IV. ENVIRONMENTAL DATA

Environmental Concentrations

Pegues [58] conducted a series of samplings to demonstrate ventilation on welding operations. The tests were performed in large buildings described as having excellent ventilation "which was probably much better than in most welding shops." To ascertain the influence of ventilation, some tests were conducted in an enclosure, 6 feet by 10 feet, made of a tarpaulin 6 feet wide, and open at the top. In this enclosure both electric arc and oxyacetylene welding were performed on steel with either zinc silicate or galvanized coatings. Samples were collected at various distances from the welding operation, generally 2-3 feet away. During electric welding on zinc silicate coated steel, 5 samples had amounts of zinc equivalent to zinc oxide concentrations ranging from 64.0 to 199.0 mg/cu m, with an average of 120.0 mg/cu m. Seven samples of oxyacetylene welding on the same steel showed zinc oxide concentrations between 17.0 and 46.0 mg/cu m, and an average of 27.0 mg/cu m. Four samples collected during the welding of galvanized steel with the electric arc showed zinc oxide concentrations between 31.0 and 185.0 mg/cu m, with an average of 109.0 mg/cu m, while oxyacetylene welding on galvanized steel produced a range of 30.0-107.0 mg/cu m in 5 samples, with an average of 64.0 mg/cu m. However, without the enclosure, 4 breathing zone samples employing both materials and both types of welding showed concentrations between 7.0 and 20.0 mg/cu m. Nevertheless, 8 room air samples 3 feet and 20 feet downwind from the welder produced concentrations of zinc oxide ranging from 5.0 to 31.0 mg/cu m, and 3 outdoor samples were reported to

have between 2.0 and 13.0 mg/cu m. Results of individual samples are shown in Tables X-3, X-4, X-5, and X-6.

Studies by Boekholt [59] demonstrated the effect of exposures from the use of local exhaust ventilation in enclosed spaces. Air samples collected during ship construction in Holland showed comparatively low concentrations of zinc oxide. In these investigations, welding was being done on steel plates coated with a zinc dust paint 20 μm thick in tanks having a depth of about 16 meters, with ventilation accomplished by flexible exhaust tubes placed close to the cloud of welding fume. Samples in the welders' breathing zone showed concentrations of 10 and 11 mg/cu m. Results in welding bays were also reported to show concentrations in the breathing zone of 5-13 mg/cu m. Results of individual samples are shown in Tables X-7 and X-8. The effectiveness of local exhaust ventilation is dependent on how close to the welding operation the exhaust tube opening can be placed, as well as on the volume and velocity of the air exhausted.

Stalker [60] studied lead and zinc fume hazards in 4 brass foundries, but presented little data on zinc concentrations, stating only that levels in excess of 15 mg/cu m were found in just 1 of the foundries. In that instance, however, he found an average of 182 mg/cu m for melting operations.

Elkins, [61] summarizing findings of investigations in Massachusetts covering more than 18 years starting in 1937, gave data listed in Table IV-I for zinc concentrations associated with selected operations. The years when the measurements were taken were not stated, however, the limit used in Massachusetts during the entire period was 15 mg/cu m.

TABLE IV-1

ZINC CONCENTRATIONS IN SELECTED OPERATIONS

Operation	No. of Samples	No. of Hazardous Concentrations
Galvanizing	8	0
Metal melting	12	4
Metal pouring	66	29
Welding	7	1

Steel and Sanderson, [62] investigating toxic fumes produced from various types of coated welding electrodes, found zinc oxide concentrations produced by burning such electrodes to range from 1.07 to 2.76 mg/cu m. While such concentrations were not considered high, if such coated welding electrodes were used, these concentrations would be added to the existing zinc oxide concentration released when welding any zinc coated metals.

Environmental Sampling and Analytical Methods

Common techniques for collecting particulate matter have been used successfully for sampling fumes and dust containing zinc. While the electrostatic precipitator is quite efficient, [63] filtration is recommended here, both because of its greater simplicity and because it lends itself to breathing zone sampling. Likewise, membrane filters are preferable to paper filters for personal monitoring by the procedure given in Appendix I. [64] A mixed cellulose ester membrane filter (or equivalent) with a pore size of 0.8 μm provides a highly retentive matrix for particulates and is recommended as an efficient collector of particles

encountered in freshly formed zinc oxide fume. The cellulose ester membrane filter is attached to the battery operated personal sampling pump worn by the worker, permitting sampling without interference to the worker.

