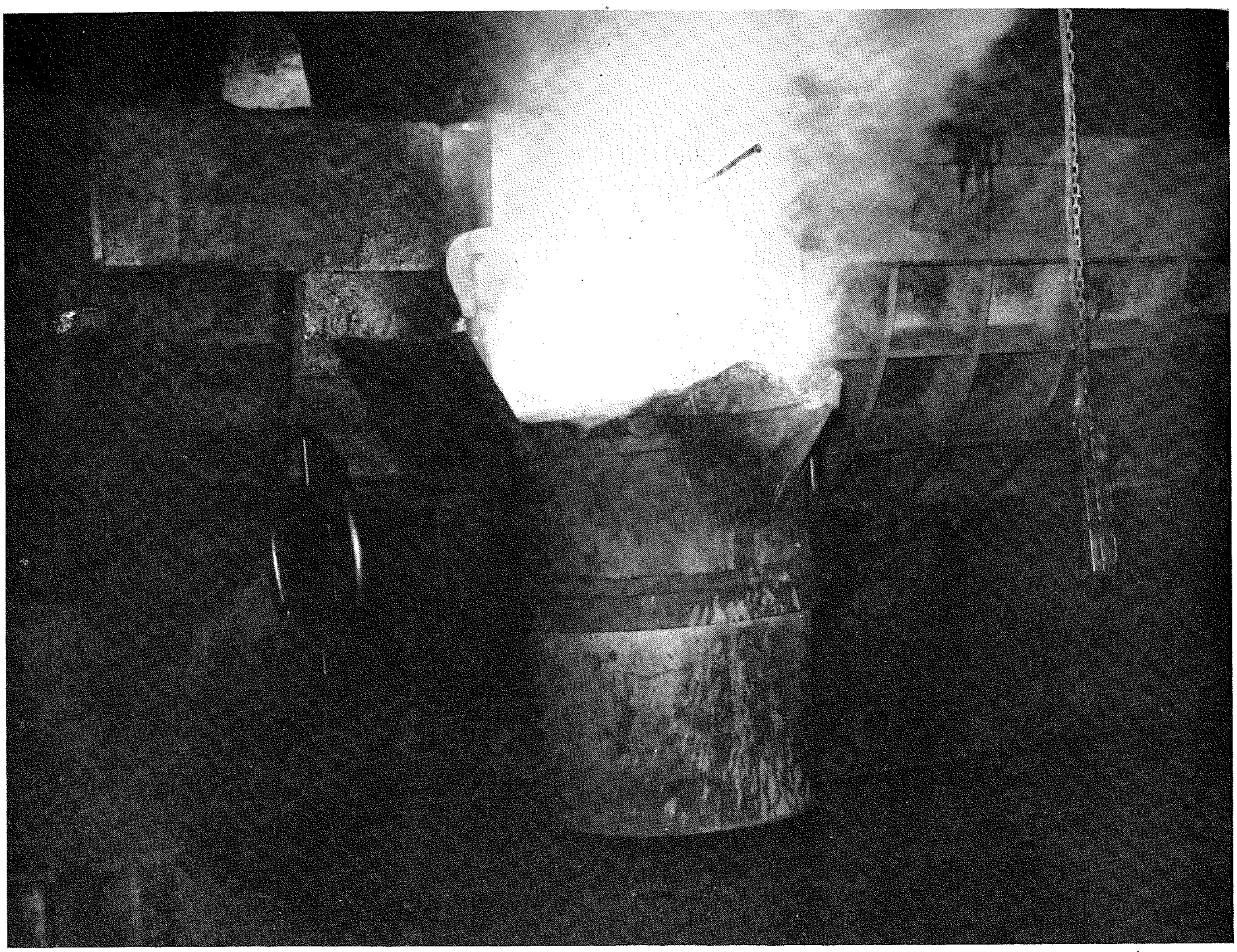
MICHIGAN'S occupational health

Volume 10, No. 2

MICHIGAN DEPARTMENT OF HEALTH
Albert E. Heustis, M.D., Commissioner

WINTER 1964-1965

THE OLD PROBLEMS ARE STILL WITH US AND NEW ONES ARE COMING ALONG



This bright flare-up effect occurs in the making of ductile iron when molten iron from the holding furnace reacts with inoculating alloys in the ladle.

FOUNDRY DUST—MERCURY—LEAD

Even now not enough is being done to keep up. The old standby problems are still very much with us and perhaps we have some room for refinement on how we handle and interpret these. We have been aware of lead, mercury and foundry dust problems for years and yet these old standbys need constant and continuing attention. People and job responsibilities change, processes change, raw materials and ingredients change, so that none of these common occupational health problems is ever solved "permanently." On the contrary, constant awareness and periodic sam-

