

IX. APPENDIX I

METHOD FOR SAMPLING COAL TAR PRODUCTS

To determine the concentrations of coal tar products in the occupational environment, samples should be collected on 0.8 micrometer pore size silver membrane filters (37 mm diameter) preceded by Gelman type A or equivalent glass fiber filters encased in 3-piece plastic (polystyrene) field monitor cassettes. The cassette face cap should be on and the plug removed.

Equipment

- (a) Personal sampling pump suitable for exhausting at least 1.6 liters/minute.
- (b) Thermometer.
- (c) Manometer.
- (d) Stopwatch.
- (e) Tubing.

Calibration

Since the accuracy of an analysis can be no greater than the accuracy with which the volume of air is measured, accurate calibration of sampling devices and flowmeters is essential. Frequency of calibration depends on the use, care, and handling of the sampling system. Pumps should be recalibrated if they have been abused or if they have just been repaired or

received from the manufacturer. When sampling highly polluted or dusty environments, frequent cleaning and calibration may be necessary because the orifices of flowmeters and other equipment may become contaminated.

Ordinarily, pumps should be calibrated in the laboratory both before they are used in the field and after they have been used to collect a large number of field samples. The accuracy of calibration depends on the type of instrument used as a reference. The choice of calibration procedure depends largely on where the calibration is to be performed. For laboratory testing, a 1-liter buret or wet-test meter is recommended, although other standard calibrating instruments, such as spirometer, Marriot bottle, or dry-gas meter, can be used. The actual setup will be similar for all calibration systems used. The calibration instrument should be connected to the sampling train, followed by the sampler pump. In this way, the calibration instrument will be at atmospheric pressure. Each personal sampling pump must be calibrated separately. If a buret is used for calibration, it should be set up so that the flow is toward the narrow end of the unit.

Assemble the calibration setup carefully to ensure that seals at the joints are airtight and that the length of connecting tubing is minimized. Calibration should be performed at the same conditions of pressure and temperature as those under which sampling will occur. A calibrated pump rotameter should be used to establish flow rate in the field.

Collection of Samples on a Glass Fiber Filter

Because of the large air volume to be sampled and the limited capacity of air movers available for personal monitoring, long sampling

periods are required. Inspect the filter and air mover periodically and terminate sampling if either the filter or air mover are malfunctioning.

Submit the filters in the field monitors for analysis along with three blank filters from each lot.

X. APPENDIX II

ANALYTICAL METHOD FOR COAL TAR PRODUCTS

Principle of the Method

The cyclohexane-soluble material in the particulates on the glass fiber filters is extracted ultrasonically. Blank filters are extracted along with, and in the same manner as, the samples. After extraction, the cyclohexane solution is filtered through a fritted glass funnel. The total material extracted is determined by weighing a dried aliquot of the extract.

Range and Sensitivity

When the electrobalance is set at 1 mg, this method can detect 75-2,000 $\mu\text{g}/\text{sample}$.

Precision and Accuracy

When nine aliquots of a benzene solution from a sample of aluminum-reduction plant emissions containing 1,350 $\mu\text{g}/\text{sample}$ were analyzed, the standard deviation was 25 μg [109]. Experimental verification of this method using cyclohexane is not yet complete.

Advantages and Disadvantages of the Method

(a) Advantages

This procedure is much faster and easier to run than the Soxhlet method.

(b) Disadvantages

If the whole sample is not used for cyclohexane-extraction analysis, small weighing errors make large errors in final results.

Apparatus

- (a) Ultrasonic bath, 90 Kc, 60 watts, partially filled with water.
- (b) Ultrasonic generator, Series 200, 90 Kc, 60 watts.
- (c) Electrobalance capable of weighing to 1 μ g.
- (d) Stoppered glass test tube, 150- x 16-mm.
- (e) Teflon weighing cups, 2-ml, approximate tare weight 60 mg.
- (f) Dispensing bottle, 5-ml.
- (g) Pipets, with 0.5-ml graduations.
- (h) Glass fiber filters, 37-mm diameter, Gelman Type A or equivalent.
- (i) Silver membrane filters, 37-mm diameter, 0.8-micrometer pore size.
- (j) Vacuum oven.
- (k) Tweezers.
- (l) Beaker, 50-ml.
- (m) Glassine paper, 3.5- x 4.5-inches.
- (n) Wood application sticks for manipulating filters.

