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TOXIC HAZARDS OF BERYLLIUM PROPELLANT OPERATIONS
CRITIQUE OF CURRENT SAFETY PRACTICES

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THE KETTERING LABORATORY

SEPTEMBER 1964
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TOXIC HAZARDS OF BERYLLIUM PROPELLANT OPERATIONS

CRITIQUE OF CURRENT SAFETY PRACTICES

J. CHOLAK
ROBERT A. KEHOE
L. J. SCHAFER
This is the first of a series of reports on the toxic aspects of beryllium. This study will continue over a period of several years. This critique has been made by the Kettering Laboratory of the Department of Preventive Medicine and Industrial Health, College of Medicine, University of Cincinnati, Cincinnati, Ohio, under Contract No. AF 33(657)-11036 for the Biomedical Laboratory, Aerospace Medical Research Laboratories, Aerospace Medical Division, Wright-Patterson Air Force Base, Ohio. This contract was initiated in support of Project No. 6302, "Toxic Hazards of Propellants and Materials," and Task No. 630205, "Toxic Hazards Evaluation." R. L. Patrick, Captain, USAF, MC was contract monitor for the Aerospace Medical Research Laboratories. This research was started on 1 April 1963 and was completed 30 June 1964.

J. Cholak, ChE, directed the work, R. A. Kehoe, MD, and L. J. Schafer, BSE (ChE) cooperated in the preparation of the report. Medical assistance was provided by George Roush, MD and S. L. Lerner, MD. Mrs. Irene Campbell and Miss Evelyn Widner provided bibliographic and other services.

Acknowledgement is made to R. C. Rhodes, Assistant Plant Manager and to E. P. Whaley, Manager of Technical Department, Hercules Powder Company, Magna, Utah for permission to use in Appendix II the analytical data obtained in the investigation of the material balance associated with the burning of beryllium enriched propellant.

This report is not releasable to the Office of Technical Services because it provides an insight into the effort and interest expended by the Air Force in the utilization of beryllium.

This technical report has been reviewed and is approved.

WAYNE H. McCANDLESS
Technical Director
Biomedical Laboratory
ABSTRACT

The soundness of the considerations which have been used to develop current safety practices in the handling of beryllium enriched propellants have been reviewed. The report includes a discussion of pertinent facts relating to berylliosis and the considerations which led to the promulgation of the tolerance limits. Particular emphasis is given to potential hazards arising from plant operations and test firings. Except for certain measures, industrial hygiene practices are described in general terms. The exceptions, dealing with locker and shower room facilities, protective clothing, laundering of clothing, the use of personal respiratory devices, and the disposal of solid and liquid wastes are discussed in some detail. Medical surveillance programs are outlined in full. The report concludes with a number of recommendations derived from current observations and past experience in the handling of beryllium enriched material.
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APPENDIX II - ANALYSIS OF RESIDUES FROM THE COMBUSTION OF THE PROPELLANTS
I. Introduction

Due to its lightness, great strength and stiffness, and its ability to absorb and conduct heat rapidly, beryllium and its compounds are being used successfully in various applications, or are being considered for use in some interesting future developments. Important potentially is its use as a component of propellants for rocket engines, in which it has been shown to produce a significant increase in performance.

The use and handling (preparation) of the metal and its compounds, however, have caused an appreciable number of dramatic illnesses, and, therefore, the injurious effects of contact with and absorption of these substances are matters of deep concern. Much information concerning the toxicity of beryllium has been collected, but the nature and extent of the hazard associated with its use under a wide variety of conditions are still controversial.

The purpose of this research initiated by the Air Force with the University of Cincinnati, on behalf of the Kettering Laboratory was to develop sufficient information pertinent to the fields of toxicology, occupational medicine, and industrial hygiene engineering, to safeguard the health of Air Force and industrial personnel who may work with beryllium-enriched propellants. The required information was to be derived at the facilities of the Air Force and its contractors, by observing the existing safety practices and by examining the soundness of the considerations and theories upon which they were based.

This report, therefore, is intended to give background information on some of the practices and policies currently being followed in the control of the hazards of exposure to beryllium in rocket propellants. Attention is also given to certain reports which may have been overlooked or ignored, and which suggest that our state of knowledge concerning the toxicity of beryllium is still incomplete.

Up to this time, data have been obtained in connection with the handling of beryllium only on research or pilot plant scales of production, and in the test-firing of small motors. It will be difficult to project information obtained from the observation of current practices involving relatively small quantities of beryllium, to those associated with the use of
large quantities, and, therefore, it is evident that further
data must be collected from time to time in conjunction with
the increasing scale of production, and the test-firing of
large motors. Therefore, this report must be regarded as the
prelude to a final report which can be prepared only after
much more information has been obtained in answer to some of
the questions arising from the special situations resulting
from the production and testing of the propellants.
II. **Beryllium Disease**

The history of the disease and its clinical manifestations have been so described that their repetition in this report would serve no useful purpose. Of general interest, however, is the fact that two distinct forms of the disease are recognized, one acute and the other chronic (refs 1, 2, 3).

A. **The Acute Disease**

The acute manifestations have resulted from massive exposure to dusts and fumes of a variety of compounds of beryllium. The soluble salts of beryllium have been the principal offenders, but beryllium in other forms has also produced the disease. It should not be overlooked that metal of "high purity", in the late 1940's, contained appreciable amounts of beryllium fluoride and other impurities, while the oxide contained some sulfate depending on the temperature of calcining. The role played by these impurities is not known, but it should not be dismissed summarily.

The majority of persons recover fully from the acute form of the disease, although fatalities have occurred in severe cases. The same individual may have several attacks while continuing at the same type of work. Chronic beryllium disease has developed in a number of persons who had the acute form of the disease previously. Only a few cases of the acute disease have occurred in recent years, their infrequency being the result, it is believed, of the application of improved procedures of industrial hygiene. It is possible, however, that some portion of this decrease in the incidence of the disease has resulted from the increase in the purity of the metal and the oxide, since men have continued to engage in operations which have afforded ample opportunities for exposure to high concentrations of beryllium in the air.

B. **The Chronic Disease**

The chronic form of the disease has been associated with exposure to air-borne compounds of beryllium in obviously high and, allegedly, very low concentrations. At times, the onset of symptoms has occurred many years after the cessation of exposure, some having occurred, allegedly, after an interval as long as 16 years. Other cases have developed, it appears, both after shorter periods of exposure and after shorter intervals of time following the initial exposure. The time and concentration relationships, therefore, in the occurrence of the disease, are somewhat uncertain. The disease has also occurred among persons who have resided in the neighborhood of plants in which beryllium or its compounds were produced and
from which they were emitted into the atmosphere (refs 4, 5). The evidence also indicates that some members of the households of workmen from such plants have been afflicted in consequence of their exposure to dust borne home on clothing. Most of the cases of chronic beryllium disease occurred before 1949, and while many of these were alleged to have been induced by relatively high levels of contamination of the air, others were considered to have resulted from remarkably little exposure. The fact is that practical and reliable procedures for sampling and analyzing air for its content of beryllium and for defining the characteristics of the dispersions, were not available prior to 1948. Therefore, the severity of the exposure of affected persons cannot be established, and it is impossible to relate the incidence and severity of the disease to the intensity or duration of the exposure.

Since a number of other diseases simulate the chronic form of beryllium disease, the differential diagnosis may be difficult. The Beryllium Case Registry at Massachusetts General Hospital in Boston lists 650 cases as of 1962, many with little corroborating environmental data (ref 6). Undoubtedly, the list includes many genuine cases of beryllium disease, but because experts have had to classify some of the cases as probably, or even possibly, due to the effect of beryllium, the attitude of uncertainty persists concerning the actual incidence of the disease. A review by a panel of radiologists and pathologists, of the material available for examination, coded or handled in such a manner as to remove prejudice toward berylliosis, would be valuable as one means of determining the validity of certain of the criteria which have been employed in the diagnosis of berylliosis, as recorded in the registry.

C. Toxicologic Aspects

In any consideration of the toxicologic and medical aspects of berylliosis it should be noted that the hazard from contact with the skin or direct ingestion is negligible (refs 1, 2, 3). All of the cases of systemic illness have resulted from the inhalation of dusts or fumes of compounds of beryllium, (some of which, no doubt, dependent upon the size of the particles, have been trapped in the upper respiratory tract and swallowed). Some transient dermatologic effects have also been noted, principally as a result of contact of the skin with the soluble salts of beryllium. Ulcers have resulted from somewhat prolonged contact with corrosive compounds of beryllium, or from contact of the skin with soluble salts of beryllium, or from the implantation of small amounts of such material in pre-existing wounds. Unless the offending material
is removed, completely, such lesions will persist.* On removal of the material, healing occurs rapidly and completely, with only a superficial scar remaining.

