VII. RESEARCH NEEDS

Proper assessment of the toxicity of asphalt fumes and evaluation of their potential hazard to the working population requires further animal and human studies. The following aspects of epidemiologic and toxicologic research are especially important.

Epidemiologic Studies

Detailed long-term epidemiologic studies, retrospective and prospective, of worker populations exposed to asphalt fumes are needed. Studies should involve both road workers and roofing workers. Care must be exercised to determine that these worker populations have not been exposed to fumes of tar or pitch or to dusts of asbestos or lime, because asphalt workers have frequently worked with materials containing these substances. Experimental studies have demonstrated that these substances are more toxic than asphalt fumes so that the assessments of the true hazard of asphalt fumes would be compromised by dual-exposure situations. As a minimum, epidemiologic studies should include environmental air measurements, medical and work histories, smoking and drinking histories, and body weight histories, pulmonary function studies, physical examinations with particular emphasis on respiratory, eye, and skin examinations, and comparisons with morbidity and mortality information from a carefully selected control population. Samples of urine collected from the cohort under study should be examined for mutagenic activity with tester strains of bacteria (Ames Tests). Additional studies should be performed to evaluate the phototoxic effects of asphalt or asphalt fumes.

Animal Studies

Adverse effects on the eyes and the respiratory tract of animals exposed to high concentrations of asphalt fumes [19,29,30] have been observed. These studies, however, did not include determinations of the concentrations of asphalt fumes to which the animals were exposed. Additional studies are necessary to determine the effects produced by exposure to asphalt fumes at known concentrations, especially in the range of the recommended occupational exposure limit. These studies should attempt to simulate the schedules of exposure in a normal working environment, so that their results could provide information relevant to workplace exposure conditions.

Studies of Carcinogenesis, Mutagenesis, Teratogenesis, and Effects on Reproduction

The available literature does not implicate asphalt fumes in carcinogenesis [19,30,27], although there are some indications that asphalt itself may be neoplastigenic in animal experiments in which it was applied to the skin [3,11,19,32] or injected subcutaneously [19,31-33,45]. The interplay of asphalt and other initiators and promotors of carcinogenesis should be investigated. Further research, including extensive long-term and multigeneration experiments, should be conducted to determine whether mutagenic, teratogenic, or other reproductive effects are caused by asphalt fumes. These experiments should be designed to simulate the exposure potential of a normal work situation.

Sampling and Analytic Studies

Studies are needed to improve the recommended sampling and analytical methods for asphalt fumes. These studies should be concentrated on techniques for separating the fumes from other airborne particulates. A comprehensive characterization of the chemical composition of the fumes generated by heating the asphalts derived from several crude oil sources is also needed, as is research to determine safe substitutes for benzene as an extraction solvent.

Biologic Monitoring

A simple, noninvasive method for detecting significant exposure to asphalt would be useful. A urine test that would signal such an exposure is desirable. Possibilities are detection of hydroxylated polycyclic hydrocarbons, of conjugated products with sulfuric or glucuronic acids or of increased excretions of sulfates, glucuronides, phenols, quinones, or mercapturic acids, in addition to the hydrocarbons themselves, in urine samples voided at the end of the workday or the workweek, depending on the frequency at which monitoring is desired. To be practical the monitoring method must be able to detect exposure during any 10-hour period, with 15-minute interruptions during both the morning and the afternoon periods and a 30-minute one at midday, to asphalt fumes at a concentration of not more than 2.5 mg/cu m, calculated on the basis of a 15-minute sampling period.

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IX. APPENDIX I

METHOD FOR SAMPLING ASPHALT FUMES IN AIR

The sampling method for airborne asphalt fumes is adapted from a general method for sampling airborne particulates [61,73] and is based on procedures developed by NIOSH and currently being used by OSHA.

General Requirements

Collect breathing zone samples that are representative of the individual employee's exposure. Collect enough samples to permit calculation of a TWA concentration for every operation or location in which there is exposure to asphalt fumes. At the time of sample collection, record the sampling location and conditions, equipment used, time and rate of sampling, name of the individual performing the sampling, and any other pertinent information.

Equipment for Air Sampling

(a) Filter: A 37-mm preweighed glass fiber filter, free of organic binders, mounted with backup pad in a two-piece polystyrene cassette.

(b) NIOSH-approved battery-operated personal sampling pump having a flowrate of at least 1 liter/minute.

(c) Calibration device: A calibration device such as is described in the Section on Calibration of Sampling Trains.

Calibration of Sampling Trains

Since the accuracy of an analysis can be no greater than the accuracy into which the volume of sample is measured, the accurate calibration of the sampling pump is essential. The frequency of calibration required depends on the use, care, and handling to which the pump is subjected. Pumps should be recalibrated if they have been misused or if they have just been repaired or received from a manufacturer. If the pump receives hard use, more frequent calibration may be necessary. Regardless of use, maintenance and calibration should be performed on a regular schedule, and records of these should be maintained.

