AIR POLLUTION ASPECTS

OF

BORON AND ITS COMPOUNDS

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Prepared for the
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FOREWORD

As the concern for air quality grows, so does the concern over the less ubiquitous but potentially harmful contaminants that are in our atmosphere. Thirty such pollutants have been identified, and available information has been summarized in a series of reports describing their sources, distribution, effects, and control technology for their abatement.

A total of 27 reports have been prepared covering the 30 pollutants. These reports were developed under contract for the National Air Pollution Control Administration (NAPCA) by Litton Systems, Inc. The complete listing is as follows:

Aeroallergens (pollens)
Aldehydes (includes acrolein and formaldehyde)
Ammonia
Arsenic and Its Compounds
Asbestos
Barium and Its Compounds
Beryllium and Its Compounds
Biological Aerosols
(microorganisms)
Boron and Its Compounds
Cadmium and Its Compounds
Chlorine Gas
Chromium and Its Compounds
(includes chromic acid)

Ethylene
Hydrochloric Acid
Hydrogen Sulfide
Iron and Its Compounds
Manganese and Its Compounds
Mercury and Its Compounds
Nickel and Its Compounds
Odorous Compounds
Organic Carcinogens
Pesticides
Phosphorus and Its Compounds
Radioactive Substances
Selenium and Its Compounds
Vanadium and Its Compounds
Zinc and Its Compounds

These reports represent current state-of-the-art literature reviews supplemented by discussions with selected knowledgeable individuals both within and outside the Federal Government. They do not however presume to be a synthesis of available information but rather a summary without an attempt to interpret or reconcile conflicting data. The reports are

necessarily limited in their discussion of health effects for some pollutants to descriptions of occupational health exposures and animal laboratory studies since only a few epidemiologic studies were available.

Initially these reports were generally intended as internal documents within NAPCA to provide a basis for sound decision-making on program guidance for future research activities and to allow ranking of future activities relating to the development of criteria and control technology documents. However, it is apparent that these reports may also be of significant value to many others in air pollution control, such as State or local air pollution control officials, as a library of information on which to base informed decisions on pollutants to be controlled in their geographic areas. tionally, these reports may stimulate scientific investigators to pursue research in needed areas. They also provide for the interested citizen readily available information about a given pollutant. Therefore, they are being given wide distribution with the assumption that they will be used with full knowledge of their value and limitations.

This series of reports was compiled and prepared by the Litton personnel listed below:

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Appreciation is expressed to the many individuals both outside and within NAPCA who provided information and reviewed draft copies of these reports. Appreciation is also expressed to the NAPCA Office of Technical Information and Publications for their support in providing a significant portion of the technical literature.

ABSTRACT

Certain compounds of boron are toxic air pollutants to humans and animals. Inhalation of boron compounds as dusts can be moderately toxic, causing irritation and inflammations but without permanent injury. Inhalation of boron hydrides (boranes, used as high-energy fuels) can be highly toxic, producing signs of severe central nervous system damage, and is capable of causing death through exposure to high concentrations for relatively short periods of time. Boron acts as an herbicide when applied to plant life in more than minute quantities, but is not known to affect materials.

The use of boron as an additive in petroleum fuels, and as a source of high-energy fuel, its presence in coals, and the manufacturing processes employed to produce boron compounds are believed to be limited sources of atmospheric boron. No information was discovered on concentrations of boron in the atmosphere.

No information has been found on the economic costs of boron air pollution or on the costs of its abatement. Methods of analysis are available; however, they are not sufficiently sensitive or selective for determining atmospheric concentrations of boron and its compounds.

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1. INTRODUCTION

Boron and its compounds have presented hazards to the health of humans and animals, and therefore should logically be investigated as a cause of environmental contamination. The most common health hazards have been the accidental ingestion of household chemicals, such as boric acid or borax, and absorption of boric acid from wounds or burns; these hazards, of course, are not directly relatable to environmental pollution. A less common hazard is the contamination of the atmosphere by boron dusts, mainly produced during the manufacture of boron compounds and products. The most serious hazard is the danger of atmospheric contamination by boron hydrides, or boranes—highly-toxic compounds used as high-energy fuels for rocket motors and jet engines. The use of boron as a fuel additive in the petroleum industry undoubtedly contributes to boron air pollution; however, its impact is unknown.

No data are available on the concentrations of boron in the atmospheric environment, and no measurements of this element or its compounds are known to be included in current air-monitoring programs.

2. EFFECTS

2.1 Effects on Humans

Boron and its compounds are considered by Sax as moderately to highly toxic to man, through ingestion or inhalation. The most significant of the boron compounds related to air pollution are the boron hydrides (boranes), which are rated by Sax as highly toxic; these compounds, used as high-energy fuels, can cause air pollution when allowed to escape into the atmosphere, and can produce severe central nervous system irritation when inhaled, possibly causing death or permanent injury. Other compounds of boron are not highly toxic, and therefore are not considered industrial poisons. However, inhalation of these compounds (such as boron oxide, boric acid, etc.) in the form of dusts can be moderately toxic without causing death or permanent injury.

2.1.1 Boranes

The boranes, the most highly toxic of the boron compounds, consist chiefly of pentaborane, decaborane, and diborane. Others are known and still others are being developed, but at this time these are the most significant. Of these, pentaborane is the most toxic, while decaborane and diborane are only slightly less so. Instances of human exposure to these compounds have occurred; however, adequate data were not available to ascertain the concentration or the actual nature of the particular compound. Rozendaal, in 1951, reported a syndrome resembling metal fume fever after exposure to diborane while exposure to pentaborane produced marked

central nervous system irritation. Diborane produces chest tightness, cough, headaches, nausea, chills, drowsiness, and dizziness. These symptoms appear promptly and last a relatively short time. Pentaborane produces the same symptoms, but with more pronounced dizziness, headache, and drowsiness. Convulsions, semicoma, disorientation, a persistent leukocytosis, and signs of liver damage were reported in one extreme case of pentaborane intoxication.

The incidence of acute borane intoxication in humans has been low despite the number of persons who have worked with and around these compounds. This is largely attributable to the safety procedures employed to avoid inhalation, skin contact, and ingestion of boron compounds.

Table 1 in the Appendix indicates probable results from a small exposure to pentaborane vapors for various time periods.

