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October 15, 1992

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Office of Pollution Prevention and Toxics  
Environmental Protection Agency  
401 M Street., S.W.  
Washington, D.C. 20460  
Attn: Section 8(e) Coordinator (CAP Agreement)

Dear Coordinator:

8ECAP-0025

On behalf of the Regulatee and pursuant to Unit II B.1.b. and Unit II C of the 6/28/91 CAP Agreement, E.I. Du Pont de Nemours and Co. hereby submits (*in triplicate*) the attached studies. Submission of this information is voluntary and is occasioned by unilateral changes in EPA's standard as to what EPA now considers as reportable information. Regulatee's submission of information is made solely in response to the new EPA §8(e) reporting standards and is not an admission: (1) of TSCA violation or liability; (2) that Regulatee's activities with the study compounds reasonably support a conclusion of substantial health or environmental risk or (3) that the studies themselves reasonably support a conclusion of substantial health or environmental risk.

The "Reporting Guide" creates new TSCA 8(e) reporting criteria which were not previously announced by EPA in its 1978 Statement of Interpretation and Enforcement Policy, 43 Fed Reg 11110 (March 16, 1978). The "Reporting Guide states criteria which expands upon and conflicts with the 1978 Statement of Interpretation. Absent amendment of the Statement of Interpretation, the informal issuance of the "Reporting Guide" raises significant due processes issues and clouds the appropriate reporting standard by which regulated persons can assure TSCA Section 8(e) compliance.

For Regulatee,

Mark H. Christman  
Counsel  
Legal D-7158  
1007 Market Street  
Wilmington, DE 19898  
(302) 774-6443

mm  
3/9/95

**ATTACHMENT 1**

Submission of information is made under the 6/28/91 CAP Agreement, Unit II. This submission is made voluntarily and is occasioned by recent changes in EPA's TSCA §8(e) reporting standard; such changes made, for the first time in 1991 and 1992 without prior notice and in violation of Regulatee's constitutional due process rights. Regulatee's submission of information under this changed standard is not a waiver of its due process rights; an admission of TSCA violation or liability, or an admission that Regulatee's activities with the study compounds reasonably support a conclusion of substantial risk to health or to the environment. Regulatee has historically relied in good faith upon the 1978 Statement of Interpretation and Enforcement Policy criteria for determining whether study information is reportable under TSCA §8(e), 43 Fed Reg 11110 (March 16, 1978). EPA has not, to date, amended this Statement of Interpretation.

After CAP registration, EPA provided the Regulatee the June 1, 1991 "TSCA Section 8(e) Reporting Guide". This "Guide" has been further amended by EPA, EPA letter, April 10, 1992. EPA has not indicated that the "Reporting Guide" or the April 1992 amendment supersedes the 1978 Statement of Interpretation. The "Reporting Guide" and April 1992 amendment substantively lowers the Statement of Interpretation's TSCA §8(e) reporting standard<sup>2</sup>. This is particularly troublesome as the "Reporting Guide" states criteria, applied retroactively, which expands upon and conflicts with the Statement of Interpretation.<sup>3</sup> Absent amendment of the Statement of Interpretation, the informal issuance of the "Reporting Guide" and the April 1992 amendment clouds the appropriate standard by which regulated persons must assess information for purposes of TSCA §8(e).

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<sup>2</sup>In sharp contrast to the Agency's 1977 and 1978 actions to soliciting public comment on the proposed and final §8(e) Policy, EPA has unilaterally pronounced §8(e) substantive reporting criteria in the 1991 Section 8(e) Guide without public notice and comment. See 42 Fed Reg 45362 (9/9/77), "Notification of Substantial Risk under Section 8(e): Proposed Guidance".

<sup>3</sup>A comparison of the 1978 Statement of Interpretation and the 1992 "Reporting Guide" is appended.

Throughout the CAP, EPA has mischaracterized the 1991 guidance as reflecting "longstanding" EPA policy concerning the standards by which toxicity information should be reviewed for purposes of §8(e) compliance. Regulatee recognizes that experience with the 1978 Statement of Interpretation may cause a review of its criteri. Regulatee supports and has no objection to the Agency's amending reporting criteria *provided that* such amendment is not applied to the regulated community in an unfair way. However, with the unilateral announcement of the CAP under the auspices of an OCM enforcement proceeding, EPA has wrought a terrific unfairness since much of the criteria EPA has espoused in the June 1991 Reporting Guide and in the Agency's April 2, 1992 amendment is new criteria which does not exist in the 1978 Statement of Interpretation and Enforcement Policy.

The following examples of new criteria contained in the "Reporting Guide" that is not contained in the Statement of Interpretation follow:

- o even though EPA expressly disclaims each "status report" as being preliminary evaluations that should not be regarded as final EPA policy or intent<sup>4</sup>, the "Reporting Guide" gives the "status reports" great weight as "sound and adequate basis" from which to determine mandatory reporting obligations. ("Guide" at page 20).
- o the "Reporting Guide" contains a matrix that establishes new numerical reporting "cutoff" concentrations for acute lethality information ("Guide" at p. 31). Neither this matrix nor the cutoff values therein are contained in the Statement of Interpretation. The regulated community was not made aware of these cutoff values prior to issuance of the "Reporting Guide" in June, 1991.
- o the "Reporting Guide" states new specific definitional criteria with which the Agency, for the first time, defines as 'distinguishable neurotoxicological effects'; such criteria/guidance not expressed in the 1978 Statement of Interpretation.<sup>5</sup>
- o the "Reporting Guide" provides new review/ reporting criteria for irritation and sensitization studies; such criteria not previously found in the 1978 Statement of Interpretation/Enforcement Policy.
- o the "Reporting Guide" publicizes certain EPA Q/A criteria issued to the Monsanto Co. in 1989 which are not in the Statement of Interpretation; have never been published in the Federal Register or distributed by the EPA to the Regulatee. Such Q/A establishes new reporting criteria not previously found in the 1978 Statement of Interpretation/Enforcement Policy.

