

Health Hazard Evaluation Report

HETA 85-540-1816
INTERNATIONAL ASSOCIATION
OF FIRE FIGHTERS
WASHINGTON, D.C.

#### PREFACE

The Hazard Evaluations and Technical Assistance Branch of NIOSH conducts field investigations of possible health hazards in the workplace. These investigations are conducted under the authority of Section 20(a)(6) of the Occupational Safety and Health Act of 1970, 29 U.S.C. 669(a)(6) which authorizes the Secretary of Health and Human Services, following a written request from any employer or authorized representative of employees, to determine whether any substance normally found in the place of employment has potentially toxic effects in such concentrations as used or found.

The Hazard Evaluations and Technical Assistance Branch also provides, upon request, medical, nursing, and industrial hygiene technical and consultative assistance (TA) to Federal, state, and local agencies; labor; industry and other groups or individuals to control occupational health hazards and to prevent related trauma and disease.

Mention of company names or products does not constitute endorsement by the National Institute for Occupational Safety and Health.

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INTERNATIONAL ASSOCIATION
OF FIRE FIGHTERS
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#### I. SUMMARY

On September 20, 1985, the National Institute for Occupational Safety and Health (NIOSH) received a request for technical assistance from the International Association of Fire Fighters (IAFF), Health and Safety Department, Washington, D.C., to assess the toxicity of Chimfex, a commercially available chimney fire extinguishing product.

Area air sampling was performed in a simulated "worse case" situation (minimal ventilation and no containment once the Chimfex fire extinguishing product was ignited) using a fire fighter training facility located in Cincinnati, Ohio. Contaminants measured in area air samples included total zinc (Zn), zinc oxide (ZnO), sulfur dioxide (SO2), and barium oxide (BaO). The concentrations of zinc oxide fume obtained from two tests ranged from 6.4 to 48 milligrams per cubic meter (mg/m3), levels exceeding the NIOSH recommended 15 minute ceiling limit for ZnO of 15 mg/m3. The Occupational Safety and Health Administration (OSHA) Permissible Exposure Limit (PEL) and the American Conference of Governmental Industrial Hygienists (ACGIH) Threshold Limit Value (TLV) for ZnO is 5.0 mg/m3 for an 8-hour time weighted average (TWA). Because the brief (4 minute) burn time of each Chimfex resulted in test periods of 11 and 22 minutes, the NIOSH recommended ceiling limit was selected for evaluating the sample results.

Cadmium, unexpectedly found in three of four area air samples, ranged from 0.01 to 0.02 mg/m³ (concentrations calculated over respective sampling period). These levels were below the OSHA 15-minute ceiling limit of 0.3 mg/m³ and the ACGIH TLV-ceiling level of 0.05 mg/m³. These levels, however, were selected by OSHA and the ACGIH to prevent such critical health effects as chronic renal damage and acute pulmonary toxicity and may not provide adequate protection from potential carcinogenic effects. NIOSH recommends that cadmium and its compounds be regarded as potential occupational carcinogens, that exposures be minimized, and that appropriate controls be used to reduce exposure.

Sample results for  $SO_2$  and BaO were below applicable OSHA PELs and ACGIH and NIOSH recommended exposure limits.

Direct-reading colormetric detector tubes were used to measure concentrations of  ${\rm CO_2}$ ,  ${\rm NO_X}$  and  ${\rm SO_2}$  during each of the tests. The concentrations of these substances were also below applicable OSHA PEL's and ACGIH and NIOSH recommended limits.

Based on these results, it has been determined that a potential health hazard from airborne exposure to zinc oxide fume may exist among users of the Chimfex fire extinguishing product if used in poorly ventilated and/or confined spaces. Recommendations for product labeling changes and respiratory protection are included in Section VIII of this report.

Key Words: SIC 2899 (Chemicals and chemical preparations), fire extinguishing, Chimfex, zinc oxide, sulfur dioxide, barium oxide, cadmium oxide, carbon dioxide, oxides of nitrogen, respiratory protection.