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PROBLEMS—Continued

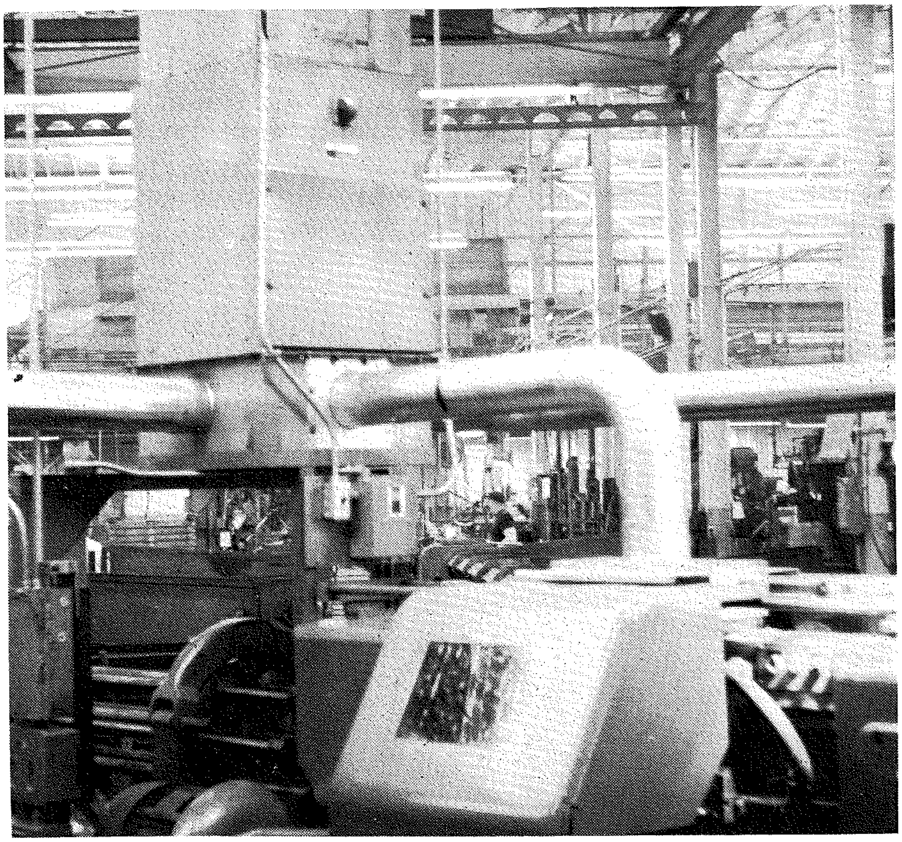
pling is called for. We have demonstrated an increasing tendency in our organization to collect biological samples —particularly from lead workers, sometimes in mercury exposure. This same technique is now being applied as a monitoring procedure among agricultural workers who are using methyl bromide for control of the cereal-leaf beetle. The fumigation procedures must be carefully controlled.

OIL MIST CONTAMINATES WORKROOM AIR

The Division of Occupational Health is also concerned about oil exposure in industry, both because of what we have seen—extreme cases of oil contamination of the workroom air—and because of complaints which we have received. The ACGIH threshhold limit value for oil mist is 5 milligrams per cubic meter. Wagner, Wright and Stokinger (1) working with five species of animals (dog, rabbit, rat, hamster, mouse) studied petroleum base mineral-oil mists at concentrations of 5 milligrams per cubic meter and 100 milligrams per cubic meter. They concluded that the 5 milligram concentration level would present no toxic hazard upon prolonged exposure but that protracted exposure at approximately 100 milligrams per cubic meter would in time produce harmful physiological effects. In comparison (and with this 5mg m^3 threshhold in mind) it is interesting to note the results of some recent studies conducted by our staff people (all general air samples):

OPERATION	*mg Per Cubic Meter*
Cold heading	13–20
Valve body assembly	24–27
Hob cutter grinders	7–11
Machining—oil mist lubrication	3–28
Machining—oil mist lubrication (same operation—oil change)	2.6–3.3
Loading ammonium nitrate-oil mixture before blasting (10-20 minutes per 8 hours)	220–750

We are presently sampling for oil mist with standard size Greenburg-Smith impingers containing perchlorethylene and analyzing the samples with a Beckman infrared spectrophotometer (at a 3.42 micron wavelength). Whenever atmospheric samples are collected, material samples are also brought back to the lab so that the infrared unit can be calibrated with the material actually used in the plant. As a further check, we evaporate the sample down and do a gravimetric.



Hooding on this automatic machining operation confines the oil mist. It exhausts through a dry-type extended-surface collector

BERYLLIUM ALLOY DUST CAUSES CONCERN

According to one of the major producers of beryllium, there is as much or more beryllium alloy material used in Michigan than in any other state. Our past experience should reflect what might be expected anywhere where beryllium and its alloys are handled and should suggest what a successful control program should include in any particular plant. Plant activity with the metal has been intermittent in Michigan, however, so we cannot claim credit for any totally successful control program based on a reasonably long experience factor. There just isn't enough work being done with beryllium to allow such a long-term judgment to be made. On the other hand, we *have* had sufficient experience with the metal to give some general indications of where problem areas are, and when control has been successful.

The hygienic standards of two micrograms per cubic meter as a threshold limit value, the 25 micrograms per cubic meter level as a maximum allowable concentration for any period of time, and the average monthly concentration maximum of 0.01 micrograms per cubic meter in the neighborhood of any plant handling beryllium compounds, should serve as a base for discussion.

One company has established a rather extensive pilot plant project involving the use of pure beryllium powder. There has been close cooperation between the company and our Division in regard to the engineering and medical control program and this plant has instituted a complete control program as designated in our *Summer 1963 issue of Michigan's Occupational Health* bulletin. Local exhaust ventilation is provided at all operations. The housekeeping procedures are excellent. Complete sanitation facilities including an in-plant laundry are provided, entry to the work area is through a double set of doors, and all street clothing is kept separate from work clothing. We have monitored the workroom and the neighborhood air.

No beryllium was found in the neighborhood air either before or after operations were started and our continuous in-plant monitoring program has shown the presence of some beryllium in the air—but always in concentrations considerably below the threshhold limit value. This success story should be qualified with the information that it is a carefully operated type pilot plant program involving just a few specially trained people who are cognizant of the hazard associated with beryllium and who are not involved in any way in what might be considered a production-type operation. We expect that these controls, which are exceptional in every respect, will successfully prevent any high workroom or neighborhood concentrations from developing.

Experience in two plants machining beryllium copper alloy (0.4 to 0.7 percent beryllium) on Warner and Swazey tracing lathes, Excello grinders, and with portable grinding and polishing operations, has enabled us to come to certain generalized conclusions.

1. We do not find excessive quantities of beryllium in those air samples collected at operations where coolants are used.

2. We find significant concentrations of beryllium at those operations not using coolants and it is apparent that the levels can exceed threshold limit values depending upon machine speed or rate of production. This is a clear indication of the need for ventilation control on most grinding machines and lathes.

3. The coolant becomes contaminated with beryllium particulate material and necessitates efficient filtration of the coolant as well as frequent change so as to both minimize the build-up of beryllium in the oil and prevent dissemination of hazardous quantities in the workroom air during use of the lubricant.