Chemical methods for the analysis of zinc content of samples have been thoroughly studied and extensively used for many years, and though relatively slow, they are satisfactory. [2,49,61,65-83] The methods most generally used employ dithizone separations. Margerum and Santacana [66] tested 8 methods, [67,70-73,78,79,84] employing radiozinc to aid in determining efficiencies, and recommended a dithizone method using bis(2-hydroxyethyl)dithiocarbamate (also called diethanol dithiocarbamate) as a complexing agent, as proposed by Serfass and Levine. [84] Very satisfactory results were obtained even in the presence of substantial amounts of 10 other metals as impurities--Cd, Co, Cu, Hg, Ni, Fe, Pb, Mn, Cr, and Sn.

Instrumental methods have also been used for the determination of zinc. These have included X-ray spectroscopy, [85] polarography, [86] and atomic absorption. [86,87] Because of speed and accuracy the atomic absorption method is replacing the dithizone method. [87] Appendix II presents details for a recommended atomic absorption method. This is based on Method No. 173 of the Physical and Chemical Analysis Branch of NIOSH. [88]

Control of Exposure

Since the principal hazard of zinc oxide is its fume, control efforts are directed primarily against the operation or processes in which zinc is subjected to elevated temperatures. Included in these process^

galvanizing, brass foundry operations, and welding. In each of these, effective control usually depends upon suitably designed and properly utilized local exhaust ventilation. [89,90] In welding and similar operations, the nature of the work may require the employee to change the location of his work frequently. Under such circumstances the exhaust system must accompany him. This may require the use of flexible exhaust ducts or other arrangements which enable the hood or the duct opening to be placed at the most effective location, preferably within a few inches of the flame or arc.

In foundry operations, careful design and location of exhaust hoods are required to control fumes from furnaces without interfering with operations. Unless centralized pouring is used, there is likewise a need for a flexible exhaust system which can accompany the pouring.

Since galvanizing is usually performed at a fixed location, the operations lend themselves to standard exhaust ventilation principles and practices. [89,90]

In some instances, general ventilation may prove sufficient to keep fume concentrations within the limits specified in the standard. Reliance should not be placed upon the natural ventilation, however, unless tests under conditions of minimal ventilation have conclusively demonstrated that the standards are met.

Where exhaust ventilation is required, the design principles presented in the 1974 edition of Industrial Ventilation - A Manual of Recommended Practice [89] or subsequent editions and in Fundamentals Governing the Design and Operation of Local Exhaust Systems, Z9.2-1971 (ANSI), [90] should be used.

Where dust problems may arise from production, processing, packaging, or other handling of zinc oxide, conventional ventilation, enclosure, and housekeeping procedures should usually suffice for adequate control.

V. DEVELOPMENT OF STANDARD

Basis for Previous Standards

Cook, [91] in his comprehensive listing of Maximum Allowable Concentrations of Industrial Atmospheric Contaminants published in 1945, cited 15 mg Zn/cu m as the Maximum Allowable Concentration (MAC) for zinc oxide then used by California, Massachusetts, New York, Utah, and the United States Public Health Service. As the basis for this MAC, Cook cited Drinker et al [6] as having found that 14 mg/cu m of zinc oxide, measured as zinc, produced no reaction on the average subject after an exposure of 8 hours. Drinker et al [6] did not specifically define "average," but apparently referred to a healthy adult of either sex, "breathing at an average rate of 9 liters a minute." They recommended a concentration of 15 mg/cu m as the threshold limit.

The paper by Drinker et al, [6] cited by Cook, [91] did not state clearly how the 15 mg/cu m was derived. It seems that it was not based on the dose-response slope calculated by Drinker. [6] Drinker referred to the work by Batchelor et al [34] but examination of the Batchelor paper does not reveal any specific statement regarding absence of effects at concentrations of zinc oxide below 14 or 15 mg/cu m. Sampling in industrial environments as described by Batchelor et al [34] led to a generalization by Drinker et al [6] that metal fume fever was not observed at levels below 14 mg/cu m. This was apparently the basis for the 15 mg/cu m standard.