Another matter of importance with some bearing on the potential hazard is the variable toxicity shown by the different compounds of beryllium. The mineral, beryl, source for the extraction of beryllium, has never been implicated as a cause of berylliosis. Other minerals, phenokite and bertrandite, are also innocuous. These observations would appear to indicate that beryllium is toxic only in certain chemical and physical forms. The soluble salts are definitely toxic, but the toxicity of the insoluble compounds, particularly the oxide, has been shown to depend on the temperature of calcining in its preparation from the hydroxide or the sulfate. "Low-fired" oxide, prepared below 1100°C, has been found to be more toxic than the oxide prepared by calcining above 1100-1200°C. One of the reasons for the difference may be that calcining increases the size of the particles of the oxide and affects its crystallinity. The particles of "high-fired" oxide are reported as being generally more crystalline and much larger in size than those of the "low-fired" oxide (ref 7). Significant variation in the sizes of the crystals have been shown to occur when oxide was calcined at different temperatures, the average crystallite size in one test was shown to increase from 455 Å at 900 °C to 1100 Å at 1000°C, and was classed as "very large" at 1100°C (ref 7). Volatile soluble salts of beryllium may also be removed at the higher temperatures.

The preliminary findings in an investigation, at Dow Chemical Company, of low and high-fired oxides prepared from various starting materials, showed that, when the oxides were introduced intratracheally into the lungs of rats and rabbits, pathologic responses were produced only by oxide calcined below 1100°C (ref 8). These were the first successful efforts to produce lesions in the lungs of animals by the introduction of beryllium oxide. The dosages introduced into the lungs of the animals were tremendous in comparison with those to which men have been subjected in their work, varying from 25 milligrams to 100 milligrams per rat or rabbit. The lowest level at which injurious effects can be induced in the lungs has not, as yet, been determined.

Our knowledge of the toxicity of beryllium is still incomplete, and is obscure in certain areas which require special consideration and investigation. The differences in

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*The subcutaneous implantation of certain materials containing beryllium, both by accident in man, and by experiment in certain animals, has brought about the production of granulomatous lesions, which also have been extirpated by complete excision of the lesion and the implanted foreign material.
the toxicity of the low and high-fired oxide may be related to volatile impurities and the size and surface area of the respirable particles, or there may be other factors. The chemical characteristics of various other compounds also seem to be important, and, therefore, whenever feasible, environmental monitoring programs must include the identification of the species of particles in the air. The range in size of the particles should also be determined, or at least explored, so as to differentiate respirable from irrespirable particles, and to provide some clue as to the ultimate deposition and disposition of the particles within the respiratory tree.
III. Hygienic Standards

An Advisory Committee to the U. S. Atomic Energy Commission studied the problem of hygienic standards, and in 1949 made the following recommendations:

1. "The in-plant concentration of beryllium should not exceed 2 micrograms per cubic meter as an average concentration throughout an eight hour day."

2. "Even though the daily average might be within the limits of recommendation 1, no personnel should be exposed to a concentration greater than 25 micrograms per cubic meter for any period of time, however short."

3. "In the neighborhood of a plant handling beryllium compounds, the average monthly concentration should not exceed 0.01 microgram per cubic meter."

It should be noted that no differentiation has been made between the various compounds of beryllium or in relation to the sizes of the particles of beryllium dispersed in the air. These limits have not been changed, despite periodic reconsideration of available information, and have had such general acceptance in industrial operations that the American Conference of Governmental Hygienists has adopted the average concentration of 2 micrograms per cubic meter recommended by the Advisory Committee as its official threshold limit (ref 9). To date no case of either acute or chronic beryllium disease has been reported in connection with plant operations at which these standards have not been exceeded.

It is generally agreed that the limits currently used are stringent, and that they lack well defined scientific substantiation, in that they were promulgated at a time when toxicological knowledge concerning beryllium was scanty. The fact is, however, that these limits can generally be met by engineering means, and, since there are no generally acceptable alternatives, they are currently recommended for all processes in which beryllium or its compounds are used. Because of the tendency toward the application of such numbers strictly and literally, it seems desirable to review the derivation of these limits, so that those responsible for safety can have a better appreciation of the philosophy of their application.

A. Basis for Inplant Standards

The standard set by the American Conference of Governmental Hygienists makes no mention of Recommendation 2,
as formulated by the Advisory Committee noted above. It states only that the concentration should not exceed 2 micrograms per cubic meter when averaged over 8 hours. Although no reference is made to the limitation of the concentration to an absolute maximum, Recommendation 2 of the Advisory Committee is generally followed. The reasons for this and the other limits have been given by Eisenbud (ref 10) in the proceedings of The Workshop on Beryllium, held January 5 and 6, 1961 at the Kettering Laboratory of the University of Cincinnati and are as follows:

1. **Basis for Recommendation 2**

   It has been observed that acute pneumonitis, with fatal results, may originate from a single massive exposure to certain air-borne compounds of beryllium, usually the soluble salts. (Eisenbud also considered the low-fired beryllium oxide to be highly toxic.) Eisenbud also found 8 men who had been working with beryllium sulfate under stable conditions for a long period of time, but who had no history of respiratory illness of any kind. The conditions of exposure suggested to him that the maximum concentration to which they had been exposed did not exceed 15 micrograms of beryllium per cubic meter of air. For the purpose of preventing the acute disease, therefore, the decision was made to adopt the value of 25 micrograms as the maximum permissible concentration for even the shortest period of exposure. Eisenbud stated that the margin of safety was unknown, but in his opinion it was not excessively large as indicated by the following quotation: "I am of the opinion that brief exposure to 100 micrograms of beryllium, as beryllium fluoride, beryllium sulfate or beryllium chloride per cubic meter, is capable of inducing illness" (ref 10). (Note the reference to soluble salts and the omission of the oxide.)

2. **Basis for Recommendation 1**

   Since at that time there were no environmental data that could be correlated with clinical evidence of occupational berylliosis, and since the meaning of the available data was ambiguous, an assumption made on the basis of the available information, was the motivating factor, as is shown by the following quotation from the paper presented by Eisenbud at The Beryllium Workshop (ref 10).

   "Having no empirical basis for the establishment of a maximum allowable concentration, what did we do? Dr. Willard Machle and I (while riding in a taxi in 1949) decided that, as a first approximation, we would simply make the assumption that beryllium was as toxic as any other metal on a molar basis, atom for atom. This would mean that if it were a heavy metal, it would be toxic at a level of about 100 micrograms per cubic meter. Since the heavy metals have atomic weights of the order of say 220 or so, and beryllium has an atomic weight of 9, we divided 100 micrograms per cubic meter by 25. This gave us a
concentration of 4 micrograms per cubic meter. We argued a bit about whether it should be one or two or five and decided to use 2 micrograms per cubic meter."

Since 1949, data have been gathered which seem to indicate that, in so far as the inplant limits are concerned, the margin of safety is considerably greater than was considered to be the case by Eisenbud. A paper by William B. Harris, also in the Beryllium Workshop, entitled "Documentation of Analytical Findings Significantly in Excess of Permissible Limits" (ref 11) reported that it was difficult in the industrial establishments of A.E.C. contractors to maintain the two standards (25 micrograms and 2 micrograms) of tolerable exposure. Harris has written, "I feel reasonably sure that the cases of illness which occurred were caused by operations which gave rise to concentrations in the milligram rather than the microgram range. In certain operations, men actually had to go into the equipment and break it open, or possibly it broke open by itself. I am convinced that even soluble beryllium fluoride, which we believe to be the worst of the beryllium compounds, can be breathed for relatively short periods in concentrations well over 100 micrograms per cubic meter without causing illness."

Machle, in 1948, also reported that the above target values had been exceeded many fold without apparently producing the chronic disease (ref 12). Some investigations of environmental conditions in plants engaged in the processing of beryllium and certain of its alloys, support the observations and impressions of Machle and of Harris. Data derived in a number of industrial operations were presented by Cholak (ref 13) and Zielinski (ref 14) in the Workshop on Beryllium. In the investigation reported by Cholak and reproduced in part as Appendix I of this report, industrial conditions with reference to beryllium, were appraised through the analysis of 635 samples collected by automatic sequential samplers operated simultaneously and continuously for 4 days in each of several areas of an alloy plant (ref 13). This plant operated on an "around the clock" basis (3 shifts) in production on a large scale. The weighted average concentration in the individual areas ranged from 21.6 to 149.4 micrograms of beryllium per cubic meter of air. Over individual periods of 2 hours, the average concentration ranged from 0.2 to 1050 micrograms per cubic meter of air, while the concentration of beryllium in the air of the plant, as determined by averaging all of the results obtained, was found to be 60.3 micrograms per cubic meter, during the period of investigation. Of interest was the fact that much of the beryllium was present as fume, and since the plant had been in operation from 1953 through 1960, there is reason to believe that the quantities of beryllium found in the air in 1960 were lower than those which prevailed earlier, especially during the period in which the new plant was being "broken in". So far as is known, no case of berylliosis has occurred in this plant, now in operation for 11 years, during which there has been an acceptable program of medical supervision of the employees.
B. Basis for the Standard Adopted for the Limitation of Atmospheric Contamination with Beryllium in the Neighborhood of an Industrial Establishment

Recommendation 3 by the Advisory Committee relates to the limitation which causes the most concern to the handlers of motor fuels which are enriched by beryllium. The limit of 0.01 microgram per cubic meter of air averaged monthly was derived from the so-called "neighborhood cases", which were reported in the vicinity of production plants (refs 4, 5, 10). The basis for the limit consisted of epidemiological survey and an assumption concerning the maximum emission of beryllium compounds from the stacks of one plant (ref 4). According to Eisenbud the limit has a factor of safety of 10 based on his finding that people at the periphery had been exposed in the past to concentrations as high as 0.1 microgram per cubic meter (ref 10). He also believed that the concentration could not have been 100 times higher (1.0 microgram per cubic meter), since his calculations showed that, had this been the case, twice as much beryllium would have been discharged than was entering the process (ref 10).

