichlorofluoromethane	0.244
Chloroform	0.240
Maleic anhydride	0.215
Ethyl acrylate	0.207
Bisphenol A	0.202
Methyl isobutyl ketone	0.199
Glycerol tri(polyoxypropylene) ether	0.192
Glycerol, synthetic	0.191
Ethyl acetate (85%)	0.161
Decyl alcohols	0.157
Nonyl phenol, ethoxylated	0.142
Dodecylbenzene sulfonic acid	0.139
Tridecylbenzene sulfonic acid, sodium salt	0.138
Ethylene glycol monoethyl ether	0.136
Sodium and potassium salts of coconut oil acids	0.133
Toluene 2,4-diamine	0.133
Di-isodecyl phthalate	0.123
Ethylene glycol monobutyl ether	0.107
Sorbitol	0.105
Acrylic acid	0.100
Isooctylalcohols	0.100
m-Xylene	0.099
Cresylic acid (refined)	0.098
Ethylene glycol monomethyl ether	0.097
Diethanol amine	0.094
Isobutyl alcohol	0.092
Triethylene glycol	0.089
Polypropylene glycol	0.089
1-Chloro-4-nitrobenzene	0.088
Monoethanolamine	0.087
Pentaerythritol	0.085
Di-isooctyl phthalate	0.085
n-Butyl acrylate	0.084
Triethanolamine	0.083
α and *β* Pinenes	0.081
Dimethyl amine	0.078
Nonyl phenol	0.078
Hexamethylenetetramine	0.077
Benzyl chloride	0.075
n-Butyl acetate	0.074
Lignin sulfonic acid, sodium salt	0.074
p-Dichlorobenzene	0.070
Melamine	0.068
Dicyclopentadiene	0.067
o-Dichlorobenzene	0.066
Sodium carboxymethyl cellulose	0.065
Ethylene diamine	0.062
n-Propyl alcohol	0.060
α-bis (*p*-chlorophenyl)-*βββ*-trichloroethane (DDT)	0.059
n-Octyl-*n*-decyl phthalate	0.059
Fumaric acid	0.053

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Sales 1977" (Anon., 1978c). Selected data on these, the synthetic organic products, are summarized in Table 4 with the approximate corresponding SIC classifications (Anon., 1972). Production and growth data for the 28 largest volume petrochemical products, derived from a compilation of the 50 highest volume chemicals produced in the U.S. in 1977 (Anon., 1978), is presented in Table 5. Although organic chemical products made from other sources are included in Table 5, the quantities produced from these sources are minor relative to the petroleum based products.

V. CHARACTERIZATION OF PROCESSES

The major petrochemical operations are located in or near crude oil refineries, pipelines, or other facilities that supply the required feed materials. These primary feeds are produced from three main reforming sources by the refineries:

1. Synthesis gas, CO, and hydrogen, for manufacturing C-1 (monocarbon) chemicals, e.g., methanol.
2. Liquefiable refinery gases and light naphthas, for producing acyclic olefins, ethylene, propylene, butadiene, etc.
3. Heavy reformates, for producing cyclic products, benzene, toluene, xylene, etc.

The prime products made from these sources feed the other conversion processes from which all the many intermediate synthetic organic chemicals are produced. These intermediates are used, in turn, to manufacture the many thousands of end use chemical products such as dyes, pigments, and medicinal chemicals (Gibbs *et al*., 1968).

For the purpose of this study, the major processes for manufacturing the principal petrochemicals and nearly all the derivatives have been classified by the reaction type involved, as follows:

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Table 4. Synthetic Organic Chemicals (Anon., 1978c)

	Production			Sales						
				Quantity			Value			
	Billion lb.		Annual Increase	Billion lb.		Annual Increase	Billion $		Annual Increase	SIC Equivalent (approximate)
	1972	1977	%	1972	1977	%	1972	1977	%	
	(a)			(a)			(a)			
Primary products from petroleum & natural gas	106	126.1	3	56	61.0	2	2	5.8	25	2911
Synthetic cyclic organic chemical intermediates	15	18.7	5	7	8.0	3	1+	2.6	20±	2911
Micellaneous cyclic and acyclic chemicals	90	87.0	-1	45	38.7	-1	5	7.9	10	2869
Total petroleum based organic chemicals	211	231.8	2	108	107.7	-0	8	16.3	15	--
Miscellaneous end-use chemicals and chemical products	39	68.8	12	33	51.1	10	8	21.9	25	(b)
Total synthetic organic chemicals	250	300.6	4	141	158.8	2	16	38.2	22	--

(a) Adjusted to 1977 classifications (Approx.)
(b) Includes end-use products - dyes, pigments, medicinal chemicals classified under SIC 2865

Table 5. Organics Scored Biggest Gains Among the 50 Top-Volume Chemicals (Anon., 1978)

Rank			Production				Average annual change			
			Billions of lb		Common units[b]					
1977	1976[a]		1977	1976	1977	1976	1976–77	1975–76	1972–77	1967–77
1	1	**Sulfuric acid**	68.80	67.00	34,400 tt	33,501 tt	2.7%	4.2%	2.1%	1.9%
2	2	**Lime**[c]	37.78	38.10	18,888 tt	19,050 tt	−0.9	5.0	−0.4	1.9
3	3	**Ammonia**, anhydrous	32.35	33.43	16,176 tt	16,716 tt	−3.2	2.0	1.3	3.3
4	4	**Oxygen**, high and low purity	31.86	31.70	385 bcf	383 bcf	0.5	8.5	1.9	5.8
5	5	**Ethylene**	24.65	22.03	24,653 mp	22,027 mp	11.9	7.5	3.6	10.8
6	6	**Nitrogen**, high and low purity	24.04	21.01	332 bcf	290 bcf	14.4	14.6	14.2	22.4
7	8	**Chlorine**, gas	21.3	20.12	10,658 tt	10,060 tt	5.9	10.5	1.6	3.9
8	7	**Sodium hydroxide**	21.0	20.29	10,483 tt	10,143 tt	3.4	5.9	0.5	3.2
9	11	**Sodium carbonate**[d]	15.97	14.92	7,986 tt	7,459 tt	7.1	4.2	1.5	4.3
10	9	**Phosphoric acid**, total	15.60	15.92	7,802 tt	7,958 tt	−2.8	3.7	3.2	5.0
11	10	**Nitric acid**	14.77	15.79	7,387 tt	7,894 tt	−6.4	4.8	−1.5	1.8
12	12	**Ammonium nitrate**[e]	13.97	14.37	6,987 tt	7,187 tt	−2.8	1.4	0.4	2.2
13	14	**Propylene**	12.56	9.76	12,563 mp	9,758 mp	28.7	12.0	9.7	11.8
14	13	**Benzene**	11.25	10.61	1,535 mg	1,448 mg	6.0	41.4	4.5	5.8
15	16	**Ethylene dichloride**	10.48	7.92	10,481 mp	7,923 mp	32.3	−0.7	6.8	16.4
16	17	**Urea**, primary solution	8.99	7.72	8,990 mp	7,721 mp	16.4	1.6	5.3	10.6
17	15	**Toluene**, all grades	7.73	8.22	1,067 mg	1,135 mg	−6.0	61.0	3.3	6.6
18	21	**Ethylbenzene**	7.30	6.13	7,302 mp	6,127 mp	19.2	27.1	5.7	11.8
19	19	**Styrene**	6.82	6.30	6,824 mp	6,301 mp	8.3	23.3	3.0	10.8
20	20	**Methanol**, synthetic	6.46	6.24	6,457 mp	6,241 mp	3.5	20.6	1.3	8.8
21	23	**Formaldehyde**, 37% by weight	6.08	5.62	6,085 mp	5,621 mp	8.3	23.3	1.5	6.4
22	18	**Xylene**, all grades	6.05	7.28	839 mg	1,010 mg	−16.9	58.1	2.7	8.4
23	22	**Vinyl chloride**	5.81	5.64	5,808 mp	5,736 mp	1.3	36.7	2.8	14.0
24	25	**Hydrochloric acid**	5.13	4.86	2,566 tt	2,428 tt	5.7	22.1	2.0	5.8
25	24	**Terephthalic acid**[f]	5.01	5.05	5,009 mp	5,051 mp	−0.8	9.5	13.6	35.7
26	28	**Carbon dioxide**, all forms	4.45	3.93	2,226 tt	1,967 tt	13.2	6.3	7.7	10.5
27	26	**Ethylene oxide**	4.42	4.18	4,421 mp	4,184 mp	5.7	−6.3	2.3	9.2
28	27	**Ammonium sulfate**	3.82	4.40	1,909 tt	2,202 tt	−13.3	4.6	0.5	−0.1
29	32	**Carbon black**	3.48	3.02	3,477 mp	3,023 mp	15.0	9.7	1.9	4.0
30	29	**Ethylene glycol**	3.47	3.36	3,470 mp	3,357 mp	3.4	−11.9	−1.5	7.4
31	30	**Butadiene** (1,3-), rubber grade	3.19	3.25	3,187 mp	3,254 mp	−2.1	25.3	−1.9	2.0
32	31	***p*-Xylene**	3.02	3.20	3,017 mp	3,199 mp	−5.7	28.7	7.3	29.9
33	33	**Cumene**	2.64	2.69	2,639 mp	2,690 mp	−1.9	34.3	3.0	13.3
34	35	**Acetic acid**, synthetic	2.58	2.43	2,579 mp	2,430 mp	6.1	10.6	3.1	6.5
35	34	**Sodium sulfate**[g]	2.51	2.52	1,256 tt	1,258 tt	−0.2	2.5	−1.0	−0.8
36	36	**Calcium chloride**[h]	2.42	2.40	1,212 tt	1,200 tt	1.0	2.5	0.7	0.4
37	37	**Phenol**, synthetic	2.38	2.18	2,384 mp	2,183 mp	9.2	25.0	5.0	8.4
38	37	**Aluminum sulfate**	2.32	2.18	1,162 tt	1,089 tt	6.7	−6.3	−0.4	1.2
39	37	**Cyclohexane**	2.24	2.18	2,242 mo	2,177 mp	3.0	25.5	−0.5	2.6
40	40	**Acetone**	2.14	1.92	2,145 mp	1,922 mp	11.6	17.2	4.7	6.7
41	41	**Propylene oxide**	1.90	1.79	1,897 mp	1,795 mp	5.7	17.8	5.0	13.3
42	42	**Isopropyl alcohol**	1.87	1.72	1,873 mp	1,720 mp	8.9	13.1	0.9	−0.9
43	45	**Adipic acid**	1.85	1.51	1,853 mp	1,515 mp	22.3	12.7	4.9	9.1
44	45	**Acrylonitrile**	1.64	1.52	1,642 mp	1,518 mp	8.2	24.9	9.5	14.5
45	47	**Vinyl acetate**	1.60	1.48	1,604 mp	1,481 mp	8.3	14.8	6.5	16.6
46	44	**Sodium silicate**	1.56	1.57	779 tt	786 tt	−0.9	8.6	3.6	2.7
47	43	**Acetic anhydride**	1.50	1.51	1,504 mp	1,507 mp	−0.1	3.4	−0.9	−0.3
48	49	**Titanium dioxide**	1.36	1.43	678 tt	716 tt	−5.3	18.5	−0.4	1.5
49	48	**Sodium tripolyphosphate**	1.30	1.46	648 tt	730 tt	−11.2	−5.2	−7.5	−3.8
49	50	**Ethanol**, synthetic	1.30	1.18	1,304 mp	1,181 mp	10.4	−17.3	−5.9	−3.2

a Revised. b tt = thousand tons, bcf = billion cubic feet, mp = million pounds, mg = million gallons. c Except refractory dolomite. d Synthetic and natural. e Original solution. f Includes both the acid and the ester without double counting. g High and low purity. h Solid and liquid. **Sources:** Bureau of the Census, Bureau of Mines, International Trade Commission, and C&EN estimates

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Process #1	High pressure catalytic synthesis, such as methanol from synthesis gas
Process #2	Dehydrogenation of acyclic light crudes by pyrolysis, producing ethylene and other olefins.
Process #3	Dehydrogenation of cyclic heavy crudes, producing aromatics, benzene, etc.
Process #4	Oxidation processes for acyclic products
Process #5	Oxidation processes for cyclic products
Process #6	Halogenation processes for acyclic products
Process #7	Halogenation processes for cyclic products
Process #8	Alkylation and dealkylation processes
Process #9	Chlorohydrin oxidation process
Process #10	Hydration processes
Process #11	Esterification processes
Process #12	Ammonia reaction processes
Process #13	Hydrogenation processes
Process #14	Acid reactions with aromatic chemicals (e.g., nitration)

Table 6 outlines each of the above processes, giving the main reaction, the range of required process conditions, and the steps involved. Also included are the principal products made by each process, the number of principal establishments using the process, and an approximation of production workers exposed. The classifications are based soley on main overall reaction types; individual steps and reaction conditions (e.g., temperature and pressure) required for the production of specific products differ considerably. Further, specific processes differ in complexity and in the number of unit operations employed, and involve one or more of many differing preparatory and finishing unit operations.

Table 6. Summary of Principal Processes for Petrochemical Manufacture

Process		Main Reaction	Principal Unit Operations	Process Conditions	Major Products	Principal Installations (Approx. No.)	Workers (Approx. No.)
No.	Name						
1	Synthesis Gas Reactions	Catalytic reaction of carbon monoxide and hydrogen <u>Type of Reaction</u> $CO + 2H_2 \xrightarrow{Cat} CH_3OH$	Compression of gases Heated catalytic converter Condensation Distillation	3000-5000 psi and 300°C to 600°C (Recent Plants 750 psi)	Methyl Alcohol Acetylene by Sachsse Process	20	3,000
2	Dehydrogenation for Acyclic Products	Pyrolysis of refinery gases and light naphthas with steam <u>Type of Reaction</u> $C_nH_{2n+2} \xrightarrow{Cat} C_nH_{2n} + H_2$	Preheating Reacting in tubular or other type furnace Quenching Liquefaction Fractionation	800-900°C and 500 psi	Ethylene Propylene Acetylene by Wolff Process	60	10,000
3	Dehydrogenation for Cyclic Products	Pyrolysis of refinery distillates with recycled hydrogen (hydroforming) <u>Type of Reaction</u> $C_5H_8CH_3 \xrightarrow{Cat} C_6H_6 + 2\ 1/2H_2$	Staged preheat and reaction Solvent extractor Washing ⎫ Stripping ⎬ Undex Process Fractionation ⎭	500°C and 200 to 1000 psi	Benzene Toluene Xylene	50	8,000
4	Oxidation for Acyclic Products	Catalytic oxidation of C-1 - C-4 hydrocarbons with air or oxygen <u>Type of Reaction</u> $C_nH_{2n} + 1/2O_2 \xrightarrow{Cat} C_nH_{2n}O$	Mixing Gas or vapor phase reaction Cooling Absorbing Stripping Fractionating	<300-400°C 100 psi ±	Acetaldehyde from ethylene Acetic acid from acetaldehyde Acetic anhydride from acetaldehyde Acetone from isopropyl alcohol Formaldehyde from methyl alcohol Ethylene oxide from ethylene Ethyl acrylate from propylene	100	10,000
5	Oxidation for Cyclic Products	Catalytic oxidation of aromatic hydrocarbons with air or oxygen <u>Type of Reaction</u> $C_6H_{12} + 2O_2 \xrightarrow{Cat} HOOC(CH_2)_4COOH$	Reacting with air in vapor or liquid phase Condensing Distilling Crystallizing Drying	<250°C <200 psi	Adipic acid from cyclohexane Cyclohexanone from cyclohexane Benzoic acid from toluene Terephthalic acid from p-xylene Maleic anhydride from benzene Phthalic acid from naphthalene Phenol from cumene	60	8,000

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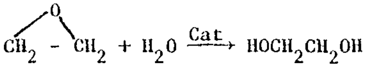
Table 6. Summary of Principal Processes for Petrochemical Manufacture (Cont'd)

Process		Main Reaction	Principal Unit Operations	Process Conditions	Major Products	Principal Installations (Approx. No.)	Workers (Approx. No.)
No.	Name						
6	Halogenation of Acyclic Products	Catalytic reaction of C-1-C-4 hydrocarbons with halogens Type of Reaction $CH_4+2Cl_2 \xrightarrow{Cat} CH_2Cl_2 + 2HCL$ $CH_2:CH_2 + Cl_2 \longrightarrow ClCH_2CH_2Cl$	Vapor and liquid phase reaction with halogen or halogen acid Absorption Scrubbing Fractionation Acid recovery	<700°C <100 psi	Chloro methanes Fluorochlorocarbons from carbon tetrachloride Ethylene dichloride Ethylene dibromide Perchlorethylene Chloroacetic acid	80	15,000
7	Halogenation of Cyclic products	Catalytic reaction of chlorine with aromatic products Type of Reaction $C_6H_6+2Cl_2 \xrightarrow{Cat} C_6H_4Cl_2+2HCl$	Vapor or liquid phase reaction Scrubbing Neutralizing Fractionation Acid disposal recovery	<200°C <50 psi	Chlorobenzenes Benzyl chloride	15	2,000
8	Alkylation and Dealkylation	Catalytic Synthesis of acylic hydrocarbons with aromatic hydrocarbons (and reverse) Type of Reactions $C_6H_6+CH_2CH_2 \xrightarrow{AlCl_3} C_6H_5CH_2CH_3$ $C_6H_5CH_3+H_2 \longrightarrow C_6H_5+CH_4$	Liquid and vapor phase reaction under pressure with catalyst Flash separator Scrubbing Fractionation	alkylation <300° <700 psi dealkylation 700°C 1200 psi	Ethylbenzene from ethylene and benzene Cumene from propylene Benzene from toluene Naphthalene from methyl naphthalene	30	5,000
9	Chlorohydrin Oxidation	Hypochlorination of propylene with hydrolysis with lime Type of Reactions $CH_2:CHCH_3+HOCl \longrightarrow$ $CH_2ClCH(OH)CH_3+Ca(OH)_2 \longrightarrow$ $CH_3\underset{\diagdown O \diagup}{CH - CH_2}+CaCl_2+H_2O$	Reaction of propylene with chlorine in water Separation of unreacted gases Hydrolysis Separation by flashing Condensing Fractionation	<100°C <50 psi	Propylene oxide	9	2,000

Table 6. Summary of Principal Processes for Petrochemical Manufacture (Cont'd)

Process		Main Reaction	Principal Unit Operations	Process Conditions	Major Products	Principal Installations (Approx. No.)	Workers (Approx. No.)
No.	Name						
10	Hydration	Hydrating oxide Typical Reaction $\overset{O}{CH_2 - CH_2} + H_2O \xrightarrow{Cat} HOCH_2CH_2OH$	Reaction in pressure system Vacuum distillation for glycols Vapor phase reaction under pressure for alcohols Neutralizing Distillation	For glycols <200°C <200 psi For alcohol 300°	Ethylene glycol Propylene glycol Ethanol from ethylene Isopropyl alcohol from propyl sulfate	40	5,000
11	Esterification	Formation of organic salts by reactions with organic and other acids Typical Reactions $CH_2{=}CH_2 + CH_3COOH + 1/2O_2 \longrightarrow CH_3COOCH{:}CH_2 + H_2O$	Reaction in batch and tubular reactors Cooling, condensing-washing Fractionation	<200°C <150 psi	Vinyl and ethyl acetates Ethyl sulfate	20	3,000
12	Reactions with ammonia	Catalytic Reaction of ammonia with olefins alcohols and aromatic chloride Typical Reaction $C_3H_6 + NH_3 + 1\ 1/2\ O_2 \longrightarrow CH_2{:}CH.CN + 3H_2O$	Reaction in batch autoclave or fluid bed reactors Cooling Stripped Neutralized Fractionated	<500°C <800 psi	Acrylonitrile Aniline Alkyl Amines	25	4,000
13	Hydrogenation	Catalytic reaction of hydrogen with aromatic chemicals Typical Reaction $C_6H_6 + 3H_2 \xrightarrow{Cat} C_6H_{12}$	Exothermic reactions conducted in series with alternate direct cooling followed with recovery and purification steps	<300°C <1000 psi	Cyclohexane from benzene Hexamethylene diamine from adiponitrile	25	3,000
14	Acid Reactions with Aromatic Chemicals	Nitration and sulfonation of aromatics Typical Reaction $C_6H_6 + HNO_3 \xrightarrow{H_2SO_4} C_6H_5NO_2 + H_2O$ $C_6H_6 + H_2SO_4 \longrightarrow C_6H_5SO_3H + H_2O$	Reaction of aromatics with nitric or sulfuric acids Acid separation Neutralization Distillation	<100°C 0 psig	Nitrobenzene Benzenesulfonic acid	15	3,000

The number of installations or plants listed in Table 6 for each process has been estimated from the listing for the main products in each group in the 1977 U.S. International Trade Commission report (Anon., 1978c) with additions from the SRI 1978 Directory of Chemical Producers (Anon., 1978d). Similarly, the number of production workers for each process was estimated from the number of locations and the complexity of the process on the basis of the total number of production workers approximated for the entire industry in Section III. A sample calculation in presented in Appendix D.