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<sup>4</sup>The 'status reports' address the significance, if any, of particular information reported to the Agency, rather than stating EPA's interpretation of §8(e) reporting criteria. In the infrequent instances in which the status reports contain discussion of reportability, the analysis is invariably quite limited, without substantial supporting scientific or legal rationale.

<sup>5</sup> See, e.g., 10/2/91 letter from Du Pont to EPA regarding the definition of 'serious and prolonged effects' as this term may relate to transient anesthetic effects observed at lethal levels; 10/1/91 letter from the American Petroleum Institute to EPA regarding clarification of the Reporting Guide criteria.

In discharging its responsibilities, an administrative agency must give the regulated community fair and adequate warning to as what constitutes noncompliance for which penalties may be assessed.

Among the myriad applications of the due process clause is the fundamental principle that statutes and regulations which purport to govern conduct must give an adequate warning of what they command or forbid.... Even a regulation which governs purely economic or commercial activities, if its violation can engender penalties, must be so framed as to provide a constitutionally adequate warning to those whose activities are governed.

Diebold, Inc. v. Marshall, 585 F.2d 1327, 1335-36 (D.C. Cir. 1978). See also, Rollins Environmental Services (NJ) Inc. v. U.S. Environmental Protection Agency, 937 F. 2d 649 (D.C. Cir. 1991).

While neither the are rules, This principle has been applied to hold that agency 'clarification', such as the Statement of Interpretation, the "Reporting Guide" nor the April 1992 amendments will not applied retroactively.

...a federal court will not retroactively apply an unforeseeable interpretation of an administrative regulation to the detriment of a regulated party on the theory that the post hoc interpretation asserted by the Agency is generally consistent with the policies underlying the Agency's regulatory program, when the semantic meaning of the regulations, as previously drafted and construed by the appropriate agency, does not support the interpretation which that agency urges upon the court.

Standard Oil Co. v. Federal Energy Administration, 453 F. Supp. 203, 240 (N.D. Ohio 1978), aff'd sub nom. Standard Oil Co. v. Department of Energy, 596 F.2d 1029 (Em. App. 1978):

The 1978 Statement of Interpretation does not provide adequate notice of, and indeed conflicts with, the Agency's current position at §8(e) requires reporting of all 'positive' toxicological findings without regard to an assessment of their relevance to human health. In accordance with the statute, EPA's 1978 Statement of Interpretation requires the regulated community to use scientific judgment to evaluate the significance of toxicological findings and to determining whether they reasonably support a conclusion of a substantial risk. Part V of the Statement of Interpretation urges persons to consider "the fact or probability" of an effect's occurrence. Similarly, the 1978 Statement of Interpretation stresses that an animal study is reportable only when "it contains reliable evidence ascribing the effect to the chemical." 43 Fed Reg. at 11112. Moreover, EPA's Statement of Interpretation defines the substantiality of risk as a function of both the seriousness of the effect and the probability of its occurrence. 43 Fed Reg 11110 (1978). Earlier Agency interpretation also emphasized the "substantial" nature of a §8(e) determination. See 42 Fed Reg 45362, 45363

(1977). [Section 8(e) findings require "extraordinary exposure to a chemical substance...which critically imperil human health or the environment"].

The recently issued "Reporting Guide" and April 1992 Amendment guidance requires reporting beyond and inconsistent with that required by the Statement of Interpretation. Given the statute and the Statement of Interpretation's explicit focus on substantial human or environmental risk, whether a substance poses a "substantial risk" of injury requires the application of scientific judgment to the available data on a case-by-case basis.

If an overall weight-of-evidence analysis indicates that this classification is unwarranted, reporting should be unnecessary under §8(e) because the available data will not "reasonably support the conclusion" that the chemical presents a substantial risk of serious adverse consequences to human health.

Neither the legislative history of §8(e) nor the plain meaning of the statute support EPA's recent lowering of the reporting threshold that TSCA §8(e) was intended to be a sweeping information gathering mechanism. In introducing the new version of the toxic substances legislation, Representative Eckhart included for the record discussion of the specific changes from the version of H. R. 10318 reported by the Consumer Protection and Finance Subcommittee in December 1975. One of these changes was to modify the standard for reporting under §8(e). The standard in the House version was changed from "causes or contributes to an unreasonable risk" to "causes or significantly contributes to a substantial risk". This particular change was one of several made in TSCA §8 to avoid placing an undue burden on the regulated community. The final changes to focus the scope of Section 8(e) were made in the version reported by the Conference Committee.