As in the case of industrial berylliosis, there are no quantitative environmental data which relate the occurrence of "neighborhood cases" to the intensity of the exposure which appears to have induced them. In an investigation of the neighborhood cases in Pennsylvania, as reported by Lieben and Metzner (ref 5), analyses of the atmosphere, carried out in 1958 at 10 stations, yielded beryllium in concentrations as high as 0.30 microgram per cubic meter in a few 48 hour samples obtained near the plant (ref 15). In the same investigation it was also reported that the levels of mean concentration, over periods of 48 hours, were of the order of 0.028 microgram per cubic meter at stations located within 0.5 mile from the plant, 0.0107 microgram per cubic meter at stations 0.6 to 1 mile distant, and 0.0014 microgram per cubic meter at a station situated more than 2 miles from the plant (ref 16). Of the 21 alleged neighborhood cases in Pennsylvania, Lieben and Metzner reported that 12 had lived 4 miles or more from the plant (ref 5). As pointed out by these investigators, the monitoring program was conducted some time later than the period during which the cases were induced (ref 5). In the opinion of some persons of experience, it is unreasonable to believe that the beryllium to which neighborhood cases were exposed consisted of that dispersed in the air at their place of residence. An example is given by Dattoli et al of a secretary who paid a weekly visit for several years, to the grave of a relative, located in a cemetery across the street from a beryllium refinery (ref 17). Other neighborhood cases can be explained, in all likelihood, on the basis of the handling or laundering of the dusty clothing of workmen, or of other indeterminate frequent, intermittent types of exposure to significant concentrations of particulate compounds of beryllium, most likely the oxide.
It is obvious, therefore, that opinion and assumption, weighted, as they have been, by professional judgment, and the necessity for caution, have been the principal means of establishing the threshold limits in current use, rather than precise knowledge of specific environmental conditions and their effects. From an examination of all of the available environmental data, the margins of safety appear to be greater than they need be. Stokinger reports that many industrial hygienists believe that a single level of 5 micrograms of beryllium per cubic meter of air should serve for all purposes (ref 18). While he does not believe that the limiting value in the air breathed by healthy, adult workmen in industry should be applied to community air, he suggests that consideration should be given to revising the community air limit to 10 or 15 times its present value (ref 18). The application of definite standards of air quality to the problems of industrial hygiene, (in this instance to those concerned with beryllium), therefore, requires some understanding of their toxicologic and clinical background, and demands the exercise of sound judgment in their application to the special situations which may result from the use of rocket fuels enriched by beryllium.
IV. Industrial Hygiene Practice Related to Beryllium Propellant Used

A. General Considerations

In work with propellants enriched by beryllium, consideration must be given to potential hazards that fall into three categories, namely those due to processing the propellant, those involved in static testing of the fuels and engines, and those which may arise from accidents or emergencies. Considerable experience has been gained in the general processing of beryllium and its compounds, so that standardized practices of industrial hygiene are generally applicable to all operations (ref 2). The application of certain principles and procedures to other types of hazards must be based on the magnitude of the hazard, the permissible degree of risk, if any, and the exercise of judgment in the interpretation of results of analyses of beryllium in the air, on the background of the threshold limit values in current use.

The prevention of occupational illness is accomplished through the application of well established medical and technical principles and procedures of industrial hygiene. These include adequate sampling and analysis of the air, precise engineering of processes, the use of properly engineered equipment for the collection of dust and fume, good housekeeping, and instruction and supervision of exposed personnel in personal hygiene and in specific measures of personal safety, satisfactory disposal of contaminated wastes, and adequate medical surveillance.

There is no need to detail exact procedures which are readily available in a number of Air Force reports (refs 2, 22) and in the general literature (ref 1), but rather to discuss these matters in general terms. It has been evident, on site visits, that some procedures were being applied blindly to situations which were not at all comparable to those encountered in plants engaged in the extraction of beryllium, for which such procedures were designed. These situations will be reviewed in greater detail in Section B.

Generalizations useful in selecting and devising measures of control may be listed as follows:

1. Operations that produce large quantities of dust should be isolated. Such operations should be enclosed as completely as possible, and should be provided with local exhaust ventilation.
2. New equipment should be so designed as to limit or prevent the contamination of the atmosphere with materials being processed.

3. Manual operations should be reduced to a minimum. Every effort should be made to use automatic equipment for conveying and transferring materials and for charging kilns, furnaces, hoppers and like receptacles. Such equipment should be provided with exhaust ventilation.

4. Changes in processes may reduce or eliminate, or they may increase or create health hazards. Therefore, each step and each anticipated change in a process should be reviewed to determine whether rearrangement or substitution will make the process less hazardous.

5. The employment of local exhaust ventilation is the most effective method for the control of air contaminants within work areas, and this often involves the use of hoods of various types. There is no universally applicable hood. The type used for each operation will depend on the operational and maintenance requirements, and the accepted practice for good control of dust. Each operation and machine will require individual consideration before a suitable hood and dust-collecting system can be designed.

B. Processing of Propellants Enriched by Beryllium

The chief hazard arises from the use of powdered beryllium metal, which may contain particles of such size as to be respirable, although the optimum size for use in the formulation of propellants is considered to be irrespirable. Contamination of the air from this source is easily controlled by providing exhaust ventilation at points where dusts may be emitted (ref 2). Metal may be weighed out at stations provided with exhaust ventilation, either over a grill with downdraft suction or in a partial enclosure similar to a chemical laboratory hood. The movement of air at the opening of the hood or at the face of the grill should be maintained at 150-200 fpm to capture dusts which may become suspended in the air. Dry boxes (with or without exhaust ventilation) may also be used if available, but, as a rule, such complete enclosures are not essential to control the environment. Powdered metal may also be shipped for use in pre-weighed bags of a plastic material that will dissolve in the plasticizers or other materials used to formulate the propellant. Powdered beryllium may also be stored in automatic weighing hoppers or in other closed hoppers. Once the powder has been incorporated into the other ingredients, it will be fixed, and the product can be handled manually in the usual manner. Such machining or filing as may be necessary should be carried out under exhaust ventilation.
1. Special Measures

(a) Gloves: Unless gloves are required for other reasons there is no need to use them to handle the powder or finished product. Gloves should be worn when soluble salts of beryllium are to be handled (see section on chronic diseases). These must be kept scrupulously clean on the inside: if they are not to increase, rather than to reduce, the hazard.

(b) Clothing: A daily change of clothing may be mandatory for workmen in certain operations. In general, daily change of clothing is not required of the general operator when the environment is satisfactorily controlled. Maintenance personnel, and those who are called upon to clean up contaminated areas and equipment, however, should be required to change work clothes daily. In most operations, a coverall over street clothes, or a laboratory coat, will prove satisfactory.

If the work environment is contaminated significantly with beryllium-containing dust, it is best to launder clothing of workmen on the premises. Should commercial laundries be utilized, they should be informed concerning the nature of the contaminant in order that suitable precautions may be taken. It is highly desirable to wet soiled clothing as soon as it is removed, in order to minimize the amount of dust that may be dispersed into the atmosphere.

Safety shoes or other work shoes may be required at some operations. Ideally, such shoes should be left at the plant, but, under appropriate circumstances, they may be taken out of the plant after being wiped clean with a damp cloth to remove accumulated dust.

(c) Showers and Lockers: Bathing is recommended at the end of each work period. Ideally, separate lockers for street and work clothing should be made available, and the lockers should not be interchangeable. The locker and shower rooms employed in connection with certain operations may be so arranged, that the workmen must enter and leave the area through them. When the hazards are controlled adequately otherwise, there is no need for special or separate locker or shower rooms, provided the facilities used by other workmen in the plant are satisfactory and are so located as to be reasonably convenient for workmen in the beryllium operations.

(d) Respiratory Protection: Individual respiratory protective devices should not be used in routine operations in lieu of engineering control of the environment. When control of the general environment is impractical for application to certain infrequent operations of production and maintenance, respirators should be used. The degree of contamination of
the atmosphere, under such conditions, will generally be unknown, and satisfactory respiratory protective devices, (filter type, supplied air, or self-contained units) should be worn by all persons in the affected areas. Such operations should be supervised continuously by a responsible person who is thoroughly familiar with the necessary precautions and the equipment employed. Respirators approved by U. S. Bureau of Mines for fume will provide adequate protection during short periods of work in areas in which the air is contaminated with beryllium in concentrations below 100 micrograms per cubic meter. During prolonged periods of work in an atmospheric environment in which beryllium compounds are dispersed in concentrations above 100 micrograms per cubic meter, air-supplied respirators of appropriate design should be utilized. Since workmen generally cannot be relied upon to maintain this equipment in a safe, clean, and efficient state, the task of inspecting, cleaning and servicing the equipment should be delegated to a specific, responsible individual or group.