2.1.2 Boric Acid, Sodium Borates, and Boron Oxide

These compounds are not considered by Sax 31 to be highly toxic; however, under certain circumstances they do possess a moderate degree of toxicity. Sax rates them generally as moderately toxic when ingested or inhaled, with the most common danger to health occurring through accidental ingestion. The medical literature contains many instances of accidental poisoning due to ingestion of borates or boric acid. While it has been contended that death may result from the ingestion of 15 to 30 g of borax or 2.5 g of boric acid,

Vertan in 1929 reported administering doses of 15 to 30 g of boric acid to several hundred humans without serious effects. Borax soap mixtures have been in use for many years, and mild solutions of boric acid have been used routinely as an eye wash. However, Sax cautions that the careless use of borax as a skin cleanser should be discouraged, as well as the continuous use of boron solutions for irrigation of body cavities.

2.1.3 Other Boron Compounds

No evidence is available concerning the toxicity of other boron compounds. Boron carbide and boron nitride can possibly be considered as nuisance dusts. 31

2.2 Effects on Animals

2.2.1 Commercial and Domestic Animals

No record has been found of accidental boron intoxication in livestock. Owen²⁸ reported in 1944 on the experimental dosing of two dairy cows which were alternately fed a control ration of 16 ppm boron and a ration containing 1 percent borax (283 ppm boron) over periods of 42 days. No ill effects were noted, and no decrease in milk output resulted. Of the ingested borax, 98 percent was excreted, and the remaining 2 percent appeared in the milk. The boron concentration of the milk rose from a normal level of 0.7 ppm to 2 ppm as a result of the experiment.

2.2.2 Experimental Animals

2.2.2.1 <u>Boranes</u>²

Experiments with the boranes on animals have indicated the highly toxic nature of these compounds. Internal administration of pentaborane has produced death, preceded by list-lessness, incoordination, tremors, convulsions, and coma. Inhalation of highly concentrated diborane produced death of hamsters within 25 minutes. Small quantities (0.2 ml) of borane fuel administered to the eyes produced severe eye irritation in rabbits.

Tables 2 and 3 in the Appendix present data on the toxicity of the boranes.

2.2.2. Boric Acid, Sodium Borates, and Boron Oxide

Studies of animals experimentally dosed with boric acid have revealed that this compound can be regarded as moderately toxic to all species of animals. Acidic solutions of 5 percent boric acid were nonirritating to eye and skin, while alkaline solutions produced a slight irritation which subsided within hours without residual injury. Boron oxide applied to the skin of a rabbit produced reddening of the skin, but no other symptoms. Levinskas cites several laboratory experiments in which boron compounds were administered to animals by inhalation without serious injury. In one instance, borax particles 5 μ^{\star} or less in diameter were administered to the lungs of guinea pigs three times daily on alternate days, with total dosage amounting to 150,000 μg .

^{*\}u: micron(s).

No damage to the lungs resulted. In another case, rats and guinea pigs were exposed to an atmosphere containing boron oxide particles for 6 hours per day over a period of 6 weeks. No ill effects were noted even with exposure to $40,000~\mu g/m^3$ boron oxide.

Table 4 in the Appendix presents data on the toxicity of boric acid, and Table 5 in the Appendix lists data on the toxicity of sodium borates.

2.2.2.3 Other Boron Compounds

Organic compounds such as borate esters were found to be moderately toxic to experimental animals when ingested or when applied to the skin; experiments involving mice produced acutely toxic reactions. However, inhalation of vapors produced no ill effects.

Table 6 in the Appendix lists toxic effects of the borate esters; Table 7, (Appendix) data on organoboron compounds; Table 8 (Appendix) the toxicities of the boron halides; and Table 9 (Appendix) data on other miscellaneous compounds. Additional data on characteristics and toxicities of boron compounds can be found in Table 10 in the Appendix.

2.3 Effects on Plants

Small quantities of boron are required for all plant life, and borates are accordingly found in commercial fertilizers. However, large quantities are extremely toxic, and boron can therefore be used as an effective herbicide. Due to its destructive effect on vegetation, boron used as an herbicide

does not appear to play a significant role in accidental poisoning of animals.

Many treatises have been prepared on the boron needs of plant life; Brenchley covered the subject well in the Botanical Review in 1947.

2.4 Effects on Materials

No information has been found indicating that damage to materials results from the presence of atmospheric boron.

2.5 Environmental Air Standards

The American Industrial Hygiene Association ¹⁷ has prepared guides for diborane and pentaborane. The Manufacturing Chemists Association has prepared a Chemical Safety Data Sheet on boron hydrides. However, the most recent standard for these compounds was issued by the American Conference of Governmental Industrial Hygienists in 1967.

Threshold Limit Values (TLV) for these compounds are:

Diborane 0.100 ppm (100 μ g/m³) Pentaborane 0.005 ppm (10 μ g/m³) Decaborane 0.050 ppm (300 μ g/m³)

The median concentrations detectable by odor for man are 3.3 ppm (33,000 $\mu g/m^3$) for diborane, 0.8 ppm (1,600 $\mu g/m^3$) for pentaborane, and 0.7 ppm (4,200 $\mu g/m^3$) for decaborane. These values are obviously considerably greater than the established TLV.

Hygienic standards for brief exposures have not been established. However, the American Industrial Hygiene Association has suggested an Emergency Exposure Limit for pentaborane of 25 ppm (50,000 $\mu g/m^3$) for not over 5 minutes. Since

this value permits a degree of intoxication, it does not represent a completely safe limit of exposure. This same source states that exposure to 1,000 ppm (2,000,000 $\mu g/m^{\epsilon}$) for one minute is believed to cause convulsions, and in some cases death.

The American Conference of Governmental Industrial Hygienists in 1967 adopted a value of 15,000 $\mu g/m^3$ as the TLV for boron oxide. No TLV has been established for boric acid dust, but Hyatt and Milligan suggest that the concentration be kept below 2,000 $\mu g/m^3$.

No information has been found regarding environmental standards for continuous exposures over longer periods than mentioned above.

SOURCES

3.1 Natural Occurrence

Boron is widely distributed in nature, but constitutes only an estimated 0.001 percent of the earth's crust. 19 It is also present in sea water, and appears to be an essential constituent of a number of rock-forming silicate minerals, such as datolite and tourmaline. Boron occurs naturally only in combined forms, usually as an alkaline earth borate or as boric acid.