- (o) Funnels, glass-fritted, 15-ml.
- (p) Graduated evaporative concentrator, 10-ml.

Reagents

- (a) Cyclohexane, ACS nanograde reagent.
- (b) Dichromic acid cleaning solution.
- (c) Acetone, ACS reagent grade.

Procedure

(a) All extraction glassware is cleaned with dichromic acid cleaning solution, rinsed first with tap water, then with deionized water followed by acetone, and allowed to dry completely. The glassware is rinsed with nanograde cyclohexane before use. The Teflon cups are cleaned with cyclohexane, then with acetone.

(b) Preweigh the Teflon cups to one hundredth of a milligram (0.01 mg).

(c) Remove top of cassette and hold over glassine paper. Remove plug on bottom of cassette. Insert end of application stick through hole and gently raise filters to one side. Use tweezers to remove filters, and loosely roll filters around tweezers. Slide rolled filters into test tube and push them to bottom of tube with application stick. Add any particulates remaining in cassette and on glassine paper to test tube.

(d) Pipet 5 ml of cyclohexane into test tube from dispensing bottle.

(e) Put test tube into sonic bath so that water level in bath is above liquid level in test tube. Do not hold tube in hand while sonifying. A 50-ml beaker filled with water to level of cyclohexane in tube works well.

(f) Sonify sample for 5 minutes.

(g) Filter the extract in 15-ml medium glass-fritted funnels.

(h) Rinse test tube and filters with two 1.5-ml aliquots of cyclohexane and filter through the fritted-glass funnel.

(i) Collect the extract and two rinses in the 10-ml graduated evaporative concentrator.

(j) Evaporate down to 1 ml while rinsing the sides with cyclohexane.

(k) Pipet 0.5 ml of the extract to preweighed Teflon weighing cup. These cups can be reused after washing with acetone.

(l) Evaporate to dryness in a vacuum oven at 40 C for 3 hours.

(m) Weigh the Teflon cup. Use counterweighing techniques on electrobalance with full scale range of 1 mg to determine weight of aliquot to nearest microgram. The weight gain is due to the cyclohexane-soluble residue.

Calculations

The amount of cyclohexane-extractable fraction present in the sample (in mg) may be determined according to the following equation:

$$\text{mg/sample} = 2 \times (\text{wt sample aliquot (mg)} - \text{wt blank aliquot (mg)})$$

The amount of cyclohexane-extractable fraction present in the air may then be determined according to the following equation:

$$\text{mg/cu m} = \frac{\text{mg/sample}}{\text{air volume collected (cu m)}}$$

XI. APPENDIX III
MATERIAL SAFETY DATA SHEET

The following items of information which are applicable to a specific product or material shall be provided in the appropriate block of the Material Safety Data Sheet (MSDS).

The product designation is inserted in the block in the upper left corner of the first page to facilitate filing and retrieval. Print in upper case letters as large as possible. It should be printed to read upright with the sheet turned sideways. The product designation is that name or code designation which appears on the label, or by which the product is sold or known by employees. The relative numerical hazard ratings and key statements are those determined by the rules in Chapter V, Part B, of the NIOSH publication, An Identification System for Occupationally Hazardous Materials. The company identification may be printed in the upper right corner if desired.

(a) Section I. Product Identification

The manufacturer's name, address, and regular and emergency telephone numbers (including area code) are inserted in the appropriate blocks of Section I. The company listed should be a source of detailed backup information on the hazards of the material(s) covered by the MSDS. The listing of suppliers or wholesale distributors is discouraged. The trade name should be the product designation or common name associated with the material. The synonyms are those commonly used for the product, especially formal chemical nomenclature. Every known chemical designation or

competitor's trade name need not be listed.