Explanatory text and schematic flow diagrams, which more fully characterize the reaction sequences involved in each process and sources of potential hazards, are subsequently presented. Each flow diagram also indicates the nature of the main stream flow and of off stream flows at various points in the process. The information presented in both the process descriptions and the flow diagrams was drawn principally from the following sources:

The Chemistry of Petrochemicals (Astle, 1956)

Faith, Keyes, and Clark's Industrial Chemicals (Lowenheim and Moran, 1975)

"Industrial Hygiene Monitoring Manual for Petroleum Refineries and Petrochemical Process" (API, 1977)

"The Industrially Significant Organic Chemicals" (Austin, 1974)

Kirk-Othmer Encyclopedia of Chemical Technology (Anon., 1965)

"Petrochemical Handbook" (Anon., 1977b)

Petroleum Refinery Operation (Nelson, 1958)

Unit Processes in Organic Synthesis (Groggins, 1958)

Process No. 1 - Pressure Synthesis

Catalytic conversion of synthesis gas into methanol supplies feed for the manufacture of C_1 hydrocarbons such as formaldehyde and methyl compounds.

Formerly the process was run at 5000 psi and 300-600°C with zinc-chromium catalysts, which were necessitated by the presence of sulfur impurities. With recent improvements in sulfur removal, new plants are run with other catalysts at about 750 psi (Austin, 1974). The high pressure, corrosive effects of sulfur, the toxicity of the carbon monoxide and hydrogen and fouling from coke formation, add, especially in earlier installations, to safety problems and to the risk of potential occupational hazards. The process is used in about 20 principal locations for methanol and BASF or Sachsse acetylene and judged to employ about 3000 production workers.

The process as used for the production of methanol, shown by Flow Diagram No. 1, is comparatively simple with 4-5 steps. The indicated purge and vent gases released to the atmosphere require control and monitoring to minimize potentially hazardous exposures.

Process No. 2 - Dehydrogenation - (Acyclic Products)

Catalytic and thermal cracking of refinery feed stocks rich in ethane and propane produce primary acyclic chemicals such as ethylene, propylene, butadiene, etc. The reaction is controlled to minimize coke deposition at 800-900°C by steam addition. With subsequent quenching, liquefaction at about 500 psig, and purification, the process has about 15 steps. Ethylene is produced as the main product, with propylene and butadiene as coproducts, in proportions that follow the composition of the feed. The tendency to scale the equipment with coke and other decomposition products, the corrosion and toxicity caused by sulfur and carbon monoxide impurities, the tubular or fixed bed furnace operations, and the other steps in the operations add significantly to potential occupational hazards. The high volatility of the products adds also to the fire hazard (Barnwell, 1978). The process is used

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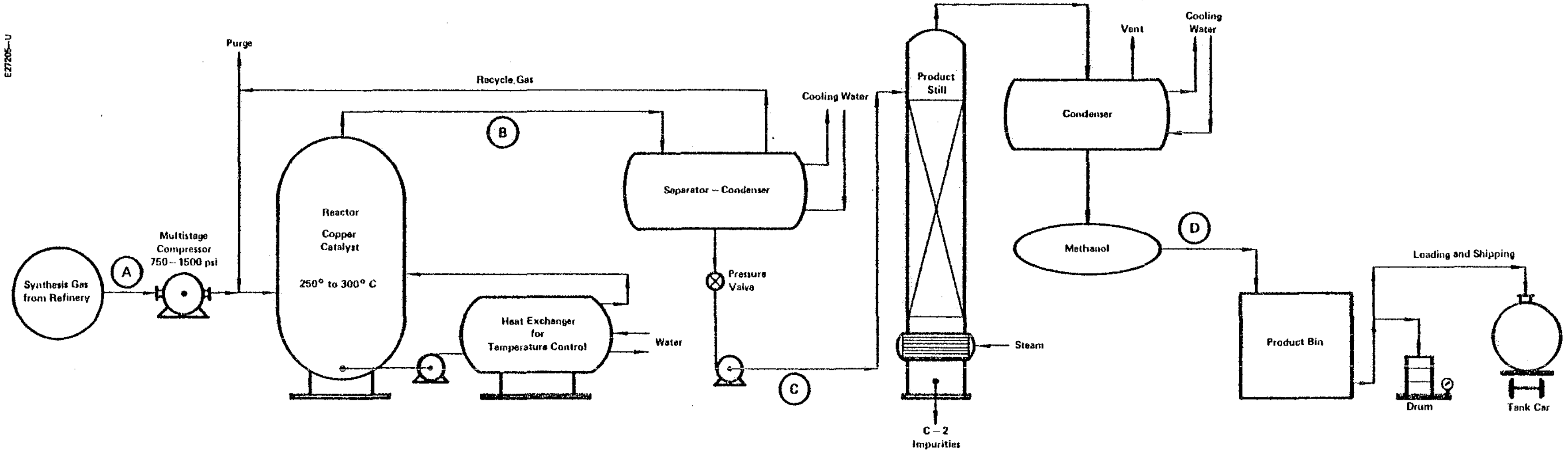
Schematic Flow Diagram No. 1

HIGH PRESSURE SYNTHESIS
(Production of Methanol)



Flow Description

	A	B	C	D
MAIN STREAM FLOW	Synthesis Gas 2 Vol. H_2 1 Vol. CO (Desulfurized)	Reactor Product 60% Methanol 40% Unreacted at Full Pressure	Condensed Impure Methanol plus C_2 Impurities	Pure Methanol 60% Yield
OFF STREAM FLOW	None	Purge of Inert Gases to Scrubber System to Outside	Product Still Bottoms Recycle to Refinery	Condenser Vent to Scrubber to Atmosphere

References:

Anon., 1977b
Austin, 1974
Lowenheim and Moran, 1975
Shreve, 1967

in about 60 major installations operated by 42 companies. It is judged that about 10,000 production workers are employed. Process No. 2 consumes about 2 pounds of feed stocks per pound of ethylene produced, or approximately 50 billion pounds per year.

Flow Diagram No. 2 outlines a typical acyclic product dehydrogenation process. Potential stresses as listed by API arise from the hydrocarbons, hydrogen sulfide, and carbon monoxide associated with the process (API, 1977). Also, the fire hazard, heat, and noise add to potential stresses in the operation. The off stream vents, wastes, and purges to the outdoor environment tabulated on the flow diagram require careful control and monitoring. These conditions give this process a high health hazard potential relative to the other processes.

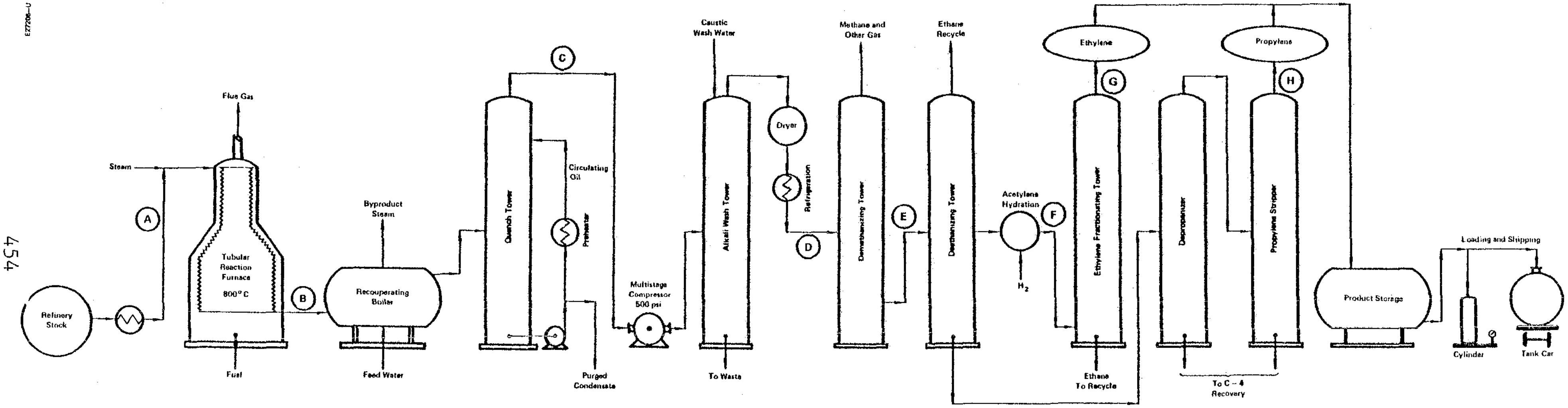
Process No. 3 - Dehydrogenation (Cyclic Products)

Catalytic cracking of feed stocks high in naphthene hydrocarbons, with hydrogen-rich recycle gas to control temperature and coke formation, produces the principal aromatics benzene, toluene, and xylenes. The reactions are operated between 200-1000 psig at furnace temperatures of 450-500°C. The operation is known as hydroforming or platforming. Fixed and moving bed furnaces are used. The reactor products are separated and purified by solvent extraction with diethylene glycol involving about 15 steps for extracting, washing, and stripping. The high pressure and temperature, the effects of sulfur, and the toxicity of benzene add to the occupational health hazards (API, 1977). The process is used in about 50 locations, operated by 30 companies, and is judged to employ on the order of 8,000 production workers.

Flow diagram No. 3 outlines a plant for producing benzene by platforming. Potential health stresses associated with the process as listed by API include, E77206-U

Schematic Flow Diagram No. 2

DEHYDROGENATION OF ACYCLIC PRODUCT
(Ethylene and Propylene by Cracking Hydrocarbons)



Flow Description

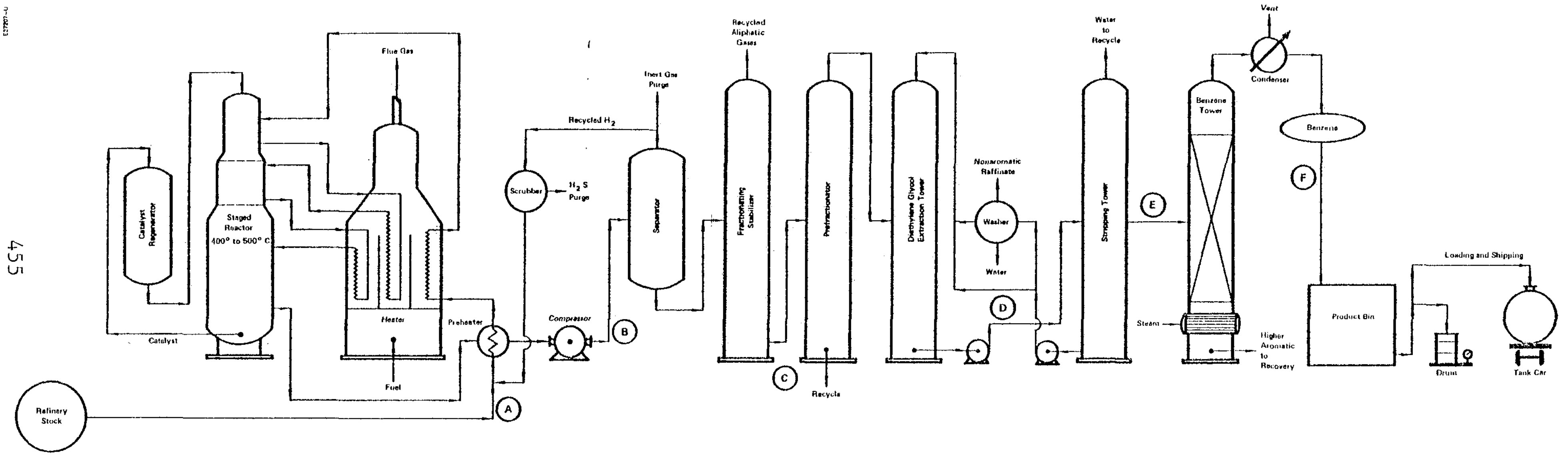
	A	B	C	D	E	F	G	H
MAIN STREAM FLOW	Preheated Feed 70% – 90% Paraffins plus Over 100% Steam	Reactor Product 40% – 50% Olefins plus Unreacted Feed and Gases	Quenched Reactor Product	Washed, Dryed and Refrigerated Product at 500 psig	Demethanized Product	Dethanized Product	Ethylene Production 40% – 80% Yield Depending on Feed	Propylene Production 3% – 20% Yield Depending on Feed
OFF STREAM FLOW	Furnace Gas to Stack and Atmosphere	Byproduct High Pressure Steam	Purged Condensate to Recycle	Caustic Washing to Waste	Methane to Recovery	Ethane to Recycle	Ethane to Recycle	C-4s to Recovery

References:

Anon., 1977b
Lowenheim and Moran, 1975
Shreve, 1967

Schematic Flow Diagram No. 3

DEHYDROGENATION OF CYCLIC PRODUCTS
(Production of Benzene from Napthenes)



Flow Description

	A	B	C	D	E	F
MAIN STREAM FLOW	Napthene Stock Mixed with Recycled Hydrogen with Platinum Catalyst 250 – 800 psig	Reaction Product at 80% Conversion plus Recycled Hydrogen	Separated and Stabilized Product	Extracted Product Diethylene Glycol	Stripped Impure Product 50% Aromatics 50% Raffinate	Benzene Product over 90% Yield of Aromatics
OFF STREAM FLOW	Furnace Gas to Stock	Recycled Hydrogen Scrubbed to Remove Sulfides Recovered as Sulfur	Separated Gas Recycled Inerts Purged to Scrubber	Nonaromatic Raffinate Recycled to Refinery	Stripped Water Recycle	Tolyene and Xylene for Recovery

References:
Anon., 1977b
API, 1977
Lowenheim and Moran, 1975
Shreve, 1967

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in addition to benzene, carbon monoxide, diphenyl, hydrogen sulfide, particulate Al_2O_3, heat, and noise. The off stream flows that exit to the atmosphere are indicated on the flow diagram; these require monitoring and control. The aforementioned factors give this process a relatively high potential for health hazards.

Process No. 4 - Oxidation of Acyclic Chemicals

The catalytic oxidation of acyclic compounds containing 1 to 4 carbon atoms is used to produce a large group of organic chemicals. The process consists usually of reacting the feed as gas or liquid with air or oxygen, at moderate pressure and temperatures. This is followed by separation and purification operations. The process is usually simple, involving 4-6 steps. The process is used in over 100 major installations which are judged to employ on the order of 10,000 production workers.

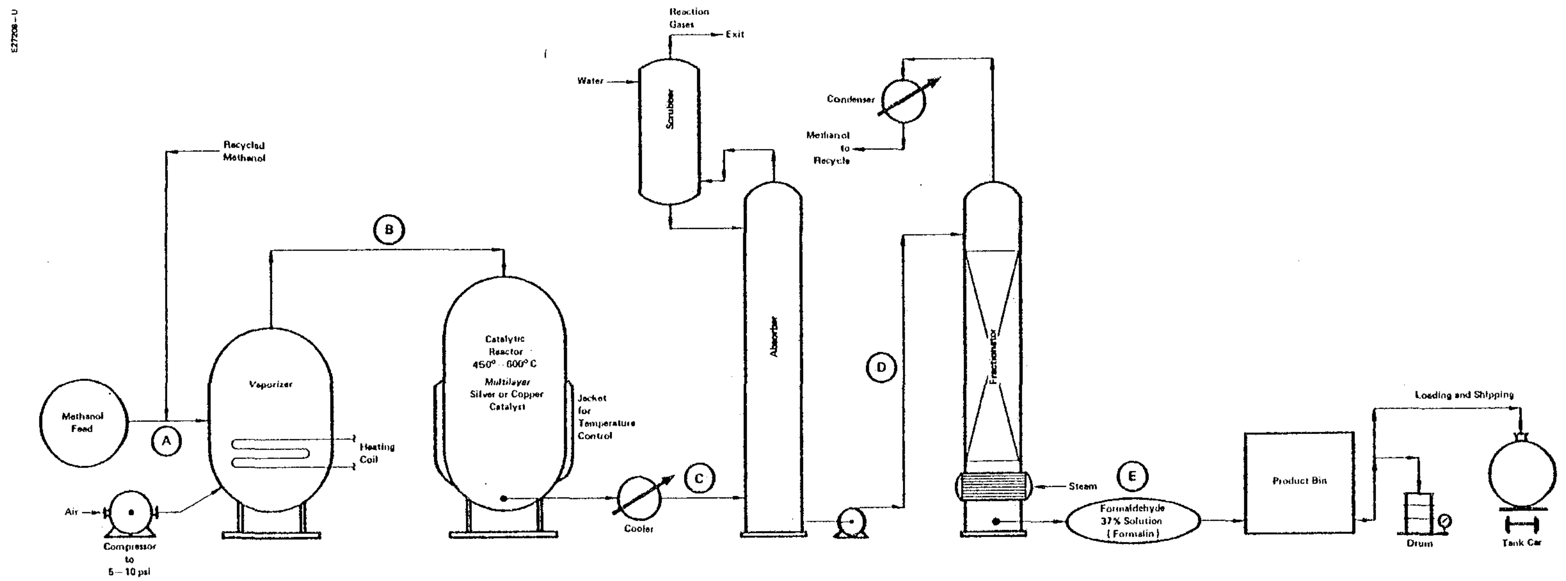
Flow Diagram No. 4 typifies the operation of this process to produce formaldehyde. The relatively simple nature of the process, the favorable temperature and pressure, and the absence of impurities minimize the risks of hazardous exposures from this process, although total worker exposure is high due to the number of products and operations in which this process is used. The toxicity of the products varies considerably, from highly toxic formaldehyde to mildly toxic acetone, and is another consideration in assessing the potential hazards of the operation.

Process No. 5 - Oxidation of Cyclic Chemicals

The catalytic oxidation of cyclic aromatic products is the base for a number of derivatives. The process is generally liquid phase at moderate temperatures up to 250°C and pressures usually below 200 psig. The processes vary in complexity with the product, ranging up to 15 steps for terephthalic

Schematic Flow Diagram No. 4

OXIDATION OF ACYCLIC PRODUCTS
(Production of Formaldehyde from Methanol)



Flow Description

	A	B	C	D	E
MAIN STREAM FLOW	Methanol Feed includes 30% – 40% Recycle	Vaporized Mixture 50% Mixture with Air	Cooled Reactor Product 60% – 70% Converted to Formaldehyde	Absorber Product Solution of Formaldehyde and Unreacted Methanol	Product Fractionated Product in Solution 85% – 90% Yield
OFF STREAM FLOW	Steam or other Heating Media for Vaporization	Cooling Water for Temperature Control	Scrubbed Reactor Gases at 18% Hydrogen 1% Oxygen 71% Nitrogen to Atmosphere	Unreacted Methanol to Recycle	None

References:
Anon., 1977b
Austin, 1974
Lowenheim and Moran, 1975
Shreve, 1967

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acid. Since many of the products are solids, filtering and drying are required. These and other steps in the separation and purification add to potential occupational hazards of the process. The products vary in toxicity from highly toxic maleic anhydride to low volatile solids, such as terephthalic acid. The process is used in over 60 locations and is judged to employ on the order of 8000 production workers.

Flow Diagram No. 5 for production of terephthalic acid from p-xylene is an example of the process. In this application, the low vapor pressure and low toxicity of the solid product reduce the potential hazards. Other operations producing liquid products may not have these advantages.

Process No. 6 - Halogenation of Acyclic Chemicals

The halogenation of acyclic chemicals is used to produce several groups of products such as the chlorofluoromethanes, chloromethanes, ethylene dichloride and ethylene dibromide. The processes may operate in the vapor or liquid phase at moderate temperature and pressure; they have varying degrees of complexity, with from 6 to 15 steps in the separation and purification of the products. Products are generally highly volatile, contributing to the risks of hazardous exposures. The halogen, as well as by-product acid, adds to corrosive conditions and potential hazards. The process is used in roughly 80 locations in which it is judged that approximately 15,000 production workers are employed. The process is used for the production of a wider variety of products than any of the other processes described, and, as indicated, requires the largest numbers of operations and production workers.