In 1946, the American Conference of Governmental Industrial Hygienists (ACGIH) published their first list of MAC's in which they endorsed the value of 15 mg/cu m for "zinc oxide fume." [92] The ACGIH MAC

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recommendation for zinc oxide fume, though the terminology eventually changed to Threshold Limit Value (TLV), remained at 15 mg/cu m until 1962 when it was revised downward to 5 mg/cu m. This figure has remained unchanged since. [93] The basis for this reduction to 5 mg ZnO/cu m, according to the ACGIH Documentation of the Threshold Limit Values, [94] was the industrial observation that zinc chills (metal fume fever) occurred in nonferrous foundries where concentrations of zinc fume rarely exceeded 15 mg/cu m. In addition, according to DE Hickish (in a written communication in 1963 to the TLV committee), metal fume fever was observed in an oxyacetylene welder who had been working on galvanized steel where very limited air sampling had subsequently indicated concentrations of 3.0-4.2 mg/cu m of zinc oxide. A question remained, however, as to whether the measurements were representative of the exposure of the welder.

The present federal standard for zinc oxide fume is an 8-hour time-weighted average of 5 mg ZnO/cu m (29 CFR 1910.1000). This standard of 5 mg ZnO/cu m is based on the ACGIH TLV originally established in 1962. [93]

Basis for Recommended Environmental Standard

Industrial exposure to zinc oxide fume by inhalation has been shown to cause metal fume fever. [8,9,12,14,46] Reports in earlier papers of prolonged or intermittent exposure to zinc oxide fume causing gastro-intestinal disturbances and other, chronic effects [35-37] have largely been discounted. [34,41,57] The reported medical data were insufficient and environmental data were either incomplete or of doubtful validity.

A report of skin lesions from frequent and prolonged coverage of the skin with zinc oxide powder [44] concluded that the material was an

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irritant but nontoxic. The lesions were found to be caused by bacterial infection and daily washing and improved personal cleanliness were sufficient to eliminate the disorder.

Drinker et al [6,29] published data which suggested that metal fume fever may also have been caused by well dispersed clouds of zinc oxide powder. Mogilevskaya [31] described clinical changes in the lungs of 13 of 19 workers engaged for 2-3 years in the manufacture of zinc powder, as well as similar changes in the lungs of experimental rats exposed to zinc oxide powder. The changes included inflammation of the upper respiratory tract (nasopharyngitis and laryngitis) in the workers and peribronchial pneumonia, sclerosis, and abnormal bronchial tissue in the rats. The author [31] concluded that zinc oxide powder and zinc powder caused changes in the upper respiratory tract and in the bronchi and peribronchial tissues. Dzukaev and Kochetkova [32] observed fibrous changes in the lungs of workers in a zinc oxide shop and demonstrated clinical changes in the lungs of rabbits. The data were difficult to interpret since the rabbits were also exposed to lead.

The lack of environmental data on zinc oxide fume could be due to the lack of interest in the metal fume fever syndrome because of its transitory nature. Experienced workers cope with the problem and usually do not bother to report it. [34] Most of the animal studies have been directed toward the elucidation of the mechanism or pathogenesis of metal fume fever. [45,50,51]

In 1944, Hammond [46] reported the incidence of metal fume fever in stone crusher repairmen who, with oxyacetylene torches, cut out the worn linings of steel crushers in which zinc and zinc alloys were used as

binders and fillers. These workers were exposed for periods of 1-3 hours to zinc oxide fume (as zinc) at 320-545 mg Zn/cu m. Eventually all these men experienced metal fume fever. There were concomitant exposures to approximately 12.4 mg/cu m of manganese fume and to 1.6 mg/cu m of lead fume. In contrast, men employed in pouring molten zinc into the crushers for unspecified periods of time were exposed at concentrations of zinc oxide fume of 8-12 mg Zn/cu m, and were never recorded as suffering metal fume fever following such work.