(b) Section II. Hazardous Ingredients

The "materials" listed in Section II shall be those substances which are part of the hazardous product covered by the MSDS and individually meet any of the criteria defining a hazardous material. Thus, one component of a multicomponent product might be listed because of its toxicity, another component because of its flammability, while a third component could be included both for its toxicity and its reactivity. Note that a MSDS for a single component product must have the name of the material repeated in this section to avoid giving the impression that there are no hazardous ingredients.

Chemical substances should be listed according to their complete name derived from a recognized system of nomenclature. Where possible, avoid using common names and general class names such as "aromatic amine," "safety solvent," or "aliphatic hydrocarbon" when the specific name is known.

The "%" may be the approximate percentage by weight or volume (indicate basis) which each hazardous ingredient of the mixture bears to the whole mixture. This may be indicated as a range or maximum amount, ie, "10-40% vol" or "10% max wt" to avoid disclosure of trade secrets.

Toxic hazard data shall be stated in terms of concentration, mode of exposure or test, and animal used, eg, "100 ppm LC50-rat," "25 mg/kg LD50-skin-rabbit," "75 ppm LC man," or "permissible exposure from 29 CFR 1910.1000," or, if not available, from other sources of publications such as the American Conference of Governmental Industrial Hygienists or the American National Standards Institute Inc. Flashpoint, shock sensitivity,

or similar descriptive data may be used to indicate flammability, reactivity, or similar hazardous properties of the material.

(c) Section III. Physical Data

The data in Section III should be for the total mixture and should include the boiling point and melting point in degrees Fahrenheit (Celsius in parentheses); vapor pressure, in conventional millimeters of mercury (mmHg); vapor density of gas or vapor (air = 1); solubility in water, in parts/hundred parts of water by weight; specific gravity (water = 1); percent volatiles (indicated if by weight or volume) at 70 degrees Fahrenheit (21.1 degrees Celsius); evaporation rate for liquids or sublimable solids, relative to butyl acetate; and appearance and odor. These data are useful for the control of toxic substances. Boiling point, vapor density, percent volatiles, vapor pressure, and evaporation are useful for designing proper ventilation equipment. This information is also useful for design and deployment of adequate fire and spill containment equipment. The appearance and odor may facilitate identification of substances stored in improperly marked containers, or when spilled.

(d) Section IV. Fire and Explosion Data

Section IV should contain complete fire and explosion data for the product, including flashpoint and autoignition temperature in degrees Fahrenheit (Celsius in parentheses); flammable limits, in percent by volume in air; suitable extinguishing media or materials; special firefighting procedures; and unusual fire and explosion hazard information. If the product presents no fire hazard, insert "NO FIRE HAZARD" on the line labeled "Extinguishing Media."

(e) Section V. Health Hazard Information

The "Health Hazard Data" should be a combined estimate of the hazard of the total product. This can be expressed as a TWA concentration, as a permissible exposure, or by some other indication of an acceptable standard. Other data are acceptable, such as lowest LD50 if multiple components are involved.

Under "Routes of Exposure," comments in each category should reflect the potential hazard from absorption by the route in question. Comments should indicate the severity of the effect and the basis for the statement if possible. The basis might be animal studies, analogy with similar products, or human experiences. Comments such as "yes" or "possible" are not helpful. Typical comments might be:

Skin Contact--single short contact, no adverse effects likely; prolonged or repeated contact, possibly mild irritation.

Eye Contact--some pain and mild transient irritation; no corneal scarring.

"Emergency and First Aid Procedures" should be written in lay language and should primarily represent first-aid treatment that could be provided by paramedical personnel or individuals trained in first aid.

Information in the "Notes to Physician" section should include any special medical information which would be of assistance to an attending physician including required or recommended preplacement and periodic medical examinations, diagnostic procedures, and medical management of overexposed employees.