# II. INTRODUCTION

On September 20, 1985, the National Institute for Occupational Safety and Health (NIOSH) received a request for technical assistance from the International Association of Fire Fighters (IAFF), Health and Safety Department, Washington, D.C., to assess the toxicity of Chimfex, a commercially available chimney fire extinguishing product manufactured by the Standard Fusee Corporation, P.O. Box 178, Boonton, New Jersey 07005.

The IAFF request was also accompanied by product information (furnished by the manufacturer) stating that the principal gases generated from the combustion of Chimfex may include  $\mathrm{SO}_2$ , sublimed sulfur, and nitrogen. According to the manufacturer, the fine solids, also dispersed in the smoke, include: ZnO fume, potassium sulfate, potassium sulfide, barium sulfate, and BaO. Small quantities of nitrogen oxides ( $\mathrm{NO}_{\mathrm{X}}$ ) and  $\mathrm{CO}_2$  may also be produced.

# III. BACKGROUND

NIOSH obtained approval from the Cincinnati Fire Department to use their training facility (a two-story brick structure referred to as the "burn house") to test two Chimfex extinguishers on December 12, 1985. The test site, an approximately 1000 square foot unheated room with an eight foot ceiling and two access doors, had a ceiling mounted passive vent which provided natural draft ventilation with the doors closed.

The area samples were positioned 4 to 5 feet from the burning Chimfex product and suspended from the floor at breathing zone height (5 feet). Two Chimfex fire extinguishers were ignited, one at a time, and area air samples were collected. Since the room received minimal ventilation during the tests, this study may be viewed as representing a worse case situation where Chimfex emissions are not confined to either a fireplace or woodstove. The burn time for each Chimfex extinguisher was approximately 4 minutes. Sampling periods for the two tests were 11 and 22 minutes.

# IV. EVALUATION DESIGN

Trace metals were collected on 37 millimeter (mm), 0.8 micron (u) pore size mixed cellulose ester filters attached, by flexible tubing, to battery operated sampling pumps calibrated at 2.0 liters per minute (lpm). Analysis was performed using inductively coupled plasma/atomic absorption spectrophotometry (ICP/AAS) according to NIOSH Method No. 7300. The limit of quantitation ((LOQ) for this sample set was 1.0 microgram (ug) per sample filter. While total Zn is quantitatively determined by this method, its physical form (i.e. elemental Zn, ZnO fume, etc.) is not identifiable.

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To identify ZnO specifically, additional area air samples were collected on 0.8 u polyvinyl chloride filters and analyzed qualitatively by x-ray powder diffraction according to NIOSH Method No. 7502. This method was used to ascertain the physical form of Zn present in the Chimfex decomposition products. It was assumed that Chimfex, once ignited, generated freshly formed ZnO fume.

Area air samples measuring sulfur dioxide (SO<sub>2</sub>) were collected according to NIOSH Method P&CAM 268 using a mixed cellulose ester filter followed by a cellulose filter impregnated with potassium hydroxide. Using battery operated sampling pumps calibrated at 2.0 LPM, these samples were positioned adjacent to the trace metal filters. Analysis was by ion chromotography and the limits of detection (LODs) for this sample set were 2ug per sample (for sulfite ions) and 4 ug per sample (sulfate ions), respectively.

Direct-reading colormetric detector tubes were used to measure concentrations of  ${\rm CO_2}$ ,  ${\rm NO_X}$  and  ${\rm SO_2}$  inside the test room during each test. The detector tube samples were taken adjacent to the air samples described in the preceding paragraphs.

# V. EVALUATION CRITERIA

As a guide to the evaluation of the hazards posed by workplace exposures, NIOSH field staff employ environmental evaluation criteria for assessment of a number of chemical and physical agents. These criteria are intended to suggest levels of exposure to which most workers may be exposed up to 10 hours per day, 40 hours per week for a working lifetime without experiencing adverse health effects. It is, however, important to note that not all workers will be protected from adverse health effects if their exposures are maintained below these levels. A small percentage may experience adverse health effects because of individual susceptibility, a pre-existing medical condition, and/or a hypersensitivity (allergy).