Ordinarily, pumps should be calibrated in the laboratory both before and after they are used in the field and after they have been used to collect a large number of field samples. If extensive field sampling is performed, calibration may also be performed periodically during sampling to ensure the continuous satisfactory operation of the pump and sampler. The accuracy of calibration is dependent on the type of instrument used as a reference. The choice of calibration instrument will depend largely on where the calibration is to be performed. For laboratory calibration, a soapbubble meter is recommended (Figure XIII-2), although other standard calibrating instruments, such as a spirometer, Marriott's bottle, or dry-gas meter, can be used.

Instructions for calibration with the soapbubble meter follow. If another calibration device is selected, equivalent procedures should be used. Since the flowrate is dependent on the pressure drop of the sampling device, the pump must be calibrated while being operated with a representative filter in the line. With a water manometer, the pressure drop should not exceed 13 inches of water.

(a) While the pump is running, check the voltage of the pump battery with a voltmeter to assure that it is adequate for calibration. Charge the battery if necessary.

(b) Turn on the pump and immerse the buret in the soap solution; draw bubbles up the inside until they are able to travel the entire length of the buret without bursting.

(c) Adjust the pump flow controller to provide the desired flowrate.

(d) Start a soapbubble up the buret and measure with a stopwatch the time the bubble takes to move from one calibration mark to another.

(e) Repeat the procedure in (d) at least three times, average the results, and calculate the flowrate by dividing the volume between the preselected marks by the time required for the soapbubble to traverse the distance.

(f) Data and records necessary for the calibration include volume measured, elapsed time, pressure drop, air temperature, atmospheric pressure, serial number of the pump, date, and the name of the person performing the calibration.

<u>Air Sampling</u>

(a) Collect personal samples as close to the employee's breathing zone as possible without interfering with the employee's work in order to characterize the exposure for each job or specific operation. Sampling flowrates should be checked frequently. If filters become clogged to the extent that the selected airflow cannot be maintained, change the filters and initiate the collection of new samples.

(b) Collect samples using a NIOSH-approved portable sampling pump whose flowrate can be determined to an accuracy of ±5% at 1-3 liters/minute. Connect the pump to the cassette, which consists of a preweighed glass-fiber filter free of organic binders, mounted on a two-piece cassette holder and supported by a backup pad.

(c) Operate the pump at a known flowrate to sample a minimum volume of 90 liters. Record the total sampling time, and other data as in Section (f) above. Record the total sampling time. A sample size of 90 liters is recommended.

(d) With each batch of 10 samples, submit one filter from the same lot used for sample collection and label it as a blank. Subject it to exactly the same handling as the samples, but do not draw any air through it.

X. APPENDIX II

ANALYTICAL METHOD (TOTAL PARTICULATE) FOR ASPHALT FUMES

A gravimetric analysis for total particulates should be performed with a preweighed glass-fiber filter [61,73].

Principle of the Method

Air samples are drawn through glass-fiber filters; the filters are then analyzed by a general gravimetric particulate method.

Range and Sensitivity

The range and sensitivity are based on the capabilities of the weighing instrument and the relationship of the particulate weight to the tare weight of the filter.

Interferences

Other particulates in the workplace air will also be collected by the filter and will cause a high reading.

Precision and Accuracy

The precision and accuracy of the gravimetric sampling method is defined by the limit of sensitivity of the balance used to weigh the filter and the interference present in the volume of sampled air.

Apparatus

(a) Balance reading to 0.005 mg.

(b) Desiccator or similar controlled humidity chamber.

Analysis of Samples

(a) A glass-fiber filter is placed in a chamber over an aqueous sulfuric acid solution for 24 hours to bring the filter to a constant weight at 50% humidity.

(b) The weight of the glass-fiber filter is recorded to the nearest 0.01 mg. A nuclear static eliminator on the balance will remove static charges that might interfere with obtaining accurate, reproducible weights of the filter.

(c) A known volume of air is drawn through the preweighed glass-fiber filter to collect airborne dust, including airborne asphalt fumes.

(d) After sampling, the filter is replaced in the chamber for 24 hours and again brought to a constant weight at 50% humidity.

(e) The filter is weighed on the balance used for the preweighing, and the weight is recorded to the nearest 0.01 mg. The difference in the initial and final weights of the filter, divided by the known volume of air sampled, equals the environmental concentration for asphalt fumes as total particulates.

Calculations

The concentration of asphalt fumes in air is expressed as the weight of the total particulates in mg/cu m of air sampled (mg/cu m).

(a) Weight of particulates:

$$Wp = Wf - Wi$$

where:

Wp = weight of particulates in mg
Wf = post-sampling weight of filter in mg
Wi = pre-sampling weight of filter in mg

(b) Volume of air sampled:

$$Vs = \frac{V \times P \times 298 \times 1{,}000}{760(T+273)}$$

where:

Vs = volume of air in cu m at standard conditions
V = volume of air sampled in liters
P = barometric pressure in mm Hg
T = temperature of sample air, C

XI. APPENDIX III

ANALYTICAL METHOD (SOLVENT EXTRACTION) FOR ASPHALT FUMES

A solvent extraction method should be used for analysis of asphalt fumes collected in dusty atmospheres.

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 [73]. 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 perform 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-μm 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) Pre-weigh 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 very 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:

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