Flow Diagram No. 6 for a chloromethane plant is representative of the process. The operation produces 4 products in about 15 steps. The off-stream vents, wastes, and byproduct acid are tabulated on the flow diagram. The

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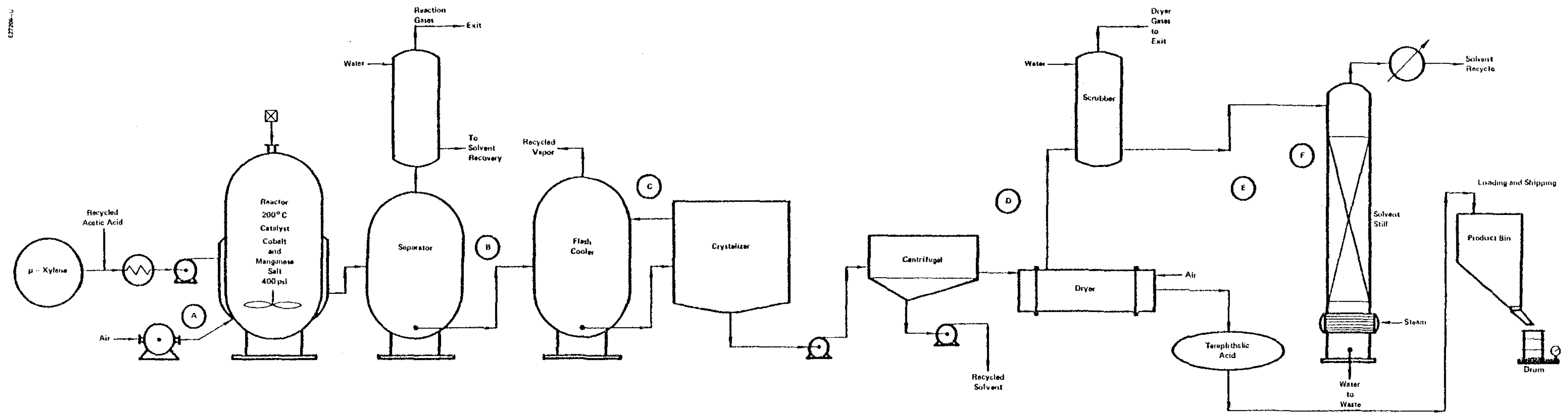
Schematic Flow Diagram No. 5

OXIDATION OF CYCLIC PRODUCTS
(Terephthalic Acid from p – Xylene)



Flow Description

	A	B	C	D	E	F
MAIN STREAM FLOW	Reactor Feed p – Xylene with Recycled Acetic Acid Solvent	Reactor Product after Venting Spent Nitrogen Gas	Flash Cooled Slurry after Vaporization	Centrifugal Product from Crystallizer	Dried TPA from Heated Air Dryer 90% Yield	Acetic Acid Recovery by Distillation
OFF STREAM FLOW	None	Water Scrubbed Nitrogen to Atmosphere Scrubber Liquid to Recovery	Flashed Vapor to Recycle	Filtrate Recycled to Feed	Scrubber Dryer Gas to Atmosphere Scrubber Liquid to Recovery	Waste Water from Distillation for Disposal

References:
Anon., 1977b
Austin, 1974
Lowenheim and Moran, 1975
Shreve, 1967

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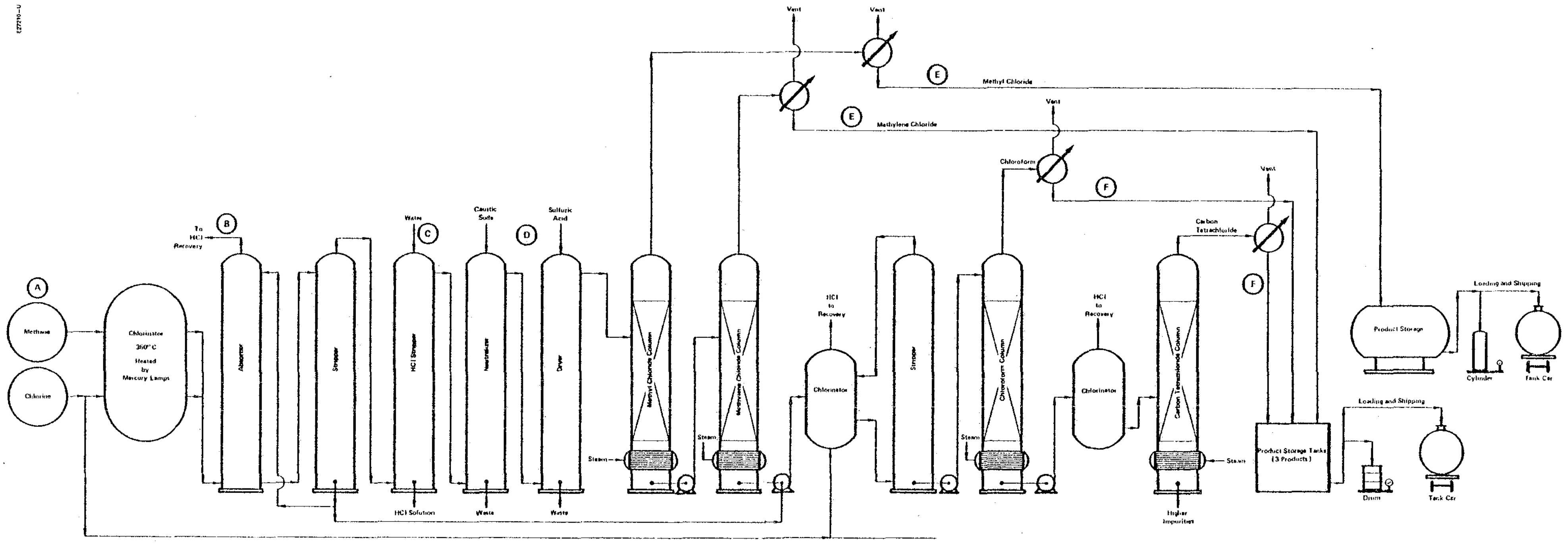
Schematic Flow Diagram No. 6

HALOGENATION OF ACYCLIC PRODUCTS
(Production of Chloromethanes)



Flow Description

	A	B	C	D	E	F
MAIN STREAM FLOW	Preheated Methane and 0.6 Mol Chlorine per Mol	Reactor Product 60% Methyl Chloride 30% Methylene Chloride 10% Other	HCl Separation for Recovery by Stripping and Washing	Neutralized and Dried Product	Fractionated Methyl and Methylene Chloride Products Over 90% Recovery	Further Chlorination and Fractionation Chloroform and Carbon Tetrachloride
OFF STREAM FLOW	None	None	HCl Washed and Disposed as Product	Waste from Neutralizer and Acid Dryer to Disposal System	Condenser Vents to Atmosphere	HCl to Recovery Condenser Vents to Atmosphere Heavy Ends to Disposal

References:

Austin, 1974
Lowenheim and Moran, 1975
Shreve, 1967

corrosive conditions, the complexity of the process, and the large exposure of total production workers give the process a high rating with respect to potential hazards.

Process No. 7 - Halogenation of Cyclic Chemicals

The halogenation of cyclic chemicals is used to produce a group of products such as the dichlorobenzenes. The process is comparatively simple, consisting of liquid phase reaction near atmospheric temperatures and pressure. The process also requires by-product hydrochloric acid recovery, neutralization, and distillation operations. There are about 15 locations using the process, employing roughly 2000 production workers.

Flow Diagram No. 7 for the chlorination of benzene typifies the process. Although comparatively simple and with few applications, the corrosive effect of chlorine and hydrochloric acid, the toxicity of benzene, and the small batch-type operations usually employed gives the process a comparatively high potential hazard rating.

Process No. 8 - Alkylation and Dealkylation Process

Alkylation of cyclic chemicals is performed usually at ambient or moderately elevated temperatures and pressures; dealkylation applications are performed at higher temperatures and pressures. The operations are simple, requiring 4-6 steps for the separation and purification of the product and recycle stream. There are about 30 locations in which the process is used, judged to employ about 5000 production workers.

Flow Diagram No. 8 outlines the alkylation of benzene with ethylene to produce ethylbenzene as a typical operation in this process. This is similar to the alkylation of benzene with propylene to produce cumene, which is another API selected petrochemical process. The purge, vent, and waste streams are

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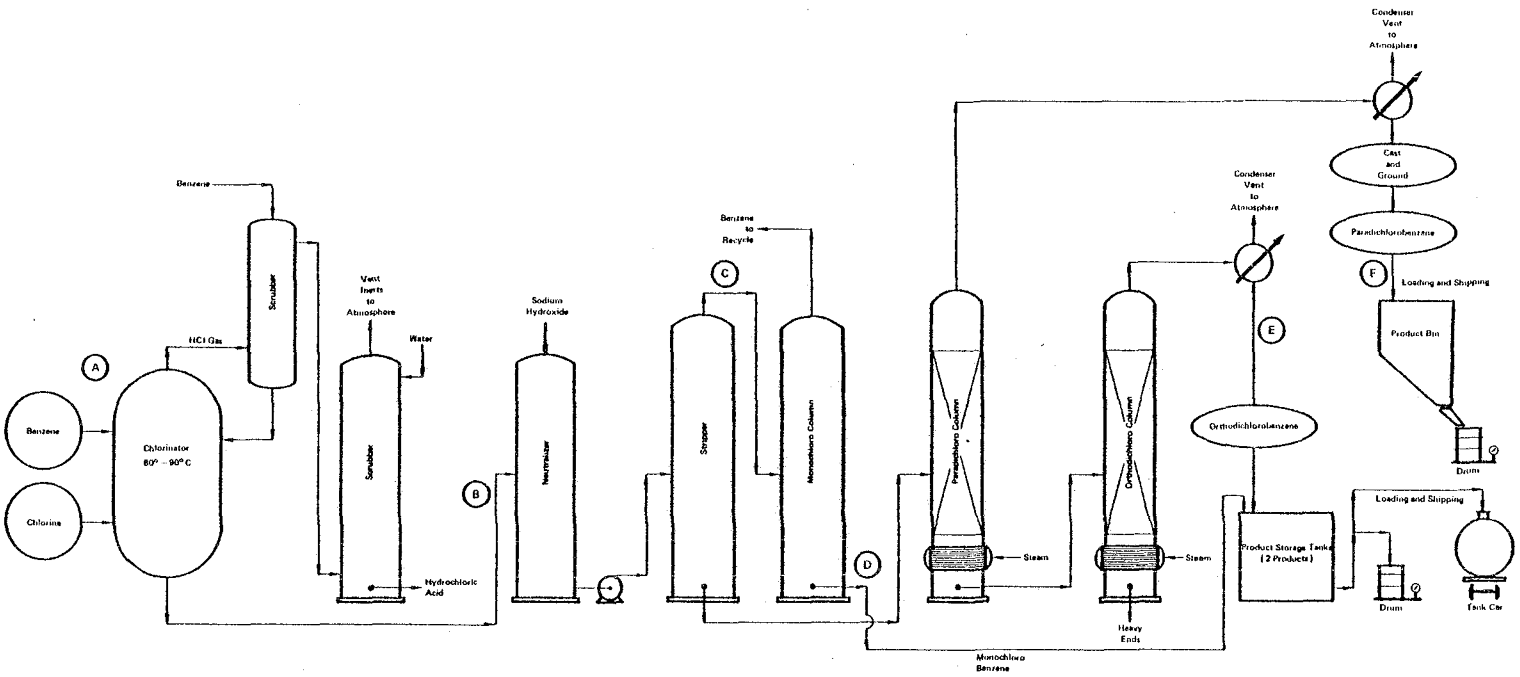
Schematic Flow Diagram No. 7

HALOGENATION OF CYCLIC PRODUCTS

(Production of Chlorobenzenes)



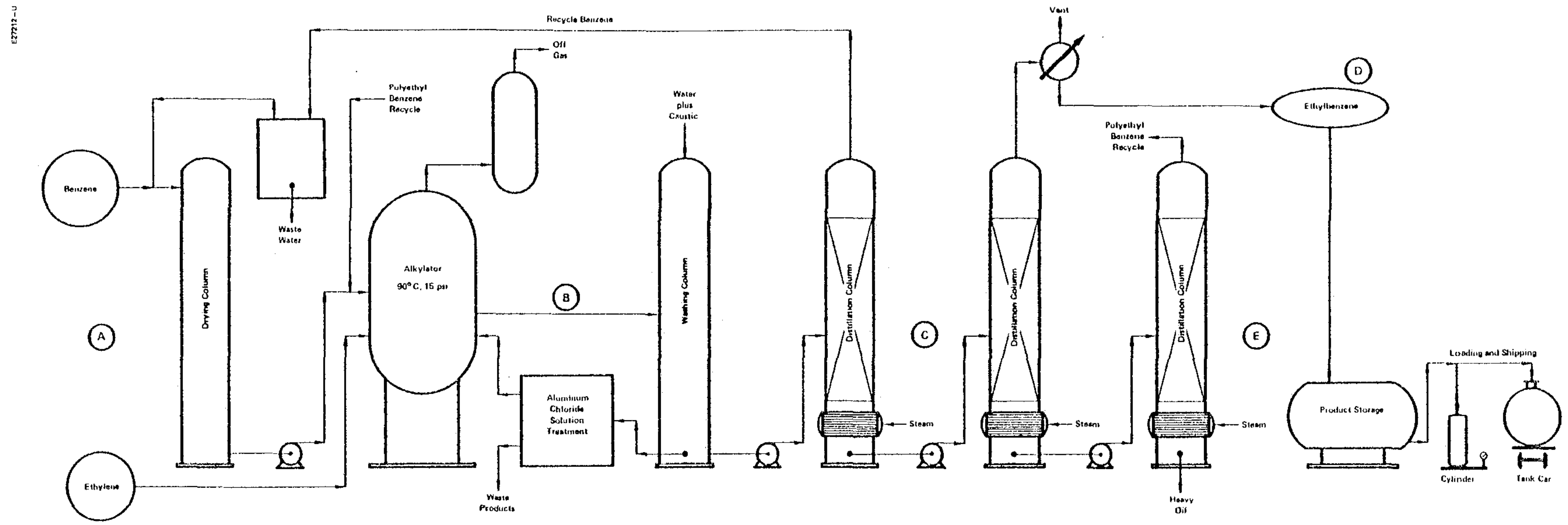
Flow Description

	A	B	C	D	E	F
MAIN STREAM FLOW	Preheated Benzene and Chlorine with Iron Filing Catalyst	Mixed Mono and Dichloro Benzene after Hydrochloric Acid Separation	Neutralized Products Separated for Fractionation	Monochloro Benzene Product 85 % – 90 % Total Recovery	Paradichloro (Cast and Ground) Benzene Products	Orthodichloro Benzene Products
OFF STREAM FLOW	None	Byproduct Hydrochloric Acid and Scrubber Vent Gas to Atmosphere	None	Benzene for Recycle	Condenser Vent to Atmosphere	Condenser Vent to Atmosphere Heavy Ends to Disposal

References:
Austin, 1974
Lowenheim and Moran, 1975
Shreve, 1967

Schematic Flow Diagram No. 8

ALKYLATION PROCESSES
(Alkylation of Benzene to Ethylbenzene)



Flow Description

	A	B	C	D	E
MAIN STREAM FLOW	Benzene and 30% Ethylene plus Recycle	Alkylation with Aluminum Chloride Catalyst and Recycle	Washed Neutralized Product after Removal of Excess Benzene	Distilled Ethylbenzene 99% Recovery	Recovery of Polyethylbenzene for Recycle
OFF STREAM FLOW	Removal of Moisture to Waste	Scrubbed Off Gas to Atmosphere	Waste Products from Aluminum Chloride Treatment	Vent from Condenser to Atmosphere	Heavy Oils for Disposal

References:
Anon., 1977b
Austin, 1974
Lowenheim and Moran, 1975

tabulated on the flow diagram. Other potential hazards associated with the process are benzene, propylene, acids, and catalysts, in addition to noise and heat (API, 1977).

Process No. 9 - Chlorohydrin Oxidation Process

The chlorohydrin oxidation process is used to produce propylene oxide and epichlorohydrin. The process is no longer used significantly for making ethylene oxide, since direct oxidation is more economical (Austin, 1974). The process consists of production of the chlorohydrin by reacting propylene with a chlorine water solution at ambient temperature and pressure. The chlorohydrin is hydrolyzed with lime to the oxide, which is recovered by distillation. The process is relatively simple, requiring 6 steps. Disposal of the waste calcium chloride is a critical problem and adds to potential risks. The process is used in 9 locations, and estimated to employ on the order of 2000 production workers.

The chlorohydrin process for production of propylene oxide is illustrated in Flow Diagram No. 9. The off stream flows of purge and waste materials to the environment are also indicated on the flow diagram. These flows and the corrosion conditions resulting from the use of chlorine add potential hazards to the process; however, the number of workers engaged in the process is comparatively small.

Process No. 10 - Hydration Processes

Hydration of organic oxides, olefins, and organic salts is used to produce glycols and alcohols. The glycol processes are comparatively simple and operate at moderate temperatures and pressure. The hydration of ethylene, however, requires 1000 psig and 300°C. The products are of generally low toxicity, which lessens the risk for hazards. Approximately 40 applications of the process are judged to employ on the order of 5000 production workers.

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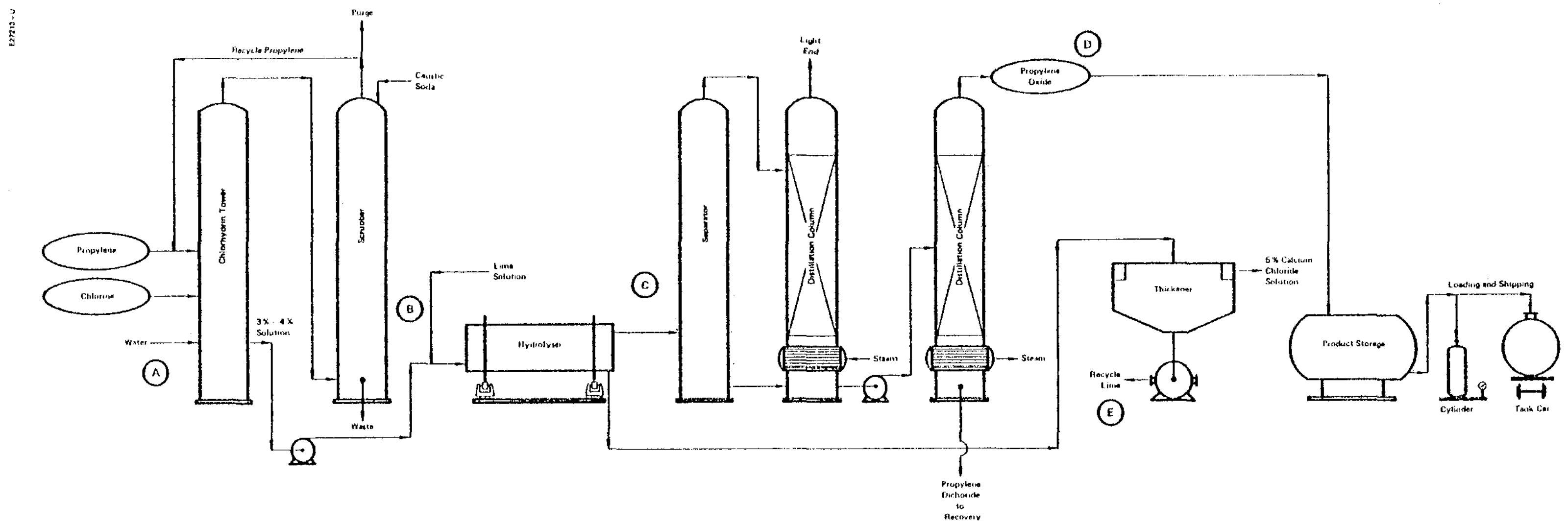
Schematic Flow Diagram No. 9

CHLORHYDRIN PROCESS
(Production of Propylene Oxide)



Flow Description

	A	B	C	D	E
MAIN STREAM FLOW	Propylene with Chlorine (1: 1.6) plus Water	3% - 4% Chlorhydrin Solution plus 10% Lime Solution	Flashed Propylene Oxide from Hydrolyser	Propylene Oxide 75% - 80% Recovery	Recycled Lime from Thickener
OFF STREAM FLOW	Purge of Inert Gases from Scrubber to Recovery or Disposal	Waste from Caustic Washing to Disposal	None	Light Ends to Recovery and Dichloride	5% Calcium Chloride Solution to Disposal

References:
Austin, 1974
Lowenheim and Moran, 1975

Flow Diagram No. 10 for the catalytic hydration of ethylene to ethyl alcohol typifies this process.

