VI. DEVELOPMENT OF STANDARD

Basis for Previous Standards

In 1967, the American Conference of Governmental Industrial Hygienists (ACGIH) [113] adopted a threshold limit value (TLV) of 0.2 mg/cu m for coal tar pitch volatiles (CTPV), described as a "benzene-soluble" fraction, and listed certain carcinogenic components of CTPV. The TLV was established to minimize exposure to the listed substances believed to be carcinogens, viz, anthracene, BaP, phenanthrene, acridine, chrysene, and pyrene [113]. This TLV was promulgated as a federal standard under the Occupational Safety and Health Act of 1970 (29 CFR 1910.1000). No foreign standards were found for exposure to coal tar pitch or creosote.

In 1973, NIOSH [114] published the "Criteria for a Recommended Standard--Occupational Exposure to Coke Oven Emissions," recommending work practices to minimize the harmful effects of exposure to coke-oven emissions and inhalation of coal tar pitch volatiles. In 1974, OSHA established a Standards Advisory Committee on Coke Oven Emissions to study the problem of the exposure of coke-oven workers to CTPV and to prepare recommendations for an effective standard in the assigned area. In 1975, the Committee recommended a limit of 0.2 μg/cu m for BaP (Federal Register, 41:46742-46787, October 22, 1976).

In 1976, OSHA promulgated a federal standard on coke oven emissions designed to reduce employee exposure to carcinogenic chemicals (Federal Register, 41:46742-46787, October 22, 1976). The standard was based on evidence collected from epidemiologic and animal experiments, which indicated that the chemicals present in coke oven emissions could produce skin and lung cancer in humans and animals. Cited epidemiologic studies by Doll et al [54,55], Redmond et al [50], and Reid and Buck [56] were said to have shown that employees exposed to coke oven emissions had a high risk of dying from lung and bladder cancer. Kidney cancer in coke oven workers was also reported by Redmond et al [50]. However, it was pointed out that the route by which carcinogens from coke oven emissions reached the kidney was not known. Particulate carcinogens may be absorbed after ingestion or inhalation or be absorbed through the skin. Doll et al [55] reported excess bladder cancer in British gas workers.

The incidence of skin cancer, especially on the scrotum, among coke oven workers was also considered, although there were no deaths from skin cancer [3]. Furthermore, it was stated that the incidence of skin cancer among coke oven workers was not related to the job or geographic location of workers in the coke plant. Data from several animal studies showed that repeated application of coal tar or its fractions containing BaP at 0.01% or more produced squamous-cell carcinomas in mice. It was stated that, although there were no deaths in coke oven workers from skin cancer, the possibility of a skin cancer hazard could not be dismissed. Variations in human response could be related to factors like the type of operation, the materials produced, personal hygiene, and medical surveillance. To the extent that such factors could be controlled, they were deemed appropriate for inclusion in the standard. Furthermore, OSHA also considered the increased incidence of non-malignant respiratory diseases, such as chronic bronchitis, pneumoconiosis, emphysema, and fibrosis, in promulgating the present standard.

It was concluded that coke oven emissions induced lung and genitourinary tract cancer in the exposed population. It was also concluded that coal tar products were carcinogenic to animal skin and were related to increased skin cancer mortality in human populations similar to coke oven workers. Thus, protective measures designed to reduce employee exposure to coke oven emissions were warranted. A standard for the benzene-soluble fraction of total particulate matter present during the destructive distillation or carbonization of coal was set; this standard set forth specific minimum engineering controls and work practices designed to reduce exposure to coke oven emissions.

Basis for the Recommended Standard

(a) Permissible Exposure Limits

Exposure to coal tar products (including coal tar, coal tar pitch, and creosote) in the occupational environment has been reported to affect the skin and eyes [45,46]. Leb et al [45] and Susorov [46] reported photosensitization, mild photophobia, temporary conjunctivitis, and decreased visual acuity in coal briquette loaders exposed to coal tar pitch dust. These authors [45,46] pointed out that the workers did not wear any protective clothing, special glasses, or respirators, and that fewer effects were observed in nighttime workers than in daytime workers. This 4- to 5-hour exposure to coal tar pitch dust produced upper respiratory effects in the workers, together with some decrease in visual acuity. Gibbs and Horowitz [52] found that mortality from lung cancer increased with exposure to tar in workers in aluminum reduction plants using the Soderberg processes. However, the mortality in these workers was not significantly increased when compared with the mortality in the local communities, apparently reflecting an increased rate of lung cancer in those communities.