Respirators (approved filter type) should be worn at all open test firing sites, particularly immediately after a firing, while work must be done on the motor or the launch pad.

(e) Disposal of Wastes and Decontamination of Equipment

(i) Liquid Waste: The exact treatment of liquid waste will depend upon its volume and type, as well as the nature and location of the area of drainage. Wash waters from laundering or general cleaning operations containing low concentrations of beryllium may be discharged directly into community sewers. Large quantities of waste materials, heavily contaminated with beryllium oxide or metal particles, such as that derived from gas scrubbing equipment, should pass to sedimentation tanks before being re-used in the scrubber or before being discharged to streams. Such waters may also be filtered, but such drastic treatment is usually unnecessary. If soluble salts are present, chemical treatment may be employed to precipitate out the beryllium. The sludge may be filtered off, or allowed to settle out in sedimentation tanks or open lagoons. The supernatant water may then be discharged to sewers or streams, or re-used as cooling water or for the scrubbing of gases. Liquid wastes should not be discharged into community sewers, streams, lakes or seas without the knowledge and approval of local authorities. Sludges removed from holding tanks or lagoons may be collected and drummed for disposal by burial on land or by barging to sea.

So far as is known, the U. S. Public Health Service has not set a threshold limit for beryllium in potable or recreational waters (ref 19). Some experimental observations on the soluble salts of beryllium have demonstrated toxic e
effects upon certain species of fresh water fish at levels of concentration near 0.10 part per million. The soluble salts were found to be more toxic in soft, than in hard waters (ref 20).

(ii) Solid Wastes: Heavily contaminated scrap paper, waste rags and similar material should be stored in covered containers for later, supervised disposal. Lightly contaminated material in small quantities may be handled in accordance with ordinary, but satisfactory, plant procedures. Large quantities of heavily contaminated material may be buried at isolated locations or burned in suitably designed or supervised incinerators, so as to prevent pollution of the air. Disposal of such wastes will require the exercise of judgment based on quantitative considerations. Obviously, large quantities of heavily contaminated waste will require more consideration than a few rags or small quantities of paper associated with cleaning operations conducted on a small scale.

C. Accidental Explosions or Fires

A matter of concern is the effect of an accident or "burn" of a large quantity of material, on (a) the plant personnel and (b) those in the neighborhood adjacent to the plant. In-plant accidents require some "disaster control procedure" for protecting the employees and preventing other damage. The handling of incidents involving beryllium-containing fuel may require some such advance planning as that designed to handle other accidents in industry. Personnel should be cleared from the affected area. Those engaged in fighting the fire or in the subsequent decontamination of the area and equipment, should employ suitable clothing and appropriate respiratory protective equipment.

Inhabited areas adjacent to the plant may be affected, depending on the quantity of material burning, the path of the plumes of smoke and combustion products, and the meteorological conditions. If practical, such areas can be evacuated until the emergency is over. From the aspect of the exposure of persons to potentially hazardous conditions, the factor of the frequency of occurrence of accidents is of more importance than the relatively brief periods involved in any one accident. The safety regulations which apply in hazardous industries such as the manufacture of explosives, greatly reduce the risk of an accident, and the industry's record indicates that while accidents may be dramatic (resulting sometimes in fatalities) they occur so infrequently that persons in the neighborhood are subjected to no greater risk (so far as health is concerned) than that involved in the accidental release of a highly toxic gas such as chlorine, nitrogen dioxide or hydrogen sulfide (Poza Rica, 1951). The immediate effect would, in all probability, be much less severe than that associated with exposure
to the three gases noted.

The hazard to health would be reduced further by the fact that much of the beryllium would not burn, or if burned, would yield particles of non-respirable size. Some data, concerning the nature of the compounds and the sizes of particles produced in the burning of a solid beryllium propellant, are presented in Appendix II. The experience derived from the destructive fire of a beryllium refinery in Lorain, Ohio on September 21, 1948 is also of interest in considering the hazard. The fire, because of the contribution made by a large quantity of magnesium metal, blazed furiously for about 4 to 5 hours, while another 24 hours elapsed before it was finally extinguished. Zielinski considers that this incident, from the toxicological view point, was responsible for the largest, single massive exposure that had ever occurred, involving a population estimated at 4000 persons (ref 21). No cases of the acute disease developed, and now, after 14 years, no case of the chronic disease has appeared. The concentration of beryllium in the air, at 2 stations in the direct path of the plume on September 22, 1948, were shown to have averaged 0.0015 and 0.0033 microgram per cubic meter, as compared to 0.014 and 0.0016 microgram per cubic meter at the same 2 stations on September 20, and 0.0017 microgram per cubic meter at the first station on September 24, 1948, 2 days following the fire (ref 21). Zielinski reported that the beryllium formed particles of beryllium oxide of denser and larger crystallites, which he thought reduced the toxicity of the oxide. It has also been reported that at monitoring stations in the area, at which samples had been collected for 24 to 72 hours, continuously, from 1947 through 1955, only a few of the 1400 samples collected at 5 stations situated at distances ranging from 500 to 6000 feet from the plant exceeded 0.01 microgram per cubic meter. However, one result of 2.15 microgram per cubic meter was obtained by the analysis of one 24 hour sample collected on May 5, 1948 (ref 21).

It is also important to note the experience of one producer of solid propellant, in so far as accidents are concerned. This plant has been producing solid propellants in ton quantities since 1945. It has been reported that, in handling solid rocket propellants, only 3 mishaps have occurred in the 19 years of operation of the plant.

Most of the accidents that have occurred have resulted from the increased sensitivity caused by the metallic contamination of the material being mixed. The industry has investigated the sources and the chances of contamination, and the risks of explosion are being reduced by changes in equipment, such as seals and glands, and by controlling the purity of the materials used to formulate the propellants. The inclusion of beryllium, of itself, has been reported as having no effect on increasing the sensitivity of the propellant to shock.
These factors, along with the fact that any such exposure of persons in the neighboring population will be discontinuous, offers assurance that the danger to the health of such persons is slight. From the aspect of production, such slight risk should not put a limit on the size of the grain or that of the motors to be produced at any location where experience and the record are favorable with respect to accidents.

D. Test Firing

This operation has caused the greatest concern for the health of people, especially those who live near or within a few miles of such sites. This concern derives from the possibility of exposure to excessive concentrations of beryllium in the air, which might come from a malfunctioning motor or an accidental explosion, or from the puff emissions from a motor while undergoing a regular static firing test. The first type of incident has already been covered in the preceding section. The emission from a normal firing test has generated considerable concern, so much so that tests are closely supervised and are generally carried out in closed systems employing suitable gas cleaning equipment, or in sparsely settled areas under such meteorological conditions that the combustion products travel away from inhabited dwellings or towns (ref 22). To date, relatively small motors only, have been tested in closed systems or fired in the open. Although it is possible to construct closed systems to test larger motors it may be more practical and economical to ship large motors to a central, remote and sparsely settled facility, where testing can be done without fear of the potential hazard.

In considering the hazard, the assumption is generally made that all of the beryllium involved is completely oxidized to beryllium oxide, and that all of the particles are respirable. On this assumption, the next step is to determine the theoretical diffusion patterns for motors of various sizes and to calculate the center line concentrations at fixed distances in the plume of exhaust gases. This is done by the application of Sutton's formula (ref 23), which requires the selection of such widely varying values for four parameters, that it is difficult to develop predictions with a consistent degree of accuracy. There are other difficulties, so that the predictions may not be directly applicable to the source of the emission generated by a rocket engine (ref 22). The predicted, intermittently occurring, center line concentrations are generally compared to the A.E.C. limit of 0.01 microgram per cubic meter, and averaged over a period of 3 months to determine the degree of hazard. Moreover the maximum concentration of 750 ug-min./M³ (25 ug/M³ for 30 minutes) is being used by some investigators for siting test facilities (ref 22). This limit has been set because the firing of rocket engines produces peak concentrations of brief duration, in contrast to the more persistent conditions in industry. It is admitted that these limits, out of caution, are set at overly low levels, but the claim is -
made that they are justified because of the long latent period in the development of chronic beryllium disease, that the standards can be met by the employment of suitable engineering measures, and that the revision of the standards must be preceded by adequate investigation of men who have worked for prolonged periods of time under known environmental conditions which exceed current standards.