The word "substantial" means "considerable in importance, value, degree, amount or extent". Therefore, as generally understood, a "substantial risk" is one which will affect a considerable number of people or portion of the environment, will cause serious injury and is based on reasonably sound scientific analysis or data. Support for the interpretation can be found in a similar provision in the Consumer Product Safety Act. Section 15 of the CPSA defines a "substantial product hazard" to be:

"a product defect which because of the pattern of defect, the number of defective products distributed in commerce, the severity of the risk, or otherwise, creates a substantial risk of injury to the public."

Similarly, EPA has interpreted the word 'substantial' as a quantitative measurement. Thus, a 'substantial risk' is a risk that can be quantified, *See*, 56 Fed Reg 32292, 32297 (7/15/91). Finally, since information pertinent to the exposure of humans or the environment to chemical substances or mixtures may be obtained by EPA through Sections 8(a) and 8(d) regardless of the degree of potential risk, §8(e) has specialized function. Consequently, information subject to §8(e) reporting should be of a type which would lead a reasonable man to conclude that some type action was required immediately to prevent injury to health or the environment.

## Attachment

**Comparison:**

Reporting triggers found in the 1978 "Statement of Interpretation/ Enforcement Policy", 43 Fed Reg 11110 (3/16/78) and the June 1991 *Section 8(e) Guide*.

<b>TEST TYPE</b>	<b>1978 POLICY CRITERIA EXIST?</b>	<b>New 1991 GUIDE CRITERIA EXIST?</b>
<b>ACUTE LETHALITY</b>		
Oral	N}	Y}
Dermal	N}	Y}
Inhalation (Vapors)	} <sup>6</sup>	} <sup>7</sup>
aerosol	N}	Y}
dusts/ particles	N}	Y}
<b>SKIN IRRITATION</b>	N	Y <sup>8</sup>
<b>SKIN SENSITIZATION (ANIMALS)</b>	N	Y <sup>9</sup>
<b>EYE IRRITATION</b>	N	Y <sup>10</sup>
<b>SUBCHRONIC (ORAL/DERMAL/INHALATION)</b>	N	Y <sup>11</sup>
<b>REPRODUCTION STUDY</b>	N	Y <sup>12</sup>
<b>DEVELOPMENTAL TOX</b>	Y <sup>13</sup>	Y <sup>14</sup>

<sup>6</sup>43 Fed Reg at 11114, comment 14:

"This policy statements directs the reporting of specific effects when unknown to the Administrator. Many routine tests are based on a knowledge of toxicity associated with a chemical. Unknown effects occurring during such a range test may have to be reported if they are those of concern to the Agency and if the information meets the criteria set forth in Parts V and VII."

<sup>7</sup>Guide at pp.22, 29-31.

<sup>8</sup>Guide at pp-34-36.

<sup>9</sup>Guide at pp-34-36.

<sup>10</sup>Guide at pp-34-36.

<sup>11</sup>Guide at pp-22; 36-37.

<sup>12</sup>Guide at pp-22

<sup>13</sup>43 Fed Reg at 11112

"Birth Defects" listed.

<sup>14</sup>Guide at pp-22

NEUROTOXICITY	N	Y <sup>15</sup>
CARCINOGENICITY	Y <sup>16</sup>	Y <sup>17</sup>
MUTAGENICITY		
<i>In Vitro</i>	Y <sup>18</sup>	Y <sup>19</sup>
<i>In Vivo</i>	Y}	Y}
ENVIRONMENTAL		
Bioaccumulation	Y}	N
Bioconcentration	Y} <sup>20</sup>	N
Oct/water Part. Coeff.	Y}	N
Acute Fish	N	N
Acute Daphnia	N	N
Subchronic Fish	N	N
Subchronic Daphnia	N	N
Chronic Fish	N	N
AVIAN		
Acute	N	N
Reproductive	N	N
Reprodcutive	N	N

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<sup>15</sup>Guide at pp-23; 33-34.

<sup>16</sup>43 Fed Reg at 11112  
"Cancer" listed

<sup>17</sup>Guide at pp-21.

<sup>18</sup>43 Fed Reg at 11112; 11115 at Comment 15

"Mutagenicity" listed/ *in vivo* vs *invitro* discussed; discussion of "Ames test".

<sup>19</sup>Guide at pp-23.

<sup>20</sup>43 Fed Reg at 11112; 11115 at Comment 16.

**CAS#:** 75-63-8; 1511-62-2

**Chem:** Trifluorobromomethane; Difluorobromomethane

**Title:** An investigation of the Toxicity of Proposed Fire Extinguishing  
Fluids

**Date:** 10/50

**Summary of effects:** Summary of narcosis findings in the chemicals  
tested/ reviewed.

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CHEMICAL CORPS  
MEDICAL DIVISION  
ARMY CHEMICAL CENTER  
MARYLAND

CMLEN-52

Medical Division Research Report No. 23

AN INVESTIGATION OF THE TOXICITY OF PROPOSED FIRE EXTINGUISHING FLUIDS

Part I - Summary

by

William H. Chambers

Eugene H. Krackow

Part II - The Approximate Lethal Concentration to Rats  
by Inhalation of Vapors for 15 Minutes

by

Charles C. Comstock

Francis P. McGrath

Stanley B. Goldberg

Lorraine H. Lawson

Part III - The Pathology in Rats Produced by Inhalation  
of Vapors of Proposed Fire Extinguishing Compounds

by

J. K. MacNamee

October 1950

Publication Control No. 5030-23

LABORATORIES  
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*PART I - SUMMARY*