In another study [53] of aluminum industry workers, a similar increase in lung cancer mortality was found in potroom workers using the horizontal Soderberg process. The presence of relatively high amounts of tarry substances (69.5-97 and 27-2,130 mg/cu m in plants with horizontal and vertical Soderberg process, respectively) and BaP levels (0.6-9.4 and 29-56 μg/cu m) in the air of aluminum reduction plants has also been associated with increased lung cancer mortality [51]. Doll et al [55] reported high respiratory cancer mortality in coke-oven workers. Redmond et al [50] found that coke-oven workers employed for 5 years or more had a high risk of dying from lung and kidney cancer; non-oven workers had a high risk of developing cancers of the colon, pancreas, buccal cavity, and pharynx, while byproducts workers had no increased risk of dying from any cancer [50,55,56]. From these epidemiologic studies, it is concluded that exposure to crude coal tar, coal tar pitch, and mixtures containing these substances in the occupational environment can cause lung cancer and possibly cancer of internal organs, such as the colon, pancreas, buccal cavity, and pharynx. This conclusion that exposure to coal tar causes lung cancer is supported by animal data discussed below.

Long-term exposure (1-43 years) to coal tar pitch has been reported to cause malignant tumors on the hands, face, and neck of briquette-factory workers [40]. However, the investigators did not specify the source or chemical nature of the pitch to which the workers had been exposed. Skin tumors have been reported in many studies [40,47] with so many samples that one can infer that coal tar pitches from all sources may be considered potent skin tumorigens.

Multiple skin applications of coal tar [67-69], coal tar pitch [12,69], and creosote produced skin tumors in rats and mice [63,72].

Kinkead [77] reported on the effects of aerosolized coal tar on various animal species. Mice and rats were exposed continuously for 90 days to aerosolized coal tar at concentrations of 0, 0.2, 2, 10, and 20 mg/cu m. Rabbits and hamsters were also exposed for 90 days, but only at 20 mg/cu m. Cumulative mortality of exposed animals was proportional to exposure concentration. Exposure also resulted in decreased body weights in all species tested.

McConnell and Specht [78] reported on lesions and microscopic changes in the liver, kidneys, and lungs of the animals exposed to coal tar aerosols by Kinkead [77]. In mice, the incidences of epithelial tumors at 0.2, 2, 10, and 20 mg/cu m of aerosolized coal tar were 0, 8, 37.5, and 27.8%, respectively. There were no tumors in the controls. The latent period for skin tumor development also was dose-dependent.

Sasmore [79] studied tissues from mice, rats, hamsters, and rabbits exposed to aerosolized coal tar. Lungs, liver, kidneys, spleen, lymph nodes, adrenals, bladder, and skin were examined microscopically. The incidences of lung tumors in mice exposed to coal tar at 0.2, 2, and 10 mg/cu m were 39%, 58%, and 77%, respectively. Controls had a 30% incidence of such tumors. Sasmore [79] also suggested that inhalation of aerosolized coal tar contributed to an increased incidence of lung tumors in rats at a concentration of 2 or 10 mg/cu m and of kidney tumors at 10 mg/cu m. In hamsters, a lymphosarcoma in the spleen was noted at a concentration of 10 mg/cu m; no effects were observed in any of the rabbit organs. MacEwen et al [80] showed a 100% and 82% incidence of lung tumors in male and female rats, respectively, exposed to aerosolized coal tar, intermittently for 18 months.

The data from this study [77-79] and from the study of MacEwen et al [80] show that exposure to aerosolized coal tar produced an increased incidence of lung tumors in mice and rats.