In another plant, a non-ferrous jobbing foundry which works with beryllium from time to time, it has been found that the furnace room air (general air samples) stays just about at the threshold limit value or a little higher than the threshold limit value and the air samples collected at hand and machine grinding on castings including a cut-off wheel operation showed values ranging from 1 to 7 micrograms per cubic meter — with

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Air Used in Ordinary Sewage Treatment Must Meet Extreme "Super Clean" Standards

In the activated sludge process for treating sewage, it is necessary to bubble air through the aeration tank liquors so as to effect an oxygen transfer. In most of the larger of the present day plants compressed air is blown through submerged porous diffusers so as to form fine bubbles thereby affecting higher oxygen transfer efficiencies. Various *diffusers are used such as ceramic plates, ceramic tubes or Saran-wound tubes. With all of these, a severe problem of plugging of the diffuser media occurs, either due to particles on the interior of the diffuser carried by the air itself, or because of the constituents in the sewage. The maintenance problem caused by plugged diffuser media is severe if it must be cleaned or changed more than once per year. A severe hardship is created on the plant operating personnel and the treatment capacity is reduced. On the other hand, without diffusers the oxygen transfer efficiency is materially reduced and this also affects treatment capacity. The main problem is getting the air clean.*

In past years, some of the larger sewage treatment plants have installed conventional bag-type dust collectors for the purpose of filtering the outside air before it is passed to the compressor and to the diffuser piping system. The fabric collector media in itself was not found to be efficient enough for the job and it has been necessary for these plants to install asbestos pre-coating equipment to achieve the desired air cleaning efficiency. The accepted general rule-of-thumb of air cleanliness for Saran-wound tubes has been 0.09 milligrams per thousand cubic feet of air. Translated into the commonly used air pollution terminology this amounts to about 3.5 micrograms per cubic meter or 0.000002 grains per cubic foot.

In a way it seems absurd that that such a high quality of air—a quality which meets so-called "white room" standards—is required for diffusion into sewage tanks. But this is the case in large treatment plants throughout the country.

In an effort to evaluate the performance of a different type of air cleaning system consisting of a dry electrostatic agglomerator followed by a dry fiberglass extended-surface filter, a series of tests were run by a collector manufacturer in conjunction with the operators of the New York City sewage treatment plant.[3] They found that they had to sample for a *continuous two-week period* in order to pick up a weighable quantity of dust on the clean-air side of the equipment, and they further found that for this sampling task Whatman paper thimbles were unsatisfactory because of their fragility and hygroscopic nature and aluminum-oxide thimbles presented similar problems in addition to being very difficult to handle. The weighing error introduced with either of these collection devices would make any sample data useless. The media finally selected was a commercially available resin-bound fiberglass paper which enabled a reasonably good weighing procedure and which on the basis of dioctyl phthalate efficiencies was found to be in the 99.9 percent range as compared to 69 percent for the ceramic thimble and 90 percent for the Whatman thimble.

We were asked to render advice on a proposed installation and suggested that the dry media portion of the system being recommended be installed and tested first. This was done and our tests of the installation which involved a series of samples collected over periods of time ranging from one to two weeks showed that the clean air loading averaged 0.18 milligrams per thousand cubic feet (average of 6.4 micrograms per cubic meter). Inasmuch as the desired maximum clean air loading was 0.09 milligrams per thousand cubic feet, the next step was to install the electrostatic agglomerator on the up-stream side of the dry filter unit. Sampling done after this installation was completed indicated an average of 0.025 milligrams per thousand cubic feet or about 1 microgram per cubic meter. A rough calculation of air cleaning efficiency based on an inlet air quality of 90 micrograms per cubic meter indicates a collection efficiency of *99 percent.* However, the startling consideration here is the degree of refinement used in such an operation which, as noted above, produces air of exceptional quality. As an approximate means of comparison (relating the final clean air loading to dust count and using a figure of 300 million particles per cubic foot for 1 micron mineral dust) the air being supplied to the diffuser would have a count of about *7500 particles per cubic foot.*

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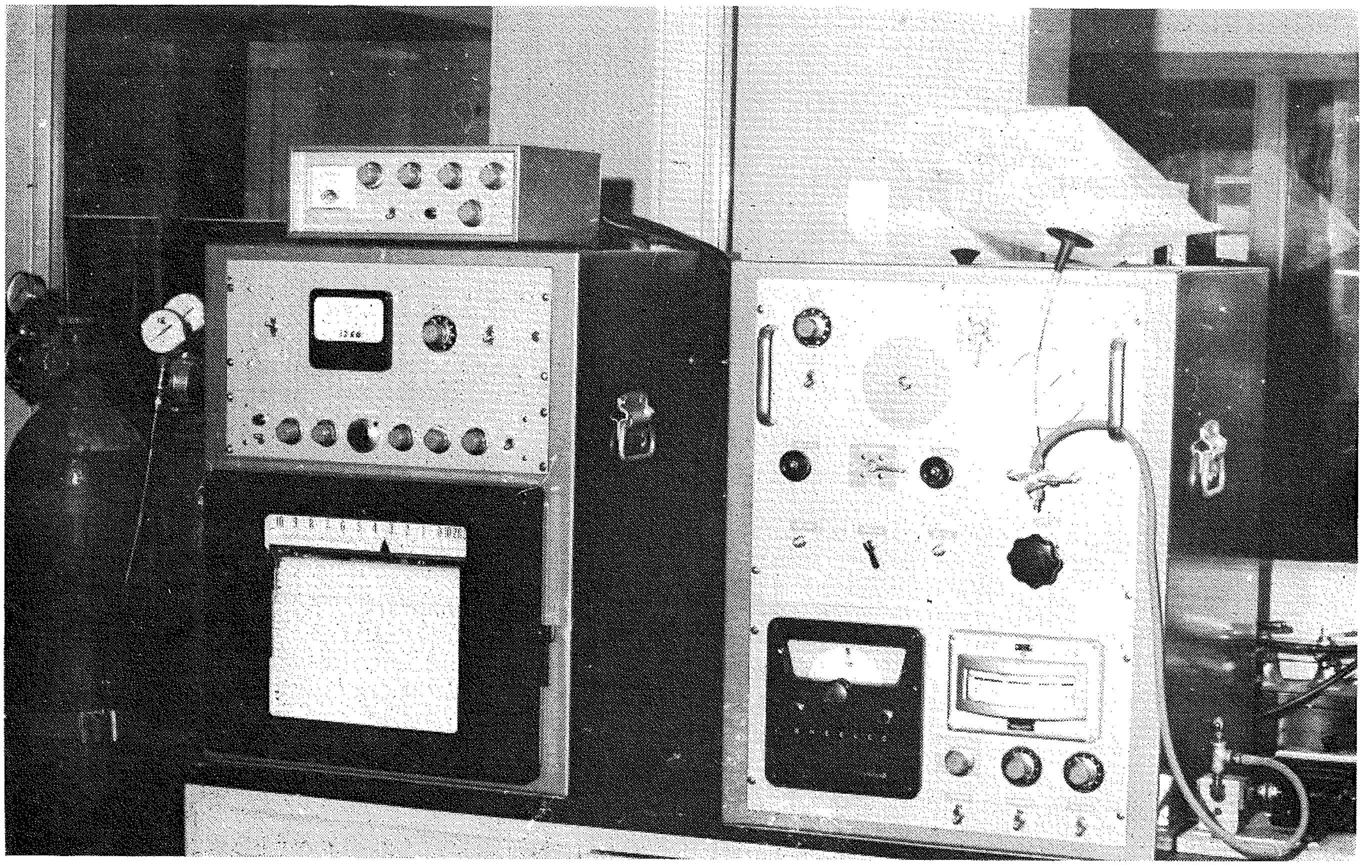
CONVENIENT BAG-SAMPLING TECHNIQUE SPEEDS FIELD AIR SAMPLING PROCEDURES