In addition, some hazardous substances may act in combination with other workplace exposures, the general environment, or with medications or personal habits of the worker to produce health effects even if the occupational exposures are controlled at the level set by the evaluation criterion. These combined effects are often not considered in the evaluation criteria. Also, some substances are absorbed by direct contact with the skin and mucous membranes, and thus potentially increase the overall exposure. Finally, evaluation criteria may change over the years as new information on the toxic effects of an agent become available.

The primary sources of environmental evaluation criteria for the workplace are: 1) NIOSH Criteria Documents and recommendations, 2) the American Conference of Governmental Industrial Hygienists' (ACGIH) Threshold Limit Values (TLV's), and 3) the U.S. Department of Labor (OSHA) occupational health standards. Often, the NIOSH recommended exposure limits (RELS) and ACGIH TLV's are lower than the corresponding OSHA standards. Both NIOSH RELS and ACGIH TLV's usually are based on more recent information than are the OSHA standards. The OSHA standards also may be required to take into account the feasibility of controlling exposures in various industries where the agents are used; the NIOSH RELS, by contrast, are based primarily on concerns relating to the prevention of occupational disease. In evaluating the exposure levels and the recommendations for reducing these levels found in this report, it should be noted that industry is legally required to meet those levels specified by an OSHA standard.

A time-weighted average (TWA) exposure refers to the average airborne concentration of a substance during a normal 8- to 10-hour workday. Some substances have recommended short-term exposure limits or ceiling values which are intended to supplement the TWA where there are recognized toxic effects from high short-term exposures.

No environmental exposure criteria exist specifically for Chimfex. The toxicities of individual chemical components contained in Chimfex are discussed below.

#### Zinc Oxide

Inhalation of freshly formed ZnO fume causes an influenza-like illness termed metal fume fever. 1-4 Symptoms, which appear several hours following exposure, include chills, lassitude, malaise, frontal headache, low-back pain, muscle cramps, and vomiting. 2 Irritation of the nasal passages, coughing, and fever was observed in subjects exposed to a test concentration of 600 milligrams per cubic meter (mg/m<sup>3</sup>) of ZnO fume. 3 Chills have been reported in workers from exposure to concentrations of ZnO fume below 5.0 mg/m<sup>3</sup>. 4

NIOSH recommends a 15-minute ceiling exposure limit for ZnO of 15 mg/m<sup>3</sup> in addition to an 8-hour TWA of 5.0 mg/m<sup>3</sup>. Both the OSHA PEL and the ACGIH TLV are set at 5.0 mg/m<sup>3</sup> for an 8-hour TWA.<sup>5</sup>, 6 Since the sampling periods used in this evaluation were brief (11 and 22 minutes), the NIOSH REL was selected for evaluating the ZnO sample results.

#### Cadmium

Cadmium is a toxic heavy metal which may enter the body either by ingestion or by inhalation of Cd metal or oxide. Once absorbed into the body, Cd accumulates in organs throughout the body, but major depositions occur in the liver and kidneys. Acute inhalation exposure to high levels of Cd can cause pneumonia or pulmonary edema, as well as liver and kidney damage. Chronic exposure may lead to emphysema of the lungs and kidney disease.

A recent epidemiological study has demonstrated a statistically significant excess of lung cancer mortality among workers exposed to CdO. 10 A chronic inhalation exposure study with rats has provided toxicological evidence that exposure to cadmium chloride aerosol can cause a dose-dependent incidence of malignant lung tumors. Based on these data, NIOSH recommends that Cd and its compounds be regarded as potential occupational carcinogens, that exposures be minimized and that appropriate controls be used to reduce worker exposure. 10

#### Barium Oxide

An odorless white solid, BaO can cause local irritation of the eyes, nose, throat, bronchial tubes, and skin. 11 More soluble forms of Ba, such as the oxide, carbonate, and nitrate, tend to be more injurious, particularly acutely. Heavy industrial exposures to dusts of BaO may produce a benign pneumoconiosis termed baritosis. Barium oxide is strongly alkaline in aqueous (water) solution and can cause severe burns of the eyes and irritation of the skin. 11

The OSHA PEL for barium is  $0.5 \text{ mg/m}^3$  for an 8-hour TWA, the same as the ACGIH TLV-TWA. 5,6 There is currently no NIOSH REL for this compound.