In a recent study [30] conducted by NIOSH to evaluate the health hazards of roofers exposed to coal tar pitch, 67% (23/34) of the workers examined had skin reactions such as burning sensation, irritation, and blistering. Fifty percent (17/34) had eye effects of varying severity, described as slight burning, slight conjunctival erythema, lacrimation, and swelling of the lids. Four of these workers experienced inability to close their eyes and interference with vision. Of the six workers showing clinical evidence of conjunctivitis, four were exposed to PPOM at reported concentrations of 0.21-0.49 mg/cu m, and two were exposed at concentrations less than 0.20 mg/cu m.

Lijinski and coworkers [72], Roe and associates [81], and Boutwell and Bosch [73] found an increased incidence of skin tumors in mice from creosote application. Cabot et al [71] concluded from studies in mice that creosote enhanced the skin tumorgenicity of BaP. Unfortunately, Lijinski et al and Roe et al did not characterize their creosote samples by source or composition. It is conceivable that their samples included coal tar, but it seems appropriate to conclude from the evidence available that creosote, whether or not containing tar, is a potent skin irritant, leading, on sufficient exposure, to skin tumors. Roe et al [81] also found lung tumors in creosote-exposed mice. Thus creosote, like coal tar pitch, can cause lung and skin tumors in workers.

In deriving the workplace environmental limit for coal tar products, NIOSH has considered numerous possibilities and variables. Extraction of samples with cyclohexane and calculation of the cyclohexane extractables has been found to be the optimum general method for analysis. It has been found, after experience with the particular analytical procedures currently available, that 75μg is the smallest quantity of extractables that can be reliably analyzed using the procedure described in Appendix II. If less than 75 μg of extract is obtained, the analysis cannot reliably indicate the presence of extractables in the sample of airborne coal tar products, though they may actually be present. Improvement of the analytical method and further testing may lead to future reliable analysis of less than 75 μg of cyclohexane extractables, but now this is not possible.

In considering the possible sampling regimens that could be used for coal tar products, NIOSH has reached four conclusions. First, the sampling time should be minimized to allow observation of variations of workplace environmental concentrations. This will allow a better understanding of the patterns of varying emissions from processes, and the development of better control measures. Second, personal sampling of each employee's breathing zone is the best method for sampling coal tar products the employee inhales; personal sampling pumps and cassette filter holders most easily accomplish this sampling goal. Third, the equipment used for personal sampling should be as reliable, portable, and uncumbersome as possible, but should be generally available. Fourth, the sampling volume should be as large as possible, to allow more precise measurement of the volume sampled.

In accomplishing these aims, three factors bear on the sampling regimen. First, portable personal sampling pumps that are available have useful maximum pumping rates of about 1.6 liters/minute. Second, the normal workshift is about 8 hours. Third, some time is usually necessary within a workshift to set up and maintain the sampling regimen. It is evident from these factors that, during the average 8-hour workshift, about 750 liters of air can be sampled. It has been stated that one objective of sampling for coal tar products is to keep sampling time short. However, this objective is not overriding, and NIOSH has decided that filtering a larger volume of air, ie, at least 750 liters, is a more important objective in the accurate characterization of the concentrations of airborne coal tar products in the breathing zones of employees. Therefore, NIOSH has concluded that at least 750 liters of breathing zone air must be sampled using a personal sampling device. Because the quantity of cyclohexane extractable material that can be reliably analyzed is 75 µg, it is apparent that the resulting workplace concentration limit, based on the factors noted above, viz, the lowest reliable detectable concentration of coal tar products, is 0.1 mg of cyclohexane extractables/cu m.

As explained before, the limit of detection of the analytical method is 75 µg. This method may be improved to increase its sensitivity, allowing amounts less than 75 µg to be detected reliably. If this were to occur, it is suggested that one of the objectives not realized above be reconsidered and the sampling time be decreased. With the recommended sampling and analytical method, one can analyze for coal tar products at concentrations of 0.1 mg/cu m or greater by sampling for an entire 8-hour work shift. If the concentration in the workplace air averages less than 0.1 mg/cu m for 8 hours, one can not be certain of the concentration of airborne coal tar products. In this situation, filtering more than 750 liters of air would be necessary to show that the workplace environmental concentrations of cyclohexane extractables from coal tar products are less than 0.1 mg/cu m.