With respect to the latter statement, attention is called to the discussion in the sections describing the derivation of the threshold limits, and to several papers in the Beryllium Workshop in which no difficulties were said to have developed when work was carried out for appreciable periods of time under conditions which deviated considerably from the A.E.C. limit (refs 11, 13, 14). In addition, in Appendix I a detailed report of a survey in a metallurgical plant not under surveillance by the A.E.C. is reproduced. It may be noted that samples were collected continuously and automatically and, therefore, they covered all of the fluctuations that occurred. Furthermore, the average value of samples collected for 2 hours was 1050 micrograms of beryllium per cubic meter of air in an area in which 97 per cent of the dispersed particles were smaller than 5 microns in diameter. This value is singled out because it represents a finding which, when calculated as microgram-minutes/M³, amounted to 126,000 (1050 x 120). It is highly significant that this maximum value was measured in 1960 seven to eight years after the plant began its operations, when conditions were much improved, in all likelihood, over those which prevailed when the operations were in their earlier stages. Still more significant is the fact that, up to the present, 11 years after the initiation of these operations, no cases of chronic disease have been found among the workmen in this plant.

Another consideration in anticipating the levels of concentration of air-borne materials that result from the spread of a plume, arises from the fact that the concentration at the center of the plume may shift widely in position while the latter is passing over a habited house or area. In the case of repeated test firings, even under the same conditions, with respect to the direction of the wind, it is possible that the center line of the puff will not repeat itself in relation to any area affected by a prior puff.

In considering the limit being proposed it is pertinent to point out that the current A.E.C. recommendation, with respect to outside air, as adopted in 1957 (ref 3), has been liberalized on the basis of extensive experience to permit the following conditions.

(1) An average monthly concentration in excess of 0.01 microgram per cubic meter, but not exceeding 0.05 microgram per cubic meter, calls for corrective procedures. Such neighborhood
concentrations will not be permitted to exist for more than
60 days without specific A.E.C. approval.

(2) An average monthly concentration in excess of
0.05 microgram per cubic meter calls for cessation of operations
until corrective measures are taken to reduce the level to at
least 0.01 microgram per cubic meter.

It would seem practical and sensible not to call
attention to a permissible peak concentration expressed as 750
micrograms-minutes per cubic meter as a limiting factor in
permitting test firing, since this number has no more scientific
basis than do the threshold limits being applied in industry
and as air quality standards. Since the exhaust plume from the
rocket firing is not likely to remain static but will move rapidly,
when the conditions are favorable for test firing, the exposure
to peak concentrations is likely to be relatively short in
duration. Therefore, the average concentration over a 24 hour
day would appear to be a better expression of the hazard than
is the peak concentration. The peak concentration of 25
micrograms per cubic meter was set to eliminate the possibility
of acute illness, induced by exposure to the soluble salts
of beryllium. There is no evidence to indicate that beryllium
oxide, free from soluble salts, can produce the acute form of
the disease. An average concentration not exceeding 0.05 micro-
gram per cubic meter over a period of 30 days would be more
conservative than the 60 day limitation recommended by the
Atomic Energy Commission, or the 0.10 or 0.15 microgram per
cubic meter mentioned for consideration by Stokinger (ref 18).
The current limit of 0.01 microgram per cubic meter of air has
been exceeded near Salt Lake City, Utah on days when test firing
was not underway and when the wind was from the southwest.
It is probable that this degree of contamination of the atmos-
phere is the expression of the entrainment of particles of
beryllium-containing ore by the atmospheric streams which pass
over superficial deposits in the Topaz Mountains of Utah.
V. Medical Control

In order to plan and implement an effective medical program, the physician must be familiar with the potential hazards to health that may be associated with the use of beryllium and its compounds. He must familiarize himself with the physical and chemical properties of the materials, and the manner of their production and use. He must collaborate closely with the technical personnel in industrial hygiene in the development of plans and procedures for performing routine operations safely and for formulating plans for use in emergencies. He must receive and review all reports which are concerned with industrial hygiene.

The precise details of a medical program will depend upon circumstances. The procedures designed for individuals and groups may require re-examination and modification, subsequent to changes in operation. Medical examinations of employed personnel should be carried out prior to the placement of the individual, periodically during his employment, and at the termination of his work with beryllium. Because of the long latent period in the development of chronic beryllium disease, medical examinations cannot be relied upon to establish the adequacy of current measures of environmental control in meeting the accepted standards; this can be achieved only by regular inspection and monitoring of the air.

In visits to contractors and Air Force facilities it was found that the program of medical control generally followed the procedures described in a report made under Air Force contract AF 33(600)37211, which is repeated below for convenience (ref 2). One of the objectives of the current investigation was to review all cases of alleged illness due to exposure to beryllium in the production and use of propellants. No such cases have come to this contractor's attention. All alleged cases, whether industrial or non-industrial, will need to be reviewed (medically and environmentally) to establish the basis for the allegation. Although medical programs have been described in a number of reports, specific details are described again for the sake of completeness, and for the convenience of physicians not acquainted with the earlier reports.

A. MEDICAL EXAMINATIONS

1. Schedule of Examinations

   a. Preplacement Examinations: All employees whose intended work involves exposure to beryllium should be examined before being subjected to such exposure. The health and safety
programs should be outlined in detail to all new employees by
the physician, who should make certain that each person under-
stands the necessity for observing the precautions and safety
regulations that are in effect within the plant.

b. Periodic Examinations: The frequency with which
examinations are carried out after the individual has been
placed in employment, should be determined by the plant physician
in accordance with the type, frequency, and severity of the
potential occupational hazard. Medical examinations carried
out annually are believed to be adequate for persons engaged in
routine machining and fabricating operations that are well
controlled from the aspect of industrial hygiene.

c. Terminal Examinations: Every employee should be
given a medical examination at the termination of his employment.

d. Miscellaneous: Employees should be instructed
and encouraged to report to the medical department whenever they
experience any unusual, prolonged, or unexplained respiratory
symptoms.

2. Scope of Examinations

a. Preplacement Examinations:

(1) History: A detailed medical and occupational
history should be obtained by the physician. Previous episodes
of significant respiratory illness should be recorded in detail.

(2) Physical Examination: A thorough general
physical examination should be made, including a careful in-
spection of the skin of the entire body.

(3) Laboratory Procedures: The laboratory procedures
should include: a complete blood count (hemoglobin, hematocrit,
red and white cell counts, and differential white cell count);
sedimentation rate; an ordinary clinical examination of the
urine; chest x-ray examinations made in full inspiration and
expiration, on 14 x 17 inch (all chest x-ray films, should be
kept as a part of the permanent medical record); and any other
procedure that may be indicated. Timed-vital capacity deter-
minations, obtained carefully with the employment of suitable
equipment, are desirable, since they comprise valuable basic
data and are useful to the physician in the appraisal of the
pulmonary status of the employee.

b. Periodic Examinations:

(1) History: A complete review of systems should be
made in the course of the yearly examination. An interval
history, with emphasis on the skin and the respiratory system,
should be obtained and recorded whenever more frequent periodic
examinations are indicated.

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(2) **Physical Examinations**: A thorough general physical examination should be given yearly to all persons whose work has subjected them to exposure to beryllium. More frequent examinations may be desirable in certain cases.

(3) **Laboratory Observations**: The tests recommended at the time of the periodic and terminal examinations should be the same as those of the preplacement examination, unless others are indicated. The examining physician must determine what tests, if any, are required for the more frequent examinations, e.g., vital capacity determinations, etc.

Analyses of specimens of urine for their content of beryllium are not necessary and, in the present state of our knowledge, are of no value in medical control programs.

**B. MEDICAL STANDARDS FOR EMPLOYMENT**

Persons being considered for work with beryllium should have good general health and must possess the physical and mental capabilities for fulfilling the requirements of the job. From the mental standpoint, they should be stable emotionally, mature, and intelligent. In view of the inadequate nature of the information concerning the pathogenesis and disease-producing potentials of beryllium and its compounds, the conditions outlined below may be considered as causes for disqualification. The physician, however, must weigh the significance of these conditions in relation to the exposure and the nature of the anticipated work.

1. **History**
   a. A history of asthma, hayfever, eczema, or other allergic manifestations of significant degree.
   b. A history of frequent or chronic respiratory infections, or conditions such as chronic cough, bronchitis, or tuberculosis.

2. **Physical Examination**
   a. Chronic pulmonary disease including emphysema.
   b. Heart disease.
   c. Kidney disease.
   d. The inability, for any reason, to wear mechanical respiratory devices.

3. **Other Examinations**
   a. Roentgenologic evidence of chronic pulmonary or cardiac disease.
b. Hematologic abnormalities.

c. Abnormalities of the urine, that reflect kidney disease.

d. Emotional instability, hypochondriasis.
VI. Recommendations

Since it is obvious that the requirements for the safe production and use of propellants which contain beryllium are unique in some respects, and that information is lacking to set up standards for certain situations, the following recommendations are made:

1. The Air Force should provide a consultant service to provide information to its contractors and to its own facilities as to the safe handling and use of propellants which contain beryllium. The collection and circulation of information should be the responsibility solely of a central agency, and contractors should be advised, prior to the preparation of bids or plans for production facilities, to consult this agency. It has been observed, when the personnel who represent contractors undertake to review the information available on the toxicity of beryllium, that, because of lack of knowledge of the problem or lack of training and experience in industrial hygiene, they often are unable to separate facts from fancies. Frequently this results in accepting the most alarming statements as facts, and in formulating excessively cautious programs that often are very expensive and, sometimes, entirely unnecessary. This criticism applies not only to practices that may be developed for the safe handling of beryllium, but to other precautionary practices for which responsibility has been assigned to project engineers.