(f) Section VI. Reactivity Data

The comments in Section VI relate to safe storage and handling of hazardous, unstable substances. It is particularly important to highlight instability or incompatibility to common substances or circumstances, such as water, direct sunlight, steel or copper piping, acids, alkalies, etc. "Hazardous Decomposition Products" shall include those products released under fire conditions. It must also include dangerous products produced by aging, such as peroxides in the case of some ethers. Where applicable, shelf life should also be indicated.

(g) Section VII. Spill or Leak Procedures

Detailed procedures for cleanup and disposal should be listed with emphasis on precautions to be taken to protect employees assigned to cleanup detail. Specific neutralizing chemicals or procedures should be described in detail. Disposal methods should be explicit including proper labeling of containers holding residues and ultimate disposal methods such as "sanitary landfill" or "incineration." Warnings such as "comply with local, state, and federal antipollution ordinances" are proper but not sufficient. Specific procedures shall be identified.

(h) Section VIII. Special Protection Information

Section VIII requires specific information. Statements such as "Yes," "No," or "If necessary" are not informative. Ventilation requirements should be specific as to type and preferred methods. Respirators shall be specified as to type and NIOSH or US Bureau of Mines approval class, ie, "Supplied air," "Organic vapor canister," etc. Protective equipment must be specified as to type and materials of construction.

(i) Section IX. Special Precautions

"Precautionary Statements" shall consist of the label statements selected for use on the container or placard. Additional information on any aspect of safety or health not covered in other sections should be inserted in Section IX. The lower block can contain references to published guides or in-house procedures for handling and storage. Department of Transportation markings and classifications and other freight, handling, or storage requirements and environmental controls can be noted.

(j) Signature and Filing

Finally, the name and address of the responsible person who completed the MSDS and the date of completion are entered. This will facilitate correction of errors and identify a source of additional information.

The MSDS shall be filed in a location readily accessible to employees exposed to the hazardous substance. The MSDS can be used as a training aid and basis for discussion during safety meetings and training of new employees. It should assist management by directing attention to the need for specific control engineering, work practices, and protective measures to ensure safe handling and use of the material. It will aid the safety and health staff in planning a safe and healthful work environment and in suggesting appropriate emergency procedures and sources of help in the event of harmful exposure of employees.

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MATERIAL SAFETY DATA SHEET

I PRODUCT IDENTIFICATION		
MANUFACTURER'S NAME	REGULAR TELEPHONE NO EMERGENCY TELEPHONE NO	
ADDRESS		
TRADE NAME		
SYNONYMS		
II HAZARDOUS INGREDIENTS		
MATERIAL OR COMPONENT	%	HAZARD DATA
III PHYSICAL DATA		
BOILING POINT, 760 MM HG		MELTING POINT
SPECIFIC GRAVITY (H ₂ O=1)		VAPOR PRESSURE
VAPOR DENSITY (AIR=1)		SOLUBILITY IN H ₂ O, % BY WT
% VOLATILES BY VOL		EVAPORATION RATE (BUTYL ACETATE=1)
APPEARANCE AND ODOR		

IV FIRE AND EXPLOSION DATA				
FLASH POINT (TEST METHOD)			AUTOIGNITION TEMPERATURE	
FLAMMABLE LIMITS IN AIR, % BY VOL.		LOWER		UPPER
EXTINGUISHING MEDIA				
SPECIAL FIRE FIGHTING PROCEDURES				
UNUSUAL FIRE AND EXPLOSION HAZARD				
V HEALTH HAZARD INFORMATION				
HEALTH HAZARD DATA				
ROUTES OF EXPOSURE				
INHALATION				
SKIN CONTACT				
SKIN ABSORPTION				
EYE CONTACT				
INGESTION				
EFFECTS OF OVEREXPOSURE				
ACUTE OVEREXPOSURE				
CHRONIC OVEREXPOSURE				
EMERGENCY AND FIRST AID PROCEDURES				
EYES				
SKIN				
INHALATION				
INGESTION				
NOTES TO PHYSICIAN				