Process No. 11 - Esterification Processes

Production of esters by reacting organic and other acids with organic chemicals is used to manufacture products such as vinyl acetate and ethyl acetate. The processes are generally simple, but are usually batch (which adds appreciably to risk from potential hazards). The process is used in about 20 locations, and is judged to employ about 3000 production workers.

The production of vinyl acetate by reacting ethylene with acetic acid is shown by Flow Diagram No. 11 as an example of the esterification process.

Process No. 12 - Ammonia Reaction

Ammonia is used for producing amines and nitriles from hydrocarbon feeds. Moderate temperatures of 300°C-400°C and pressures up to 800 psi are required. Batch type autoclaves are used for reactors in some cases. The products are characteristically highly toxic. The operations are comparatively simple, involving strippers and distillation operations for purification and separation of the product. The process is used in 20-30 locations in which it is judged that 3000-4000 production workers are employed.

Flow Diagram No. 12 for the production of acrylonitrile from propylene is an example of the ammonia reaction process. The inert gases, other vents, and the light ends that contain HCN require careful monitoring to control escape to the atmosphere.

Process No. 13 - Hydrogenation

Hydrogenation is used to saturate some unsaturated hydrocarbons as well as to dealkylate alkyl aromatics. Operations are moderately simple, requiring about 6 steps. Pressures up to 1000 psi and temperatures up to 300°C are

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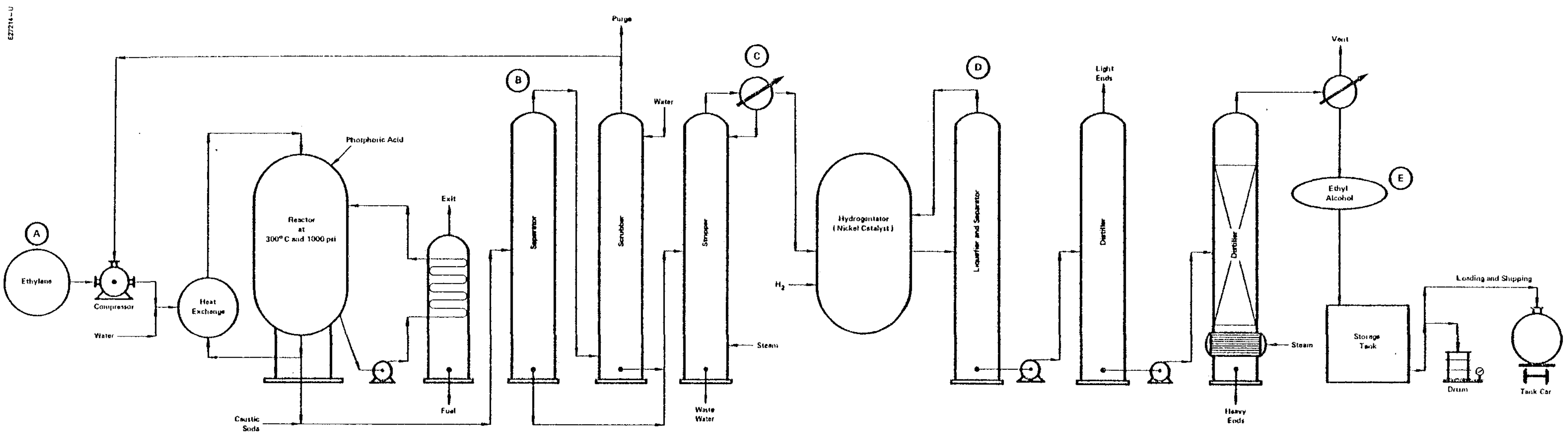
Schematic Flow Diagram No. 10

HYDRATION PROCESS
(Production of Ethyl Alcohol from Ethylene)



Flow Description

	A	B	C	D	E
MAIN STREAM FLOW	Ethylene Recycle and Water Feed	Hydration Reactor Product Phosphoric Acid Catalyst	Product from Steam Stripping	Product after Hydrogenation to Convert Olefins	Ethyl Alcohol 90 + % Recovery after Removal of Light Ends to Disposal
OFF STREAM FLOW	None	Recycled Gas with Purge to Disposal	Waste Water	None	Heavy Ends to Disposal

References:
Austin, 1974
Lowenheim and Moran, 1975
Shreve, 1967

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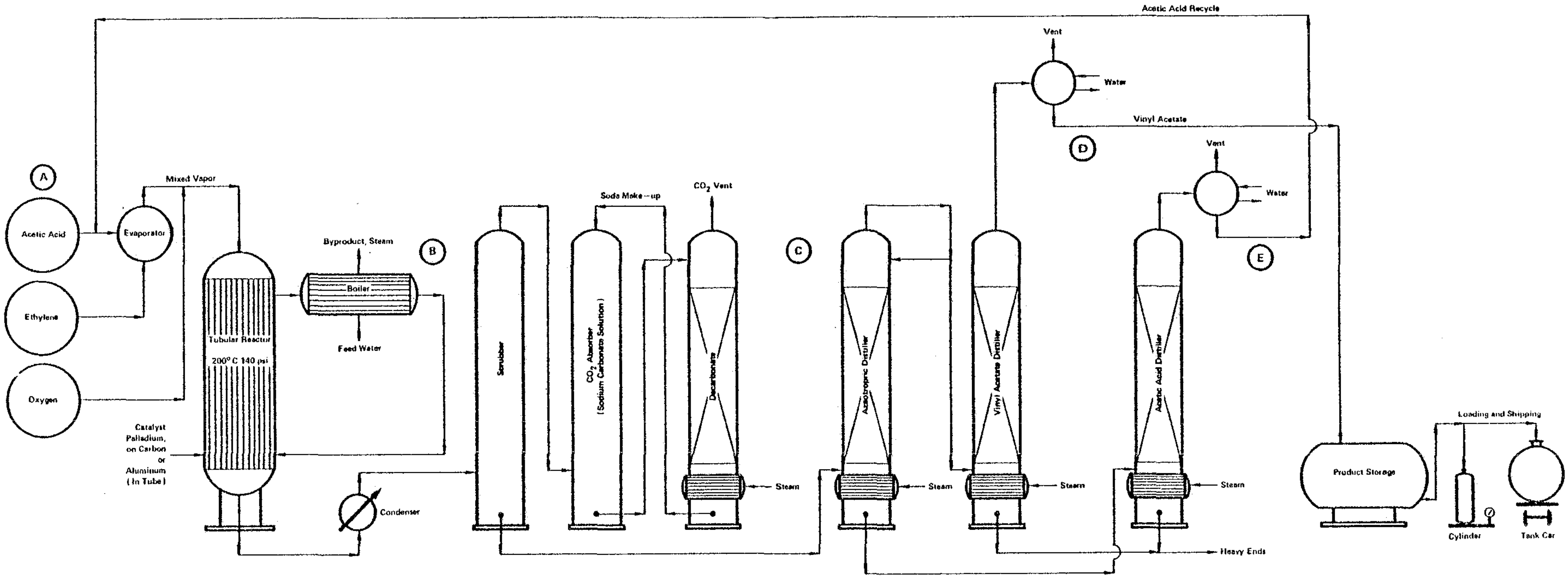
Schematic Flow Diagram No. 11

ESTERIFICATION

(Production of Vinyl Acetate from Acetic Acid and Ethylene)



Flow Description

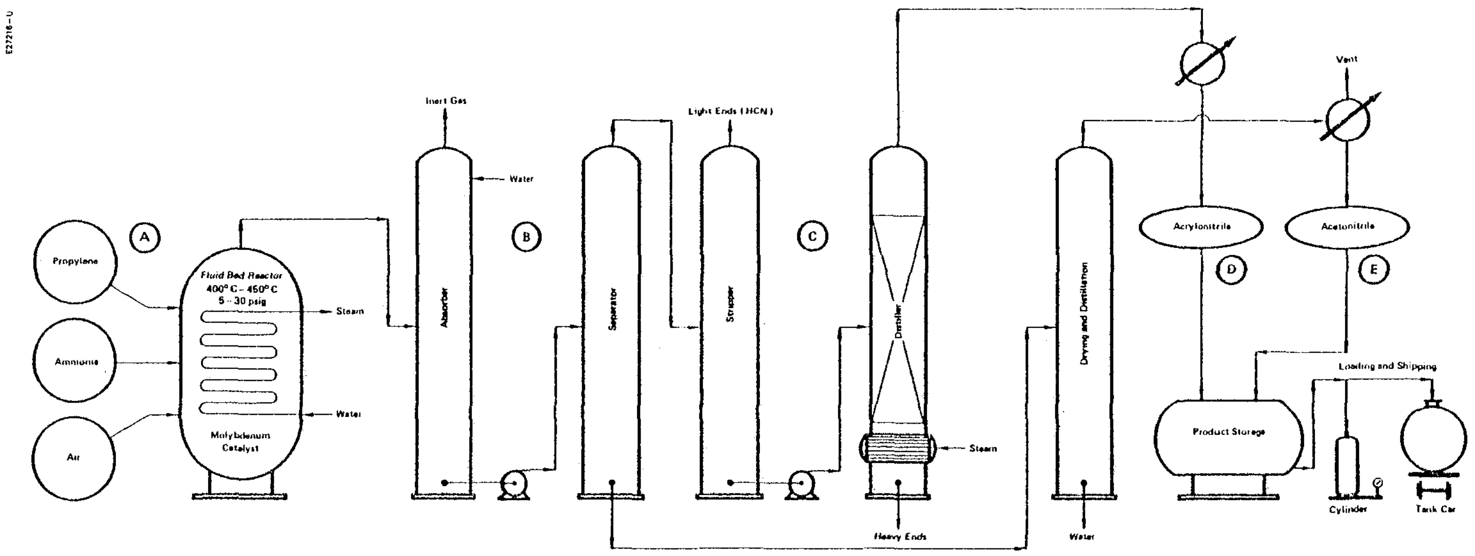
	A	B	C	D	E
MAIN STREAM FLOW	Mixture of Acetic Acid and 50 % Ethylene Vapor plus Oxygen	Catalytic Reactor Product with Excess Reactants and CO_2	Vinyl Acetate in Acetic Acid Solution after CO_2 Removal	Vinyl Acetate after Distillation 90 % Plus Recovery	Recovered Excess Acetic Acid for Recycle
OFF STREAM FLOW	None	Byproduct, Steam from Reaction	CO_2 Removed from Scrubber for Disposal	Heavy Ends to Disposal Condenser Vent to Atmosphere	Heavy Ends to Disposal Condenser Vent to Atmosphere

References:
Anon., 1977b
Austin, 1974
Lowenheim and Moran, 1975

Schematic Flow Diagram No. 12

AMMONIA REACTION PROCESS

(Production of Acrylonitrile)



Flow Description

	A	B	C	D	E
MAIN STREAM FLOW	Propylene with Equal Ammonia and Two – Parts Air Feed	Reaction Product Separated from Inert Gases by Solution	Crude Acrylonitrile Separated from Acetonitrile	Distilled Acrylonitrile Product (70% Yield)	Distilled Acetonitrile Product (15% – 20% of D)
OFF STREAM FLOW	None	Fixed Gas, Nitrogen and Unreacted Propylene for Recovery	Light Ends, Including HCN (3% Product) for Disposal	Condenser Vent to Atmosphere Heavy Ends for Disposal	Condenser Vent to Atmosphere Water for Disposal

References:
Anon., 1977b
Austin, 1974
Lowenheim and Moran, 1975
Shreve, 1967

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required. The process is used in about 25 locations that are judged to employ 3000 production workers.

The hydrogenation of benzene to produce cyclohexane shown in Flow Diagram No. 13. API lists the potential health hazards that are associated with this process to be cyclohexane, hydrogen sulfide, aromatic and cycloparaffinic hydrocarbons, catalysts, and noise and heat (API, 1977).

Process No. 14 - Acid Reactions with Aromatic Chemicals

Nitration and sulfonation of aromatic chemicals are used to produce products such as nitrobenzene and benzenesulfonic acid. The batch type reactors formerly used for nitration have been replaced by continuous processes in some new installations. Corrosion-resistant constructions are required due to the strongly acidic conditions. Temperatures and pressures are moderate and the processes are comparatively simple, involving product separation from the acids, neutralizing, washing, and distillation. The sulfonation operation formerly used for phenol production has been largely replaced by the cumene process. There are about 15 principal locations using the process, employing on the order of 3000 production workers.

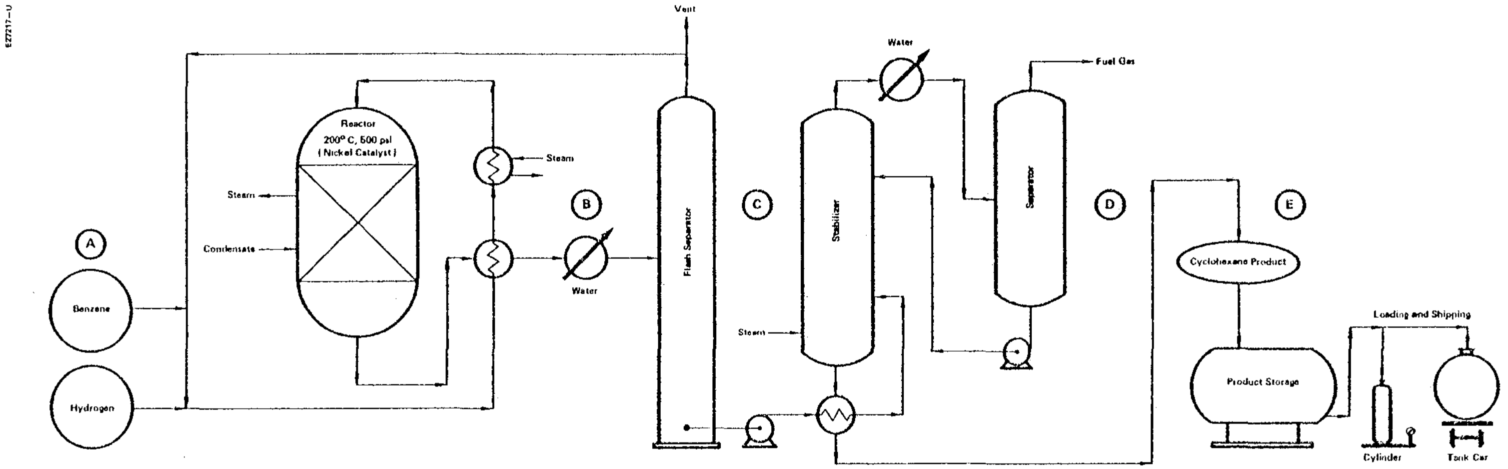
The nitration of benzene shown by Flow Diagram No. 14 is an example of the process. Disposal of spent acids and washings requires close control to avoid serious contamination.

VI. ENGINEERING CONTROLS

The 14 processes described in Section V differ in respect to the types of chemical reactions employed, but many production details are common to all. With several exceptions, most of the operations are in liquid or vapor phase; consequently, the major equipment used to prepare and purify the products is similar to tower type separators, quenchers, washers, and fractionating

Schematic Flow Diagram No. 13

HYDROGENATION PROCESS
(Production of Cyclohexane)



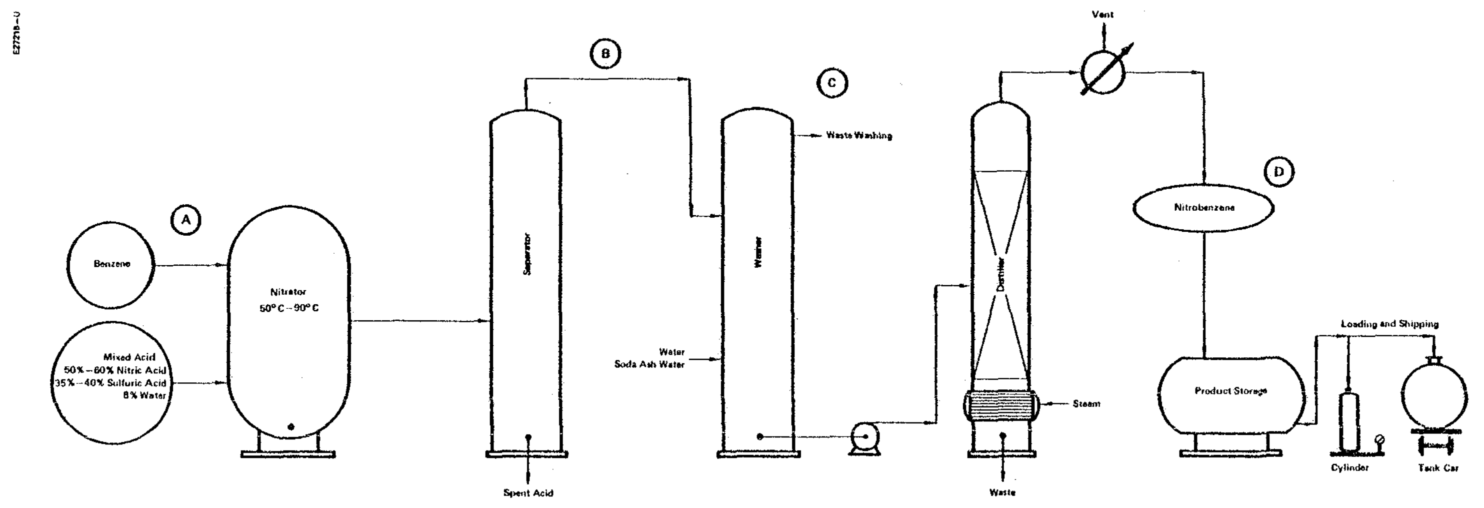
Flow Description

	A	B	C	D	E
MAIN STREAM FLOW	Benzene, Hydrogen and Recycle Hexane Feed to Reactor Preheater	Partly Condensed Reactor Product for Gas Separator	Product Reboiled to Remove Residue Gas	Light Overhead Separated to Vent Residual Gas	Cyclohexane Product from Reboiler 99% Recovery
OFF STREAM FLOW	None	Byproduct Steam to Recovery Vent Inert Gas for Disposal	None	Residual Gas for Disposal as Fuel	None

References:
Anon., 1977b
API, 1977
Austin, 1974
Lowenheim and Moran, 1975

Schematic Flow Diagram No. 14

ACID REACTION PROCESS
(Production of Nitrobenzene)



Flow Description

	A	B	C	D
MAIN STREAM FLOW	Benzene Reacted with Mixed Acids at Controlled Temperature	Nitrated Product Separated from Spent Acid	Nitrated Product Washed with Water and Alkali	Distilled Nitrobenzene 95% Plus Recovery
OFF STREAM FLOW	None	Spent Acid to Disposal for Recovery	Washings for Disposal	Condenser Vent to Atmosphere Distiller Bottoms to Waste

References:
Austin, 1974
Lowenheim and Moran, 1975
Shreve, 1967

columns. Also, conventional tubular heat exchanges, compressors, pumps, condensors, and connecting piping are used in all the processes. The only pieces of equipment that differ significantly are the reactors. Otherwise, the principal differences between the processes, as discussed in Section V, are in such characteristics as pressure, temperature, volatility, toxicity, and corrosive and scaling tendencies.

The potential hazards inherent in each process that are directly related to engineering design can be inferred from the process descriptions and flow diagrams presented in Section V. In the totally enclosed and gas tight continuous operations, escape of the chemicals to the air is automatically controlled and exposure of production workers does not normally exceed acceptable levels. Exit gases and vapors are discharged, however, at condenser and scrubber vents, by air dryers, and by purging operations. Process wastes from washers and neutralizers are additional sources of potential chemical exposure, as are leaks from seals on pump, compressor and agitator shafts. Further, potentially hazardous exposures may result during sampling, weighing, packaging, and shipping of products, or from cleaning, filling, and venting tank cars, trucks, and storage vessels.