2. Monitoring of the air in production and test areas, and in inhabited areas adjacent to plants, should be maintained as regular operating procedure. More information on the concentration of beryllium in the air is needed, as the use of beryllium is scaled upward toward the final operational magnitude. It is as important to obtain well documented negative data as it is to secure positive data, to serve as future guide lines in developing programs of industrial hygiene. This phase of the projected work should be tied in with the epidemiological investigation of the population at risk in industries in which the contamination of the atmosphere with beryllium has exceeded the target concentrations promulgated by the Atomic Energy Commission. A review, by a panel of experts, of the medical, radiologic and histologic evidence available from cases of berylliosis listed in the Beryllium Case Registry should be a part of the epidemiological investigation, in order to establish the validity of the information in the Registry.

3. In areas where test firing is done, the air should be monitored in conjunction with meteorological observations and continuing observations of the diffusion of exhausts from larger
motors, test fired at suitable remote sites, in order to plan properly for the selection of sites to be used in the static testing of the larger rocket motors in the open air.

4. Certain limited toxicological investigations should be initiated. There is no need to repeat the unsuccessful investigations of the past involving the respiratory exposure of animals to beryllium oxide. However, the available information should be reviewed and appraised critically. Since, according to one investigator, the introduction of massive doses of low-fired oxide into the trachea of rabbits and rats has apparently produced pulmonary granulomas, it would appear desirable to repeat the investigation, with graduated lower doses, in order to determine the least dose which, when introduced intra-tracheally, will produce these or any other definite lesions.

5. Further to the investigation suggested in item 4, it is necessary to explore the physical and chemical nature of the particles, as well as the impurities in low-fired beryllium oxide which is capable of producing granulomas. The presence of water-soluble or ionizable material, such as the hydroxide, sulfate, chloride and fluoride, should be determined in the low-fired and high-fired oxide (and in metal) as a possible explanation of differences in the behaviour of these materials.

6. The chemical and physical nature of combustion products of the open burning of various types of beryllium-bearing rocket propellants should be investigated. A start along this line has been made, but there is a need for a more intensive investigation with better analytical methods than are being used presently.

7. The hazard posed by the accidental explosion or burning of propellants at manufacturing operations or test launch sites should be considered as no greater than that which may result from other dramatic industrial accidents.

8. Consideration should be given to the liberalized regulations suggested by the Atomic Energy Commission for providing a safe outside atmosphere. It is suggested that an average concentration not exceeding 0.05 microgram per cubic meter, averaged over a period of 30 days during each quarter (90 days), be adopted as permissible.

9. The peak concentration, expressed as 750 ug-min/M³ (25 micrograms for 30 minutes) should be dropped from consideration, as being too restrictive, and having no basis in fact. If a time-concentration value is to be adopted it should be selected on the basis of a sounder criterion than that which was applied in establishing the limit for controlling exposure to soluble salts of beryllium in the prevention of the acute form of the disease.
REFERENCES


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Appendix I

Environmental Conditions During the Period
May 2-6, and December 13, 1960 in an Alloy Plant

Introduction

"Master Alloy" consisting of 4 per cent of beryllium and 96 per cent of copper, was produced by heating and melting beryllium oxide, copper scrap, dross, and carbon in an arc furnace. The product or "Master Alloy" may be sold as such, or may be used to produce a variety of other alloys containing a lower content of beryllium.

The production of "Master Alloy" began with beryllium hydroxide, which was calcined in a closed system to produce beryllium oxide. All of the operations, except cropping and sawing, were carried out in closed systems or under ventilated canopy hoods. The alloys were produced on a schedule of three shifts per day during a five-day week. Between 30 and 40 workmen were employed in the operations of the alloy plant.

Procedures

Particulate material was collected continuously, from the air, on paper tapes of American Iron and Steel Institute (A.I.S.I.) smoke samplers at 7 locations. Solid particles from approximately 0.5 cubic meter of air were deposited on the tape during each hour of the period of sampling. Continuous sampling was started on the afternoon of May 2, and continued through Friday morning of May 6, 1960. The samplers were set up in the center of each area, about 4 to 6 feet above the level of the floor. The paper tapes were then returned to the laboratory, where every 2 spots were combined into a 2 hour sample, which was analyzed for beryllium.

The levels of concentration of beryllium in the air at the breathing zone of the individual operators were determined from the analyses of dusts collected on Whatman #41 filter papers placed in Staplex high volume samplers. This equipment was operated intermittently, for various periods of time, during the daylight hours of this visit.

During a later visit, on December 13, 1960, a number of samples of dust were removed from the air in various areas of the plant upon millipore filters placed in a Staplex high volume sampler. These samples were collected in order to determine
the levels of the concentration of beryllium and the sizes of the particles dispersed in the atmosphere of the plant.

Results

Table 1 gives the mean, median, and the range of the concentration of beryllium in the air during each 2 hour period at each of several locations in the plant. In Table 2 are listed the levels of concentration that were exceeded during 75, 50 and 25 per cent of the time of the total periods of sampling in each location. Table 3 compares the average concentration of beryllium in the air at various locations during each of the three work shifts. Table 4 compares the findings obtained by the analysis of samples collected with the A.I.S.I. smoke sampler with those of samples collected intermittently by the high volume sampler. The frequencies of the occurrence of certain sizes of the particles in the air of the plant are given in Table 5. Figure 1 shows the fluctuation in the average concentration of beryllium in the air of the cropping area of the plant, as determined over periods of 2 hours.

Discussion

The weighted average of the concentration of beryllium, as obtained in the centers of 7 areas in the plant (Table 1), by the analyses of the material deposited thereon during every successive period of 2 hours (2 spots on the tape)over the total period of 90 hours, was 60.3 micrograms per cubic meter of air. The values ranged from 0.03 to 1050.00 micrograms of beryllium per cubic meter. The air of the oxide area, where beryllium hydroxide is received and calcined to the oxide, was found to be more heavily contaminated than any other with beryllium dusts. The average concentration of beryllium in the air at this area as determined from samples collected over the period of 2 hours, was found to be 149.4 micrograms per cubic meter of air. The maximum average concentration, in any period of 2 hours, was 1050.0 micrograms per cubic meter of air. Air in other areas - of the plant contained beryllium at levels which averaged, (in samples collected over periods of 2 hours) from 21.6 micrograms per cubic meter, in the mixing area, to 87.6 micrograms per cubic meter, in the arc furnace area.

In the entire plant, the concentration of beryllium exceeded 28.4 micrograms per cubic meter during 50 per cent of the time (Table 2), 62.9 micrograms per cubic meter of air during 25 per cent of the time, and 12.9 micrograms per cubic meter of air during 75 per cent of the time. The median concentration, during the sampling period of 2 hours, in individual areas varied from 14.4 micrograms per cubic meter of air, in the mixing area, to 72.5 micrograms per cubic meter of air, in the oxide area. The data show that the levels ranged from 6.5 micrograms per cubic meter, to 33.3 micrograms per cubic meter of air, during 75 per cent of the total number of hours of sampling. During 25 per cent
of the time, the concentration of beryllium in the air varied from 29.1 micrograms per cubic meter, at the Oliver saw, to 140 micrograms per cubic meter of air, in the oxide area.

When the data for the three shifts were compared it was found that the concentration of beryllium in the air was generally higher during the 4 p.m. to midnight shift, than during the others (Table 3). A number of factors may have contributed to this finding, including the variability in the habits of the workmen in association with less supervision and perhaps the differences in climatological conditions during different periods of the day.

The concentration of beryllium in the air of the plant increased to its highest average level on the last work day of the week. This is indicated by the graph in Figure 1, in which are plotted the fluctuations in the average (2 hour) concentration during the period of continuous sampling in the cropping area, practically in the center of the plant. This pattern may be explained by the fact that the plant is shut down over the week ends, and the concentration of beryllium in the air mounts from this low point as the operations continue during the week. The high concentration of beryllium in the air in the cropping area on the afternoon of May 5 (Figure 1) was due to the shutting off of the exhaust system, in order to control the rise in temperature of the furnace, thereby protecting the fabric of the bags employed for collecting dust.

Examination of the data in Table 4 shows that, except for May 6th, the average daily concentration of beryllium in the air, as obtained by the technique of continuous sampling, was higher than that obtained by intermittent sampling. In the latter case, the average is likely to be biased in one direction or the other, because of the unpredictable character of the hourly fluctuations in the concentration of beryllium in the air (Figure 1).

The particles of beryllium dispersed into the air of this plant arise in part, as fume from the furnaces and the casting operations, and as larger particles which escape from the enclosed conveyor system by which the raw materials are handled at the arc furnace. Almost all of the particles of dust removed from the atmosphere were of such size as to be considered as respirable (Table 5).