Analysis of a bag sample collected in the field is usually done with a gas chromatagraph in the laboratory

Bag sampling has developed into an important technique not only in air pollution work but in occupational health as well. Its successful use depends upon the availability of supporting instrumentation particularly the gas chromatograph, and also the infrared spectrophotometer. Sampling for a specific gas or a mixture in the breathing zone of a worker is easily done, and with most stable compounds there is little or no physical and chemical change of the sample during transport to the laboratory. The analytical data produced by gas chromatographic analysis is quantitative even in ranges considerably below threshold limit values. Other advantages include speed of analysis, the ability to work with unknown materials (thereby avoiding the decision of what instrument to use for sampling the unknown atmosphere), the ability to identify the individual component of a gas mixture even in the low concentration range, ease of shipment of the sample, and the psychological significance to the worker or plant manager of *seeing an actual physical amount of gas being collected.*

In utilizing the bag sampling procedure in conjunction with the gas chromatograph it is important that the sample be run within about 24 hours if reasonably good results are to be obtained, since with some gases a diffusion effect takes place. The speed factor is particularly important where the contaminant is an unkown, in which case the gas should be run through the chromatograph as soon as possible utilizing a universal-type adsorption column (our chomatograph is a Model 20 Barber-Colman with a 25 percent Apiezon L on Chromosorb W in ¼-inch OD stainless steel, 10-feet-long column). Either the hydrogen-flame-ionization or argon-ionization detector can be used for analysis.

There are several polymeric film materials. Some heat-seal, some are double layers of two different films, and some are aluminized. Scotch-pak, Mylar and Saran are typical. The selection of a film material should, if possible, be based on the contaminant to be sampled since most gases even if they are nonreactive with the plastics, do demonstrate a diffusion loss. Baker and Doerr[4] have noted that moisture (whether present originally or having permeated into a bag on storage) is a factor to be considered in analysis where oxides such as SO_2 and NO_2 are involved. Hydrocarbons do not appear to be affected by moisture. Chemical reaction and permeability are involved with the soluable oxides, but diffusional parameters and perhaps other factors control hydrocarbon loss. A considerable amount of information on bag sampling systems for specific contaminants has been presented in the literature.

It is obviously important that the bags be made as leakproof as possible and that a technique (we use an automobile tube valve stem) be developed for getting the sample into and out of the bag container without dilution, and that where possible "decay" curves be run on any known materials that are to be sampled. Bags can be re-used but if this is to be done they should be purged several times and then a chromatogram run on the bag before it is re-used. Internal standards may be desirable to compensate for procedure and instrument variables.

Depending upon the instrumentation available, there is no problem in determining concentrations of benzene below 10 parts per million as an impurity in toluene or xylene solvent mixtures and some hydrocarbons lend themselves to an easy sampling and analytical procedure. We have not been successful in sampling styrene or ozone with this technique and have also determined that Mylar (2 mils in thickness) is the best all around film material for our use. It does not readily heat seal but a thermoplastic heat sealing tape can be used for making up the bags.

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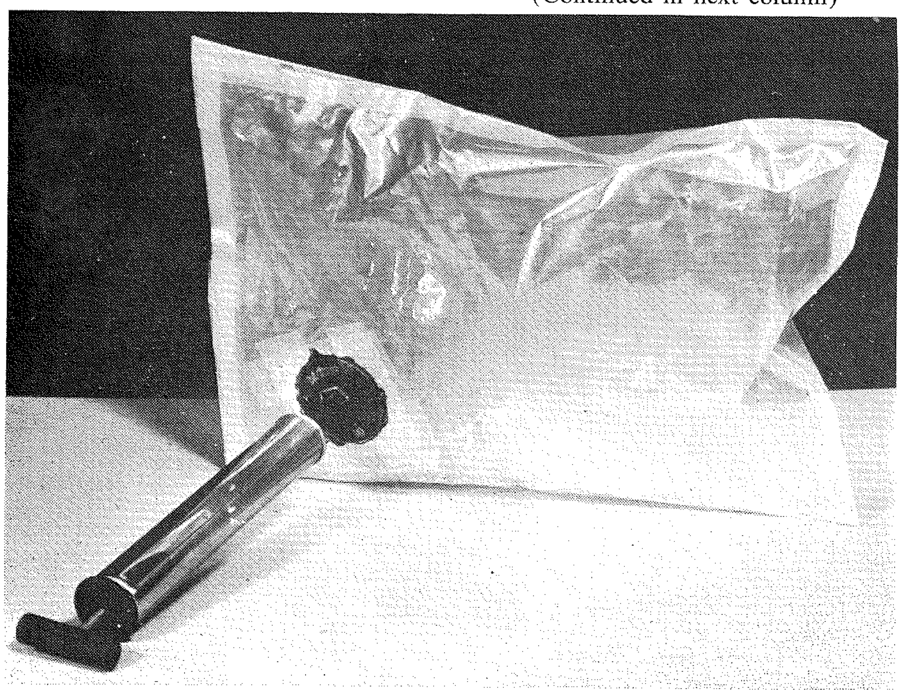