Although boron is widespread in nature, large deposits of commercially valuable boron minerals are found only in a very few localities, and these are primarily areas of formerly intense volcanic activity where precipitation and natural drainage have not produced leaching and drainage to the sea. The United States supplies most of the boron minerals required by the free world. The Kramer deposit, located near the town of Boron, Calif., contains an estimated 100,000,000 tons of borax and kernite, and is the principal source of borate. The remainder of the borax produced in this country comes almost entirely from Searles Lake, near Trona in the Mohave Desert, although minor deposits are located elsewhere in the southwestern region of the United States.

Boron is a known constituent of coals. Abernethy and Gibson¹ report that selected coals of the United States averaged more than 0.1 percent of boron in the ash examined. Values of boron concentration in coal ash measured 0.005 to

0.65 percent in the Northern Great Plains, 0.008 to 0.096 percent in West Virginia, and 0.21 percent in North Dakota. Boron contents in the basic coal were determined to be 116 ppm for the Great Plains, 96 ppm for the Eastern Interior, and 25 ppm for the Appalachian regions of the United States. No information was found on the emissions to the atmosphere resulting from these concentrations.

3.2 Production Sources

Although elemental boron does not occur in nature, it can be produced—usually in the laboratory—by three general techniques: (1) chemical reduction with active elements, (2) electrolytic reduction, and (3) thermal decomposition. The most common method for producing large amounts of elemental boron is the exothermic reduction of boron trioxide with magnesium. The product of this reaction, known as "Moissan's boron," is relatively impure amorphous boron, which usually is refined by various leaching processes.

Few applications of elemental boron are presently known. It is most commonly used in the metallurgical field, as a deoxidizer and degassifier; as a p-type doping agent for silicon or germanium semiconductors; and in certain nuclear applications involving thin films of elemental boron for neutron counters. It is considered to have definite potential as a heat-and oxidation-resistant raw material for space-age electronic and optical devices.

Crystalline boron, in large samples, is relatively nonreactive; however, powdered boron reacts readily and

sometimes violently with certain chemical agents—most violently with oxidizing agents—in some cases igniting or exploding.

Use of boron minerals and compounds has shown a steady increase in recent years. Figures from the Minerals Yearbook for 1966 reveal the following trends: 26

Sold or used by producers 1956-60 1961 1962 1963 1964 1965 1966

Gross weight (tons) 575 603 647 700 776 807 866

Value \$40,573 46,936 49,336 54,981 60,871 64,180 68,209

The distribution of boron compounds used in various industries in 1965 was approximately as follows:

Heat-resistant glass, glass wool, and fiberglass	32%
Soaps and cleaners	16%
Porcelain enamels	13%
Synthetic fertilizers and herbicides	8%
Miscellaneous (leather tanning, metallurgy,	31%
corrosion control, nuclear shielding,	
flameproofing, etc.)	

The principal producers of boron minerals and compounds in the United States are:

U.S. Borax and Chemical Corporation American Potash and Chemical Corporation Stauffer Chemical Company Kern County Land Company

3.3 Product Sources

The compounds of boron are normally divided into six general groups: (1) boron oxides, boric acid, and borates, (2) boric acid esters, (3) refractory boron compounds, (4) boron halides, (5) boron hydrides, and (6) organic boron

compounds. Within each grouping there exist a large number of individual compounds, some of pronounced commercial importance, and others primarily significant to the problem of air pollution.

3.3.1 Boron Oxide, Boric Acid, and Borates

These compounds consist of several compounds having very definite commercial importance, used in over 100 different industries. Borax and boric acid are the most important of these compounds, with many other compounds—mainly in the borates—having lesser importance.

Boron dusts of unknown composition are emitted to the atmosphere by the iron industry. Analysis of two samples taken from a baghouse serving a gray iron furnace in the Los Angeles area revealed concentrations of 0.050 percent and 0.054 percent (500 and 540 $\mu g/g$) of boron in the total samples.

3.3.1.1 Boric Acid

Boric acid (H_3BO_3) is usually manufactured by adding sulfuric or hydrochloric acid to granulated borax or colemanite. The resulting solution is then cooled to the proper temperature, and boric acid crystals are removed by filtration. The American Potash and Chemical Corporation also extracts boric acid by recovery from plant-end liquors and lake brine at Searles Lake, Trona, Calif.

Boric acid has a wide variety of industrial uses. It is used in glazing in the ceramics industry, as raw material in making chemicals such as boron trifluoride and boron carbide, and in making boron alloys that are used in hardening

steel. Boric acid is used as a nonirritating, mildly antiseptic pharmaceutical solution, and for years has been a common household preparation for washing the eyes. It is also used in cosmetics, dye stabilizers, latex paints, solutions for electroplating, and flameproofing; in photography; and for other purposes.

3.3.1.2 Borax

Borax ($Na_2B_4O_7$ - $10H_2O$), commercially the most important of the borates, is manufactured by crushing borate ore and dissolving the borax, then removing the insoluble rock and dry particles through successive solutions and separator screens. It is also produced by an evaporation process, using the borax brine recovered from Searles Lake.

Borax has wide and varied applications in industry. It is an important ingredient in the manufacture of glasses and ceramics; its mild alkaline and preservative properties are important to the leather-tanning industry; it is extensively used as a detergent or in combinations with soap; and it is frequently used in cosmetics that require a mild alkaline base. When combined with boric acid or used separately in solution, borax is an effective fire retardant and preservative for wood and wood products. A significant use of borax is its application as an additive to prevent the growth of microorganisms in such petroleum fuels as gasoline, diesel and aircraft turbine fuels, home heating oil, and other fuels and solvents. 19

In agriculture, borax is an essential component of

many artificial fertilizers. Most soils that have been under cultivation for long periods of time become deficient in elemental boron, which is vital to the health of many commercial crops. However, care must be used in the addition of borax, for when used in large amounts, it then acts as a nonselective herbicide.

3.3.1.3 Other Borates

Other borate compounds include sodium tetraborate pentahydrate, used in antifreeze solutions as a rust inhibitor, in liquid starches, and in the manufacture of other borates; kernite, one of the most important of borate ores, found with borax in the Kramer deposits; anhydrous borax, made by dehydrating and fusing borax, and used chiefly as the source of sodium borate in high-quality glasses and glazes; ammonium pentaborate, used as a component of electrolytes and of fire-retardant preparations; and many other similar compounds.