## AN INVESTIGATION OF THE TOXICITY OF PROPOSED FIRE EXTINGUISHING FLUIDS

## Part I - Summary

Detailed reports on the screening of ten (10) candidate fire extinguishing compounds and four (4) "comparator" or control compounds compose Parts II and III of this Medical Division Research Report. The "comparator" compounds were carbon tetrachloride ( $\text{CCl}_4$ ), methyl bromide ( $\text{CH}_3\text{Br}$ ), chlorobromomethane ( $\text{CH}_2\text{ClBr}$ ), and carbon dioxide ( $\text{CO}_2$ ). The experimental work consisted of acute toxicity tests by inhalation in rats and a study of the resultant pathological effects upon these rats of the pure vapors and of the combustion products of these compounds from pyrolysis at  $800^\circ\text{C}$ . Observations were also made estimating the time of onset of narcosis in these experiments. Since the animals were exposed in a gas chamber to high concentrations around the lethal dose level, the data on narcosis should be considered as only a rough approximation. After the initial screening data were obtained, it became apparent from several conferences and meetings between representatives of this laboratory, Engineer Research and Development Laboratories of the Corps of Engineers, and the USAF, in which information was exchanged regarding the performance of the various fire extinguishing agents and toxicity, that from the point of view of performance, two compounds are of foremost interest at this time as promising new fire extinguishing agents, namely, trifluorobromomethane ( $\text{CF}_3\text{Br}$ ) and difluorodibromomethane ( $\text{CF}_2\text{Br}_2$ ).

Trifluorobromomethane ( $\text{CF}_3\text{Br}$ )

The undecomposed  $\text{CF}_3\text{Br}$  was among the least toxic of all the compounds included in these tests (Part II, Table 15). The combustion products of  $\text{CF}_3\text{Br}$  from pyrolysis at  $800^\circ\text{C}$ , through an iron pipe were more toxic than the undecomposed vapor, being approximately 1/4 to 1/2 as toxic as pyrolyzed  $\text{CH}_2\text{ClBr}$  and 1/25 to 1/50 as toxic as pyrolyzed  $\text{CCl}_4$ . The vapors from pyrolyzed  $\text{CF}_3\text{Br}$  are roughly of the same order of toxicity as the vapors of undecomposed  $\text{CCl}_4$ , which would indicate that under the conditions of these experiments a 15 min. inhalation of 10,000 - 20,000 ppm approaches a dangerous degree of exposure for man.

Comparative narcotic effects are shown in the accompanying data (Tables A and B, Part I). The figures indicate that in the lethal range of concentration there is little choice among the 4 compounds in respect to the onset of narcosis but in the sublethal ranges,  $\text{CF}_3\text{Br}$  appears to be definitely superior to the other 3 compounds when considered on the basis of mg./liter of vapor.

Pathology on animals exposed to lethal or near lethal concentrations of the pure vapor showed damage involving the respiratory system and typical congestion of liver, spleen, and kidneys, with no cellular changes in the latter three organs. No animals were exposed at low enough concentrations to determine the threshold concentration for the appearance of

pathological changes. There is indication that exposure to lethal concentrations of pyrolyzed vapor will produce severe pulmonary edema and hemorrhage.

The comparative values found in these animal experiments on acute single exposures point to the low order of health hazard from  $CF_3Br$ . There is no indication that respiratory protection against acute exposure is needed by personnel handling  $CF_3Br$  in large quantities. Crash concentrations of  $CF_3Br$  such as may result from the accidental discharge of a fire extinguisher do not appear to offer any practical toxic hazard.

#### Diffluorodibromomethane ( $CF_2Br_2$ )

Diffluorodibromomethane dispersed as the un Decomposed vapor is considerably more toxic than  $CF_3Br$ . Its toxicity is of the same order of magnitude as  $CH_2ClBr$ , but somewhat less toxic than  $CCl_4$ . The vapors decomposed at  $800^\circ C$  appear slightly more toxic than those of pyrolyzed  $CB$  ( $CH_2ClBr$ ) but approximately 1/6 to 1/4 as toxic as the pyrolyzed vapors of  $CCl_4$ .

The data on narcosis (Tables A and B, Part I, and Tables 5 and 6, Part II) indicate that the narcotic effect in the sublethal ranges of  $CF_2Br_2$  is greater than that of  $CF_3Br$  since it appears at a definitely lower concentration.

Pathological studies indicate that single acute exposures to the un Decomposed vapors of the order of 4 000 ppm for 15 mins. can produce significant pulmonary lesions. This is not a threshold concentration, but the lowest one to which animals were exposed in this study. The permissible acute exposure may be considerably lower than 4 000 ppm for 15 mins., but when it is anticipated that personnel may experience such an exposure, precautions and adequate preventive measures should be provided. There is indication that exposure to a concentration of approximately 1 000 ppm of pyrolyzed vapors for 15 mins. will produce no deleterious permanent effects.

#### General Conclusions

- 1 From the acute screening studies,  $CF_3Br$  appears to be the most promising candidate fire extinguishing agent from the standpoint of toxicity.
- 2 Further work would be necessary to determine whether  $CF_2Br_2$  offers any advantages over  $CH_2ClBr$  from a toxic hazard aspect.
- 3 Information on the comparative narcotic properties of  $CF_3Br$ ,  $CF_2Br_2$ ,  $CH_2ClBr$ , and  $CCl_4$  is meager. It would seem desirable to consider further study of these agents from the point of view of narcosis.
- 4 Toxicity tests of decomposition products in the presence of fires (gasoline fires particularly) are indicated before final acceptance of any of the new compounds.