Samples are collected with the use of a simple plastic bag and an ordinary football pump

PROBLEMS—Continued

most in excess of the threshold limit value. On a time-weighted basis, the controls provided in this plant are barely acceptable and recommendations for improvement have been submitted and are being followed. This type operation as well as all others where beryllium is handled on an intermittent basis presents a challenge to us in terms or the extent of control programming we insist be done.

Two studies were conducted to determine the concentrations of beryllium in the workroom air at an electric discharge machining operation where pure sheet beryllium was being handled. In this operation, the metal to be cut is submerged in oil and a preformed discharge electrode adjusted to a point near the metal. When the high voltage is applied to the electrode, the electric arc cuts the desired hole or other predetermined shape into the metal. Concentrations of beryllium at the working area of the operation were found to be *above the threshold limit* value at a distance of 16 inches from the arc and appreciable amounts were found several feet from the machine. Based on the data obtained, it is apparent that local exhaust ventilation is needed at such machines when beryllium is being processed. Also, the amount of beryllium found in the oil indicated a need for frequent cleaning, concern about oil misting, and a safe disposal method.

We are maintaining a close surveillance on all users that we know about.

(Continued in next column)

Phosphine Gas Released in Machining of Nodular Iron

Nodular iron, also known as ductile iron or spheroidal graphite iron is a form of iron containing graphite in spheroidal form rather than in the flake form found in ordinary cast iron. Ductile iron can be made with the ladle addition of cerium or, as is commonly done in Michigan, by the controlled addition of magnesium in the form of a copper or a nickel alloy to the melt. Where the magnesium alloy is used as the inoculant it usually contains about 10 to 20 percent of magnesium and about 1 to 2 percent of this alloy is added to the ladle at the time of tapping. This procedure leaves a small magnesium content in the metal—about 0.04 to 0.10 percent.

When ductile iron is freshly fractured or machined it emits a characteristic odor similar to that of acetylene and this odor becomes more pronounced when the freshly exposed surfaces are in a moist atmosphere. It has been theorized that the odor is probably due to the presence of phosphine (and possibly arsine) since phosphine gas results when a hydrolyzable phosphide is formed in iron by the reaction of magnesium with phosphorus ($3Mg + 2P = Mg_3P_2$). Then when the metal is fractured or machined, the phosphide is hydrolyzed by moisture in the air to phosphine ($Mg_3P_2 + 6H_2O \rightarrow Mg(OH)_2 + 2PH_3$).

Phosphine is a highly toxic gas having a TLV of 0.05 parts per million. The health problem attributable to phosphine from ductile iron machining was perhaps first uncovered in Europe in 1955 when it was reported that illness had arisen among workers in the Saar who were machining nodular iron rolls. The workmen complained of pains in the eyes, the stomach, and the nose with some nosebleeding. It was believed that the illness was caused on the inhalation of magnesium phosphide dust which on contact with moisture in the nose and throat would generae phosphine in concentrations sufficient to cause difficulty. There followed in England a detailed study by Matthew[2] who found that phosphine gas *was in fact produced* in concentrations that varied with the depth of cut and machine speed — a higher concentration developing with greater roughing. Dust lying around the machine contributed significantly to the concentrations of phosphine determined in the breathing area of the