3.3.2 Boric Acid Esters

Esterification of boric acid with alcohols or phenol, or of boric oxide with alcohols results in a wide family of compounds with special characteristics. These compounds are suitable for use as additives to fuels and lubricants, as antiknock agents in gasoline, as inhibitors of growth of microorganisms in diesel and aviation fuels, as additives to kerosene jet fuel to prevent icing, and as an oxidation preventive. Various compounds are effective as curing agents for epoxy resins. Various esters have been used in nuclear-shielding materials and as ingredients in

nuclear-detecting devices.

In general, therefore, the esters of boron have limited, specialized uses, the most significant of which are their uses as fuel additives for automobile power sources.

3.3.3 Refractory Boron Compounds

Metal borides, boron carbide, and boron nitride comprise this group of boron compounds. Metal borides, formed usually by direct interaction of metallic boron with other metals, are metallic substances with high electrical conductivities, high melting points, extreme hardness, relatively low coefficients of expansion, and high degrees of chemical stability. These compounds are used primarily as structural parts of rocket engines, jet turbines, and other equipment subjected to high temperatures and chemically reactive agents. Boron carbide, produced by the reduction of boric oxide by carbon at high temperatures, possesses great hardness and electrical conductivity, and is used as an abrasive, in jet engine parts, and as a semiconductor. nitride, prepared by heating boric oxide with sodium, potassium, or calcium cyanide, is used in the manufacture of crucibles and other heat-resistant items and for high-voltage electrical insulation.

3.3.4 Boron Halides

Boron halides include boron trichloride, boron tribromide, boron triiodide, and sub-halides of boron. The use of these compounds is limited almost exclusively to chemical manufacturing and metallurgy.

3.3.5 Boron Hydrides

Boron hydrides, or boranes, consist of a large group of boron compounds of growing importance and of definite significance to a study of air pollution. Of these, the most important are considered to be diborane (gas), pentaborane (liquid), tetraborane (liquid which boils at 18°C), and decaborane (solid).

3.3.5.1 Diborane (B_2H_6)

Diborane is manufactured by the reaction of sodium borohydride with boron fluoride, using dimethyl ether or diethylene glycol as a solvent. Gaseous boron fluoride is passed into a solution of sodium borohydride, and the evolved diborane is fractionated from the solvent. To avoid thermal decomposition, the temperature is kept at 35°C or less. Diborane is a colorless, poisonous gas, normally stable but explosively ignitable at room temperatures in air containing traces of other boranes or moisture. The major use of diborane has been its conversion to higher boranes and their derivatives, which are used as high-energy fuels and propellants. Diborane is also used in the manufacture of amine complexes and as a catalyst in polymerization.

3.3.5.2 Tetraborane (B_4H_{10})

Tetraborane is normally produced by the pyrolysis of diborane. It is a colorless, poisonous gas which decomposes slowly at room temperature and rapidly at higher temperatures. In the presence of impurities and in moist air it ignites

explosively. No use can be identified in the literature for this compound.

3.3.5.3 Pentaborane (B_5H_9)

Pentaborane is a colorless liquid with strong toxic properties. When stored for long periods at room temperatures, pentaborane is very stable and does not decompose. However, in the presence of impurities and in moist air, pentaborane vapors explode spontaneously. Anderton⁶ notes that it is the best of the synthetic fuels for jet aviation motors, and is probably the fuel that will be used for turbojet and ramjet motors in the near future. Kracknell²⁰ considered it to be 1.6 times better than kerosene with respect to weight calorific power.

Analyses of exhaust-gas samples indicated ³² no appreciable hazard from any of the exhaust-gas constituents; and although boron or boron compounds are produced as a result of combustion of the boranes, they have not been identified or quantitatively evaluated, as have other constituents.

3.3.5.4 Decaborane $(B_{10}H_{14})$

Decaborane is a solid, and is toxic. It is the most stable borane, does not react with oxygen of the air at room temperature, and can be worked with in air. At temperatures of 100°C, decaborane vapors explode spontaneously. This compound is used in the vulcanization of rubber, but its most significant use is as a fuel for rockets and other propellants.

3.4 Environmental Air Concentrations

Neither quantitative nor qualitative data have been found in the literature on the concentration, distribution, or variation of boron or boron compounds in the atmosphere.

4. ABATEMENT

Little evidence can be found to indicate that action is being taken to reduce air pollution by boron, except in the areas involving use of the high-energy fuels. And even in these specific areas, the efforts to date have been largely concerned with preventing accidental spilling of the fuels.

5. ECONOMICS

No information has been found on the economic costs of boron air pollution, or on the costs of its abatement.

Data on the production and consumption of boron are presented in Section 3.

6. METHODS OF ANALYSIS

Several devices for detecting pentaborane in air are available, but they are nonspecific (i.e., they detect other compounds with similar chemical properties). A coulometric borane monitor was developed by Braman et al. which was based on the oxidation of boranes with electrolytically generated iodine. This instrument, with a sensitivity of approximately ± 0.02 ppm (40 $\mu g/m^3$) pentaborane in air, unfortunately was susceptible to overloading when excessive concentrations of electroactive materials present in the air desensitized it.

A boron hydride monitor that converted hydrides to boric acid by pyrolysis and then determined the presence of boric acid by colorimetry was described by Fristom, Bennett, and Berl. However, this monitor was not automated. Kuhns Forsythe, and Masi²¹ have outlined a hand-held device for automatic detection of boron hydrides in air, based on the reduction of boron hydrides with triphenyltetrazoleum chloride. These devices provided sensitivity in the 0.1 ppm range, but were not continuous monitors and were subject to interference from all oxidizing or reducing material in air.

Hill and Johnston 15 reported on ultraviolet spectrophotometric detection of decaborane, but this method proved unsuitable for use with other boranes.

Braman and Gordon and Braman reported on a directreading, automatic, temperature-insensitive instrument capable of detection of pentaborane down to concentrations of 0.05 ppm (100 $\mu g/m^3$). This device used the flame-emission principle of detection: in the presence of boranes, a small hydrogen flame takes on a greenish cast, the intensity of which is proportional to the borane concentration. This device can be operated continuously over an 8-hour period using a self-contained hydrogen supply and storage batteries.

Development of an atmospheric monitoring device to detect and record several toxic components, including pentaborane, is reported by the Mine Safety Appliances Company. This device also features pyrolysis to form boric oxide from borane, followed by detection of the boron by using n-amylamine reagent. The company claims a detectability of 0.01 ppm (20 $\mu g/m^3$), with rapid response and continuous operation.