Hazardous chemical exposure is particularly difficult to control during equipment repair and maintenance (API, 1977; Selikoff, 1977). The frequency of maintenance outages, scheduled and unscheduled, is related to the following characteristics of the processes:

Complexity of the process. Maintenance requirements, outages, and reliability are directly related to the number of steps or unit operations. The number of required operating personnel is affected also.

Temperature and pressure conditions. Maintenance requirements increase as the level of these factors rises.

Corrosive conditions. Maintenance needs, frequency of outages, and equipment replacement are directly affected by corrosion.

Fouling conditions. Deposition of scale from suspended solids and corrosion products requires outages for cleaning the equipment.

The risk of exposure is the greatest during unscheduled outages; these unplanned outages may be minimized if a program of scheduled maintenance is followed. The length of time between scheduled shutdowns is 12-24 months for most operations and about 6-12 months for cracking. Five hundred to 1000 man hours are usually required per shutdown in a 1000 bbl/day capacity plant (API, 1977).

Good engineering design is required for the effective control of occupational hazards. This involves the selection, location, sizing, and specification for all items of the installed equipment. The selection process involves the following engineering responsibilities:

(1) Correct sizing of the equipment units for uninterrupted, reliable, and controlled specified performance. Example: correct sizing of the piping and the balancing of liquid flow systems in order to avoid spillages, overflows, etc.

(2) Specifying equipment with adequate strength to withstand the required operating pressures and temperatures and other process conditions such as corrosion, wear, and fouling. Example: selection of safe reactor tank wall thickness of a corrosion-resistant material.

(3) Proper location and layout arrangement of equipment for accessibility, convenience, and safe operating attention. Example: assuring adequate clearances between equipment and convenient location of controls.

(4) Simplification of equipment for effective control and easy maintenance in order to facilitate cleaning, repairs, and replacement. Example: simplified heat exchanger design for convenient cleaning and repairing; selecting pumps that are designed to avoid leakage.

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(5) Selection of effective equipment for accurately measuring, recording, metering, and reliably controlling process parameters, rates, concentrations, product quality, etc. Example: selecting a computerized system to control an azeotropic distillation system; selecting control valves that are easily calibrated with proper sizing for sensitive response, and rugged construction for minimum repairs and adjustments; inclusion of a manual or spare method of control during outages. Reliable supply of the actuating energy, e.g. air, electricity, etc. is also necessary. The API publications listed in the reference section provide more complete information on these control factors.

(6) Provisions for controlling and monitoring all forms and locations of emissions, leakages, overflow, drains, spills, breaks, vents, pressures, reliefs, and wastes that escape the system. These include ventilation systems, scrubbers, drain liquor collection systems, waste receivers, and disposal pond systems. Example: ventilating system for a packing and loading area to control concentration of product vapor to acceptable limits through adequate change rate of the room atmosphere; collection and disposal of liquid from scrubber on the emitted or recirculated air. Detailed specifications depend on the local conditions and particular applications.

Training in safe maintenance and operating practices is also essential for effective hazard control. Operating codes and manuals have been developed for this purpose by NIOSH, OSHA, and API, and are covered by several of the referenced publications (Anon., 1976; 1977a; 1978; API, 1977; Cocks and Rogerson, 1978).

VII. POTENTIAL HEALTH HAZARDS

A. Chemical and Physical Agents

Due to the diversity of specific hazards encountered in the petrochemical industry, this information is presented in tabulated form in Table 7 for chemical agents and Table 8 for physical hazards. Only the major toxic effects, derived from both human and animal studies, are summarized; detailed discussion of the characteristic toxic properties of the end-product petrochemicals (Table 2) and other compounds encountered during production (Section V) is beyond the scope of this report.

Table 7. Toxicological/Physiological Properties of Specific Substances (API, 1977)

Substance	Toxicological/Physiological Effects	
	Acute	**Chronic**
Ammonia	temporary blindness and intolerable irritation of mucous membranes at concentrations above 200 ppm	irritation of eyes and mucous membranes; odor threshold is 20 ppm or less
Asbestos	no significant immediate effects unique to exposure to asbestos	generalized, diffuse fibrosis resulting in impairment of O_2 transfer, respiratory insufficiencies and cardiac failure; carcinogenic potential
Asphalt	no significant immediate effects unique to asphalt fumes	no evidence of chronic toxicity of asphalt fumes
Benzene	potent narcotic action at 200 ppm	unique among hydrocarbons as *myelotoxicant*; toxic action on bone marrow resulting in blood changes, aplastic anemia and death; can be absorbed through skin
Butadiene	relatively weak narcotic action and moderate irritation at high concentrations (5000 ppm)	mild irritation at concentrations of 2000-5000 ppm only apparent effect
Cadmium oxide	nausea, vomiting, salivation, choking attacks, diarrhea, loss of consciousness and abdominal pains; catarrhal and ulcerative gastroenteritis, pulmonary infarcts, and subdural hemorrhages; death due to pulmonary injury after short exposure to approximately 50 mg/M^3	rats exposed to 0.1-10 ppm Cd for one year showed no toxic effects. However, Cd content in the liver and kidneys increased proportionately indicating eventual toxicity. Results show storage in lungs, kidneys, liver, bone, teeth and blood, resulting in anemia, liver cirrhosis and splenic hyperplasia
Carbon dioxide	pronounced stimulation of respiratory center at 50,000 ppm; weakly narcotic at 30,000 ppm	no apparent chronic toxicity where sufficient O_2 supply is available
Carbon monoxide	pounding of heart, headache, dizziness, nausea, unconsciousness and death at concentrations above 1200 ppm	similar to acute effects but less severe; no adverse *subjective* response at concentrations of 100 ppm or less
Carbonyl sulfide	animal studies have indicated CNS depressant, paralysis of respiratory system and death	no adverse experience in humans; animal studies have indicated exposures to 1300 ppm for

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Table 7. Toxicological/Physiological Properties of Specific Substances (Cont'd) (API, 1977)

Substance	Toxicological/physiological Effects	
	Acute	Chronic
		½ hour produced intoxication; 3200 ppm for 1 hour caused death
Chromium	Cr^{3+} salts including Cr_2O_3 are considered to have a low order of toxicity. However, chromates are readily absorbed through the skin	chromate exposure causes lesions of the mucosa, submucosa of the respiratory tract as well as changes in the spleen and kidneys. History of lung cancer among chromate workers
Cobalt carbonyls*	no reports of significant effects unique to cobalt carbonyls; by analogy to nickel carbonyl, acute pulmonary distress is a potential consequence of overexposure.	no reports of adverse human experience; animal studies indicate a low toxicity lower than nickel carbonyl due probably to lower volatility
Coke	no significant effects unique to coke dust	no evidence of chronic toxicity
Crude oil	compositions and toxicological properties of crude oils vary tremendously; toxicities of component fractions (paraffinic, naphthenic and aromatic) and associated impurities and trace substances (compounds of sulfur and nitrogen) determine toxicological properties of crude oil.	
Cumene	potent narcotic; depression of CNS and respiratory system; skin and eye irritation	chronic effects similar to but less severe than acute effects; readily absorbed through intact skin
Cyclohexane (see naphthenic hydrocarbons)	moderately narcotic and irritating to eyes and mucous membranes	no reports of adverse experience in humans
Diphenyl (biphenyl)	no significant effects other than irritation of eyes, nose and throat	mild irritation of upper respiratory tract; no reported cases of injury in humans
Ethylene	considered an "inert" gas; defined by ACGIH as simple asphyxiant without significant physiological effects	
Ethylene dibromide	weakly narcotic, CNS depression, injury to lungs, liver and kidneys; lethal exposures resulting from pneumonia	chronic effects similar to acute effects but less severe; animals experienced injury to liver and kidneys after exposure to 50 ppm for 6 months but tolerated 24 ppm with no apparent effects; severely irritating and injurious to intact skin
Ethylene dichloride	severe irritation of eyes, nose and throat; CNS depression; gastro-	chronic symptoms similar to but less severe than acute effects;

Table 7. Toxicological/Physiological Properties of Specific Substances (Cont'd) (API, 1977)

Substance	Toxicological/Physiological Effects	
	Acute	Chronic
	intestinal tract injury; mental confusion, dizziness, nausea and vomiting; liver and kidney damage; pulmonary edema	nausea and vomiting are striking symptoms of chronic exposure to tolerable concentrations
Formaldehyde	primary irritation of eyes, respiratory tract and skin at 20 ppm	similar to acute effects; itching of eyes and skin, dry and sore throats, unusual thirst after sleeping, some evidence of sensitizasitization
Furfural	depression of CNS; cramps, convulsions, irritation of mucous membranes; animal studies (rats) indicated exposures to 300 ppm were fatal	irritation of eyes, nose and throat; headache; rarely reported cases of individual respiratory sensitization
Casoline	composition of gasoline varies significantly; in most cases, the aromatic hydrocarbon components will determine predominantly the toxicological/physiological properties of the mixture	
Hexamethylene tetramine	no reports of significant acute toxicity	no reported evidence of chronic toxicity other than occasional evidence of skin irritation
Hydrocarbons, paraffinic	as a class, these compounds are narcotic and irritating to mucous membranes, the severity of effects increasing generally with increasing molecular weight (methane, ethane and propane are considered "inert," or simple asphyxiants; generally paraffin series butane through nonane exhibits increasing anesthetic effects	chronic effects (irritation and mild narcosis) similar to but less severe than acute effects
Hydrocarbons, olefinic	lower molecular weight members of the olefin series (ethylene, propylene, butylene), diolefins and acetylene are simple asphyxiants and relatively weak narcotics, anesthetic potency increases generally with increasing hydrocarbon chain length in ethylene series; no serious injuries resulting from industrial exposure to this class of hydrocarbons have been reported	chronic effects consist primarily of mild narcotic action and irritation
Hydrocarbons, naphthenic	these cyclic saturated compounds are characterized by a	chronic effects are primarily mild anethesia and conjunctivitis

Table 7. Toxicological/Physiological Properties of Specific Substances (Cont'd) (API, 1977)

Substance	Toxicological/Physiological Effects	
	Acute	Chronic
	low degree of acute toxicity; lethal exposures of animals resulted in excitement, loss of equilibrium, stupor, coma and death due to respiratory paralysis	
Hydrocarbons aromatic	with the exception of the unique properties of benzene (which see) the aromatic hydrocarbons are characterized as strong and potent narcotics and are capable of irritating the eyes, nose, throat and respiratory tract	generally, headache, fatigue, slight nausea, irritation of eyes, nose, throat and respiratory tract (see also toluene and xylenes)
Hydrocarbons, polycyclic aromatics	no significant immediate effects unique to polycyclic aromatic compounds	some specific polycyclic aromatic (PCA) compounds are capable of inducing abnormal growth in tissues; animal studies (primarily mice) have demonstrated that several PCA's can elicit skin cancers after repeated contact leading to involvement of peripheral blood, spleen, lymph nodes and bone marrow
Hydrogen fluoride	moderate to severe irritation of the conjunctiva and respiratory tract; 120 ppm the highest concentration tolerated by man for one minute	chronic effects similar to acute but less severe; sour taste in mouth; prolonged exposures presumably would lead to fluorosis; concentrated aqueous solutions are extremely injurious to skin although there may not be pain associated with contact
Hydrogen sulfide	even brief exposures to concentrations 600 ppm can result in unconsciousness and death; severe pulmonary irritation and respiratory paralysis	irritation of eyes, mucous membranes and respiratory system; painful conjunctivitis; photophobia, olfactory nerves readily fatigued to the point that odor is not perceptible
Hydroquinone	animal studies have indicated increased motor activity; hypersensitivity to stimuli, dyspnea and cyanosis; no significant acute injuries reported in man	most significant chronic effect is characteristic eye injury consisting of lens curvature changes sometimes long after exposure
Iron oxide	no significant acute toxicity attributable to iron oxide	"siderosis," also known as mottling of the lungs, is considered to be that of benign pneumoconiosis because it does not lead to fibrous profileration; it is of low or-

Table 7. Toxicological/Physiological Properties of Specific Substances (Cont'd) (API, 1977)

Substance	Toxicological/Physiological Effects	
	Acute	Chronic
		der of severity and usually requires six to ten years of exposure before diagnosable roentgenographic changes occur; no evidence of physical impairment is associated with these clinical findings
Iron pentacarbonyl	no reported human exposures; animal studies indicate toxicity is similar to $Ni(CO)_4$, i.e., respiratory distress, limb weakness and tremors	no data available on chronic effects
Kerosine	composition varies somewhat but principal components are C_5-C_{16} paraffins; acute effects include headache, fatigue, tinnitis, irritation of eyes and respiratory tract, unconsciousness	chronic effects similar to acute but less severe; conjunctivitis and bronchitis, irritation of mucous membranes
Lead, alkyl	readily absorbed through skin in acutely toxic amounts; except that gastrointestinal complications are absent; development of symptoms are similar to inorganic lead intoxication, severe overexposure, results in tremors, profound cerebral involvement, delirium tremens-like attacks unconsciousness and/or death	development of chronic effects similar to that for inorganic leads
Lead, inorganic	gastrointestinal disorders, colic, constipation in extreme overexposures; effects described as "chronic" can result after even brief exposures	continuation of acute symptoms, presence of stippled cells, anemia, weakness (and in some cases paralysis) of extensor muscles primarily of the wrists, encephalopathy in severe poisonings
Manganese	no significant immediate effects unique to manganese	causes a disease known as "manganism" characterized by unaccountable laughter, euphoria, impulsiveness, and insomnia followed by overpowering somnolence; also encountered: cramps, headache, sexual excitement followed by impotence, as poisoning develops one approaches absolute detachment; manganese poisoning is usually permanently disabling unless treated

Table 7. Toxicological/Physiological Properties of Specific Substances (Cont'd) (API, 1977)

Substance	Toxicological/Physiological Effects	
	Acute	Chronic
Mercaptans (methyl and ethyl)	severe eye irritation, depression of CNS, pulmonary edema, injury to the respiratory system causing death due to respiratory paralysis	headache, nausea, irritation of eyes and mucous membranes
Methanol	depression of CNS; acidosis cerebral edema and hemorrhages; optic nerve neuritis leading to atrophy and blindness; fatalities result from severe depression of respiratory center	conjunctivitis, headache, giddiness, insomnia, gastrointestinal disturbances, failure of vision
Naphtha	toxicity varies directly with aromatic hydrocarbon content; effects include narcotic action and disturbances of the gastrointestinal system, photosensitivity	similar to but less severe than acute effects; chronic effects predominantly associated with aromatic hydrocarbon content
Nickel	severe, transient pneumonitis; animal studies have revealed evidence of acute toxicity in the form of pathological changes in the lung, pneumonia and hyperplasia of lymphoid tissue	evidence of significant increased incidence of lung cancer among exposed workers; dermatitis, or "nickel itch", is most prevalent effect; evidence exists that nickel is both a skin and respiratory tract sensitizer
Nickel carbonyl	frontal headache, dizziness, tightness in chest, limb weakness, nausea, vomiting; delayed effects usually develop several hours after exposure and include pain and tightness in chest; dry cough, shortness of breath, cyanosis and convulsions; in lethal exposures, death usually results from respiratory failure	some evidence of increased incidence of nasal and lung cancers; studies with animals tend to confirm human experience although specific cause-and-effect relationships have not been established
Nitric acid	delayed but eventually irritating and corrosive to moist tissue, inhalation of harmful concentrations may not be immediately noticed	chronic bronchitis, chemical pneumonia, erosion of the teeth
Nitrogen dioxide	coughing, choking, headache, abdominal pain and nausea followed by a "symptom-free" period of 6-72 hours after which fatigue, uneasiness, hyperpnea, dyspnea and pulmonary edema edema develop; in fatal overexposures, cyanosis, coughing, fro-	chronic bronchitis, irregular cardiac actions, respiratory complications, recurrent asthmatic-like attacks and, rarely, pulmonary fibrosis and emphysema

Table 7. Toxicological/Physiological Properties of Specific Substances (Cont'd) (API, 1977)

Substance	**Toxicological/Physiological Effects**	
	Acute	**Chronic**
	thy expectoration and unconsciousness follow	
Oil	toxicological and physiological properties vary considerably as a function of composition of the oils; properties determined by relative amounts of paraffinic, olefinic, naphthenic and aromatic fractions and, often more importantly, various special additives	
Phenol	intense burning at point of contact, cyanosis, muscular weakness, tremors, convulsions and collapse may develop after inhalation, ingestion or skin contact	except for cases of absorption through the skin, there are no reports of adverse chronic effects in industrial environments; can be absorbed readily through skin in toxic amounts
Phosphoric acid	irritating and corrosive to eyes, nose, throat and upper respiratory tract although effects are not as pronounced as with nitric or sulfuric acids	similar to acute effects but less severe
Propylene	similar to ethylene; generally considered a simple asphyxiant and without significant toxicity	
Residuum	toxicological/physiological properties are determined primarily on the composition of the various "bottoms" products; of particular concern is the carcinogenic potential associated with polyclic aromatic hydrocarbons present in varying concentrations in some residual material	
Silica (crystalline)	no significant acute toxicity unique to crystalline silica	cumulative and progressive development of pneumoconiosis (silicosis); increase in pulmonary density progressing to diffuse development of nodules which increase to the size where they in terfere with pulmonary function; dyspnea; emphysema, chronic bronchitis
Sodium hydroxide	severely irritating to upper respiratory tract, ulceration of nasal septum passages, general discomfort	similar to acute effects but less severe
Sulfuric acid	severe irritation of eyes and upper respiratory system	similar to acute effects but less severe; tracheobronchitis, stomatitis, conjunctivitis, gastritis, erosion of teeth
Toluene	strong narcotic action, extreme	similar to but less severe than

Table 7. Toxicological/Physiological Properties of Specific Substances (Cont'd) (API, 1977)

Substance	Toxicological/Physiological Effects	
	Acute	**Chronic**
	fatigue, mental confusion, nausea, headache and dizziness in trations >400 ppm	acute effects; primary effect at concentrations < 200 ppm is irritation of eyes and respiratory tract
Xylenes	strong narcotic action when concentration exceeds 200 ppm	headache, fatigue, irritability, nausea, anorexia, irritation of eyes, nose and throat
Zinc oxide	inhalation of freshly formed fume produces characteristic "metal fume fever" with symptoms resembling influenza, e.g., chills, fever, elevated body temperature; recovery invariably is complete within 48 hours even without symptomatic treatment	no evidence of chronic toxicity

Table 8. Physiological Properties of Specific Physical Stresses (API, 1977)

Stress	Physiological Effects	
	Acute	**Chronic**
Cold	frostbite as a result of local damage to tissues usually to the skin and muscles of the hands and feet; condition sometimes irreversible requiring amputation in severe exposures to cold result from extreme fatigue due to prolonged shivering	lowering of body temperature, shivering; tendency toward arthritis and/or viral infections
Heat	*heat stroke:* sharp rise in body temperature; dry warm skin; confusion; delirium and convulsions *heat exhaustion:* rapid, shallow breathing; weak, slow pulse; moist, clamming, pale skin *heat shock:* cramps, weakness, nausea, fatigue and dizziness *heat fatigue:* lassitude, irritability, fatigue	no evidence of chronic effects attributable to exposure to heat
Noise	extremely excessive noise (> 140 dB) can produce severe pain and damage to the hearing mechanism; less severe exposures result in either or both permanent and temporary threshold shift (decrease in hearing ability)	gradual decrement in hearing ability; psychological effects; interference with communication
Radiation, Ionizing	all forms of ionizing radiation are capable of damaging tissue of the body; increasing penetration ability from alpha, beta, gamma to X-rays; extent of damage dependent upon energy of radiation and relative sensitivity of tissue contacted	chronic efects include dermatitis, sterility, leukopenia, leukemia, anemia, bone necrosis, glandular dysfunction, fatal injury, cataracts and tumor induction
Radiation, Non-ionizing	*microwaves* can result in significant heating of body tissue, the organs most susceptible being those least able to dissipate heat (e.g., eyes, testicles, etc.)	similar to acute effects but less severe; actual effects are related to wavelength, power intensity, and duration of exposure
	infrared radiation does not penetrate below superficial skin layers; thus, primary effect is to heat the skin and tissues immediately below	excessive exposure of eyes reportedly has resulted in cataract-like formations
	ultraviolet radiation results primarily in effects on the skin surface and eyes although more severe than infrared radiation	most common overexposure is to direct sunshine which can result in tumor development; some evidence of synergistic effects with various chemicals

B. Human Exposure and Epidemiological Studies

Assessment of the relative risk to employees of the petrochemical industry involves analysis of several types of informational studies. Geographical studies have found increased rates of cancer of the lung, nasal cavities and sinuses, and skin in counties with petroleum industries (Blot and Fraumeni, 1976; Blot *et al.*, 1977). Studies such as these do not consider occupation, residency, or other etiological factors, and, as a result, are useful only as indicators of probable links to disease. More direct studies have found a 1.6 greater chance of lung cancer in petrochemical workers (Menck and Henderson, 1976). In-depth epidemiological studies of petroleum refinery workers have reported no significant increases in total cancer mortality rates or in mortality rates from skin (Wade, 1963; Baird, 1967) or respiratory tract cancer (Baird, 1967; Thériault and Goulet, 1979). Increased mortality caused by disease and cancer of the digestive system (particularly the esophagus and stomach) does, however, appear to be associated with exposure to petroleum refinery environments (Thériault and Goulet, 1979; Hanis *et al.*, 1979). In contrast to the findings of Baird (1967) and Thériault and Goulet (1979), Hanis *et al.* (1979) also reported significantly increased incidences of cancer of the trachea, bronchus and lung in refinery workers.