(b) Sampling and Analysis

As described in Chapter IV, the optimum method for sampling uses a combination glass fiber filter and silver membrane filter in a cassette and a personal sampling pump capable of operating at 1.6 liters/minute.

Coal tar, coal tar pitches, creosote, and coal tar pitch volatiles are analyzed by determining the weight of cyclohexane-extractable material that can be extracted from the filters with the aid of ultrasonication as described in Appendix II.

(c) Medical Surveillance and Recordkeeping

It is proposed that medical surveillance be made available to employees and that it include preplacement and periodic examination of the lungs, the upper respiratory tract, and the skin. Pulmonary function tests, chest X-rays, and sputum cytology examinations should be performed to aid in detecting any developing or existing adverse effects of coal tar, coal tar pitch, and creosote on the lungs. Examination of the upper respiratory tract should be directed to the detection of possible adverse effects, including hyperplastic or premalignant changes. Preplacement and interim medical histories should supplement the information obtained from the medical tests. Periodic examinations should be given at least annually to workers frequently exposed to coal tar, coal tar pitch, and creosote to permit early detection of adverse effects on the respiratory organs and of sensitization to coal tar, coal tar pitch, and creosote. In areas of high particulate exposure, special attention should be given to the oral mucosa.

There are likely limitations on the number of sputum cytology examinations which can be accomplished by the facilities now available. Efforts should be made to increase the number of qualified laboratories available for routine analysis of cytologic specimens; these efforts should standardize procedures and increase the feasibility of performing these examinations.

Because of the slow development of carcinogenic effects of coal tar products, all medical records should be maintained for at least 30 years beyond the duration of employment.

(d) Personal Protective Equipment and Clothing

All employees assigned to areas of high exposure should wear clean long-sleeved shirts, shoe covers, head coverings, and rubber gloves. Respirators may be needed by employees working with hot coal tar pitch or with creosote. Employees working with hot coal tar pitch should wear goggles to protect the eyes.

(e) Informing Employees of Hazards

At the beginning of employment, all employees must be informed of the hazards from exposure to coal tar products. Brochures and pamphlets may be effective as aids in informing employees of hazards. In addition, signs warning of the danger of exposure to coal tar products must be posted in any work area where there is a likelihood of occupational exposure. A continuing education program, which includes training in the use of protective equipment and information about the advantages of medical examination, should be available to the employees.

(f) Work Practices

Engineering processes should be designed and operated to minimize leaks of hazardous substances, such as hot coal tar pitch, coal tar, or creosote, from pipes and valves. For operations that might increase the concentration of airborne coal tar products in the work environment, adequate ventilation must be maintained at all times. In case of an accidental leak or spill, anyone entering the area must be appropriately clothed and wear suitable respiratory protective devices. If the coal tar products contact the skin or eyes, the affected person should wash thoroughly with water and soap, flush the eyes with water, and consult a physician if necessary.

(g) Monitoring and Recordkeeping Requirements

Periodic sampling to characterize each employees' exposure is needed. This should be accomplished with due consideration of changes in environmental and process changes. Environmental and medical records need to be retained primarily to give a factual basis for the protection of the worker's health or decisions on the worker's health and rights.

VII. RESEARCH NEEDS

Proper assessment of the toxicity of coal tar products and evaluation of their potential hazard to the working population require additional research in humans and animals.

Epidemiologic Studies

Further epidemiologic studies are needed to estimate the risks of morbidity and mortality resulting from exposure to coal tar products in US workers in processes such as coal tar distillation, wood treatment with creosote, and manufacture of carbon electrodes using coal tar pitches. There is a need for more data on exposure to coal tar products in the occupational environment to determine the association between exposure and observed effects.

Animal Studies

Potential effects of long-term exposure to coal tars, pitches, and fractions of coal tar on various physiologic systems in humans and animals require investigation. Well-planned inhalation studies in several animal species are needed to determine the effects of coal tar aerosols and coal tar pitch volatiles.