In a comprehensive 1964 review of analytical methods for determining the presence of boron, Nemodruk and Karalova listed the following methods. Photometric methods are widely used, and are especially suitable for determining micro amounts—at concentrations of 0.05-0.20 μ g, these methods produce 90% or better accuracies. Coulometric titration is said to provide determination of amounts as low as 0.2 μ g. Spectral analysis is one of the most widely used methods in metallurgy, capable of determining 5 \times 10⁻⁵ percent concentrations of boron. Fluorimetric analysis is also used, with sensitivity to 0.1 μ g of boron. And radioactive methods are also available, based on the ability of boron's nuclei to

absorb thermal neutrons—this method is considered simple, and highly efficient, is capable of providing 100 determinations in 8 hours, and has sensitivity to 0.1 μg .

7. SUMMARY AND CONCLUSIONS

Boron compounds, in general, are toxic to humans and animals when ingested. Most boron compounds are moderately toxic by inhalation, while certain compounds, such as the high-energy borane fuels, are highly toxic when inhaled. Dusts of some boron compounds are considered merely nuisance dusts; others, such as dusts of boric acid and boron oxide, are moderately toxic.

Borane poisoning in animals has produced listlessness, incoordination, convulsions, coma, and death. Similar symptoms have been observed in humans exposed to the boranes, although none have died. The incidence of acute borane intoxication in humans has been low, and adequate data on exposure, concentrations, and reactions are lacking.

Environmental problems concerning boron and its compounds are generally limited to the particular areas where the production of boron compounds emits dust particles to the atmosphere. However, the highly toxic nature of the borane fuels poses a constant threat of environmental pollution wherever they are produced, stored, or used. Recognition of this hazard has resulted in strict safety measures which have minimized accidental exposures.

The use of boron additives in petroleum fuels and the presence of boron in coals, possibly contribute quantities of boron to the atmosphere, but no assessment has been made of the amount of these contributions or of their impact

as air pollutants.

Data are not available on the concentration of boron or its compounds in the atmosphere. This absence of recorded data indicating qualitatively or quantitatively the presence of boron compounds suggests that their presence in the atmosphere may not be fully understood, and the exact nature of boron as an air pollutant may not be fully appreciated. Environmental monitoring of boron concentrations should be considered, particularly near industrial plants engaged in boron production or use and near borane fuel sites.

Normal entrapment and precipitation procedures applicable to most particulate pollutants should be effective in controlling or reducing the amount of boron compound dusts emitted into the atmosphere. No specific methods for abatement of atmospheric borane compounds have been identified, but strict regulatory practices are used to prevent accidental emissions. No information has been found on the economic costs of boron air pollution or on the costs of its abatement.

Methods of analysis are available, but these are not sufficiently sensitive or selective for determining atmospheric concentrations of boron and its compounds.

Based on the material presented in this report, further studies in the following areas are suggested:

(1) Determination of ambient air concentrations of boron compounds, with special emphasis upon localities producing or using the boron hydride fuels. This will involve

the development of better methods of analysis for boron and its compounds than are currently available.

(2) Expansion of research on the characterization and analysis of exhausts from motor vehicles—to include boron along with other fuel additives.

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APPENDIX

Exposure Time	Concentra	tion in Air	
(min)	(ppm)	(µg/m³)	Expected Effects in Humans
5	390	780,000	
15	130	260,000	Convulsions, death
30	65	130,000	
60	30	60,000	
5	200	400,000	
15	65	130,000	Convulsions
30	30	60,000	
60	15	30,000	
5	100	200,000	
15	30	60,000	Some decrement in
30	15	30,000	performance and slight
60	8	16,000	signs of toxicity
5	25	50,000	
15	8	16,000	Emergency exposure limits;
30	4	8,000	some temporary impairment
60_	2	4,000	of judgment

APPENDIX

_				LD _{5 0} _	
Compound	Species	Sex	Route	(hd/dg)	Remarks
Pentaborane	Rat		Intraperitoneal	11,100	Mineral oil solution
Decaboraneb	Mouse	M	Intraperitoneal	33,200	SOLUCION
		M	Oral	(30,500-36,200) 40,900	
	Rat	M	Intraperitoneal	(33,400-50,200)	
		M	Oral	(21,400-25,600) 64,300	
		М	Percutaneous	(57,500-71,800) 740,000 (67,600-80,900)	Decaborane- dioxane - 3 in 1 oil
	Rabbit	М	Percutaneous	71,000 (32,000-155,000)	mixture "
	Dog	F	Intraperitoneal	Up to 25,000	3 of 3 died within 3 da
Boron hydride fuel HEF-2 HEF-3; Hi-Cal 3	Rat Guinea pig Rabbit Rat		Oral Percutaneous Intravenous Percutaneous Intravenous Intraperitoneal Oral Percutaneous	240,000 >3,200,000 7,000 1,000,000-3,200,000 13,000 20,000-71,000 40,000 317,000-502,000	within 3 da.
	Guinea pig		Intraperitoneal Percutaneous	18,000-40,000 160,000 158,000-251,000	
	Rabbit		Intravenous	4,000 - 6,000 6,000	
			Percutaneous	80,000 57,000 - 105,000	
	Cat		Percutaneous	126,000	

(continued

TABLE 2, (Continued)

ACUTE ORAL AND PARENTERAL TOXICITY OF BORANES

				LD_{50}	
Compound	Species	Sex	Route	(µg/q ^a)	Remarks
Dimethyl- amine-					
borane	Rat	M	Intraperitoneal	50,500	
				(45,900-55,600)	
		F		39,000	
				(32,500-46,800)	
		M	Oral	59,200	
				(52,900-66,300)	
	Guinea pig	M	Intraperitoneal	55,900	
				(34,900-89,500)	
	Rabbit	M	Intraperitoneal	35,100	
				(21,900-56,100)	
Trimethyl-	Rat	M	Intraperitoneal	176,000	Dioxane soln
amine - borane				(159,000-193,000)	diluted with water
Pyridine- borane	Rat	M	Intraperitoneal	73,600	No range calculable
		M	Oral	95,400	
				(85,200-107,000)	
	Rat	F	Intraperitoneal	64,800	
			-	(58,900-71,300)	
	Guinea pig	M	Intraperitoneal	54,000	No range
	1 3		_		calculable
		М	Percutaneous	220,000	No range
					calculable
Triethyl-	Rat	M	Intraperitoneal	22,700	12.4% soln
borane			_	(14,700-35,200)	in Nujol
			Oral	235,000	
				(214,000-258,000)	8.9% soln in Nujol

a95% Confidence limits are shown in parentheses.

b_{Agar-saline} suspensions, except as noted.