Blot and Fraumeni (1976) correlated the incidence of lung cancer with occupation by county in the United States from 1950-1969. Each county was classified according to the number of people employed by a particular industry. If the number was at least 0.1 percent of the county's total population, that county was considered as an "industry country." Of the 3056 counties surveyed, 185 were petroleum industry counties, 147 of which had at least 0.1 percent of the population employed in the industry and 38 had more than 1 percent employed. Mortality rates from lung cancer were increased in counties with a higher degree of urbanization. After adjusting for demographic influences, lung cancer mortality was significantly higher in counties with four industries: paper, chemical, petroleum, and transportation. The rates increased as the percentage of workers involved in the industries increased. The predicted annual increases in age-adjusted lung cancer mortality rates among white males for the petroleum industry were estimated at 0.98 ± .45/100,000 population for 0.1-1.0 percent employed counties and 1.32 ± 1.00/100,000 population for 1.0 percent employed counties. The median increase for lung cancer mortality in petroleum industry counties was 6 percent for counties with more than 1 percent of the population employed and 3 percent in the lower concentration counties. Among the heavy concentration counties, 65 percent exhibited increased rates of lung cancer mortality. Slight, though not significant, increases in lung cancer mortality were also seen when information concerning white females was analyzed. Industrial correlations for non-white males were the same as for white males but increases were significant only for the chemical industry. When interpreting the increased rates of cancer in petroleum industry counties, the influence of other factors including urbanization, geographic region, socioeconomic status, and cigarette smoking must be considered. The county mortality data used did not specify occupation, location or length of residency. In order to better assess the occupational risk to petroleum workers, more specific and complete information is required.

Cancer mortality in petroleum industry counties (PIC) was further evaluated in a comparison of the mortality rates of various cancers in 39

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U.S. counties engaged heavily in the industry, and 117 comparable counties with no involvement in the industry (Blot et al., 1977). The two groups of counties were matched for geographic region, population size, and various demographic indicators. Nonpetroleum industries were equally divided between the two groups. There was, however, a tendency for chemical plants to occur in PIC counties at a much higher rate than in control counties; 11 of the 39 PIC versus 6 of the 117 control counties had equal numbers of workers employed in the chemical and petroleum industries. Table 9 presents the ratios of age-adjusted mortality rates for various cancers during 1950-1969. Mortality rates from cancer were significantly elevated for: all tumor sites combined; nasal cavity and sinuses; lungs; skin; testis; stomach; and rectum. The ratios of mortality rates were also separated according to population size. Cancers of the nasal cavity, lung, and skin were high regardless of population whereas cancers of the stomach, rectum, and testis increased in highly populated counties. The influence of the chemical industry on cancer rates should be considered in any interpretation of these results. The rates of lung and skin cancers in the 11 PIC with chemical industries was 10 percent higher than in PIC without; for nasal cancer the increase was 50 percent in PIC counties with chemical industries versus those without.

In an attempt to correlate rates of lung cancer to occupation, Menck and Henderson (1976) reviewed 2,161 death certificates mentioning lung cancer for 1968-70 and 1,777 cases of lung cancer in Los Angeles County for 1972-73. The Standard Mortality Ratio (SMR) was calculated according to the following formula: ratio of observed deaths plus incident cases to expected deaths plus incident cases; the SMR for all occupations

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Table 9. Ratios of Age-adjusted Mortality Rates, 1950 to 1969, Among White Males in Petroleum Industry Counties to Those in Control Counties by Cancer Site (Blot <u>et</u>. <u>al</u>., 1977)

Cancer site	Ratio
Buccal cavity and pharynx	1.04
Esophagus	1.06
Stomach	1.09*
Colon	1.02
Rectum	1.07**
Liver	1.06
Pancreas	1.05
Nasal cavity and sinuses	1.48*
Larynx	1.09
Lung	1.15*
Prostate	0.98
Testis	1.10**
Kidney	1.05
Bladder	1.02
Melanoma and other skin	1.10**
Brain	0.94**
Thyroid and endocrine	1.04
Bone and connective tissue	0.98
Hodgkin's disease	0.96
Other lymphomas	1.01
Multiple myeloma	1.05
Leukemia	1.03
All sites combined	1.06

$^{*}P < .01$

$^{**}.01 < P < .05$

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was 100. For the petroleum and coal products industry, the SMR was 160 for white males 20-64 years of age, thus indicating a 1.6 times greater chance of developing lung cancer. General air pollution and smoking habits were not considered, thus limiting interpretation of the increased risk factor.

Baird (1967) conducted an epidemiological study of cancer mortality of employees in Humbles Baytown refinery. Multiple sources of air pollution were not considered since there were no other major sources of industrial pollution on the prevailing wind side of the area. The study covered the period from 1935-1963; the average number of employees over this period was 15,437. There were 377 reported cancer deaths, equivalent to a cancer death rate of 84.4/100,000/year. Comparison with the cancer mortality rates of the surrounding geographical areas and of the United States for 1945 places the cancer death rate for petroleum refinery workers within the limits for the general public (Table 10). The relative frequency of death due to all cancers (Table 11) and the mortality rate from skin cancer and respiratory tract tumors (Table 12) did not reveal significant differences from the control group. Cancer mortality was also examined by major departments in the company, including the Pipe Line Co., production, refinery, sales, and exploration (Table 13). Differences in relative frequency were not considered significant since a small number of total deaths often raised the cancer death rate disproportionately. Another factor to consider is uneven age distribution and length of service records for the workers in each department.

The incidence of skin cancer among refinery workers was examined in a "case matching" study of three large refineries (Wade, 1963). In an effort to correct for other factors affecting the incidence of skin cancer

Table 10. Cancer Mortality Rates for Ages Over 20 in 1945*
(Baird, 1967)

Rate (all forms)	Frequency/100,000/yr.
United States	131.7
Arkansas	78.7
Louisiana	97.2
Oklahoma	102.1
Texas	88.0
Humble Companies, all employees and annuitants	84.4

*Figures for U.S. and 4 states reduced by 2% to correct for tumor mortality 0-20 year age group.

Table 11. Relative Frequency of All Cancer Deaths
(Baird, 1967)

		Deaths		
			Cancer deaths**	
Area	Year	Total*	No.	%
U.S.	1945	1,258,744	173,915	13.8
Arkansas	1945	13,203	1,457	11.0
Louisiana	1945	19,868	2,333	11.7
Oklahoma	1945	16,991	2,171	12.8
Texas	1945	52,850	5,801	11.1
Humble Companies	1935-1955	1,481	179	12.1

*Figures for U.S. and 4 states reduced by 10.2% to correct for mortality occurring in age group 0-20 years.

**Figures for U.S. and 4 states reduced by 2% to correct for tumors occurring in age group 0-20 years.

Table 12. Mortality Rates from Skin Cancer and Respiratory Tract Tumors (Baird, 1967)

Group	Skin Cancer Deaths/100,000/yr.	Respiratory Tract Tumors Deaths/100,000/yr.
United States (1945)	5.96	30.8
Arkansas (1945)	5.40	14.9
Louisiana (1945)	4.96	25.2
Oklahoma (1945)	8.95	14.7
Texas (1945)	7.40	16.5
Above states combined	6.93	17.6
Humble Companies' employees and annuitants (1935-1963)	3.88	17.3

Table 13. Cancer Mortality Experienced by Major Departments (Baird, 1967)

Occupational group	Average population	Cancer deaths	Total deaths	Death rate/100,000/yr.		Relative frequency (%)
				Total	Cancer	
Pipe Line Co.	2373	76	578	830	110	13.2
Production	4892	162	846	595	114	19.2
Refinery (Baytown)	6239	96	839	465	52	11.2
Sales	843	23	121	500	95	18.9
Exploration	1090	20	71	225	63	23.0
Total employees	15437	377	2455	541	81	15.0

other than exposure to oil slurry (a residue from catalytic cracking); the control and exposure groups were matched for age, company service, race, sex, complexion, hair color, personal hygiene, family history of cancer, and exposure to other etiologic factors. During the time of the study, 1949-1961, 45 neoplasms occurred in the control group and 46 in the exposed group, of which 53.5 percent and 58.7 percent, respectively, were skin lesions. It was noted that all skin cancers of the extremeties occurred in the exposed group. The age of the first appearance of skin cancer did not, however, seem to be job-related. The age of the first appearance of skin cancer did not differ significantly in the two groups of workers. The oil fractions tested are known to be carcinogenic to laboratory animals; absence of such an effect in the workers of this study may indicate the effectiveness of the protective program aimed at minimizing exposure, or a longer latency period necessary for the development of such cancers.

In a cohort epidemiologic study, Hanis and coworkers (1979) examined the cancer mortality experience from 1964 to 1973 of 15,032 Imperial Oil Limited refinery employees. The study population was composed of both active workers and company annuitants who were exposed on a daily basis to crude petroleum or its products, and subdivided into refinery and non-refinery, and exposed, moderately exposed, and non-exposed groups. Of the 15,032 workers, 1511 deaths occurred of which 301 were due to cancer; a total of 865 employees were lost to follow-up. Disease of the circulatory system and malignant neoplasms together accounted for nearly 80% of all deaths (Table 14); analysis of deaths from causes other than cancer have not yet been published.

Table 14. Percentage Distribution of Deaths in the Study Population by Major Cause, 1964-1973 (Hanis *et al.*, 1979)

Cause of Death*	No.	%
Malignant neoplasms (140-209)	301	19.9
Diseases of circulatory system (390-458)	905	59.9
Diseases of respiratory system (460-519)	90	6.0
Diseases of digestive system (520-577)	51	3.4
Accidents, poisonings, and violence (800-999)	59	3.9
All other	105	6.9
Total	1,511	100.0

*ICDA Codes, 8th Revision (1965) shown in parentheses.

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An examination of the distribution of deaths by cause and age revealed that only five cancer deaths occurred in employees under the age of 40. The distribution of cancer deaths at ages 40 and over in the exposure and refinery groups and their controls is shown in Table 15. In all groups, the sites accounting for the largest percentages of deaths were trachea, bronchus and lung, and the digestive tract -- particularly the intestines in the exposed and unexposed and other digestive system organs in the moderately exposed workers. There were no cancers of the small intestines.

Mortality from all malignant neoplasms in the exposed group was significantly higher than that in the nonexposed employees (Table 16). The two sites for which mortality was significantly higher and which accounted for the largest part of the excess cancer mortality in the exposed group were esophagus and stomach, and trachea, bronchus and lung. The risk of death from cancer of the esophagus/stomach and lung in the exposed group was, respectively, more than three and about twice that in the nonexposed. In the exposed group, increasing risks of both cancers occurred with increasing duration of employment (Table 17).

When refinery workers were compared with non-refinery workers without consideration of exposure to petroleum in either group, the refinery workers were found to have almost twice the risk of cancer of the intestines (including rectum) and other digestive organs (Table 18). The mortality in the refinery group from neoplasms of the lymphatic and hematopoietic systems was about half that in the non-refinery group. In contrast to the findings with the exposed/nonexposed worker groups, the age-adjusted mortality rates for intestinal cancer in refinery workers did not increase with duration of employment, the rates being 7.3, 5.9, and 7.5/10,000 person-years for the categories 11-20 years, 21-30 years, and over 30 years, respectively.

Table 15. Percentage Distribution of Cancer Deaths in the Exposure and Refinery Comparison Groups, 1964-1973* (Hanis et al., 1979)

Site of Cancer†	Cancer Deaths				
	Nonexposed (N=65)	Moderately Exposed (N=16)	Exposed (N=215)	Non-Refinery (N=132)	Refinery (N=164)
Buccal cavity and pharynx (140-149)	1.5%	—	2.8%	2.3%	2.4%
Esophagus and stomach (150, 151)	4.6	12.5%	13.0	11.4	17.0
Large intestine and rectum (153, 154)	18.5	6.2	13.5	10.6	17.1
Other digestive organs (155-159)	12.3	31.2	9.3	9.1	12.8
Trachea, bronchus, lung (162)	20.0	12.5	31.2	29.5	26.2
Other respiratory organs (160, 161, 163)	1.5	—	1.4	1.5	1.2
Bone, connective tissue, skin (170-174)	7.7	6.2	2.3	5.3	2.4
Prostate (185)	10.8	—	8.4	7.6	9.1
Urinary organs (188, 189)	7.7	—	6.5	6.8	6.1
Other and unspecified sites (190-199)	7.7	6.2	5.6	4.5	7.3
Lymphatic and hematopoietic system (200-209)	7.7	25.0	6.0	11.4	4.3
Total	100.0	99.8	100.0	100.0	99.9

*Age groups less than 40 excluded from this table.
†ICDA Codes, 8th Revision (1965) shown in brackets.

Table 16. Age-Adjusted* Cancer Mortality Rates for Specific Sites in Exposed and Nonexposed Workers, 1964-1973† (Hanis et al., 1979)

Site of Cancer‡	Age-Adjusted Mortality Rates per 10,000 Person-Years				
	Nonexposed	Moderately Exposed		Exposed	
	Rate	Rate	Relative Risk	Rate	Relative Risk
All sites (140-209)	32.3 (65)¶	18.4 (16)	0.57	39.7 (215)	1.23§
Esophagus and stomach (150,151)	1.6 (3)	1.7 (2)	1.06	5.2 (28)	3.25§
Intestines and rectum (153, 154)	6.1 (12)	1.5 (1)	0.26	5.3 (29)	0.88
Other digestive organs (155-159)	3.9 (8)	2.6 (5)	0.67	3.5 (20)	0.90
Trachea, bronchus, lung (162)	6.6 (13)	2.6 (2)	0.39	12.5 (67)	1.89§
Prostate (185)	3.8 (7)	—	—	3.2 (18)	0.84
Urinary bladder, kidney (188, 189)	2.4 (5)	—	—	2.6 (14)	1.08
Lymphatic hematopoietic system (200-209)	2.6 (7)	4.9 (4)	1.88	2.3 (13)	0.88

*Direct adjustment using the study population as standard
†Age groups less than 40 excluded from this table
‡ICDA codes, 8th Revision (1965) shown in brackets
§Indicates that the exposed rates differed significantly from the nonexposed at $p < 0.05$, Chi square, d.f. = 1[9]
¶Numbers of deaths upon which rates are based shown in parentheses

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Table 17. Age-Adjusted[*] Stomach and Lung Cancer Mortality Rates in Exposed Workers by Duration of Employment, 1964-1973[†] (Hanis et al., 1979)

Duration of Employment (Years)	Cancer Mortality Rates/10,000 Person-Years (Exposed Workers) Esophagus and Stomach	Cancer Mortality Rates/10,000 Person-Years (Exposed Workers) Trachea, Bronchus and Lung
11-20	3.0 (4)[‡]	10.1 (11)
21-30	5.8 (11)	14.7 (27)
31+	7.8 (13)	19.6 (29)

[*] Direct adjustment with the study population, age ≥40, > 10 years service as the standard

[†] Age groups less than 40 excluded from this table

[‡] Numbers of deaths upon which rates are based are shown in parentheses

Table 18. Age-Adjusted[*] Cancer Mortality Rates for Specific Sites in Refinery/Non-Refinery Workers, 1964-1973[†] (Hanis et al., 1979)

Site of Cancer[‡]	Age-Adjusted Mortality Rates/10,000 Person-Years Refinery	Non-Refinery	Relative Risk
All sites (140-209)	40.6 (164)[¶]	31.4 (132)	1.29[§]
Esophagus and stomach (150, 151)	4.5 (18)	3.7 (15)	1.22
Intestines & rectum (153, 154)	6.9 (28)	3.5 (14)	1.97[§]
Other digestive organs (155-159)	5.1 (21)	2.8 (12)	1.82[§]
Trachea, bronchus, lung (162)	10.9 (43)	9.2 (39)	1.18
Prostate (185)	3.3 (15)	2.6 (10)	1.27
Urinary bladder, kidney (188, 189)	2.5 (10)	2.1 (9)	1.19
Lymphatic and hematopoietic system (200-209)	1.7 (7)	3.7 (15)	0.46

[*] Direct adjustment using the study population as standard

[†] Age groups less than 40 excluded from this table

[‡] ICDA Codes, 8th Revision (1965) shown in brackets

[§] Indicates that the refinery rates differed significantly from the non-refinery at $p<0.05$. Chi square, d.f. = 1(*)

[¶] Numbers of deaths upon which rates are based shown in parentheses

The excess cancer mortality in the exposed and refinery workers was also generally consistent in comparisons specific for refinery/exposure subgroup (Table 19) and geographic area, although small numbers of deaths in some categories introduced difficulties in interpretation.

Table 20 shows the age-adjusted cancer mortality rates by job titles for various sites, and ratios of the job-specific mortality rates to the study population rate (Hanis *et al.*, 1979). Rates for the specific cancers that were about twice as high in the particular groups of jobs relative to the study population included: (1) intestinal cancer, in service workers (laundry workers, custodians, watchmen and inspectors), mechanics, boilermakers, and pipefitters; (2) other digestive organ cancers in engineers; (3) stomach cancer in service workers, garage workers and route salesmen; and (4) lung cancer in office workers, workers in utilities, building trades and boilermakers.