5. Further experimentation is indicated to evaluate the hazards from long term chronic exposure incident to plan and filling operations.

Appended Data on Narcosis

The hazards involved from the narcotic effects in the use and application of fire extinguishers are difficult to evaluate from the present study which was concerned with relatively high concentrations to determine approximate lethal concentrations. Observations of the estimated time of onset of narcosis are summarized in Table A, which shows narcosis times for CF<sub>3</sub>Br, CF<sub>2</sub>Br<sub>2</sub>, CH<sub>2</sub>ClBr, and CCl<sub>4</sub> at the approximate lethal concentrations (ALC). The lowest concentrations in which narcosis was noted for these compounds are tabulated in Table B.

Table A  
Narcosis at Approximate Lethal Concentrations  
(15 min. Exposure)

<u>Undecomposed Vapors</u>				<u>Decomposed at 800°C.</u>			
Compound	Narcosis Time Min	ALC		Compound	Narcosis Time Min.	ALC	
		mg./l	ppm			mg./l.	ppm
CF <sub>3</sub> Br	1	5 070	834 000	CF <sub>3</sub> Br	10	90	14 000
CF <sub>2</sub> Br <sub>2</sub>	1	470	55 000	CF <sub>2</sub> Br <sub>2</sub>	3	16	1 900
CH <sub>2</sub> ClBr	1	340	64 000	CH <sub>2</sub> ClBr	10	22	4.200
CCl <sub>4</sub>	5	180	29 000	CCl <sub>4</sub>	-	2	300

Table B  
Narcosis Below Approximate Lethal Concentrations  
(15 min. Exposure)

<u>Undecomposed Vapors</u>				<u>Decomposed at 800°C.</u>			
Compound	Narcosis Time Min	Concentration		Compound	Narcosis Time Min.	Concentration	
		mg./l	ppm			mg./l.	ppm
CF <sub>3</sub> Br	15	1 970	323 244	CF <sub>3</sub> Br	10	63	10 310
CF <sub>2</sub> Br <sub>2</sub>	7	83	9 628	CF <sub>2</sub> Br <sub>2</sub>	9	6	702
CH <sub>2</sub> ClBr	5	142	26 980	CH <sub>2</sub> ClBr	7	8	1 520
CCl <sub>4</sub>	8-10	7	11 130	CCl <sub>4</sub>	4	1.5	159

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*PART II - THE APPROXIMATE LETHAL CONCENTRATION TO RATS  
BY INHALATION OF VAPORS FOR 15 MINUTES*

Medical Division Research Report No. 23

AN INVESTIGATION OF THE TOXICITY OF PROPOSED FIRE EXTINGUISHING FLUIDS

Part II - The Approximate Lethal Concentration to Rats  
by Inhalation of Vapors for 15 Minutes

ABSTRACT

OBJECT.

The object of this work was to determine the approximate lethal concentration of undecomposed and pyrolyzed vapors of various compounds proposed for use as fire extinguishing agents.

RESULTS.

1. A screening method is described for inhalation toxicity determinations using a small number of animals.

2. The approximate lethal concentrations of 14 fire extinguishing compounds to rats exposed 15 mins. are given. Compounds examined were the following: Carbon tetrachloride, Chlorobromomethane, Methyl bromide, Bromotrifluoromethane, Dibromodifluoromethane, Dibromotetrafluoroethane, Dibromotrifluoromonochloroethane, Ethyl bromide, Perfluoromethylcyclohexane, Carbon tetrafluoride, Methyl iodide, Dibromodifluoroethane, Chlorodifluoromonobromomethane and Carbon dioxide.

3. The approximate lethal concentrations of the vapors of the same compounds heated to 800°C. are given.

CONCLUSIONS.

1. The inhalation toxicities of 10 of the 14 compounds tested are increased on pyrolysis at 800°C. Vapors of methyl bromide and methyl iodide are less toxic after pyrolysis and this heating did not affect the toxicities of  $CF_4$  and  $CO_2$  due to the thermal stability of these compounds.

2. The toxicity of methyl bromide determined by the ALC method checked closely with the toxicity determined by a statistically valid LC50 method.

3. The least toxic of the undecomposed vapors tested for acute inhalations toxicity were those of  $CF_3Br$ ,  $CF_4$  and  $CF_2BrCl$ . Of the vapors pyrolyzed over an iron surface at 800°C, the least toxic were  $CF_4$ ,  $CO_2$ ,  $Cl_3I$ .

RECOMMENDATIONS

1. That because the sublethal effects, such as pulmonary irritation of  $CF_2Br_2$  and  $CF_3Br$ , may be cumulative additional toxicity studies are indicated before either of these compounds are adopted as fire extinguishing agents.

2. That work be continued on these fire extinguishing fluids to determine the inhalation toxicity of vapors decomposed by heat from other than a heated iron surface.

## Medical Division Research Report No. 23

## AN INVESTIGATION OF THE TOXICITY OF PROPOSED FIRE EXTINGUISHING FLUIDS

Part II - The Approximate Lethal Concentration to Rats  
by Inhalation of Vapors for 15 Minutes

## I. INTRODUCTION.

## A. Object.

The object of this work was to determine the approximate lethal concentration of undecomposed and pyrolyzed vapors of various compounds proposed for use as fire extinguishing agents.