CDissolved in physiological saline.

 $d_{\mbox{\footnotesize Dissolved}}$ in propylene glycol.

TABLE 3

ACUTE INHALATION TOXICITY OF BORANES

				LC ₅₀	Exposure period	Observation period
Compound	Species	Sex	ppma	µg∕m³	(hours)	(days)
Diborane	Mouse	F	29 (27 - 32)	33,000	4	14
	Rat	M^{b}	40 (35 - 45)	45,000	4	14
		$\mathtt{M}^{\mathtt{C}}$	(33 – 43) 80 (73 – 93)	91,000	4	14
Dimethyl- amine-						
diborane	Mouse	M	63 (55 - 123)	182,000	4	14
	Rat	M	86 (77 - 99)	248,000	4	14
Pentaborane	Mouse	\mathbf{F}	3.4	8,700	4	14
		М	10.9 (10.5- 11.3)	28,000	2	2 hr
	Rat	M	6.0	15,000	4	14
		М	17.8	46,000	2	2 hr
Decaborane	Mouse	М	25.7 (22.8- 28.0)	122,000	4	2
	Rat	M M	46 >95.2 ^d	230,000 >475,000	4 4	14 14
Boron hydride fuel						
HEF-2	Mouse		11		4	
	Rat		12		4	
HEF-3; Hi-Cal 3	Mougo		6		4	
ni-Cai 3	Mouse Rat		23		4	
Triethyl- borane	Rat	М	700 (667 – 735)	2,800,000 (2,670,000- 2,940,000		7

a_{95%} Confidence limits are shown in parentheses.

centration.

b_{Animals 2 months old.}

CAnimals 5 months old.

TABLE 4 $\mbox{ACUTE ORAL AND PARENTERAL TOXICITY OF BORIC ACID^2 }$

Species	Route	Dosage g/kg*	Remarks
Mouse	Oral	>4.1 3.45 ± 0.16	LD ₅₀
	Subcutaneous		LD ₅₀ LD ₅₀
	Subcucaneous	2.07 ± 0.17 1.74 ± 0.13	LD ₅₀ soln adjusted to pH 7.4 with NaOH
	Interperitoneal	0.8	4 or 5 survived 2 wk
	Intravenous	1.78 ± 0.12	$ ext{LD}_{50}$ injected as 2 cc of 5% soln/min
		2.11	LD ₅₀ soln adjusted to pH 6.9 with NaOH
		2.42	L D ₅₀ soln adjusted to pH 7.4 with NaOH
		1.52	LD ₅₀ soln adjusted to pH 8.8 with NaOH
		1.24	LD _{so} soln adjusted to pH 9.4 with NaOH
Rat	Oral	5.14	LD ₅₀ 95% confidence limits 4.74-5.58
		2.66 - 0.22	LD _{5 ○}
	Subcutaneous	1.4	LD _{5 O}
	Intraperitoneal	0.8	5 of 5 survived 2 wk
	Intravenous	1.33 ± 0.11	LD ₅₀ injected as 2 cc of 5% soln/min
Guinea pig	Subcutaneous	1.20 [±] 0.03	LD ₅₀
Rabbit	Oral	4.0	Lethal dose
	Intravenous	0.9	4 of 5 died 1 of 5 died
_		0.8 >1.0	LD _{BO}
Dog	Oral	2.0	3 of 6 died within 43 hr
	Subcutaneous	1.0	2 of 4 died
	Intravenous	0.4	No observed effect

^{*}Value following $LD_{\delta\,0}$ is standard error.

TABLE 5 $\mbox{ACUTE ORAL AND INTRAVENOUS TOXICITY OF SODIUM BORATES} ^2$

Compound	Species	Route	Dosage (q/kg)	Remarks
Borax	Mouse	Oral Intravenous	2.0-3.0 1.32	LD ₅₀ LD ₅₀ injected in 1 sec
Sodium per- borate mono- hydrate	Guinea pig Rat Rabbit	Oral Oral Intravenous	5.33 0.65 0.078	LD ₅₀
-	Cat	Intravenous	0.6-0.9	LD ₅₀ anesthetized animals. 3% soln injected at 1 cc/min
Sodium metaborate	Rabbit	Intravenous	0.3	No toxic effects noted

TABLE 6 ACUTE ORAL TOXICITY AND EYE IRRITATION OF BORATE ESTERS 2

Compound	LD _{5 O} , ml/kg (mouse)	Vehicle ^a	Eye b irritation (rabbit)
Thisthyl bombo			
Friethyl borate	2.1		mild
Fri-n-propyl borate	2.08		mild
Friisopropyl borate	2.5		mild
Fri-n-butyl borate	2.15		moderate
Friisobutyl borate	2.4		mild
Fri-sec-butyl borate	2.1		mild
<pre>Iri(methylisobutylcarbonyl) borate</pre>	1.6		severe
<pre>Tri-n-amyl borate</pre>	1.24		moderate
<pre>Fri-n-hexyl borate</pre>	2.13		moderate
<pre>Fri-n-octyl borate</pre>	1.29		moderate
<pre>Fri(2-octyl) borate</pre>	3.3		mild
<pre>Fri(2-ethylhexyl) borate</pre>	3.3		${\tt mild}$
<pre>Fri-n-dodecyl borate</pre>	1.66		moderate
Trioleyl borate	6.2		mild
<pre>Frihexylene-glycol biborate</pre>	1.72		moderate
<pre>Fri-o-cresyl borate</pre>	0.40		corneal scars
<pre>Fri-o-chlorophenyl borate</pre>	<0.23		corneal scars
Tristeraryl borate	6.2 ^C	aqueous suspension	mild
<pre>Iri(2-cyclohexylcyclohexyl) borate</pre>	2.05 ^C	aqueous suspension	moderate
<pre>Fri(2-phenylcyclohexyl) borate</pre>	3.4 ^C	aqueous suspension	
Triethanolamine borate	6.2 ^C	15% aqueous soln	mild
Trioctyleneglycol borate	5.1°	10% olive-oil solnd	mild
Triphenyl borate	0.2°	5% aqueous soln ^q	corneal scars
Friphenylcyclohexyl borate	$1.\overline{24}^{\text{C}}$	5% olive-oil solnd	severe
<pre>Fri(diisobutylcarbonyl)</pre>	3.7 ^C	5% olive-oil soln ^d 10% olive-oil soln ^d	moderate
borate			
Triisopropanolamine borate	7.2 ^C	10% aqueous soln	mild

aUndiluted liquid administered except as noted. See text for grading of injury. $^{\rm c}_{\rm g/kg}$. Solution warmed to $40^{\rm o}_{\rm C}$.