Thériault and Goulet (1979) assessed the survival status of 1205 men who were employed for more than five years in a Canadian oil refinery from 1928 through 1976, and reviewed death certificates. It resulted that of the 1205 refinery workers, 190 were lost to follow-up and 108 died; the study group accounted for 1015 men or 84% of the total study population. An examination of observed and expected numbers of deaths (based on reference Quebec population) revealed that the oil refinery workers showed a standard mortality ratio lower than expected for all causes of death (SMR = 78.43; Table 21). The SMR's for specific causes, though sometimes differing from 100, were not statistically different. When mortality was studied according to duration of employment, it appeared that workers employed for less than 20 years since the first exposure had statistically lower SMR's for all

Table 19. Age-Adjusted* Intestinal, Other Digestive Organ, Stomach and Lung Cancer Mortality Rates in Refinery/Exposure Subgroups, 1964-1973† (Hanis <u>et</u> <u>al</u>., 1979)

Subgroup	Age-Adjusted Cancer Mortality Rates/10,000 Person-Years			
	Intestines (153, 154)‡	Other Digestive Organs (155-159)	Esophagus and Stomach (150, 151)	Trachea, Bronchus, and Lung (162)
Refinery exposed	7.2 (26)§	4.4 (17)	4.7 (17)	11.9 (42)
Refinery moderately exposed	8.8 (1)	6.7 (2)	3.3 (1)	—
Refinery nonexposed	5.5 (1)	9.3 (2)	—	—
Non-refinery exposed	1.7 (3)	1.9 (3)	6.0 (11)	13.6 (25)
Non-refinery moderately exposed	—	15.2 (3)	5.1 (1)	7.2 (2)
Non-refinery nonexposed	6.4 (11)	3.2 (6)	1.9 (3)	6.9 (13)

*Direct adjustment using the study population as standard

†Age groups less than 40 excluded from this table

‡ICDA codes, 8th Revision (1965) shown in brackets

§Numbers of deaths upon which rates are based shown in parentheses

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Table 20. Age-Adjusted* Cancer Mortality Rates by Site and by Specific Job, 1964-1973† (Hanis et al., 1979)

Job Title‡	Age-Adjusted Cancer Mortality Rates/10,000 Person-Years							
	Intestines (153, 154)		Other Digestive Organs (155-159)		Esophagus and Stomach (150, 151)		Trachea, Bronchus and Lung (162)	
	Rate	Risk Ratio§	Rate	Risk Ratio	Rate	Risk Ratio	Rate	Risk Ratio
Services: laundry, custodial, watchmen, inspectors (N=156) (RE)	11.9¶ (3)	2.3	—	—	11.9 (3)	3.0	—	—
Mechanics, boiler-makers, pipe fitters (N=1496) (E)	9.8 (13)	1.9	5.4 (8)	1.4	4.0 (5)	1.0	12.7 (17)	1.3
Operations, processing, field supervisors, dewaxing, asphalt stills, crude stills, clay press (N=1303) (RE)	6.7 (7)	1.3	4.5 (5)	1.1	4.8 (5)	1.2	9.1 (10)	0.9
Office workers (including executives) (N=2546) (NE)	6.1 (11)	1.2	2.6 (5)	.6	—	—	22.5 (12)	2.2
Garage workers, route salesmen (N=807) (NR, E)	4.2 (2)	.8	3.5 (2)	.9	9.0 (4)	2.2	12.0 (7)	1.2
Plant clerks (N=609) (ME, E)	3.6 (2)	.7	—	—	—	—	17.9 (9)	1.8
Utilities, building trades, boilerhouse (N=226) (RE)	3.4 (2)	.7	—	—	5.3 (2)	1.3	22.3 (5)	2.2
Engineers (N=625) (ME)	—	—	9.2 (4)	2.3	3.7 (2)	0.9	—	—
Packaging, shipping (N=494) (E)	—	—	—	—	4.4 (2)	1.1	10.6 (5)	1.1
Study population	5.1 (42)	1.0	4.0 (33)	1.0	4.0 (33)	1.0	10.0 (82)	1.0

*Direct adjustment using the study population as standard

†Age groups less than 40 excluded from this table

‡Refinery and exposure groups are shown in parentheses: R=refinery, NR=Non-refinery, E=exposed, ME=moderately exposed, NE=nonexposed

§Ratio of rate in subgroup to study population rate

¶Numbers of deaths upon which rates are based are shown in parentheses

Table 21. Observed and Expected Number of Deaths and Standard Mortality Ratio (SMR) Among Oil Refinery Workers (1928-1976) According to the Time Elapsed Since Start of Exposure (Thériault and Goulet, 1979)

Disease Category (ICDA*)	-20 Years Since 1st Expos.		+20 Years Since 1st Expos.		Total	
	Obs/Exp.†	SMR	Obs/Exp.	SMR	Obs/Exp.	SMR
Malignant neoplasms (140-209)	7/8.36	83.73	18/20.18	89.19	25/28.54	89.29
Central nervous system diseases (320-349)	1/0.70	142.85	0/0.65	—	1/1.35	74.07
Cardiovascular diseases (390-458)	12/19.07	62.92	40/42.56	93.98	52/61.63	84.37
Respiratory system diseases (460-519)	0/1.57	—	3/4.29	69.93	3/5.86	51.19
Digestive system diseases (520-577)	0/2.70	—	7/3.92	178.57	7/6.62	105.74
Genitourinary system diseases (580-607)	0/1.27	—	0/1.27	—	0/2.54	—
Accidents and violence (800-999)	12/11.44	104.89	1/5.82	17.18‡	13/17.26	75.31
Others	1/7.77	12.87‡	6/6.73	89.15	7/13.90	50.36
All causes (001-999)	33/52.28	63.12‡	75/85.42	87.80	108/137.70	78.43‡

*International Classification of Diseases, Eighth Revision

†Expected deaths based on age specific death rates of Quebec males

‡Statistically significant

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causes of death and for the category "other diseases" when compared with the reference population.

The Thériault and Goulet (1979) study also showed no significant difference in the total cancer mortality death rate between the refinery workers and the reference Quebec population (SMR = 89.29; Table 22). A detailed examination of the cancer types indicated that (1) lung cancer was less frequent than expected (3 vs 7.42); and (2) an unusual appearance of three brain cancers in workers within an interval of less than 20 years since the start of exposure (SMR = 652.17). The investigators noted that though cancers of the digestive system were not statistically higher than expected (12 vs 10.22), the high number of deaths caused by the cancer of the digestive system organs (SMR = 117), in combination with the diseases of the digestive system, deserves additional study. Table 23 presents a list of workers who died of cancer by type of cancer, age at death, occupation, time elapsed between start of work and death, and number of years of service. Table 24 gives the distribution of workers who died of cancer by occupational categories.

Additional reports of high incidences of brain tumors, glioblastoma multiforma, in employees of Union Carbide and Monsanto in Texas City, Texas are currently under investigation (OHSL, 1979). Eleven cases of brain tumors have been reported in the Union Carbide plant since 1962. The difficulty in analysis arises from the fact that workers are exposed to a wide variety of chemicals and the problem of separating their individual exposure factors. At the Union Carbide plant, 60 employees are regularly exposed to vinyl chloride, which has been linked with glioblastoma and angiosarcoma of the liver. Studies by the Manufacturing Chemists Association

Table 22. Observed and Expected Number of Deaths Due to Malignant Neoplasms and Standard Mortality Ratio (SMR) Among Oil Refinery Workers According to Time Elapsed Since Start of Exposure (Thériault and Goulet, 1979)

	-20 Years Since 1st Expos.		+ 20 Years Since 1st Expos.		Total	
Disease Category (ICDA*)	Obs/Exp.†	SMR	Obs/Exp.	SMR	Obs/Exp.	SMR
Nose, tongue, orbit (140-149)	0/0.21	—	0/0.59	—	0/0.79	—
Digestive system (150-159)	3/3.10	96.77	9/7.12	126.40	12/10.22	117.41
Larynx, lung, pleura (160-163)	0/1.80	—	3/6.68	44.91	3/8.48	35.37
Bone, skin (170-173)	0/0.23	—	1/0.19	526.31	1/0.42	238.09
Kidney, genital (185-189)	0/0.58	—	3/1.97	152.28	3/2.55	117.64
Brain, central nervous sytem (190-192)	3/0.46	652.17‡	0/0.31	—	3/0.77	389.61
Leukemia, lymphoma (200-209)	1/0.90	111.11	2/1.46	136.98	3/2.36	127.11
Other cancers	0/1.08	—	0/1.87	—	0/2.95	—
All neoplasms (140-209)	7/8.36	83.73	18/20.18	89.19	25/28.54	89.29

*International Classification of Diseases, Eighth Revision
†Expected deaths based on age specific death rates of Quebec males
‡Statistically significant

Table 23. List of Workers Who Died of Cancer (Among 1015 Men Who Worked for Over 5 Years at the Oil Refinery) (Thériault and Goulet, 1979)

No.	Type of Cancer	Age at Death	Occupation at the Refinery	Time Elapsed Between Starting Work & Death	No. of Years of Service
1	Stomach (151)	51	Maintenance	24	15
2	Stomach (151)	55	Maintenance	33	29
3	Stomach (151)	43	Laboratory	21	21
4	Stomach (151)	50	Office	23	23
5	Rectum (154)	57	Laboratory	13	13
6	Rectum (154)	67	Operations	18	15
7	Pancreas (157)	65	Maintenance	29	23
8	Pancreas (157)	71	Operations	30	8
9	Intestinal (159)	45	Maintenance	14	14
10	Brain (191)	43	Operations	18	6
11	Lung (162)	77	Maintenance and others	25	15
12	Lung (162)	80	Office	42	19
13	Liposarcoma of the legs (170)	79	Maintenance	36	13
14	Prostate (185)	74	Office	29	17
15	Prostate (185)	66	Maintenance	23	19
16	Bladder (188)	51	Maintenance	21	21
17	General lymphoma (200)	68	Maintenance	25	20
18	Myelogenous leukemia (205)	43	Operations	13	13
19	Intestine (153)	72	Operations and office	36	28
20	Brain (192)	41	Maintenance	13	12
21	Lymphosarcoma (200)	56	Office and maintenance	29	29
22	Pancreas (157)	43	Maintenance	25	19
23	Lung (162)	46	Maintenance	20	8
24	Intestinal (153)	73	Office	40	28
25	Brain (191)	41	Maintenance-operations	19	18

Table 24. Cancer Distribution According to Occupational Categories (Thériault and Goulet, 1979)

Occupational Categories	No. of Workers	No. of Cancers Observed	No. of Cancers Expected*	Obs/Exp.
Operators	299	4	5.5	0.73
Office Employees	168	4	3.8	1.05
Maintenance	321	11	9.9	1.11
Others (belong to several groups)	227	6	5.8	1.03
Total	1015	25	25	

*Expected numbers based on age adjusted death rates in the study population
$\chi^2 = 0.55$; dl = 3; $p = .91$

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revealed 12 cases of glioblastoma multiforma versus the six expected in a group of vinyl chloride workers. Inferences cannot be drawn, however, because of the inadequate information on type and length of exposure. Dow Chemical has reported negative results in studies of their plants in Texas, Michigan, and Louisana. OSHA is presently conducting an epidemiological study in the Texas plants.

Carpenter and coworkers (1975a-h; 1976a-e; 1977) have conducted numerous studies on the response of animals and humans to the vapors of various petroleum hydrocarbons. The hydrocarbons tested were those with approximate benzene concentrations of less than 2 percent. The results of the human responses to the vapors are presented in Table 25.

VIII. PERTINENT NIOSH PUBLICATIONS

A. Criteria Documents

Subject	NIOSH Publication No.
Acetylene	76-195
Acrylonitrile	78-116
Alkanes	77-151
Ammonia	74-136
Asbestos	72-10267
Asbestos (revised)	77-169
Asphalt Fumes	78-106
Benzene	74-137
Benzene (revised)	NIOSH only
Cadmium	76-192
Carbon Dioxide	76-194
Carbon Disulfide	77-156
Carbon Monoxide	73-11000
Chlorine	76-170
Chloroform	75-114
Chloroform (revised)	NIOSH only
Chromium (VI)	76-129
Dibromochloropropane	78-115
Epichlorohydrin	76-206
Ethylene Dibromide	77-221
Ethylene Dichloride	76-139
Formaldehyde	77-126
Hot Environments	72-10269

Table 25. Human Response to Various Petroleum Hydrocarbon Vapors (Carpenter et al., 1975a–h; 1976a–e; 1977)

Varnish makers' and Painters' Naphtha	Odor threshold, human	Between 0.007 and 0.0007 mg/1 (1.5 and 0.15 ppm) based on a correction factor of 70% obtained from the measured to metered ratio in the subacute study.
	Sensory threshold, human	Concentrations up to 2.1 mg/1 (450 ppm) caused only slight or transitory responses
Stoddard Solvent	Odor threshold, human	Between 0.005 mg/1 (0.09 ppm) and 0.005 mg/1 (0.9 ppm) (based on a correction factor of 50% obtained from the measured to metered ratio in the subacute study)
	Sensory threshold, human	A concentration of 0.85 mg/1 (150 ppm) caused only slight or transitory response in 15 min. in 1 subject but 2.7 mg/1 (470 ppm) was unacceptable. This substantiates the current TVL of 1.15 mg/1 (200 ppm)
Rubber Solvent	Odor threshold, human	0.04 mg/1 (10 ppm). Based on a correction factor of 64% obtained from the measured to metered ratio in the subacute study.
	Sensory threshold, human	1.6 mg/1 (430 ppm) caused only slight or transitory responses and should be well tolerated by most people.
Mixed Xylenes	Odor threshold, human	Between 0.006 and 0.005 mg/1 (0.14 and 1.4 ppm). (Based on a correction factor of 59% obtained from the measured to metered ratio in the subacute study)
	Sensory threshold, human	Concentrations of 0.46 mg/1 (110 ppm) or less should not be objectionable to most people
"60 Solvent"	Odor threshold, human	Approximately 0.01 mg/1 (2.0 ppm) corrected
	Sensory threshold, human	ca. 1.3 mg/1 (260 ppm); midpoint between 0.86 and 1.7 mg/1
"70 Solvent"	Odor threshold, human	Between 0.00052 and 0.0052 mg/1 (0.1 and 1.0 ppm); approximately 0.004 mg/1 (0.7 ppm) based on a correction factor of 52% obtained from the measured to metered ratio in the subacute study
	Sensory threshold, human	Concentrations of 0.32 mg/1 (59 ppm) or less caused only slight or transitory responses and should be tolerated by most individuals.

Table 25. Human Response to Various Petroleum Hydrocarbon Vapors (Carpenter et al., 1975a-h; 1976a-e; 1977) (Continued)

"140° Flash Aliphatic Solvent"	Odor threshold, human	Approximately 0.004 mg/1 (0.6 ppm)
	Other sensory thresholds, human	Saturated vapor (0.31 mg/1 or 49 ppm) caused a mild drying sensation in the eyes of one volunteer; all volunteers experienced some degree of olfactory fatigue, but no other effects were seen
"80 Thinner"	Odor threshold, human	Approximately 0.004 mg/1 (0.9 ppm)
	Other sensory thresholds, human	0.45 mg/1 (100 ppm) probably will be tolerated by most individuals
"50 Thinner"	Odor threshold, human	Between 0.005 and 0.05 mg/1, the most probable corrected measured concentration being 0.01 mg/1 (2.5 ppm)
	Other sensory thresholds, human	1.7 mg/1 (430 ppm)
Deodorized Kerosene	Odor threshold, human	0.0006 mg/1 (0.09 ppm)
	Other sensory thresholds, human	Substantially saturated vapor at 25°C acceptable for daily inhalation
"40 Thinner"	Odor threshold, human	Between 0.0002 and 0.002 mg/1, the most probable concentration is 0.001 mg/1 (0.17 ppm)
	Sensory thresholds, human	0.21 mg/1 (35 ppm) did not cause adverse effects but was considered disagreeable by two of six
"Toluene Concentrate"	Odor threshold, human	0.01 mg/1 or 2.5 ppm after application of the correction factor of 64% obtained from the measured to metered relationship in the subacute study.
	Sensory threshold, human	1.9 mg/1 or 480 ppm was considered to be a tolerable concentration for an 8-hr working day. This concentration would contain 0.87 mg/1 or 220 ppm of toluene per se.
"High Aromatic Solvent"	Odor thresholds, human	The most probable corrected concentration is 0.0004 mg/1 (0.07 ppm)
	Sensory thresholds, human	0.15 mg/1 (26 ppm) could be expected to have mildly irritating effects only upon sensitive humans

Hydrogen Cyanide	77-108
Hydrogen Fluoride	76-143
Hydrogen Sulfide	77-158
Inorganic Lead	73-11010
Inorganic Lead (revised)	78-158
Methyl Alcohol	76-148
Noise	73-11001
Phenol	76-196
Crystalline Silica	75-120
Refined Petroleum	77-192
Sodium Hydroxide	76-105
Sulfur Dioxide	74-111
Sulfuric Acid	74-128
1,1,2,2-tetrachloroethane	77-121
Tetrachloroethylene (perc)	76-185
Toluene	73-11023
1,1,1-trichloroethane	76-184
Vinyl Acetate	78-205
Vinyl Chloride	NIOSH only
Xylene	75-168
Zinc Oxide	76-104

B. Health Hazard Evaluations (HHE's)

No health hazard evaluations of petrochemical manufacturing facilities were encountered.

C. Other NIOSH Publications

Title	NIOSH Publication No.
Working with Ammonia (folder)	73-11003
Effects of Carbon Monoxide in Vigilance Performance	77-124
Irritant Effects of Industrial Chemicals: Formaldehyde	77-117
Caution: Inorganic Metal Cleaners Can Be Dangerous	76-110

IX. EXISTING STANDARDS

A tabulation of OSHA promulgated standards, NIOSH recommended criteria, and ACGIH threshold limit values (TLV) for selected petrochemicals is presented in Table 26.

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Table 26. Threshold Limit Values, OSHA Standards, NIOSH Recommended Standards

	TLV (ACGIH, 1977)		OSHA (OSHA, 1976)		NIOSH (NIOSH, 1977)	
	ppm	mg/m^3	ppm	mg/m^3	ppm	mg/m^3
Ethylene	asphyxiant	(minimal oxygen content 18% volume)	N/A	N/A	N/A	N/A
Propylene	asphyxiant	(minimal oxygen content 18% volume)	N/A	N/A	N/A	N/A
Ethylene dichloride	50	200	500 (8 hr TWA) 100 (accept. ceiling) 200 (5 min. in 3 hr ceiling)		5 (10 hr TWA) 15 (15 min. ceiling)	
Benzene (skin)	10	30	10 (8 hr TWA) 25 (accept. ceiling) 50 (10 min. ceiling)		1 (60 min. ceiling)	
Styrene	100	420	100 (8 hr TWA) 200 (accept. ceiling) 600 (5 min. in 3 hr ceiling)		N/A	N/A
Ethylbenzene	100	435	100	435	N/A	N/A
Toluene (skin)	100	375	200 (8 hr TWA) 300 (accept. ceiling) 500 (10 min. ceiling)		100 (10 hr TWA) 200 (10 min. ceiling)	
Methanol	200	260	200	260	200 (10 hr TWA) 800 (15 min. ceiling)	260
Xylene (skin)	100 (ceiling)	435	100	435	100 (10 hr TWA) 200 (10 min. ceiling)	
Formaldehyde	2 (ceiling)	3	3 (8 hr TWA) 5 (accept. ceiling) 10 (30 min. ceiling)		(30 min. minimum detectable level ceiling)	1.2
Vinyl chloride	Pending		1 (8 hr TWA) 5 (15 min. ceiling)		1 (15 min. ceiling)	
Terephthalic acid	N/A	N/A	N/A	N/A	N/A	N/A
Ethylene oxide	50	90	50	90	N/A	N/A
Ethylene glycol Particulate		10	N/A	N/A	N/A	N/A
Vapor	100	260				
Butadiene	1000	2200	1000	2200	N/A	N/A
Cyclohexane	300	1050	300	1050	N/A	N/A
Cumene (skin)	50	245	50	245	N/A	N/A
Acetic acid	10	25	10	25	N/A	N/A

Table 26. Threshold Limit Values, OSHA Standards, NIOSH Recommended Standards (Cont'd)

	TLV (ACGIH, 1977)		OSHA (OSHA, 1976)		NIOSH (NIOSH, 1977)	
	ppm	mg/m^3	ppm	mg/m^3	ppm	mg/m^3
Acetone	1000	2400	1000	2400	N/A	N/A
Phenol (skin)	5	19	5	19	(10 hr TWA) (15 min. ceiling)	20 60
Isopropyl alcohol (skin)	400	980	400	980	N/A	N/A
Propylene oxide	100	240	100	240	N/A	N/A
Acrylonitrile (skin)	20	45	20	45	4 (not greater than)	
Vinyl acetate	10	30	N/A	N/A	N/A	N/A
Adipic acid	N/A	N/A	N/A	N/A	N/A	N/A
Acetic anhydride	5 (ceiling)	20	5	20	N/A	N/A
Ethanol	1000	1900	1000	1900	N/A	N/A
Phthalic anhydride	1	6	2	12	N/A	N/A
Fluorinated hydrocarbons	N/A	N/A	N/A	N/A	N/A	N/A
Hexamethylene diamine	N/A	N/A	N/A	N/A	N/A	N/A
Caprolactam Dust	--	1	N/A	N/A	N/A	N/A
Vapor	5	20				
Carbon tetrachloride (skin)	10	65	10 (8 hr TWA) 25 (accept. ceiling) 200 (5 min. in 4 hr ceiling)		2 (60 min. ceiling)	
Cyclohexanone	50	200	50	200	N/A	N/A
Methyl methacrylate	100	410	100	410	N/A	N/A
Phosgene	0.10	0.4	0.1	0.4	0.1 (10 hr TWA) 0.2 (15 min. ceiling)	
1,1,1-Trichloroethane	350	1900	350	1900	350 (15 min. ceiling)	
1,1,2-Trichloroethane (skin)	10	45	10	45	N/A	N/A
Toluene diisocyanate	0.02 (ceiling)	0.14	0.02 (ceiling)	0.14	0.005 (10 hr TWA) 0.02 (20 min. ceiling)	
Nitrobenzene (skin)	1	5	1	5	N/A	N/A
Aniline (skin)	5	19	5	19	N/A	N/A
Ethyl hexanol	N/A	N/A	N/A	N/A	N/A	N/A
Propylene glycol	N/A	N/A	N/A	N/A	N/A	N/A
Chlorobenzene	75	350	75	350	N/A	N/A
Bisphenol	0.5	2.8	0.5 (ceiling)	2.8	N/A	1.0 (15 min. ceiling)

Table 26. Threshold Limit Values, OSHA Standards, NIOSH Recommended Standards (Cont'd)

	TLV (ACGIH, 1977)		OSHA (OSHA, 1976)		NIOSH (NIOSH, 1977)	
	ppm	mg/m^3	ppm	mg/m^3	ppm	mg/m^3
Trichloroethylene	100	535	100 (8 hr TWA)		100 (10 hr TWA)	
			200 (accept. ceiling)		150 (10 min. ceiling)	
			300 (5 min. in 2 hr ceiling)			
Maleic anhydride	0.25	1	0.25	1	N/A	N/A
Ethyl chloride	1000	2600	1000	2600	N/A	N/A
Perchloroethylene (skin)	100	670	100 (8 hr TWA)		50 (10 hr TWA)	
			200 (accept. ceiling)		100 (15 min. ceiling)	
			300 (5 min. in 3 hr ceiling)			

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X. EXPOSURE ESTIMATES

As detailed in Sections III (Statistical Information) and V (Process Characterization) approximately 80,000 workers are involved in the production of petrochemicals.