#### VI. RESULTS AND DISCUSSION.

#### A. Environmental

Concentrations of ZnO fume ranged from 6.4 to 48 mg/m³ in the two tests conducted on December 12, 1985. These levels exceed the NIOSH 15-minute REL of 15 mg/m³. The OSHA PEL and ACGIH TLV for ZnO is 5.0 mg/m³, 8-hour TWA. $^{5,6}$  Because the short (4 minute) burn time of each Chimfex resulted in test periods of 11 and 22 minutes, the NIOSH REL was selected for evaluating the sample results. Results of the trace metal analyses (for ZnO, Cd, and Ba) are shown in Table I.

Cadmium, unexpectedly found in three of four area air samples, ranged from 0.01 to 0.02 mg/m³ (concentration over respective sampling period). Because of its low boiling point (767°C) cadmium may, during the burning of a Chimfex extinguisher, volatilize and then condense to form fine airborne particles that react with oxygen to form respirable CdO fume.¹² The concentrations of CdO measured in this study were below the OSHA 15-minute ceiling standard of 0.3 mg/m³ and the ACGIH 15-minute TLV of 0.05 mg/m³. These levels, however, were selected to prevent such critical health effects as chronic renal damage and acute pulmonary toxicity and may not provide adequate protection from potential carcinogenic effects.

Area air samples for barium revealed concentrations ranging from 0.08 to 1.7 mg/m³ (concentrations calculated over respective sampling periods of either 11 or 20 minutes). Assuming no exposure to barium over the remaining 8-hour period (burn time of the Chimfex extinguisher averaged 4 minutes) the concentrations are well below the 8-hour TWA of 0.5 mg/m³ used by both OSHA and ACGIH.5,6 There is currently no NIOSH REL for barium.

Area air samples for  $SO_2$  revealed concentrations ranging from 0.39 to 0.63 mg/m<sup>3</sup>. These levels are below the NIOSH REL for  $SO_2$  of 0.5 ppm for up to a ten-hour exposure. Sulfur dioxide concentrations are presented in Table II

Detector tubes for  ${\rm CO_2}$ ,  ${\rm NO_X}$ , and  ${\rm SO_2}$  measured concentrations of these substances below their applicable OSHA PEL's and ACGIH and NIOSH recommended limits. Results of detector tube measurements are presented in Table III.

#### VII. CONCLUSIONS

Based on these sample results, ZnO fume concentrations, exceeding the NIOSH recommended 15-minute ceiling limit, may be generated when this product is used. The ZnO fume levels measured in this study are sufficient to induce zinc fume fever, muscle pain, frontal headache, blurred vision, dyspnea, and dryness of the throat. In addition, ZnO fume exposure may inflame the upper respiratory tract. 11,14

#### VIII. RECOMMENDATIONS

 A statement warning of the principal decomposition products and their corresponding health effects, especially ZnO and CdO fume, should be placed both on the container and the extinguisher device. Since the completion of Interim Report No. 1, HETA 85-540, April 30, 1986, the Standard Fusee Corporation revised their warning label on packages of Chimfex. The new label now states that zinc oxide fumes are generated and that contact with this material should be avoided. The revised warning statement label further states that the user should leave confined areas where the product is being used or use a self-contained breathing apparatus (SCBA).

- 2. Zinc oxide fume in excess of the NIOSH recommended 15 minute ceiling limit may be generated in poorly ventilated situations. In addition, CdO, a potential human carcinogen, was detected in samples collected in this investigation. Considering the numerous variables which may be encountered in using this product (i.e. condition of fireplace or woodstove; size of the room; the presence or absence of fireplace doors; etc.) the use of a NIOSH/Mine Safety and Health Administration approved SCBA with a full facepiece (operated in a pressure demand or other positive pressure mode), may be warranted when using this product. Respiratory protection is recommended whenever this product is used in poorly ventilated areas or confined space situations. As described above, the revised label on packages of Chimfex now recommend the use of SCBA when this product is used in confined areas.
- 3. It is recommended that the new label for Chimfex indicate the ingredients in addition to the ZnO fume (particularly the CdO fume) and their possible health consequences from inadvertent exposure from using this product.