lompound	Species	Route	Dosage (g/kg)	Remarks
irimathari	Mana	022-1		
!rimethyl borate	Mouse	Oral Intraperitoneal	1.29 ^a 1.0 ^a	LD ₅₀ Approx lethal dose
201400	Rat	Oral	7.91	LD _{s o}
			6.14	LD ₅₀ 95% confidence
				limit $4.97 - 7.95$
			2.8 ^a	Approx lethal dose
	Dabbit	Intraperitoneal	1.6-3.2 ^a	n n n
	Rabbit	Intraperitoneal Percutaneous	1.6-3.2 ^a 1.98	LD ₅₀ 95% confidence
		Percutaneous	1.90	limit 1.47-2.68
!rimeth-	Rat	Oral	5.16	LDs o
oxyboroxin				
Dimethylphos-				
phino borane trimer	Rat	Oral	0.0135	ID 19/ garn-oil
ctimer	Rat	Olai	0.0133	LD ₅₀ 1% corn-oil soln
	Rabbit	Oral	0.04-0.05	MLD ^b 1% corn-oil
				soln
		Percutaneous	0.06-0.8	MLD ^b 10% corn-oil
}enzene−	Mouse	Intraperitoneal	0.56	soln Lethal dose
boronic acid	Rat	Oral	0.74	LD ₅₀ 20% corn-oil
				suspension
	Guinea	Intraperitoneal	0.284	Lethal dose
	pig	0 - 1	0.60-0.65	MLD ^b 25% corn-oil
	Rabbit	Oral	0.60-0.65	suspension
		Percutaneous	4.5-5.0	MLD ^b oily paste
	Dog	Intravenous	0.45	Lethal dose
}-Amino-4-	Mouse	Intravenous	3.29	$\mathtt{L}\mathtt{D}_{\mathtt{50}}$ soln adjusted
carboxyben-			2 06	to pH 8.1
zeneboronic			2.06	LD ₅₀ soln adjusted
acid	Cat	Intravenous or	0.66	to pH 9.5 Tolerated
	C(2 C	intracarotid		
-(2-Carboxy-				
2-acetamido-				
ethyl)-benzene-			F 70	ID 001m 34
boronic acid	Mouse	Intravenous	5.72	LD ₅₀ soln adjusted to pH 7.5
				CO PII / • 3
				(continued)

(continued)

Compounds	Charia	D	Dosage	
Compounds	Species	Route	(g/kg)	Remarks
m-Carboxyben- zeneboronic acid	Mouse	Intravenous	2.56	LD ₅₀ soln adjusted to pH 7.4
<pre>p-Carboxyben- zeneboronic acid</pre>	Mouse	Intravenous	1.74	LD ₅₀ soln adjusted to pH 9.4
m-Ureido- benzene- boronic acid	Mouse	Intravenous	1.02	LD ₅₀ soln adjusted to pH 10.0
2-Acetamido- benzene-1,4- diboronic acid	Mouse	Intravenous	2.54	LD _{so} soln adjusted to pH 10.6
2-Nitrobenzene- l,4-diboronic acid	Mouse	Intravenous	1.68	LD ₅₀ soln adjusted to pH 9.3
p-Borono- phenylalanine	Mouse	Intravenous	1.52	LD _{5 n} soln adjusted to pH 10.0
<pre>m-Borono- succinanilic acid</pre>	Mouse	Intravenous	4.09	LD ₅₀ soln adjusted
B,B',B"-	Cat	Intracarotid	0.86	to pH 7.4 Tolerated
Triallyl-N,N', N"-triphenyl borazine	Mouse	Intraperitoneal	2.50 1.25	<pre>3 of 5 animals died 5 of 5 animals survived</pre>

(continued)

TABLE 7 (Continued) ACUTE TOXICITY OF ORGANOBORON COMPOUNDS 2

Species	Route	Dosage (q/kg)	Remarks
Rat	Oral	5.2	LD _{5 n} death in 2 - 5 days
Rabbit	Oral	7.0-8.0	MLD ^b death in 24-48
	Percutaneous	10	2 of 2 survived 10 days
Dabbis	Dawantanaona	0.00	2 of 3 animals died
Kappic	Percutaneous	0.62	z or 3 animars died
Rabbit	Percutaneous	1.75	All 3 animals survived
	Rat Rabbit Rabbit	Rat Oral Rabbit Oral Percutaneous Rabbit Percutaneous	Rat Oral 5.2 Rabbit Oral 7.0-8.0 Percutaneous 10 Rabbit Percutaneous 0.82

aml/kg. bMinimum lethal dose.

lompound	Species	Air Concentration (ppm)	Exposure Period (hours)	Mortality
3oron trifluoride	Mouse Rat Guinea pig	750 750 750	5.5 5.5 5.5	1/10 1/10 10/10
<pre>3oron trifluoride- dimethyl ether</pre> <pre>3oron trichloride^b</pre>	Mouse Rat Guinea pig Mouse Rat	225 485 50 20 20	14 ^a 14 ^a 3.8 7 7 14 ^a	1/4 1/2 10/10 10/10
Noron trichloride ^C	Guinea pig Mouse Rat Guinea pig	85 50 100 50 100	14 ^a 14 ^a 14 ^a 14 ^a 14 ^a	0/10 0/10 0/15 0/10 10/10

a_{Two} 7-hour daily exposures.

b Cages used continuously for 7 hours.

^CClean cages substituted every 2 hours.