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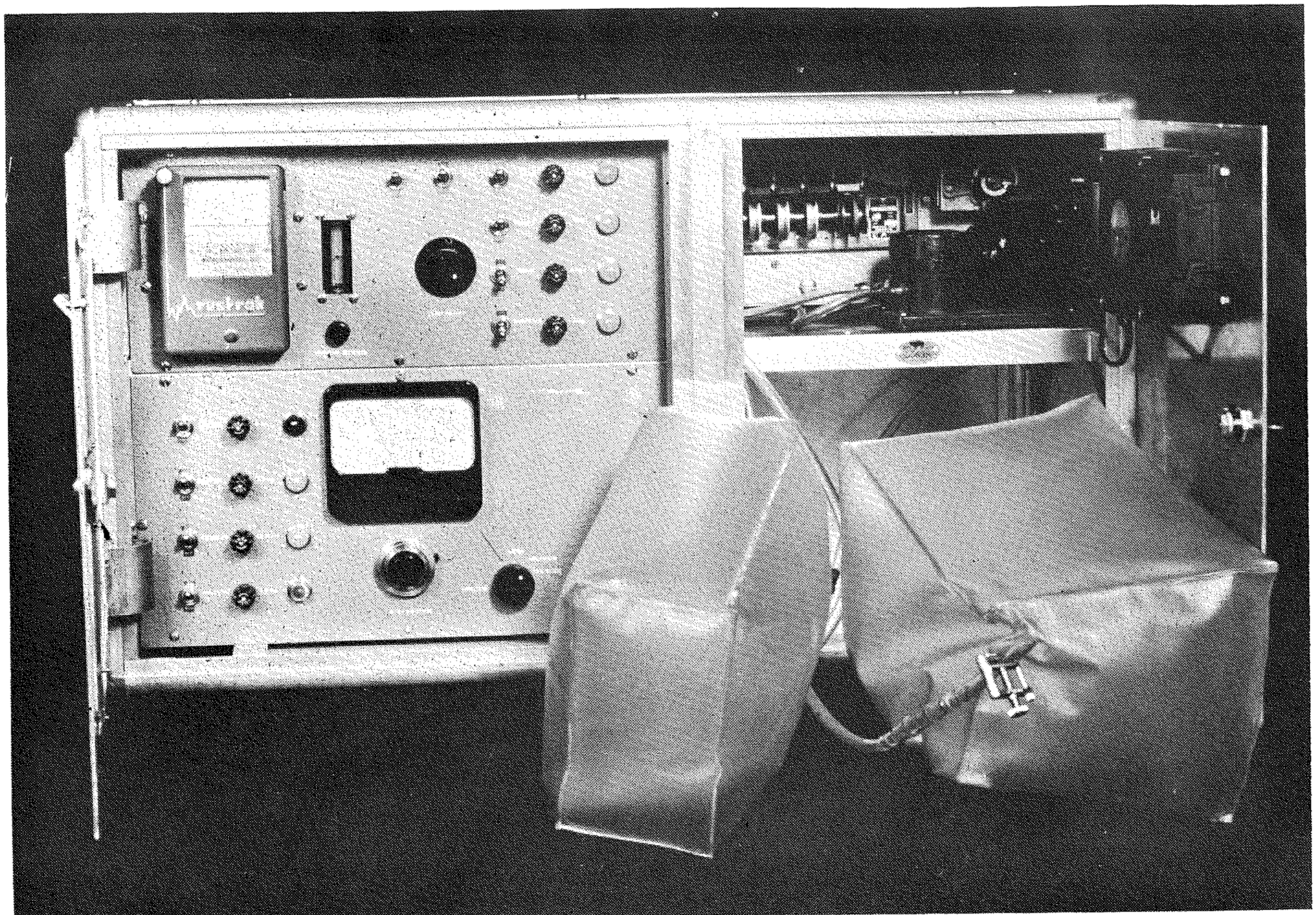
AUTOMATIC CARBON MONOXIDE INDICATOR



The automatic carbon monoxide indicator incorporates its own purging and calibration gas supply

The automatic carbon monoxide indicator lends itself to field applications where extended monitoring (of varying carbon monoxide concentrations) is desired.

This instrument is designed for continuous monitoring of carbon monoxide gas in air and will detect and record CO concentrations in the ranges of 0 to 100 parts per million and 0 to 200 parts per million at a full-scale sensitivity of plus or minus 0.5 percent. The read-out chart is shown in Figure 2. It incorporates a Beckman Model 15A infrared analyzer with a 13½ inch cell and its auxiliary components include a diaphragm pump, Rustrak recorder, a 24-hour timer, a 1-hour timer, a rechargeable air drying chamber and a rechargeable purge and calibration container. Under conditions of automatic operation, the purge and calibrate checks are built in to repeat and record on a 12-hour cycle. Under manual operation, purging and calibration can be done as needed. The instrument samples at a rate of 1/10 of a cfm, utilizes dry nitrogen as a purging gas, and 185 parts per million CO in dry nitrogen as a calibration gas. It weighs about 100 pounds. The air drying chamber which contains Drierite was included because we found that the instrument is sensitive to humidity, presenting a slight error in reading where humidity conditions in the atmosphere being sampled exceeded 50 percent RH.

We are currently using this new instrument for evaluating carbon monoxide exposures in industry, including exposures which might result from the use of unvented, gas-fired infrared heaters.

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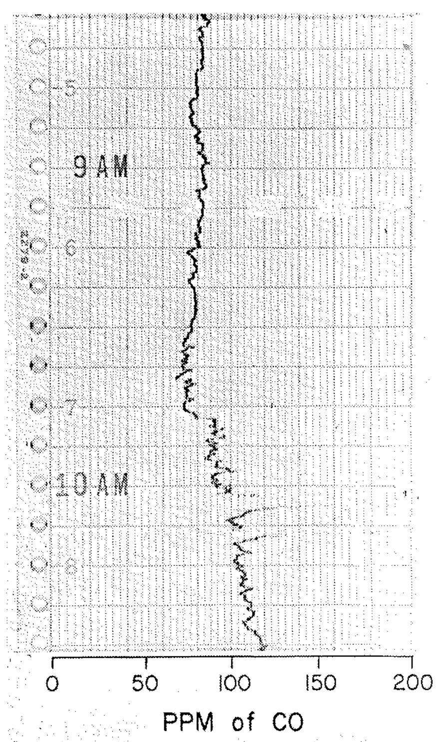
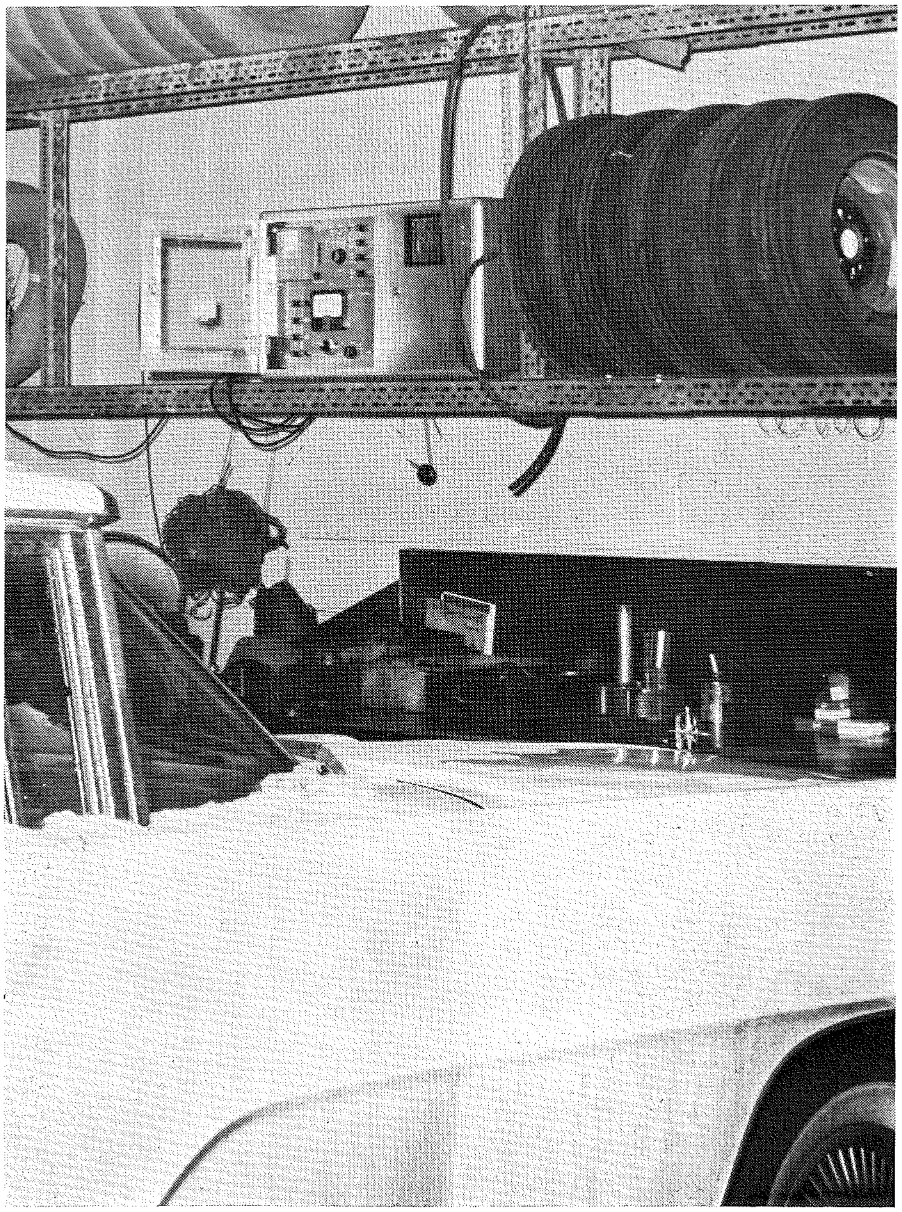