Having produced classical metal fume fever in volunteer subjects after 10 1/2-12 minutes' exposure at 600 mg/cu m of high purity, freshly generated zinc oxide fume, [5] and having observed metal fume fever in a colleague who had been exposed at an average of 52 mg/cu m for about 5 hours, Drinker et al [6] conducted an elaborate series of experiments to determine the threshold for zinc oxide fume-induced metal fume fever. Twenty-seven experimental exposures of 10 volunteers, 7 males and 3 females, were conducted at various concentrations, durations of exposure, respiration rates, and minute volumes. A dose-response slope was constructed using a rise in body temperature as the endpoint. A threshold value of 15 mg/cu m was selected by the authors who stated "We use a concentration of 15 mg per cubic meter as the threshold limit, because we have found that men exposed for eight hours to concentrations of that order do not ordinarily acquire fever." The earlier study by Batchelor et al [34] was used in support of this statement. However, the available data fail to support a threshold limit of 15 mg/cu m. Batchelor et al reported that a concentration of 57-70 mg/cu m of very finely divided zinc oxide powder inhaled slowly and deeply for 15 minutes or more was close to the

threshold for metal fume fever. [34] The recommendation of Drinker and his colleagues [6] of 15 mg/cu m as a threshold limit value was widely accepted until 1962. [93]

The basis for including zinc oxide dust comes from animal [31,32,45] and human [45,95] experimental data which indicated that symptoms of metal fume fever resulted from exposure to zinc oxide dust. Batchelor et al [34] found that an individual unaccustomed to zinc, breathing zinc oxide dust slowly and deeply at concentrations of approximately 57-70 mg/cu m for 15 minutes or more, developed a low grade metal fume fever reaction. Respiratory effects in humans and animals from zinc oxide powder consisted of pneumonia, sclerosis of bronchial tissue, and atrophic mucosal changes of the upper respiratory tract, thus suggesting chronic toxicity from zinc oxide powder. [31,32] However, the reported findings are clouded by a lack of quantitative data and the possibility of simultaneous human occupational exposures to substances other than zinc oxide. Turner and Thompson [45] reported histories of "oxide chills" in 7 out of 9 men employed in a zinc oxide packing room. The symptoms described by the workers consisted of irritation and dryness of the nose and throat and frequent headaches. The incidence of zinc oxide-induced metal fume fever seems strongly dependent on particle size with thresholds having been described for zinc oxide powder in the vicinity of 60 mg/cu m, and for oxidized zinc fumes encountered in welding operations on the order of 15 mg/cu m. Suggestions of cases of metal fume fever in the range of 5 mg/cu m are unsupported by firm data.

Although the effects of zinc fume fever are transitory, the possibility of chronic respiratory effects resulting from zinc oxide

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inhalation, whether as a fume or in larger particulate form, cannot be dismissed. It is appropriate to retain the current federal standard of 5 mg/cu m, as a time-weighted average, and to recommend a ceiling of 15 mg/cu m, as determined by a sampling time of 15 minutes, to prevent the incidence of metal fume fever associated with zinc oxide inhalation and the possible development of pathological tissue changes in the lungs.

The sampling and analytical methods presented in Appendices I and II are based on Method Number 173 of the NIOSH Manual of Analytical Methods. The analytical method as developed is not specific for zinc oxide but measures total zinc. It is recognized that analysis for total zinc is not the most desirable approach and that additional research is needed to develop a method which is specific for zinc oxide. NIOSH is currently developing a sampling and analytical method to distinguish zinc oxide from total zinc.

From the work of Drinker et al, [6,8,29] the respirable fraction of suspended zinc oxide particles, 1 μm or less in size, seems to be responsible for metal fume fever. However there is not enough justification at this time to warrant a requirement for size-selective sampling.

It is recognized that many workers are exposed to small amounts of zinc oxide or are working in situations where, regardless of the amount generated, there is only negligible contact with the substance. Under these conditions, it should not be necessary to comply with many of the provisions of this recommended standard, which has been prepared primarily to protect worker health under more hazardous circumstances. Concern for worker health requires that protective measures be instituted below the

enforceable limit to ensure that exposures stay below that limit. For these reasons, "exposure to zinc oxide" has been defined as exposure above half the TWA environmental limit, thereby delineating those working situations which do not require the expenditure of health resources for environmental and medical monitoring and associated recordkeeping. Half the environmental limit has been chosen on the basis of professional judgment rather than on quantitative data that delineate nonhazardous areas from areas in which a hazard may exist.