## B. Authority.

Authorized by the Chief, Chemical Corps, under Project 4-61-14-03, Health Hazards of Military Chemicals, Test Program 16, Cal C Research and Development Program for fiscal year 1950.

## II. HISTORICAL AND THEORETICAL.

The inhalation toxicities of common fire extinguishing fluids have been the subject of several reports (1, 2, 3, 4, 5, 6, 7, 8) of which the most comprehensive have been studies on the inhalation toxicity of  $\text{CO}_2$ ,  $\text{CCl}_4$ ,  $\text{CH}_3\text{Br}$  (4) and  $\text{CH}_2\text{BrCl}$  (9). In this work decomposition products of the fire extinguishing agents as formed by various types of fires such as gasoline, oil, artificial gas and wood, and by heated iron surfaces ( $550^\circ\text{C}$ .) were reported. Analyses of the vapors of  $\text{CCl}_4$  decomposed by passing over a heated iron surface showed 0.106% by volume of phosgene ( $\text{COCl}_2$ ), while the decomposition of  $\text{CH}_3\text{Br}$  under the same conditions produced 0.005% by vol. of carbonyl bromide ( $\text{COBr}_2$ ). In addition mortality rate and pathological changes were observed in a series of experiments with guinea pigs after 5, 30 and 60 min exposures. No pertinent data with rats could be found in the literature.

In November, 1949 the Engineer Research and Development Laboratories (ERDL) at Ft. Belvoir, Virginia submitted to this laboratory certain halogenated compounds proposed for use as fire extinguishing compounds. They had been screened for fire extinguishing ability and were proposed for use against fires in tanks and airplane engines. The following screening program (9) was jointly agreed upon by a representative of ERDL and representatives of this laboratory. a) The toxicities of the undecomposed vapors were to be determined. b) Due to the possible increased toxicity of halogenated compounds in a decomposed state the inhalation toxicity studies of pyrolyzed vapors over a heated iron surface ( $800^\circ\text{C}$ .) were to be made and c) Lethality to rats were to be determined as an approximate lethal concentration. This was an adaptation of the determination of the Approximate Lethal Dose (ALD) proposed by Deichmann (10) and previously used only for toxicity by injection and ingestion.

Analytical Studies on the products of decomposition by heat are at present being carried out at the Purdue Research Foundation and Department of Chemistry (11)

### III EXPERIMENTAL

#### A Compounds

Fire extinguishing compounds tested were

Carbon tetrachloride	$\text{CCl}_4$	Halon 104
Chlorobromomethane	$\text{CH}_2\text{ClBr}$	Halon 1011
Methyl bromide	$\text{CH}_3\text{Br}$	Halon 1001
Bromotrifluoromethane	$\text{CF}_3\text{Br}$	Halon 1301
Dibromodifluoromethane	$\text{CF}_2\text{Br}_2$	Halon 1202
Dibromotetrafluoroethane	$\text{C}_2\text{F}_4\text{Br}_2$	Halon 2402
Dibromotrifluoromonoethane	$\text{C}_2\text{F}_3\text{ClBr}_2$	Halon 2312
Ethyl bromide	$\text{C}_2\text{H}_5\text{Br}$	Halon 2001
Perfluoromethylcyclohexane	$\text{C}_6\text{F}_{11}\text{CF}_3$	
Carbon tetrafluoride	$\text{CF}_4$	Halon 14
Methyl iodide	$\text{CH}_3\text{I}$	Halon 10001
Dibromodifluoroethane	$\text{C}_2\text{H}_2\text{F}_2\text{Br}_2$	Halon 2202
Chlorodifluoromonobromomethane	$\text{CF}_2\text{BrCl}$	Halon 1211
Carbon dioxide	$\text{CO}_2$	

Carbon dioxide was obtained from the Fire Department Army Chemical Center Maryland. All the other compounds were supplied by ERDL.

#### B Animals

Wistar strain male rats weighing between 220 and 250 g were used.

#### C Procedure

##### 1 Undecomposed Vapor

Constant flow gassing chambers of 20 l capacity were operated at an air flow of 2 l/min. Concentrations of the compound were set up by introducing measured quantities of the vapor into the affluent air at a

constant rate. Each concentration was 50% higher than that next below. Only one rat was exposed at each level. Exposure time was 15 mins. in all experiments. The lowest concentration that produced death was called the Approximate Lethal Concentration (ALC). The rats were observed for mortality for 14 days, at the end of which time survivors were sacrificed for pathological examinations. Rats undergoing acute death (dead on removal from the chamber) were also examined for pathological findings. The various times required to produce narcosis during the exposure were recorded.

## 2. Decomposed Vapors

The procedure was the same as that for undecomposed vapors with the exception that prior to introduction into the gas chamber the vapors were passed through an iron pipe at 800°C. in an electric furnace and then cooled to room temperature. The rate of flow through the heated pipe was adjusted so that the vapors were in contact with the hot metal for one second.

## C. Results

The data obtained from these experiments are given in Table 1 through Table 14. The ALCs of the compounds examined are given in Table 15.