Carcinogenic effects of crude coal tar products in animals and humans are well documented. To determine the carcinogenic, teratogenic, and mutagenic potential of tars, pitches, and their respective distillation fractions, detailed animal studies are needed with each type of product sampled from several sources. Techniques are needed to detect and identify the metabolites of coal tar products in the blood and urine of exposed animals and humans. These analytical techniques would be useful in characterizing exposure to coal tar products in the occupational environment.

Analytical Techniques

Existing analytical and sampling methods for determining the concentration of coal tar products in workplace air require refinement to improve the accuracy, sensitivity, and precision of the recommended methods. Investigations of other sampling and analytical techniques should also be encouraged, especially development of an analytical approach which can conveniently and routinely identify individual constituents of coal tar products at the proposed environmental limits.

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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 μg/sample.

Precision and Accuracy

When nine aliquots of a benzene solution from a sample of aluminum-reduction plant emissions containing 1,350 μg/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 μg.

(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:

mg/sample = 2 x (wt sample aliquot (mg) - 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.

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_2O=1)		VAPOR PRESSURE	
VAPOR DENSITY (AIR=1)		SOLUBILITY IN H_2O, % 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

	Mice			Rabbits		
Fraction*	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*								
	BghiP	BaP	BeP	BkF	P	Cor	Per	A	Total
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

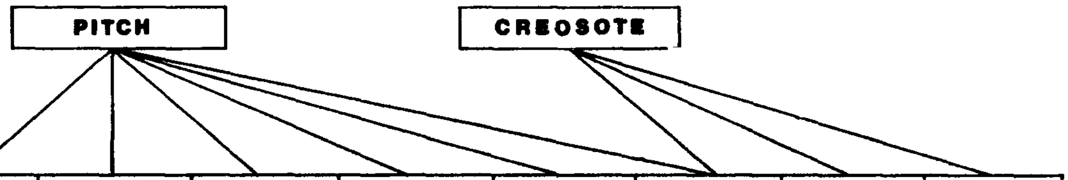
Adapted from reference 19

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



	ALUMINUM	STEEL	FOUNDRY	CARBON-GRAPHITE	ELECTRICAL	CONSTRUCTION	RAILWAY	UTILITY
TYPES OF INDUSTRIAL PROCESSES	ALUMINUM PRODUCTION	ELECTRIC STEEL PRODUCTION OXYGEN FURNACE STEEL PRODUCTION	PRODUCTION OF LARGE CASTINGS FOR INDUSTRY	PRODUCTION OF CARBON AND GRAPHITE PRODUCTS	PRODUCTION OF ELECTRICAL CONDUIT PRODUCTION OF ELECTRICAL MOTORS AND PRINTED CIRCUITS	TREATMENT OF CONSTRUCTION AND MARINE PILING PRODUCTION OF TAR BASED PIPE-LINE COATINGS TAR AS A ROAD, ROOFING, AND WATERPROOFING MATERIAL	TREATMENT OF RAILWAY TIES	TREATMENT OF UTILITY POLES
TYPICAL CONSUMER PRODUCTS	AEROSPACE EQUIPMENT PARTS ALUMINUM SIDING, DOORS, WINDOWS PACKAGING FOIL, WIRE, CANS HARDWARE	AUTOMOBILES APPLIANCES PLUMBING HARDWARE FURNITURE CONSTRUCTION MATERIAL TRANSPORTATION	MACHINE TOOLS FOR CONSUMER GOODS PRODUCERS	BATTERIES: FLASHLIGHTS HEARING AIDS RADIOS PENCILS STREETLIGHTING ARCS MOVIE PROJECTOR ARCS CLAY TARGETS	MOTORS, PARTS FOR: HOUSEHOLD APPLIANCES TELEVISION SETS PUMPS POWER TOOLS CONSTRUCTION	CONSTRUCTION OF: BUILDINGS FACTORIES PIPELINES ROADS, ETC.	IMPROVEMENT OF: RAIL-ROADWAYS	POLES FOR POWER AND TELEPHONE

FIGURE XII-1

THE IMPACT OF COAL TAR PRODUCTS

Adapted from reference 3

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