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VII. APPENDIX I

METHOD FOR SAMPLING ZINC OXIDE IN AIR

The sampling and analytical methods presented in Appendices I and II are based on those described in Method No. 173 of the Physical and Chemical Analysis Branch of NIOSH. [88]

Atmospheric Sampling

Breathing zone samples representative of the individual worker's exposure are collected. A description of sampling location and conditions, equipment used, time and rate of sampling, and any other pertinent information are recorded at the time of sample collection. Enough samples must be collected to permit calculation of a time-weighted average (TWA) exposure for every operation or location in which there is exposure to zinc oxide.

(a) Equipment

The sampling train consists of a membrane filter and a vacuum pump.

(1) Membrane filter: Samples of zinc oxide are collected in the breathing zone of the worker, using a sampler with a cellulose ester membrane filter. The filter is a 0.8 μm pore size mixed cellulose ester membrane mounted in a closed-face sampling cassette which can be attached to the worker near his breathing zone.

(2) Pump: A battery-operated pump, complete with clip for attachment to the worker's belt, capable of operation at 2 liters/min or less.

(b)   Calibration

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

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 is dependent on the type of instrument used as a reference. The choice of calibration instrument will depend largely upon where the calibration is to be performed. For laboratory testing, primary standards such as a spirometer or soapbubble meter are recommended, although other standard calibrating instruments such as a wet test meter or dry gas meter can be used. The actual setups will be similar for all instruments.

Instructions for calibration with the soapbubble meter follow. If another calibration device is selected, equivalent procedures should be used. The calibration setup for personal sampling pumps with a membrane filter is shown in Figure X-1. Since the flowrate given by a pump is dependent on the pressure drop of the sampling device, in this case a membrane filter, the pump must be calibrated while operating with a

representative filter in line.

(1)   The voltage of the pump battery is checked with a voltmeter to assure adequate voltage for calibration.   The battery is charged if necessary.

(2)   The sampling train is assembled as shown in Figure X-1.

(3)   The pump is turned on and the inside of the soapbubble meter is moistened by immersing the buret in the soap solution and drawing bubbles up the inside until they are able to travel the entire buret length without bursting.

(4)   The pump rotameter is adjusted to provide the desired flowrate.

(5)   The water manometer is checked to ensure that the pressure drop across the sampling train does not exceed 13 inches of water at 1 liter/min or 2.5 inches of water at 200 ml/min.

(6)   A soapbubble is started up the buret and the time it takes the bubble to move from one calibration mark to another is measured with a stopwatch.

(7)   The procedure in (6) above is repeated at least twice, the results averaged, and the flowrate calculated by dividing the volume between the preselected marks by the time required for the soapbubble to traverse the distance.

(8)   Corrections to the flowrate may be necessary if the pressure or temperature, when samples are collected, differs significantly from that when the calibration was performed.   Flow rates may be calculated by using the following formula:

$$q \text{ actual} = q \text{ indicated} \cdot \sqrt{\frac{P(\text{calibrated})}{P(\text{actual})} \cdot \frac{T(\text{actual})}{T(\text{calibrated})}}$$

where = q = volumetric flowrate

T = absolute temperature (Kelvin or Rankine)

P = atmospheric pressure

(9)   Use graph papers to record the air flow corrected to 25 C and 760 torr as the ordinate and the rotameter readings as the abscissa.

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

(c)   Sampling Procedure

(1)   Sampling is performed using a closed-face membrane filter cassette.

(2)   The sampler shall be operated at a flowrate of 1 liter/min and samples taken for 15 minutes.

(3)   The temperature and pressure of the atmosphere being sampled are measured and recorded.

(4)   One membrane filter is treated in the same manner as the sample filters with the exception that no air is drawn through it. This filter serves as a blank.

(5)   Immediately after sampling, personal filter samples should be sealed in individual plastic filter holders for shipment. The filters must not be loaded to the point where portions of the sample might be dislodged from the collecting filter during handling.