XI. ONGOING STUDIES

As detailed in Section VII, reports of high incidences of brain tumors in employees of Union Carbide and Monsanto in Texas City, Texas are currently under investigation (OHSL, 1979). Hanis and coworkers (1979) indicated in their cancer mortality study that Imperial Oil Limited is presently updating the study, and is in the process of designing a cancer morbidity study. An analysis of deaths from causes other than cancer in the Imperial Oil employees has not yet been, but presumably will be, published (Hanis *et al.*, 1979).

A manual search of *Tox-Tips* for the last twelve months (through December, 1978) has identified the following relevant ongoing studies:

Project Title: Epidemiologic Studies of Cancer in Louisiana
Performing Organization: Tulane University; New Orleans, Louisiana
End Date: January 1979
Source: *Tox-Tips*, No. 39, August 1979, p. 21.

Project Title: Medical and Industrial Hygiene Study of Chlorinated Hydrocarbons
Performing Organizations: NIOSH, Cincinnati, Ohio and SRI International, Menlo Park, California
End Date: September 1979
Source: *Tox-Tips*, No. 36, May 1979, p. 33.

Project Title: Mutagenic Potential of Petroleum Hydrocarbons - API Composite Motor Oils
Performing Organization: Hazelton Laboratories, Vienna, Virginia
End Date: Not Specified
Source: *Tox-Tips*, No. 35, April 1979, p.3.

Project Title: Mutagenic Potential of Petroleum Hydrocarbons - #2 Fuel Oil
Performing Organization: Hazelton Laboratories, Vienna, Virginia
End Date: Not Specified
Source: *Tox-Tips*, No. 35, April 1979, p. 5.

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Project Title: Mutagenic Potential of Petroleum Hydrocarbons - n-Hexane (pure)
Performing Organization: Hazelton Laboratories, Vienna, Virginia
End Date: Not Specified
Source: Tox-Tips, No. 35, April 1979, p. 7.

Project Title: Mutagenic Potential of Petroleum Hydrocarbons - Commercial Jet Fuel
Performing Organization: Hazelton Laboratories, Vienna, Virginia
End Date: Not Specified
Source: Tox-Tips, No. 35, April 1979, p. 9.

Project Title: Teratogenic Potential of Commercial Jet Fuel A
Performing Organization: Hazelton Laboratories, Vienna, Virginia
End Date: Not Specified
Source: Tox-Tips, No. 35, April 1979, p. 11.

Project Title: Teratogenic Potential of #2 Fuel Oil
Performing Organization: Litton Bionetics, Inc., Kensington, Maryland
End Date: Not Specified
Source: Tox-Tips, No. 35, April 1979, p. 13.

Project Title: Assessment and Validation for In-Vitro Carcinogenic Screening of Petroleum Crude Oil Fractions
Performing Organization: Litton Bionetics, Inc., Kensington, Maryland
End Date: Not Specified
Source: Tox-Tips, No. 35, April 1979, p. 15.

Project Title: Assessment and Validation for In-Vitro Carcinogenic Screening of Petroleum Crude Oil Fractions
Performing Organization: Microbiological Associates, Bethesda, Maryland
End Date: Not Specified
Source: Tox-Tips, No. 35, April 1979, p. 17.

Project Title: Teratogenic Potential of Diesel Fuel
Performing Organization: Litton Bionetics, Inc., Kensington, Maryland
End Date: Not Specified
Source: Tox-Tips, No. 35, April 1979, p. 19.

Project Title: Teratogenic Potential of Kerosene
Performing Organization: Litton Bionetics, Inc., Kensington, Maryland
End Date: Not Specified
Source: Tox-Tips, No. 35, April 1979, p. 21.

Project Title: Teratogenic Potential of n-Hexane
Performing Organization: Litton Bionetics, Inc., Kensington, Maryland
End Date: Not Specified
Source: Tox-Tips, No. 35, April 1979, p. 23.

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APPENDIX A
(Anon., 1972)

2869 Industrial Organic Chemicals, Not Elsewhere Classified

Establishments primarily engaged in manufacturing industrial organic chemicals, not elsewhere classified. Important products of this industry include: (1) non-cyclic organic chemicals such as acetic, chloroacetic, adipic, formic, oxalic and tartaric acids and their metallic salts; chloral, formaldehyde and methylamine; (2) solvents such as amyl, butyl, and ethyl alcohols; methanol; amyl, butyl and ethyl acetates; ethel ether, ethylene glycol ether and diethylene glycol ether; acetone, carbon disulfide and chlorinated solvents such as carbon tetrachloride, perchloroethylene and trichloroethylene; (3) polyhydric alcohols such as ethylene glycol, sorbitol, pentaerythritol, synthetic glycerin; (4) synthetic perfume and flavoring materials such as coumarin, methyl salicylate, saccharin, citral, citronellal, synthetic geraniol, ionone, terpineol, and synthetic vanillin; (5) rubber processing chemicals such as accelerators and antioxidants, both cyclic and acyclic; (6) plasticizers, both cyclic and acyclic, such as esters of phosphoric acid, phthalic anhydride, adipic acid, lauric acid, oleic acid, sebacic acid, and stearic acid; (7) synthetic tanning agents such as naphthalene sulfonic acid condensates; (8) chemical warfare gases; and (9) esters, amines, etc. of polyhydric alcohols and fatty and other acids. Establishments primarily engaged in manufacturing plastics materials and nonvulcanizable elastomers are classified in Industry 2821; synthetic rubber in Industry 2822; essential oils in Industry 2899; wood distillation products, naval stores, and natural dyeing and tanning materials in Industry 2861; rayon and other synthetic fibers in Industries 2823 and 2824; specialty cleaning, polishing and sanitation preparations in Industry 2842; paints in Industry 2851; urea in Industry 2873; organic pigments in Industry 2865; and inorganic pigments in Industry 2816. Distilleries engaged in the manufacture of grain alcohol for beverage purposes are classified in Industry 2085.

Accelerators, rubber processing: cyclic and acyclic
Acetaldehyde
Acetates, except natural acetate of lime
Acetic acid, synthetic
Acetic anhydride
Acetin
Acetone, synthetic
Acid esters, amines, etc.
Acids, organic
Acrolein
Acrylonitrile
Adipic acid
Adipic acid esters
Adiponitrile
Alcohol, aromatic
Alcohol, fatty: powdered
Alcohol, methyl: synthetic (methanol)
Alcohols, industrial: denatured (nonbeverage)
Algin products
Amyl acetate and alcohol
Antioxidants, rubber processing: cyclic and acyclic
Bromochloromethane
Butadiene, from alcohol
Butyl acetate, alcohol, and propionate
Butyl ester solution of 2, 4-D
Calcium oxalate
Camphor, synthetic
Carbon bisulfide (disulfide)
Carbon tetrachloride
Casing fluids, for curing fruits, spices, tobacco, etc.
Cellulose acetate, unplasticized
Chemical warfare gases
Chloral
Chlorinated solvents
Chloroacetic acid and metallic salts
Chloroform
Chloropicrin
Citral
Citrates
Citric acid
Citronellal
Coumarin
Cream of tartar
Cyclopropane
DDT, technical
Decahydronaphthalene
Dichlorodifluoromethane
Diethylcyclohexane (mixed isomers)
Diethylene glycol ether
Dimethyl divinyl acetylene (di-isopropenyl acetylene)
Dimethylhydrazine, unsymmetrical
Embalming fluids
Enzymes
Esters of phosphoric, adipic, lauric, oleic, sebacic, and stearic acids
Esters of phthalic anhydride
Ethanol, industrial
Ether
Ethyl acetate, synthetic
Ethyl alcohol, industrial (nonbeverage)
Ethyl butyrate
Ethyl cellulose, unplasticized
Ethyl chloride
Ethyl ether
Ethyl formate
Ethyl nitrite
Ethyl perhydrophenanthrene
Ethylene
Ethylene glycol
Ethylene glycol ether
Ethylene glycol, inhibited
Ethylene oxide
Fatty acid esters, amines, etc.
Ferric ammonium oxalate
Flavors and flavoring materials, synthetic
Fluorinated hydrocarbon gases
Formaldehyde (formalin)
Formic acid and metallic salts
Freon
Fuel propellants, solid: organic
Fuels, high energy: organic
Geraniol, synthetic
Glycerin, except from fats (synthetic)
Grain alcohol, industrial (nonbeverage)
Hexamethylenediamine
Hexamethylenetetramine
High purity grade chemicals, organic: refined from technical grades
Hydraulic fluids, synthetic base
Hydrazine
Industrial organic cyclic compounds
Ionone
Isopropyl alcohol
Ketone, methyl ethyl
Ketone, methyl isobutyl
Laboratory chemicals, organic
Lauric acid esters
Lime citrate
Malononitrile, technical grade
Metallic salts of acyclic organic chemicals
Metallic stearate
Methanol, synthetic (methyl alcohol)
Methyl chloride
Methyl perhydrofluorine
Methyl salicylate
Methylamine
Methylene chloride
Monochlorodifluoromethane
Monomethylparaminophenol sulfate
Monosodium glutamate
Mustard gas
Naphthalene sulfonic acid condensates
Naphthenic acid soaps
Normal hexyl decalin
Nuclear fuels, organic
Oleic acid esters
Organic acid esters
Organic chemicals, acyclic
Oxalates
Oxalic acid and metallic salts
Pentaerythritol
Perchloroethylene
Perfume materials, synthetic
Phosgene
Phthalates
Plasticizers, organic: cyclic and acyclic
Polyhydric alcohol esters, amines, etc.
Polyhydric alcohols
Potassium bitartrate
Propellants for missiles, solid: organic
Propylene
Propylene glycol
Quinuclidinol ester of benzylic acid
Reagent grade chemicals, organic: refined from technical grades
Rocket engine fuel, organic
Rubber processing chemicals, organic: accelerators and antioxidants
Saccharin
Sebacic acid
Silicones
Soaps, naphthenic acid
Sodium acetate
Sodium alginate
Sodium benzoate
Sodium glutamate
Sodium pentachlorophenate
Sodium sulfoxalate formaldehyde
Solvents, organic
Sorbitol
Stearic acid salts
Sulfonated aaphthalene
Tackifiers, organic
Tannic acid
Tanning agents, synthetic organic
Tartaric acid and metallic salts
Tartrates
Tear gas
Terpineol
Tert-butylated bis (p-phenoxyphenyl) ether fluid
Tetrachloroethylene
Tetraethyl lead
Thioglycolic acid, for permanent wave lotions
Trichloroethylene
Trichloroethylene stabilized, degreasing
Trichlorophenoxyacetic acid
Trichlorotrifluoroethane tetrachlorodifluoroethane isopropyl alcohol
Tricresyl phosphate
Tridecyl alcohol
Trimethyltrithiophosphite (rocket propellants)
Triphenyl phosphate
Vanillin, synthetic
Vinyl acetate

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APPENDIX B
(Anon., 1972)

Major Group 29.—PETROLEUM REFINING AND RELATED INDUSTRIES

The Major Group as a Whole

This major group includes establishments primarily engaged in petroleum refining, manufacturing paving and roofing materials, and compounding lubricating oils and greases from purchased materials. Establishments manufacturing and distributing gas to consumers are classified in public utilities industries, and those primarily engaged in producing coke and byproducts in Major Group 33.

Group No. Industry No.

291 PETROLEUM REFINING

2911 Petroleum Refining

Establishments primarily engaged in producing gasoline, kerosene, distillate fuel oils, residual fuel oils, lubricants and other products from crude petroleum and its fractionation products, through straight distillation of crude oil, redistillation of unfinished petroleum derivatives, cracking or other processes. Establishments primarily engaged in producing natural gasoline from natural gas are classified in mining industries. Those manufacturing lubricating oils and greases by blending and compounding purchased materials are included in Industry 2992. Establishments primarily re-refining used lubricating oils are classified in Industry 2992.

- Acid oil
- Alkylates
- Aromatic chemicals, made in petroleum refineries
- Asphalt and asphaltic materials: liquid and solid—produced in refineries
- Benzene, produced in petroleum refineries
- Benzol, produced in petroleum refineries
- Butadiene, from petroleum
- Coke, petroleum: produced in petroleum refineries
- Fractionation products of crude petroleum
- Gas, refinery or still oil: produced in petroleum refineries
- Gases, liquefied petroleum
- Gasoline blending plants
- Gasoline, except natural gasoline
- Greases: lubricating, produced in petroleum refineries
- Hydrocarbon fluid, made in petroleum refineries
- Jet fuels
- Kerosene
- Mineral jelly, produced in petroleum refineries
- Mineral oils, natural
- Mineral waxes, natural
- Naphtha, produced in petroleum refineries
- Naphthenic acids
- Oils: fuel, lubricating, and illuminating—produced in petroleum refineries
- Oils, partly refined: sold for rerunning—produced in refineries
- Paraffin wax, produced in petroleum refineries
- Petrolatums, nonmedicinal
- Petroleum refining
- Road materials, bituminous: produced in petroleum refineries
- Road oils, produced in petroleum refineries
- Solvents, produced in petroleum refineries
- Tar or residuum, produced in petroleum refineries

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APPENDIX C
(Anon., 1972)

Group No. Industry No.

286 INDUSTRIAL ORGANIC CHEMICALS

2865 Cyclic (Coal Tar) Crudes, and Cyclic Intermediates, Dyes, and Organic Pigments (Lakes and Toners)

Establishments primarily engaged in manufacturing coal tar crudes and cyclic organic intermediates, dyes, color lakes and toners. Important products of this industry include: (1) derivatives of benzene, toluene, naphthalene, anthracene, pyridine, carbazole, and other cyclic chemical products; (2) synthetic organic dyes; (3) synthetic organic pigments; and (4) cyclic (coal tar) crudes, such as light oils and light oil products; coal tar acids; and products of medium and heavy oil such as creosote oil, naphthalene, anthracene, and their higher homologues, and tar. Establishments primarily engaged in manufacturing coal tar crudes in chemical recovery ovens are classified in Industry 3312, and petroleum refineries which produce such products in Industry 2911.

Acid dyes, synthetic
Acids, coal tar: derived from coal tar distillation
Alkylated diphenylamines, mixed
Alkylated phenol, mixed
Aminoanthraquinone
Aminoazobenzene
Aminoazotoluene
Aminophenol
Aniline
Aniline oil
Anthracene
Anthraquinone dyes
Azine dyes
Azo dyes
Azobenzene
Azoic dyes
Benzaldehyde
Benzene hexachloride (BHC)
Benzene, product of coal tar distillation
Benzoic acid
Benzol, product of coal tar distillation
Biological stains
Chemical indicators
Chlorobenzene
Chloronaphthalene
Chlorophenol
Chlorotoluene
Coal tar crudes, derived from coal tar distillation
Coal tar distillates
Coal tar intermediates
Color lakes and toners
Color pigments, organic: except animal black and bone black
Colors, dry: lakes, toners, or full strength organic colors
Colors, extended (color lakes)
Cosmetic dyes, synthetic
Creosote oil, product of coal tar distillation
Cresols, product of coal tar distillation
Cresylic acid, product of coal tar distillation
Cyclic crudes, coal tar: product of coal tar distillation
Cyclic intermediates
Cyclohexane
Diphenylamine
Drug dyes, synthetic
Dye (cyclic) intermediates
Dyes, food: synthetic
Dyes, synthetic organic
Eosine toners
Ethylbenzene
Hydroquinone
Isocyanates
Lake red C toners
Leather dyes and stains, synthetic
Lithol rubine lakes and toners
Maleic anhydride
Methyl violet toners
Naphtha, solvent: product of coal tar distillation
Naphthalene chips and flakes
Naphthalene, product of coal tar distillation
Naphthol, alpha and beta
Nitro dyes
Nitroaniline
Nitrobenzene
Nitrophenol
Nitroso dyes
Oil, aniline
Oils: light, medium, and heavy—product of coal tar distillation
Organic pigments (lakes and toners)
Orthodichlorobenzene
Paint pigments, organic
Peacock blue lake
Pentachlorophenol
Persian orange lake
Phenol
Phloxine toners
Phosphomolybdic acid lakes and toners
Phosphotungstic acid lakes and toners
Phthalic anhydride
Phthalocyanine toners
Pigment scarlet lake
Pitch, product of coal tar distillation
Pulp colors, organic
Quinoline dyes
Resorcinol
Scarlet 2 R lake

Stains for leather
Stilbene dyes
Styrene
Styrene monomer
Tar, product of coal tar distillation
Toluene, product of coal tar distillation
Toluidines
Toluol, product of coal tar distillation
Vat dyes, synthetic
Xylene, product of coal tar distillation
Xylol, product of coal tar distillation

APPENDIX D

Estimated Production Worker Exposure

The following relationship (Jelen, 1970) provides a basis for estimating production worker exposure to chemicals:

$$A = \frac{\text{Operating man-hours}}{\text{Tons of product}} = T \times \frac{\text{No. of Steps in Process}}{[\text{Daily Production (Tons)}]^{0.76}}$$

where T = 10 for fully automated continuous processes

= 25 for batch manual processes

Example: Process No. 2 (Dehydrogenation of Acyclic Light Crudes)

Total Production @ 42×10^9 lb/yr (ethylene + propylene, etc.; Table 2) = 58,000 tons/day

Average Production per Plant = 500 tons/day (based on a total of 117 plants; Table 2)

Assuming that there are 10 steps in Process No. 2, and T = 10, then:

$$A = \frac{10 \times 10}{(500)^{0.76}} = 1.0 \text{ hrs/ton}$$

For an average plant operating 2000 hrs/yr,

$$\text{No. of workers} = \frac{1.0 \text{ hrs/ton} \times 500 \text{ tons/day} \times 365 \text{ days/yr}}{2000 \text{ hrs/yr}}$$

$$= 90$$

Therefore, No. of workers for all Process No. 2 = 90 x 117
= 10,500

PLASTICS AND RESINS MANUFACTURE

I. SCOPE OF PROFILE

The processes used to compound and fabricate synthetic plastic and resin products have been reviewed for the purpose of identifying occupational health hazards in the plastic and resin industry.

The compounding and fabrication processes primarily involve the conversion of plastic polymeric and resin materials into commercial products by blending with suitable additives, promotors and other materials with specific properties, by thermosetting and thermoplastic methods.

The commercial products, defined in Standard Industrial Classification (SIC) Code 3079 ("Miscellaneous Plastic Products"), are blended and fabricated from the plastic materials listed under SIC classification 2821 ("Plastic Materials, Synthetic Resins and Nonvulcanizable Elastomers"). Full descriptions of SIC categories 3079 and 2821 are given in Appendices A and B.

In many cases, the terms "plastic" and "resin" are used interchangeably. Strictly speaking, however, a resin is the more or less homogeneous polymer used as the starting material in the production of a molded article, while plastic signifies the finished product which may contain fillers, plasticizers, stablizers, pigments, and other additives.

II. SUMMARY

Table 1 presents a summary of the nine main classes of molding and finishing operations that are employed in the plastics fabricating industry, including information on principal products and related fabricating processes, classes of resins, and numbers of production workers and facilities.

In general, the principal health hazards of plastics and resins are associated with their constituent monomers. It is uncommon for a fully

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