TABLE 9

ACUTE ORAL AND PARENTERAL TOXICITY OF MISCELLANEOUS BORON COMPOUNDS²

Compound	Species	Route	Dosage (µg/kg*)	Remarks
Sodium borohydride	Mouse	Intraperitoneal	<18,000	Approx lethal dose
	Rat	Intraperitoneal	18,000	Approx lethal dose
		Oral	160,000	2 of 5 animals died
	Rabbit	Intraperitoneal	60,000	Approx lethal dose
Potassium borohydride	Rat	Oral	160,000	1 of 5 animals
Potassium fluoroborate	Mouse	Intraperitoneal	590,000 (460,000- 750,000)	LD _{6 0}
	Rat	Intraperitoneal	240,000 (130,000- 460,000)	LD ₅₀
	Rabbit	Intraperitoneal	380,000 (190,000- 780,000)	LD ₅₀
Sodium deca- hydrodecaborate	Mouse	Intravenous	1,040,000	LD _{6 0}

^{*95%} confidence limits are shown in parentheses.

TABLE 10 PROPERTIES, TOXICITY AND USES OF BORON AND SOME BORON COMPOUNDS 24

Compound	Properties, ^O C	Toxicity	Uses
Boric acid	mp 160 ⁰	Ingestion or absorption may cause nausea, vomiting, diarrhea, abdominal cramps, erythematous lesions on skin and mucous membranes, circulatory collapse, tachycardia, cyanosis, delirium, convulsions, coma. Death has been reported from less than 5 g in infants and from 5 to 20 g in adults. Chronic use may cause borism (dry skin, eruptions, gastric disturbances). Caution: several cases of fatal poisoning have occurred following its absorption from granulating wounds and abraded skin areas	For weatherproofing wood and fireproofing fabrics; as a preservative; in manufacture of cements, crockery, porcelain, enamels, glass, borates, leather, carpets, hats, soaps, artificial gems; in nickeling baths, cosmetics, printing and dyeing, painting, photography; for impregnating wicks; in electric condensers; for hardening steel. Med. use: mild topical astringent, antiseptic. Vet. use: in aqueous solution for application to wounds, ulcers, and inflamed mucous membranes, mouth washes, eye and skin lotions. Also as hot fomentations for abscesses and ulcerative skin conditions. Also in dusting powders
Boron B	mp 2150 ⁰	The element itself has low toxicity, but some boron compounds are moderately or highly toxic. See individual compounds	In nuclear chemistry as neutron absorber, in ignition rectifiers, in alloys, usually to harden other metals

Compound	Properties, ^O C	Toxicity	Uses
Boron monoxide (BO) _x	Vaporizes at 1300-1500 ^o in- to gaseous B ₂ O ₂	See Boron	
Boron nitride BN	тр 3000 ⁰		In manufacture of alloys; in semiconductors, nuclear reactors, lubricants
Boron tribromide BBr ₃	mp -45° bp 90°		In manufacture of diborane
Boron trichloride BC1 ₃	bp 12.5 [°] mp -107 [°]		In manufacture and purification of boron, as catalyst for organic reactions, in semiconductors
Boron trifluoride BF3	mp -127.1° bp -101°	May be highly irritating to the eyes, mucous mem-branes	To protect molten magnesium and its alloys from oxidation as a flux for soldering magnesium, as a fumigant, in ionization chambers for the detection of weak neutrons. By far the largest application of boron trifluoride is in catalysis with and without promoting agents

TABLE 10 (Continued)

PROPERTIES, TOXICITY AND USES OF BORON AND SOME BORON COMPOUNDS 24

Compound	Properties, ^O C	Toxicity	Uses
Boron trifluoride etherate (CH ₃ CH ₂) 2 0 · BF ₃	bp 125.70 mp -60.40	On decomposition, forms highly toxic fumes of fluorides	As catalyst in acetylation, alkylation, polymerization, de-hydration, and condensation reactions
Boron anhydride (Boron oxide) B2 ^O 3	тр 577 ⁰		In metallurgy; in analysis of silicates to determine SiO ₂ and alkalies; in blowpipe analysis
Diboron tetrachloride B ₂ Cl ₄	mp -92.6 ⁰	Details unknown. Probably a strong irritant	
Potassium borohydride KBH ₄	Decomposes at ~500°	No specific data. In general, boron hydrides are quite toxic and may cause injury to liver, kidneys, central nervous system	As reducing agent for aldehydes, ketones, and Schiff bases in non-aqueous solvents. Also to reduce acids, esters, acid chlorides, disulfides, nitriles, inorganic anions. Further used to generate diborane, as foaming agent, as scavenger for traces of aldehyde, ketones, and peroxides in organic chemicals
Sodium borohydride NaBH ₄	mp 36-37 ⁰	See note for potassium borohydride	Same as above

TABLE 10 (Continued)

PROPERTIES, TOXICITY AND USES OF BORON AND SOME BORON COMPOUNDS

Compound	Properties, ^O C	Toxicity	Uses
Sodium borate (Borax) ^{Na} 2 ^B 4 ^O 7	mp 75 ⁰	Ingestion of 5 to 10 g by young children may cause severe vomiting, diarrhea, shock, death. Also see boric acid	For soldering metals; in manufacture of glazes and enamels; for tanning; in cleaning compounds; for artificially aging wood; as preservative against wood fungus, either alone or with other antiseptics; for fireproofing fabrics and wood, curing and preserving skins
Decaborane ^B 10 ^H 14	mp 98.8 ⁰ bp 213 ⁰	Dizziness, nausea, vomi- ting, muscular tremors, and evidence of liver injury have been reported in man	In rocket propellants, as cata- lyst in olefin polymerization
Diborane ^B 2 ^H 6	mp -165° bp 92.5°	Inhalation may produce irritation of lungs, pulmonary edema. High exposures produce symptoms resembling metal fume fever. See decaborane	As a catalyst for olefin poly- merization, as rubber vulcani- zer, as reducing agent, as flame-speed accelerator, in rocket propellants, as inter- mediate in preparation of other boron hydrides, in conversion of olefins to trialkylboranes and primary alcohols, as a doping gas

APPENDIX

TABLE 10 (Continued)
PROPERTIES, TOXICITY AND USES OF BORON AND SOME BORON COMPOUNDS 24

Compounds	Properties, ^O C	Toxicity	Uses
Procaine borate ^C 13 ^H 20 ^N 2 ^O 2	mp 165-166 ⁰	Side effects: minimal systemic toxicity. Anaphylactic reactions may occur	Med. use: local anesthetic
Pentaborane ^B 5 ^H 9	mp -46.6 ⁰ bp 48 ⁰	Dizziness, nausea, vomi- ting, muscular tremors, and evidence of liver injury reported in man	In rocket propellants