VI REACTIVITY DATA
CONDITIONS CONTRIBUTING TO INSTABILITY
INCOMPATIBILITY
HAZARDOUS DECOMPOSITION PRODUCTS
CONDITIONS CONTRIBUTING TO HAZARDOUS POLYMERIZATION
VII SPILL OR LEAK PROCEDURES
STEPS TO BE TAKEN IF MATERIAL IS RELEASED OR SPILLED
NEUTRALIZING CHEMICALS
WASTE DISPOSAL METHOD
VIII SPECIAL PROTECTION INFORMATION
VENTILATION REQUIREMENTS
SPECIFIC PERSONAL PROTECTIVE EQUIPMENT
RESPIRATORY (SPECIFY IN DETAIL)
EYE
GLOVES
OTHER CLOTHING AND EQUIPMENT

IX SPECIAL PRECAUTIONS

PRECAUTIONARY
STATEMENTS

OTHER HANDLING AND
STORAGE REQUIREMENTS

PREPARED BY _____

ADDRESS _____

DATE _____

XII. TABLES AND FIGURE

TABLE XII-1

TYPICAL FRACTIONS FROM CONTINUOUS TAR DISTILLATION

Fraction No.	Synonyms	Boiling Range (C)	% of Crude Tar (by weight)
1	Crude benzene Light oil	106-107	2.4
2	Naphtha Carbolic oil Phenolic oil	167-194	3.1
3	Heavy naphtha Carbolic oil Naphthalene oil	203-240	9.3
4	Naphthalene oil	215-254	3.5
5	Wash oil Benzene absorbing oil Light creosote	238-291	10.2
6	Creosote	271-362	11.5
7	Heavy creosote Heavy oil	285-395	12.1
Residue	Medium-soft pitch	-	40.5
Liquor and losses	-	-	7.4

Adapted from reference 6

TABLE XII-2

EMPLOYMENT INVOLVING COAL TAR PRODUCTS

Product	User Industry	% of Tar Processed	Volume of Product	No. of Jobs Affected
Electrode binder pitch	Aluminum	43.2	-	28,000
	Steel	3.0	-	50,000
	Graphite	9.2	-	10,000
Core pitch	Foundry	2.2	-	2,000
Refractory pitch	Steel	2.4	-	50,000
Fiber pitch	Electrical	3.5	-	-
Misc pitch	Various	3.4	-	-
Roofing pitch	Construction	8.8	-	-
Other tars and fuel residue	Fuel	24.3	-	-
Creosote	Railway, utility, construction	-	127,000 M*gal	5,000

*M = million

Adapted from references 3 and 4

TABLE XII-3

OCCUPATIONS WITH POTENTIAL EXPOSURE TO COAL TAR PRODUCTS

Artificial stone makers	Impregnated felt makers
Asbestos goods workers	Insecticide-bomb makers
Asphalt workers	Insulation-board makers
Battery box makers	Insulators
Battery workers, dry	Lens grinders
Boatbuilders	Linemen
Brickmasons	Miners
Brick pressers	Painters
Brickyard workers	Paper conduit makers
Briquette makers	Pavers
Brushmakers	Pipeline workers
Cable makers	Pipe pressers
Carpenters	Pitchworkers
Coal tar still cleaners	Railroad track workers
Coal tar workers	Riveters
Coke-oven workers	Road workers
Corkstone makers	Roofers
Creosoters	Roofing-paper workers
Diesel engine engineers	Ropemakers
Electric equipment makers	Rubber workers
Electricians	Shingle makers
Electrode makers	Shipyard workers
Electrometallurgic workers	Soapmakers
Farmers	Smokeless fuel makers
Fishermen	Stokers
Flue cleaners	Tar paintmakers
Fuel pitch workers	Tile pressers
Furnace men	Waterproof-concrete workers
Gashouse workers	Waterproofers
Glassblowers	Wood preservers