## IV. DISCUSSION

The toxicities of most of the decomposed vapors increased markedly over those of the undecomposed compounds. However, the ALCs of  $\text{CO}_2$  and of  $\text{CF}_4$  were the same for the vapors before and after heating due to the thermal stability of these compounds at 800°C.

The ALCs of the decomposed compounds, in order of decreasing toxicity are shown in Table 15. Compounds undergoing decomposition at 800°C. showed an interesting trend in lethality related to the number and kind of halogen atoms in the individual molecule. A study of the table shows that compounds containing fluorine have reduced toxicity when compared with those containing chlorine, bromine or both. The compound containing one Cl atom and two atoms of Br was more toxic than that with two atoms of Br and no Cl.

It has already been reported that methyl bromide (4) and carbon tetrachloride (4, 11, 12) form carbonyl halides on pyrolysis. In this laboratory qualitative tests performed on the decomposition products of  $\text{CF}_2\text{Br}_2$  and  $\text{CF}_3\text{Br}$  also showed the presence of this type of compound. Because only nominal concentrations were used in this study, no analytical information was available for correlating the presence of these break-down products with lethality.

In applying the principles of the Deichmann (9, 13) ALD method to inhalation toxicity grading a table of concentration levels increasing by 50% was drawn up for the complete range of concentration used in this work. The nominal concentrations varied from these values by  $\pm 12\%$ . This was considered good agreement in view of the practical difficulties encountered in establishing predetermined chamber concentrations. Since the method has an accuracy of  $\pm 30\%$  as reported by Deichmann (9), there was no significant difference between adjacent concentration levels.

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The inhalation toxicity results obtained using two samples of methyl bromide from ERDL did not agree as shown in Table 3. The ALC for sample No. 1 was 12 mg /l for the undecomposed vapor and 248 mg. for the decomposed vapor while the corresponding values for sample No. 2 were 23 and 63 mg./l. respectively. The quantity of sample No. 1 was insufficient for further tests. Therefore the lethal concentration for 50% of the animals exposed (LC50) was determined on sample No. 2 using more animals at each level. The results shown in Table 16 were treated statistically using the method of Litchfield and Wilcoxon (14) and plotted in Chart 1. The LC50 was determined as 21 mg /l. with a range for two standard errors of 19.8 to 22.2 mg /l. This value is in very good agreement with the ALC of 23 mg /l. reported in Tables 3 and 15. A more detailed comparison of these two methods using at least six different compounds is planned to properly evaluate the ALC method.

Compound  $\text{CF}_2\text{Br}_2$  was relatively non toxic in the undecomposed state but toxic on decomposition. However, it should be noted that performance tests on this compound suggest its use as a fire extinguishing agent.

## V CONCLUSIONS

1 The inhalation toxicities of 10 of the 14 compounds tested are increased on pyrolysis at 800°C. Vapors of methyl bromide and methyl iodide are less toxic after pyrolysis and this heating did not affect the toxicities of  $\text{CF}_4$  and  $\text{CO}_2$  due to the thermal stability of these compounds.

2 A comparison of the toxicity of the second sample of methyl bromide by the ALC method with a statistically valid LC50 method showed very good agreement.

3 The least toxic of the undecomposed vapors tested for acute inhalation toxicity were those of  $\text{CF}_3\text{Br}$ ,  $\text{CF}_4$  and  $\text{CF}_2\text{BrCl}$ . Of the vapors pyrolyzed over an iron surface at 800°C the least toxic were  $\text{CF}_4$ ,  $\text{CO}_2$ ,  $\text{CH}_3\text{I}$ .

## VI RECOMMENDATIONS

1 That because the sublethal effects, such as pulmonary irritation of  $\text{CF}_2\text{Br}_2$  and  $\text{CF}_3\text{Br}$  may be cumulative additional toxicity studies are indicated before either of these compounds are adopted as fire extinguishing agents.

2 That work be continued on these fire extinguishing fluids to determine the inhalation toxicity of vapors decomposed by heat from other than a heated iron surface.

## VII BIBLIOGRAPHY

1 Lindsey Methyl Bromide vs Carbon Dioxide for Quenching Aircraft Fires Air Digest 47 120 1944

\*Composition:

99% {	C4 (n = 1) ~ 2.5%
	C6 (n = 2) ~ 30.0%
	C8 (n = 3) ~ 33.0%
	C10 (n = 4) ~ 19.0%
	C12 (n = 5) ~ 9.0%
	C14 (n = 6) ~ 1.0%

Traces mineral acid and 280 ppm I (probably an organic iodide).

*Doris F. Edwards*

Report by:

Doris F. Edwards  
Toxicologist

*Neil D. Krivanek*

Approved by:

Neil D. Krivanek  
Chief, Dermal & Ocular Toxicology Section

DFE/aph  
N.B. E-16375, page 69  
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UNITED STATES ENVIRONMENTAL PROTECTION AGENCY  
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12416A



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CECATS DATA: 1092 - 12416 SEQ. A

Submission # BEHQ: 1092 - 12416  
 TYPE: INT. SUPP FLWP  
 SUBMITTER NAME: E. I. DuPont de Nemours and Company

INFORMATION REQUESTED: FLWP DATE:  
 0501 NO INFO REQUESTED  
 0502 INFO REQUESTED (TECH)  
 0503 INFO REQUESTED (VOL. ACTIONS)  
 0504 INFO REQUESTED (REPORTING RATIONALE)  
 DISPOSITION:  
 0630 REFER TO CHEMICAL SCREENING  
 0670 CAP NOTICE