A portion of the read-out chart indicates carbon monoxide concentration from heating equipment

PROBLEMS—Concluded

workers. The use of coolants increased the moisture content at the machining point and accordingly *increased the amount of phosphine generated.* Matthew concluded that the hazard can be adequately controlled by efficient exhaust ventilation and efficient collection of the heavier dust particulates which drop into a suitable medium such as a container containing a 1 percent by volume solution of potassium permanganate. There was also occasion to verify subjective clinical systems of tightness in the chest, irritation of the eyes, loss of appetite and nausea. A review of the literature indicates that serious systematic effects are due to direct toxic action of phosphine on the cells of the central nervous and autonomic nervous systems with possible hemorrhagic effects in the brain and liver. To our knowledge, chronic phosphine poisoning has never been described.



We recently conducted studies in two tool and die plants where ductile iron was being machined to evaluate complaints of "acetylene-like" odors produced during the machining operations. It was determined in both plants as a result of sampling that phosphine was produced at the drilling, machining, and grinding operations when these operations were done dry and that the gas production was greatly increased when water base coolants were employed. Both plants studied used synthetic type lubricants—one with a ratio of 1 part coolant to 20 parts water and the other with a ratio of 1 part coolant to 40 parts water.

During dry machining, the phosphine concentrations determined ranged from 0.02 to 0.05 parts per million and increased to 0.6 to 0.75 parts per million when the milling and drilling operations *were lubricated with a coolant.* In another plant, the phosphine concentration averaged about 3 to 3.5 p.p.m. in close proximity to the tool and was found to be about twice the threshold limit value in the breathing zone. Our study findings tend to confirm those determined elsewhere and indicate that a real hazard may exist in plants where adequate ventilation is not provided. We also treated dust and turnings from these machining operations with distilled water in our laboratory and confirmed that phosphine is generated. This, of course, is significant in terms of dust inhalation with resulting deposition on moist respiratory tract surfaces.

POLYURETHANE AND MASS HYSTERIA

Polyurethane operations in Michigan are extensive. A hazard exists with all types of foaming whether conventional mold pouring, spraying, brushing or gluing scrap. The operations usually at fault, due to inadequate control, are pouring and curing, and sometimes the careless handling of scrap. The 0.01 PPM threshold limit value appears to be realistic. With reference to TDI exposures, we have seen sensitivities developed among laboratory workers, employees of subcontractors installing conveyors and ventilation equipment while a production operation is being started up, and an occasional worker. Complaints of headaches, ill feeling, and pulmonary difficulty are characteristic of some plants even with good control. Recently we experienced a *mass hysteria* situation in a plant where a new foam line had been installed but where the concentrations of TDI were *not* significant. There were some irritating cure-oven breakdown products in the atmosphere and nine men became ill. Following this, *even when windows were opened and ventilation control had been improved,* the workers, male and female, went into a hyperventilation state for two or three consecutive days necessitating the resuscitation squad and plant shutdown. We spent two 24-hour days in the plant and the company spent $40,000 on ventilation equipment and lost $100,000 in production before normal work activity resumed.

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RADIATION REGULATIONS UPDATED FOR EXPECTED LEGISLATIVE ACTION

Our 1958 Radiation Regulations have been up-dated and are now in the hands of a legislative review committee, having already been submitted to the Legislature. There are several changes which include the following:

1. **The old so-called limit of 300 mr/week has been changed to the general value of 100 millirems per week with a maximum of 5 rems per year.**

2. **The industrial radiographic installation section has been rewritten and there is an entirely new section on portable and mobile radiation sources.**

3. **There is a requirement that industrial radiographic installations utilizing isotopes be leak-tested.**

4. **Tables on shielding design have been deleted since this information is available from other sources.**

5. **There is a provision that no persons shall lease, lend or sell x-ray equipment unless such equipment will meet the requirements of the regulations.**

In line with the above, it might be interesting to note that we still sample on a continuous basis rain, air and foliage at the two reactor sites, we are continuing our milk shed sampling program as well as our municipal well water sampling program. In addition we are working actively at all of the industrial and medical radiation facilities.