The environmental conditions found to exist during this period of sampling indicate that operators of this plant are exposed, continuously, to air-borne beryllium in many times the concentration suggested as satisfactory for processors and handlers of beryllium.
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<td>Oliver Saw Area</td>
<td>90</td>
<td>21.1</td>
<td>25.6</td>
<td>&lt;2.5-92.5</td>
</tr>
<tr>
<td>All Areas</td>
<td>635</td>
<td>28.4</td>
<td>60.3</td>
<td>0.03-1050.0</td>
</tr>
</tbody>
</table>
Table 2

Concentration of Beryllium (Micrograms/M³) in Samples Arranged According to the Percentage of Their Prevalence in Time at a Number of Locations

<table>
<thead>
<tr>
<th>Location</th>
<th>75% of the Time</th>
<th>50% of the Time</th>
<th>25% of the Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxide Area</td>
<td>33.3</td>
<td>72.5</td>
<td>140.0</td>
</tr>
<tr>
<td>Arc Furnace Area</td>
<td>30.6</td>
<td>50.0</td>
<td>88.8</td>
</tr>
<tr>
<td>Mixing Area</td>
<td>7.4</td>
<td>14.4</td>
<td>24.5</td>
</tr>
<tr>
<td>Cropping Area</td>
<td>25.0</td>
<td>33.6</td>
<td>65.0</td>
</tr>
<tr>
<td>Casting Area</td>
<td>6.5</td>
<td>14.6</td>
<td>30.0</td>
</tr>
<tr>
<td>Fischer Furnace Area</td>
<td>7.1</td>
<td>28.8</td>
<td>58.5</td>
</tr>
<tr>
<td>Oliver Saw Area</td>
<td>14.3</td>
<td>21.1</td>
<td>29.1</td>
</tr>
<tr>
<td><strong>All Areas</strong></td>
<td><strong>12.9</strong></td>
<td><strong>28.4</strong></td>
<td><strong>62.9</strong></td>
</tr>
</tbody>
</table>
Table 3
The Average Concentration of Beryllium in the Air at Various Locations During the Three Shifts

<table>
<thead>
<tr>
<th>Location</th>
<th>Average</th>
<th>12 Mid.-8 AM</th>
<th>8 AM-4 PM</th>
<th>4 PM-12 Mid.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxide Area</td>
<td>149.4</td>
<td>149.5</td>
<td>108.2</td>
<td>189.7</td>
</tr>
<tr>
<td>Arc Furnace Area</td>
<td>87.6</td>
<td>61.5</td>
<td>109.8</td>
<td>89.6</td>
</tr>
<tr>
<td>Mixing Area</td>
<td>21.6</td>
<td>16.6</td>
<td>17.5</td>
<td>31.8</td>
</tr>
<tr>
<td>Cropping Area</td>
<td>52.8</td>
<td>42.2</td>
<td>45.2</td>
<td>63.7</td>
</tr>
<tr>
<td>Casting Area</td>
<td>39.8</td>
<td>33.9</td>
<td>23.2</td>
<td>57.9</td>
</tr>
<tr>
<td>Fischer Furnace Area</td>
<td>40.8</td>
<td>30.3</td>
<td>30.7</td>
<td>58.9</td>
</tr>
<tr>
<td>Oliver Saw Area</td>
<td>25.6</td>
<td>25.7</td>
<td>25.7</td>
<td>25.4</td>
</tr>
<tr>
<td>All Areas</td>
<td>60.3</td>
<td>51.6</td>
<td>52.0</td>
<td>73.9</td>
</tr>
</tbody>
</table>
Table 4

Comparison of the Averages and Ranges of Concentration of Beryllium Found in Samples Collected by Two Different Methods

<table>
<thead>
<tr>
<th>Date</th>
<th>A.I.S.I. Sampler</th>
<th></th>
<th></th>
<th>High Volume Sampler</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Number of Samples</td>
<td>Micrograms Be/M³</td>
<td>Average</td>
<td>Range</td>
<td>Number of Samples</td>
<td>Micrograms Be/M³</td>
</tr>
<tr>
<td>5-2-60</td>
<td>65</td>
<td>45.8</td>
<td>0.03-560.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>5-3-60</td>
<td>168</td>
<td>29.6</td>
<td>0.2-545.0</td>
<td>16</td>
<td>17.5</td>
<td>1.39-268.0</td>
</tr>
<tr>
<td>5-4-60</td>
<td>168</td>
<td>60.3</td>
<td>6.8-785.0</td>
<td>15</td>
<td>27.5</td>
<td>2.0-305.0</td>
</tr>
<tr>
<td>5-5-60</td>
<td>168</td>
<td>91.9</td>
<td>&lt;2.5-1050.0</td>
<td>17</td>
<td>33.9</td>
<td>2.54-218.0</td>
</tr>
<tr>
<td>5-6-60</td>
<td>66</td>
<td>69.2</td>
<td>5.7-321.0</td>
<td>7</td>
<td>96.8</td>
<td>7.3-330.0</td>
</tr>
</tbody>
</table>

Averages of the Week

<table>
<thead>
<tr>
<th></th>
<th>A.I.S.I. Sampler</th>
<th></th>
<th></th>
<th>High Volume Sampler</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>635</td>
<td>60.3</td>
<td>0.03-1050.0</td>
<td>55</td>
<td>43.9</td>
<td>1.39-330.0</td>
</tr>
</tbody>
</table>
Table 5

The Frequencies of the Occurrence of Certain Sizes of Particles Found in the Air at Various Locations. Per Cent of Total Number

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxide Area</td>
<td>97.2</td>
<td>2.2</td>
<td>0.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Arc Furnace Area</td>
<td>95.5</td>
<td>3.2</td>
<td>1.0</td>
<td>0.0</td>
<td>0.3</td>
</tr>
<tr>
<td>Mixing Area</td>
<td>96.0</td>
<td>2.7</td>
<td>0.3</td>
<td>0.3</td>
<td></td>
</tr>
<tr>
<td>Cropping Area</td>
<td>97.0</td>
<td>2.7</td>
<td>0.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Casting Area</td>
<td>98.0</td>
<td>1.0</td>
<td>0.6</td>
<td>0.6</td>
<td>0.4</td>
</tr>
</tbody>
</table>
Appendix II

Analysis of Residues
From the Combustion of the Propellants

Hercules Powder Company has set up equipment at their facility near Salt Lake City for determining the material balance associated with the burning of the propellant. The propellant is ignited in a closed system consisting of an underground tank 10 feet in diameter and 45 feet long. The vent of the tank is provided with a Cambridge absolute filter which removes the fine particles in the stream of gaseous combustion products from the burning as these are forced from the tank by the pressure developed during burning. At the other end of the tank a covered manhole is provided for entrance into the tank.

After the propellant was burned completely, a workman equipped with an air-line hose mask and suitable protective clothing entered and swept down the sides of the tank, and collected all of the solid residue. The walls were then cleaned by a Gelman vacuum pump, and the material so collected was preserved for analysis. The sweepings were screened and the materials that were retained on a number of the screens down through 200 mesh, as well as those collected on the filters, were then analyzed to determine their composition.

Hercules Powder Company reported three different sets of results. One set was obtained by the use of an x-ray method while the other two sets of data were from a spectrophotometric method. The three sets of data are included in Table 1, along with data obtained by the Kettering Laboratory in the analysis of a portion of material from the same test made available for collaborative study.

As may be seen, the quantities of beryllium recovered by Hercules Powder Company varied from 60.18 to 73.35 per cent of the total content of metallic beryllium in the propellant. The quantities recovered in the Kettering Laboratory were somewhat larger than the average of the three values reported by Hercules. Coarse particles, 75 microns or more in diameter, constituted approximately 80 per cent of the recovered residue. Hercules also reported that 38 per cent of the particles composing the "pan material" were smaller than 10 microns in diameter. Approximately 10 per cent of the beryllium was found in particles less than 10 microns in diameter.
A number of compounds of beryllium were found in the combustion products of the propellant. Table 2 gives the results of a qualitative analysis of the screen and other materials collected in Burn 11, as made in the Kettering Laboratory by our technique of x-ray diffraction. Table 3 gives the results of quantitative x-ray analysis as reported by Hercules Powder Company. The attempt made in the Kettering Laboratory to determine the concentration of the various compounds is indicated in the lower section of the table. Although there is considerable disagreement, quantitatively, between the two laboratories, the types of compounds found, and the general order of magnitude, as well as the trends, in the concentration of the compounds are obvious. Of interest is the finding (Kettering Laboratory) of soluble salts of beryllium, principally as the chloride, in some of the fractions. The small particles appeared to contain more of the soluble beryllium than did the coarse particles. Of the beryllium present on the vacuum filter, 6 per cent was as the chloride. The beryllium chloride in this fraction, as calculated, accounted for 1.25 per cent of the total beryllium recovered. Tests of the carbide and the nitrite indicated that these compounds were soluble in water only to the extent of 0.0005 per cent, in the case of beryllium carbide (85% pure Be$_2$C containing 10% BeO), and 0.00008 per cent in that of the nitrite (97% pure Be$_3$N$_2$).