VOLUNTARY ACTIONS:  
 0401 NO ACTION REPORTED  
 0402 STUDIES PLANNED/IN PROGRESS  
 0403 MODIFICATION OF WORKING CONDITIONS  
 0404 LABEL/MSDS CHANGES  
 0405 PROCESS/PLANTING CHANGES  
 0406 APP. USE DISCONTINUED  
 0407 PRODUCTION DISCONTINUED  
 0408 CONFIDENTIAL

SUB. DATE: 10/15/92 OTS DATE: 10/27/92 CSRAD DATE: 03/09/95

CHEMICAL NAME: Methane, difluorobromo -  
 CAS# 75-63-8  
1511-62-2

INFORMATION TYPE:	P F C	INFORMATION TYPE:	P F C	INFORMATION TYPE:	P F C
0201 ONCO (HUMAN)	01 02 04	EPIACLIN	01 02 04	0241 IMMUNO (ANIMAL)	01 02 04
0202 ONCO (ANIMAL)	01 02 04	HUMAN EXPOS (PROD CONTAM)	01 02 04	0242 IMMUNO (HUMAN)	01 02 04
0203 CELL TRANS (IN VITRO)	01 02 04	HUMAN EXPOS (ACCIDENTAL)	01 02 04	0243 CHEM/PHYS PROF	01 02 04
0204 MUTA (IN VITRO)	01 02 04	HUMAN EXPOS (MONITORING)	01 02 04	0244 CLASTO (IN VITRO)	01 02 04
0205 MUTA (IN VIVO)	01 02 04	EEO/AQUA TOX	01 02 04	0245 CLASTO (ANIMAL)	01 02 04
0206 REPRO/TERATO (HUMAN)	01 02 04	ENV. OCCUR/REL/FATE	01 02 04	0246 CLASTO (HUMAN)	01 02 04
0207 REPRO/TERATO (ANIMAL)	01 02 04	EMER INCI OF ENV CONTAM	01 02 04	0247 DNA DAM/REPAIR	01 02 04
0208 NEURO (HUMAN)	01 02 04	RESPONSE REQEST DELAY	01 02 04	0248 PROD/USE/PROC	01 02 04
0209 NEURO (ANIMAL)	01 02 04	PROD/COMP/CHEM ID	01 02 04	0251 MSDS	01 02 04
0210 ACUTE TOX. (HUMAN)	01 02 04	REPORTING RATIONALE	01 02 04	0299 OTHER	01 02 04
0211 CHR. TOX. (HUMAN)	01 02 04	CONFIDENTIAL	01 02 04		
0212 ACUTE TOX. (ANIMAL)	01 02 04	ALLERG (HUMAN)	01 02 04		
0213 SUB ACUTE TOX (ANIMAL)	01 02 04	ALLERG (ANIMAL)	01 02 04		
0214 SUB CHRONIC TOX (ANIMAL)	01 02 04	METAB/PHARMACO (ANIMAL)	01 02 04		
0215 CHRONIC TOX (ANIMAL)	01 02 04	METAB/PHARMACO (HUMAN)	01 02 04		

TRIAJE DATA: NON-CBI INVENTORY YES (DROPPED) NO (CONTINUE) REFTR  
 SPECIES: RAT  
 TOXICOLOGICAL CONCERN: LOW MED HIGH  
 USE: Fire extinguishing Fluids  
 PRODUCTION:

> <ID NUMBER>  
8(E)-12416A-01

> <TOX CONCERN>  
L

> <COMMENT>

CF3BR: ACUTE INHALATION TOXICITY IN RATS IS LOW CONCERN FOR A 15 MINUTE EXPOSURE. 10 ANIMALS WERE EXPOSED TO TEST MATERIAL. THE ALC FOR UNDECOMPOSED AND DECOMPOSED VAPORS OF TEST MATERIAL WERE 834,000 AND 14,000 PPM, RESPECTIVELY. CONCENTRATIONS BELOW THE ALC THAT ANIMALS WERE EXPOSED TO UNDECOMPOSED AND DECOMPOSED VAPORS WERE 323,244 AND 10,310 PPM, RESPECTIVELY. PATHOLOGY ON ANIMALS EXPOSED TO LETHAL OR NEAR LETHAL CONCENTRATIONS SHOWED DAMAGE TO THE RESPIRATORY SYSTEM AND CONGESTION OF LIVER, SPLEEN, AND KIDNEYS. REPORT WAS DIFFICULT TO READ - BAD PHOTOCOPY.

> <ID NUMBER>  
8(E)-12416A-02

> <TOX CONCERN>  
L

> <COMMENT>

CF2BR2: ACUTE INHALATION TOXICITY IN MALE RATS IS LOW CONCERN FOR A 15 MINUTE EXPOSURE. THE ALC FOR UNDECOMPOSED VAPORS AND DECOMPOSED WAS 55,000 AND 1,900 PPM, RESPECTIVELY. CONCENTRATIONS BELOW THE ALC THAT ANIMALS WERE EXPOSED TO UNDECOMPOSED VAPORS AND DECOMPOSED WERE 9,628 AND 702 PPM, RESPECTIVELY. 10 ANIMALS WERE EXPOSED TO TEST MATERIAL.

REPORT WAS DIFFICULT TO READ - BAD PHOTOCOPY.