REFERENCES:

(1) Wagner, Wm. D., White, Paul G., and Stokinger, Herbert E., "Inhalation Toxicology of Oil Mists—Part I, Chronic Effects of White Mineral Oil", American Industrial Hygiene Assn. Journal, Vol. 25, No. 1, 1964.

(2) Matthew, C. G., "Production of Phosphine While Machining Spheroidal Graphite Iron", Occupational Hygiene, Vol. 4, pp 19-35, 1961, Great Britain.

(3) Bootes, R. L., and Chasic, A. H., "Determining the Efficiency of Air Filters", Water Works and Waste Engineering, January, 1964.

(4) Baker, Robert A., and Doerr, Robert C., "Methods of Sampling and Storage of Air Containing Vapors and Gases", International Journal of Air Pollution, Vol. 2, pp. 142-158, 1959.

ERRATUM:

Please make the following correction in the last issue (Vol. 10, No. 1, Fall 1964) of Michigan's Occupational Health. Page 4, center column should read "Average level (3 Bands) $\frac{382}{3} = 94$", rather than "... = 92".

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Two Studies of Lead Exposure . . .

Torch-cutting of Leaded Steel Plate — The Casting of Lead-bearing Steel

The torch-cutting of ordinary steel plate has always presented a ventilation problem, as have the various operations involved in steel casting. But when lead enters into the picture, as it has with the increasing use of leaded steel, the problem is compounded even further. The easy-machining properties of the leaded steels are undeniable —so it's not likely that the use of leaded steel will decrease in the near future. We must recognize the health hazards it presents and remain aware of them so we can deal with such hazards realistically. The following two case studies provide some perspective on the problem.

So far as general background on this topic is concerned, the hazards inherent in the manufacture of leaded steels have been reported in the literature[1, 2, 3]. Procedures for ventilation control, and methods for medical supervision of workers with potential exposure to lead fume, have been established for the primary producers of leaded steel. A study involving atmospheric lead levels and the urinary lead levels of workers (in the manufacture of stainless steel with a 0.25 percent lead content) was reported from the state of Indiana[4]. A prior reference to the pouring of leaded steel castings in Michigan was published in an earlier issue[5]. The significance of lead exposure as a hazard to health, as well as recommendations for medical and ventilation control, have been amply presented in the literature.

An article reviewing many of the operations encountered in Michigan, including recommendations for control, appeared in a 1957 issue of this publication[6]. A 1959 issue[7] presented information on the various clinical tests and guidelines necessary for an effective medical control program. No attempt will be made to duplicate any of this information here. An Industrial Hygiene Guide on lead and its inorganic compounds is available[8].

But the purpose of this article is to report on two actual investigations of operations presenting lead-fume exposures. One involves the flame-cutting of leaded steel plate; the other involves the casting of lead-bearing steel. Each investigation will be discussed separately to retain clarity.

FLAME-CUTTING OF LEADED STEEL PLATE

The division was recently requested to evaluate the lead exposure involved in an experimental flame-cutting operation involving leaded plate. The plant visited was that of a company engaged in steel sales and warehousing. Seventeen employees in the plate department were directly or indirectly involved with the possibility of exposure to fumes created at the burning operations.

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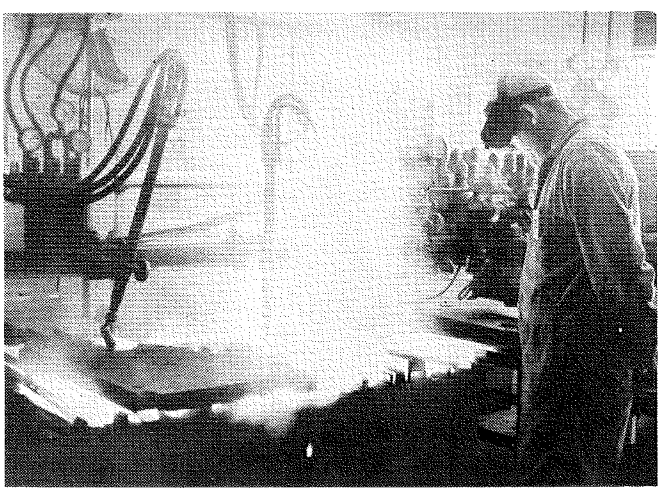

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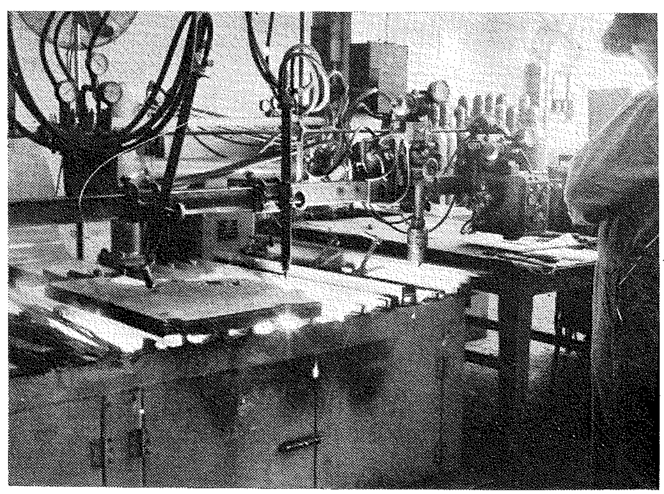

Figure 1.

(A) Leaded steel flame-cutting operation is shown with ventilation turned off, to simulate the pre-ventilation condition.

(B) The leaded steel flame-cutting operation is shown here with down-draft ventilation system in operation.