It is evident, from the few data available, that a number of compounds of beryllium, as well as beryllium metal, are present in the combustion products of the propellant. In "quiet" combustions, most of the beryllium and its compounds occur as particles greater than 75 microns in diameter. Approximately 10 per cent of the particles of beryllium or its compounds were smaller than 10 microns in diameter. Of the beryllium products retained on the vacuum filter, water soluble beryllium, calculated as BeCl$_2$, amounted to 10 per cent of the total material collected. The material in the pan (material passing a 200 mesh sieve) consisted principally of metallic beryllium and beryllium oxide.
Table 1

The Weight of Material and the Content of Beryllium in Material Retained on Various Screens

<table>
<thead>
<tr>
<th>Microns and (Mesh Size)</th>
<th>Portion of Material Collected on Screen % by Weight</th>
<th>Hercules Powder Company</th>
<th>Spectrophotometric Method</th>
<th>Kettering Laboratory</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>X-Ray Method</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Analysis 1</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>A</td>
<td>B</td>
<td>A</td>
</tr>
<tr>
<td>833 (20)</td>
<td>11.0</td>
<td>20.50</td>
<td>6.51</td>
<td>10.60</td>
</tr>
<tr>
<td>589 (30)</td>
<td>6.0</td>
<td>33.70</td>
<td>5.83</td>
<td>28.30</td>
</tr>
<tr>
<td>417 (40)</td>
<td>7.0</td>
<td>39.64</td>
<td>7.74</td>
<td>29.50</td>
</tr>
<tr>
<td>208 (70)</td>
<td>22.0</td>
<td>38.84</td>
<td>25.06</td>
<td>28.30</td>
</tr>
<tr>
<td>147 (100)</td>
<td>14.0</td>
<td>34.34</td>
<td>13.89</td>
<td>32.80</td>
</tr>
<tr>
<td>75 (200)</td>
<td>18.0</td>
<td>35.76</td>
<td>15.93</td>
<td>42.90</td>
</tr>
<tr>
<td>Pan</td>
<td>21.0</td>
<td>35.88</td>
<td>10.22</td>
<td>33.90</td>
</tr>
<tr>
<td>Vacuum Filter</td>
<td>0.73</td>
<td>8.13</td>
<td>0.98</td>
<td>43.10</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>A</td>
</tr>
</tbody>
</table>

A = Per cent Beryllium in material retained on screen
B = Per cent of total Beryllium recovered
Table 1 Continued

<table>
<thead>
<tr>
<th>Microns and (Mesh Size)</th>
<th>Hercule Powder Company</th>
<th>Kettering Laboratory</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>X-Ray Method</td>
<td>Spectrophotometric Method</td>
</tr>
<tr>
<td></td>
<td>Analysis 1</td>
<td>Analysis 2</td>
</tr>
<tr>
<td></td>
<td>A</td>
<td>B</td>
</tr>
<tr>
<td>Cambridge Filter</td>
<td>0.83</td>
<td>35.89</td>
</tr>
<tr>
<td>Per cent of total Be input recovered</td>
<td>60.18</td>
<td>64.86</td>
</tr>
</tbody>
</table>

A = Per cent Beryllium in material retained on screen
B = Per cent of total Beryllium recovered

*Calculated from average of 3 analyses by Hercules Powder Company
Table 2

Beryllium Compounds Identified from X-Ray Diffraction
Patterns of Material in Samples Collected from "Burn" #11

<table>
<thead>
<tr>
<th>Beryllium Compounds Identified</th>
<th>Material Retained on Screen of Mesh Size</th>
<th>Pan Residue</th>
<th>Material Retained on the Vacuum Filter</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>20</td>
<td>30</td>
<td>40</td>
</tr>
<tr>
<td>Beryllium Metal Be</td>
<td>Trace</td>
<td>Nil</td>
<td>Nil</td>
</tr>
<tr>
<td>Beryllium Oxide BeO</td>
<td>++++</td>
<td>++++</td>
<td>++++</td>
</tr>
<tr>
<td>Beryllium Carbide Be₂C</td>
<td>+</td>
<td>Trace or Nil</td>
<td>Trace</td>
</tr>
<tr>
<td>Beryllium Nitride Be₃N₂</td>
<td>Trace or Nil</td>
<td>Nil</td>
<td>Nil</td>
</tr>
<tr>
<td>β Beryllium Nitride Be₃N₂</td>
<td>Trace or Nil</td>
<td>++++</td>
<td>+++</td>
</tr>
</tbody>
</table>
Table 3
X-Ray Diffraction Analysis (Per Cent) of Residues of Burned Propellant Reported by Hercules Powder Company

<table>
<thead>
<tr>
<th>Product</th>
<th>Screen Size</th>
<th>833u</th>
<th>589u</th>
<th>417u</th>
<th>208u</th>
<th>147u</th>
<th>75u</th>
<th>Pan</th>
<th>Vacuum</th>
<th>Filter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Be</td>
<td></td>
<td>4.0</td>
<td>2.2</td>
<td>3.2</td>
<td>7.2</td>
<td>8.6</td>
<td>9.2</td>
<td>10.6</td>
<td>2.9</td>
<td></td>
</tr>
<tr>
<td>BeO</td>
<td></td>
<td>25.6</td>
<td>32.8</td>
<td>50.5</td>
<td>59.4</td>
<td>57.4</td>
<td>46.0</td>
<td>36.2</td>
<td>6.2</td>
<td></td>
</tr>
<tr>
<td>Be₂C</td>
<td></td>
<td>6.2</td>
<td>3.0</td>
<td>2.5</td>
<td>2.3</td>
<td>2.0</td>
<td>1.8</td>
<td>1.6</td>
<td>1.8</td>
<td></td>
</tr>
<tr>
<td>Be₃N₂</td>
<td></td>
<td>7.3</td>
<td>36.5</td>
<td>31.5</td>
<td>19.4</td>
<td>8.0</td>
<td>5.0</td>
<td>5.3</td>
<td>3.5</td>
<td></td>
</tr>
<tr>
<td>Total Be</td>
<td></td>
<td>14.3</td>
<td>35.2</td>
<td>37.5</td>
<td>46.0</td>
<td>43.6</td>
<td>27.2</td>
<td>42.0</td>
<td>24.6</td>
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</tr>
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</table>

Analysis of Propellant Residues by Kettering Laboratory

<table>
<thead>
<tr>
<th>Product</th>
<th>Analysis</th>
<th>0.0009</th>
<th>0.002</th>
<th>0.21</th>
<th>1.17</th>
<th>4.5</th>
<th>4.05</th>
<th>3.16</th>
<th>10.0</th>
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<tbody>
<tr>
<td>BeCl₂</td>
<td>(1)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Be</td>
<td>(3)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>4.0*</td>
<td>11.5</td>
<td>12.1</td>
<td>34.0</td>
<td>-</td>
</tr>
<tr>
<td>BeO</td>
<td>(2)</td>
<td>26.0</td>
<td>14.3</td>
<td>29.0</td>
<td>39.0</td>
<td>46.0</td>
<td>51.0</td>
<td>42.0</td>
<td>31.5</td>
</tr>
<tr>
<td>Be₂C</td>
<td>(3)</td>
<td>14.7</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Be₃N₂</td>
<td>(3)</td>
<td>-</td>
<td>36.8</td>
<td>34.0</td>
<td>8.0*</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>15.5</td>
</tr>
<tr>
<td>Total Be</td>
<td>(4)</td>
<td>18.0</td>
<td>23.2</td>
<td>27.0</td>
<td>22.0</td>
<td>28.5</td>
<td>31.0</td>
<td>49.5</td>
<td>20.0</td>
</tr>
</tbody>
</table>

(1) Beryllium content of portion of sample in solution in water.
(2) X-ray diffraction analysis.
(3) Calculated from excess of beryllium, after that due to BeCl₂ and BeO was subtracted from total beryllium determined chemically.
*Assuming that each contained 50% of the beryllium not accounted for.
### REPORT TITLE
TOXIC HAZARDS OF BERYLLIUM PROPELLANT OPERATIONS
Critique of Current Safety Practices

### DESCRIPTIVE NOTES
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### ABSTRACT
The soundness of the considerations which have been used to develop current safety practices in the handling of beryllium enriched propellants have been reviewed. The report includes a discussion of pertinent facts relating to berylliosis and the considerations which led to the promulgation of the tolerance limits. Particular emphasis is given to potential hazards arising from plant operations and test firings. Except for certain measures, industrial hygiene practices are described in general terms. The exceptions, dealing with locker and shower room facilities, protective clothing, laundering of clothing, the use of personal respiratory devices, and the disposal of solid and liquid wastes are discussed in some detail. Medical surveillance programs are outlined in full. The report concludes with a number of recommendations derived from current observations and past experience in the handling of beryllium enriched material.
### Key Words

<table>
<thead>
<tr>
<th>Role</th>
<th>WT</th>
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<tbody>
<tr>
<td></td>
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</tr>
</tbody>
</table>

**Hazards**  
**Toxicity**  
**Safety**  
**Beryllium**  
**Propellants**  
**Industrial Medicine**  
**Beryllium Diseases**

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