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# XI. DISTRIBUTION AND AVAILABILITY OF REPORT

Copies of this report are currently available upon request from NIOSH, Division of Standards Development and Technology Transfer, Publications Dissemination Section, 4676 Columbia Parkway, Cincinnati, Ohio 45226. After 90 days, the report will be available through the National Technical Information Service (NTIS), 5285 Port Royal, Springfield, Virginia 22161. Information regarding its availability through NTIS can be obtained from NIOSH Publications Office at the Cincinnati address. Copies of this report have been sent to:

- Standard Fusee Corporation
- 2. International Association of Firefighters, Washington, D.C.
- 3. NIOSH, Boston Region
- 4. OSHA, Region V

For the purpose of informing affected employees, copies of this report shall be posted by the employer in a prominent place accessible to the employees for a period of 30 calendar days.

TABLE I

Area Air Samples for Trace Metals

Chimfex Fire Extinguisher
Test Location: Cincinnati Fire College Training Center
Cincinnati, Ohio
HETA 85-540

December 12, 1985

	TIME		CONCENTRATION, mg/m3a		
SAMPLE No.		VOLUME (liters)	ZnO Fume	Ba	CdO Fume
D-1	1417-1428	22	6.4	0.08	<0.0001
D-2	1417-1428	22	36.0	0.67	0.01
D-3	1445-1505	40	12.0	0.34	0.01
D-4	1445-1505	40	48.0	1.7	0.02
Evaluation Cr OSHA ACGIH NIOSH	iteria:		5.0b 5.0b 15.0c	0.5 <sup>b</sup> 0.5 <sup>b</sup>	0.3 <sup>c</sup> 0.05 <sup>c</sup> d

<sup>(</sup>a) Milligrams per cubic meter

<sup>(</sup>b) 8-hour time weighted average

<sup>(</sup>c) 15-minute ceiling limit

<sup>(</sup>d) NIOSH recommends that levels be minimized and exposure kept as low as possible

# TABLE II

# Area Air Samples for SO2

# Chimfex Fire Extinguisher Test Location: Cincinnati Fire College Training Center Cincinnati, Ohio HETA 85-540

# December 12, 1985

SAMPLE NO.	TIME	VOLUME(liters)	CONCENTRATION mg/m3a	
A-2	1417-1428	22	0.63	
A-4	1445-1505	40	0.39	
B-2	1417-1428	22	0.48	
B-4	1445-1505	40	0.40	
Evaluation Cri	teria:		13 <sup>b</sup>	
ACGIH		13 <sup>c</sup>		
NIOSH			1.3 <sup>d</sup>	

<sup>(</sup>a) Milligrams per cubic meter

<sup>(</sup>b) 8-hour time weighted average

<sup>(</sup>c) Short-term exposure limit (STEL) - Maximum concentration to which workers can be exposed for a period up to 15 minutes.

<sup>(</sup>d) Up to a 10-hour time weighted average

#### TABLE III

# Detector Tube Measurements

# Chimfex Fire Extinguisher Test Location: Cincinnati Fire College Training Center Cincinnati, Ohio HETA 85-540

December 12, 1985

		CONCE	TRATION, pp	<u>a</u>	
TEST No.	TIME PERIOD	CO <sub>2</sub>	NO <sub>2</sub>	so <sub>2</sub>	
1	1417-1428	1,000	2	<1	
2	1445-1505	1,000	1	1	
Evaluation Cr	iteria:				
OSHA		5,000b	5 C	5b	
ACGIHd		15,000	5	5	
NIOSH		30,000e	1c	0.5b	

<sup>(</sup>a) Parts per million

<sup>(</sup>b) 8-hour time weighted average

<sup>(</sup>c) Nitrogen dioxide ( $NO_2$ ), 15 minute ceiling limit (d) Short-term exposure limit (STEL) - Maximum concentration to which workers can be exposed for a period up to 15 minutes.

<sup>(</sup>e) 10-minute ceiling limit

# DEPARTMENT OF HEALTH AND HUMAN SERVICES PUBLIC HEALTH SERVICE CENTERS FOR DISEASE CONTROL NATIONAL INSTITUTE FOR OCCUPATIONAL SAFETY AND HEALTH

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