Adapted from reference 115

TABLE XII-4

CARCINOGENIC EFFECTS OF COAL TAR FRACTIONS ON MICE AND RABBITS

Fraction*	Mice			Rabbits		
	Exposure Duration (wk)	First Tumor (wk)	Animals with Tumors** (%)	Exposure Duration (wk)	First Tumor (wk)	Animals with Tumors (%)
5% tar in BZ	18	11	40	14	7	85
BTE	18	8	53	14	7.5	100
BTA-1	18	-	0	14	-	0
BTA-2	18	-	0	14	-	0
EE	14	10	60	11	7.5	40
TE-2	14	9	50	11	9.5	40
EEF	14	-	0	11	-	0
EEA	14	7	50	11	6.5	100
TS-C	16	12	30	15	10	40
TS-D	16	11	50	15	12.5	40
TS-E	16	13	60	15	8.5	80
TS-F	16	10	40	15	15	20
PES**	15	10	50	14	7	100
PE-1***	15	-	0	14	-	0
PES-C	16	-	0	16	8.5	80
PES-D	16	8	50	16	7.5	60
PES-E	16	7	25	16	8	60
PES-F	16	-	0	16	7.5	60
II	28	-	0	17	6.5	100
III	20	10	70	17	8.5	100
IV	28	10	30	17	10	80
V	19	-	0	17	-	0

*See Figure III-2 and the text for derivation of fractions

**Numbers are in terms of animals at the start of experiment

***PE-1 insoluble in light petroleum ether; PES soluble in light petroleum ether

Adapted from reference 61

TABLE XII-5

AMBIENT CONCENTRATIONS OF POLYCYCLIC AROMATIC HYDROCARBONS
IN THE AIR OF SELECTED CITIES, EXPRESSED IN NG/CU M

Season and City	Compound*								Total
	BghiP	BaP	BeP	BkF	P	Cor	Per	A	
Summer 1958									
Atlanta	5.1	1.6	1.5	1.3	0.7	2.5	0.4	0.2	13.3
Birmingham	8.3	6.4	5.9	4.6	2.1	2.4	2.1	0.3	32.1
Detroit	9.5	6.0	5.3	4.9	2.8	1.8	1.7	0.4	32.4
Los Angeles	2.3	0.5	0.6	0.5	0.3	2.2	0.03	0.0	6.4
Nashville	3.4	1.4	1.2	1.0	0.6	1.3	0.2	0.1	9.2
New Orleans	4.6	2.0	3.1	1.8	0.3	2.5	0.4	0.1	14.8
San Francisco	2.6	0.3	0.5	0.2	0.1	1.6	0.01	0.02	5.4
Winter 1959									
Atlanta	8.9	7.4	4.7	6.0	6.0	4.3	1.1	0.5	38.9
Birmingham	18	25	10	13	17	3.5	5.5	2.2	94.2
Detroit	33	31	23	20	36	6.4	6.0	2.0	146.4
Los Angeles	18	5.3	8.1	5.7	6.0	12	1.6	0.2	56.9
Nashville	17	25	14	15	30	4.6	4.4	1.8	111.8
New Orleans	7.3	4.1	6.4	3.9	2.3	27	0.8	0.1	27.6
San Francisco	7.5	2.3	2.9	1.7	1.9	4.9	0.3	0.1	21.6

*Key to compound abbreviations: BghiP=benzo(g,h,i)perylene, BaP=benzo(a)pyrene, BeP=benzo(e)pyrene, BkF=benzo(k)fluoranthene, P=pyrene, Cor=coronene, Per=perylene, A=anthracene

Adapted from reference 19

TABLE XII-6

CHEMICAL COMPOSITION OF COAL TAR FUMES

Compound	Percent by Weight
Naphthalene	0.9
2-Methyl naphthalene	1.0
1-Methyl naphthalene	0.7
Dimethyl naphthalene	1.1
Dimethyl naphthalene	0.5
Trimethyl naphthalene	7.6
2,3,6-Trimethyl naphthalene	5.8
Fluorene	9.1
Xanthene	1.1
Phenanthrene and/or anthracene (reported as phenanthrene)	36.4
Carbazole and methyl phenanthrene	9.6
Methyl phenanthrene	6.0
Fluoranthrene	11.8
Pyrene	8.5
Total	100.0

Adapted from reference 98

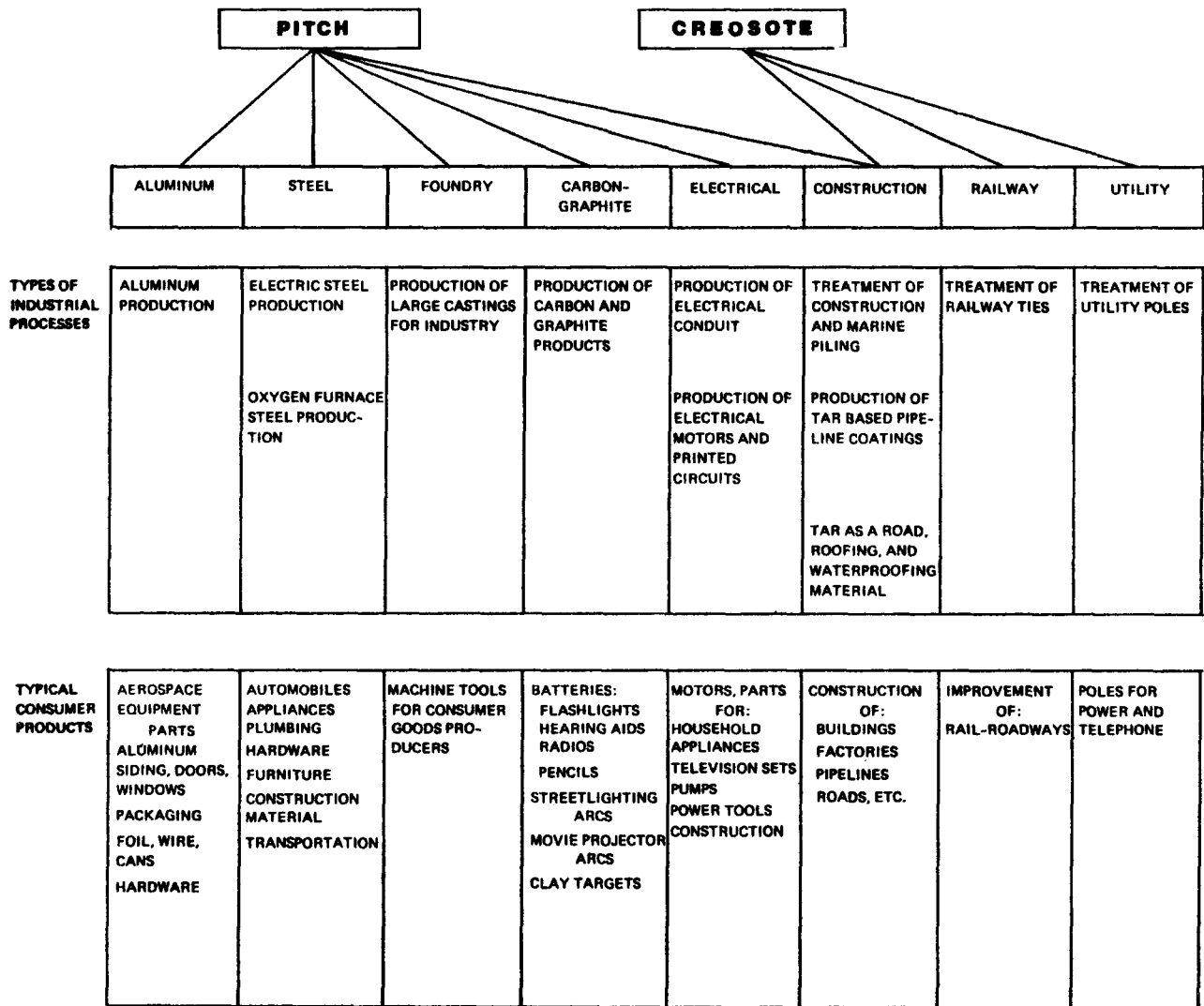


FIGURE XII-1

THE IMPACT OF COAL TAR PRODUCTS

Adapted from reference 3