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USNCBC ltr dtd 24 Oct 1974



Project NY 030 019-1
Technical Memorandum M-108

EVALUATION OF HALOGENATED HYDROCARBON AND
ALKALI-EARTH-METAL-SALT FIRE EXTINGUISHING
AGENTS FOR LOW TEMPERATURES

1 November 1955

U. S.
naval
civil
engineering
research
and
evaluation
laboratory

port hueneme,
california

A0108249

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R. J. Zablodil

SUMMARY

To improve methods and equipment for combating arctic fires, this Laboratory has been given the task of evaluating improved fire extinguishing agents for low temperatures and developing a portable fire sprinkler system for building protection. This is a final report on results stemming from tests on newly developed fire extinguishing agents for low-temperature use.

Four vaporizing halogenated-hydrocarbon-type and five water-base alkali-earth-metal-salt-type extinguishing agents were selected for test on a NAVCERELAB standardized surface Class A fire. The temperature of the agents was varied approximately 135 degrees, tests being performed at ambient (70 F), 0 F, and -65 F. Halon 2011B, calcium chloride-zinc chloride solution, and potassium carbonate solution froze between 0 F and -65 F and are therefore considered unsuitable for advance base use.

An extinguishment index was established from tests on the standardized surface Class A fire, and is the product of the agent's extinguishing time and the quantity required to extinguish the standard fire in units of pound-seconds. This index was used to evaluate and measure the agent's efficiency and effectiveness.

All of the halogenated hydrocarbon agents, except 2011B which froze, performed equally well over the entire temperature range, with an index variation from 1.9 to 2.8. The earth-metal-salt agents, excluding those that froze, varied from 4.6 to 31.0.

This report concludes that Halon agents are not practical, notwithstanding their superior extinguishment abilities, because of the toxicity and density of their pyrolyzed vapors; that fire extinguishing abilities of plain water are enhanced by the inclusion of alkali-earth-metal salts; and that solutions containing lithium chloride are superior in their extinguishment abilities to other earth-metal-salt solutions tested. Lithium chloride solutions are less viscous at low temperatures.

It is recommended that water solutions of lithium chloride and lithium chloride-calcium chloride be considered candidates for Class A first-aid fire extinguishers. It is further recommended that effective inhibitors compatible to the selected agent be developed, and that the agent be given thorough toxicity tests by the Navy Bureau of Medicine.

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Figure 1. Extinguishing fire with CO₂ at -65 F. Low vapor pressure has adversely affected discharge range.

INTRODUCTION

Within the past several years the Military has established many advanced bases in the polar regions. With these frontier bases came many new problems which had to be overcome before satisfactory base operation could be effected. One such problem is obtaining adequate protection against one of man's worst natural enemies - fire. A cursory analysis of this problem has revealed the obvious necessity for maintaining adequate protective housing from the extreme cold and high winds, and that existing fire fighting facilities and equipment do not furnish sufficient protection against a structural fire in the Arctic. It was found that most commercially available materials and equipment failed or fell short of satisfactory performance at low temperatures. For example, carbon dioxide, normally reliable, may solidify at the nozzle and plug the discharge when application is attempted at temperatures approaching -45 F. In the event of unrestricted discharge, the lower vapor pressure results in a decreased effective discharge range, making it unsatisfactory except possibly for small localized fires (see Figure 1).

Industry and laboratories throughout the country have been endeavoring to overcome these existing inadequacies by improving materials, equipment, and techniques for fighting arctic fires. Since World War II, many new low-temperature extinguishing agents have been developed giving promise of superior performance at low temperatures over those heretofore used. Under Project NY 030 019-1, "Polar Fire Fighting Methods," a program of evaluation of these new agents was initiated.

DESCRIPTION OF AGENTS

The agents chosen for this evaluation are divided into two categories:

1. Halogenated-hydrocarbon-type.
2. Water-base alkali-earth-metal-salt-type.

Halogenated Hydrocarbon Agents

These agents are of the vaporizing liquid type, similar to carbon tetrachloride, and are halogenated hydrocarbons containing atoms of fluorine and/or bromine. The action of the fluorine on these compounds produces a lower boiling point and has a stabilizing effect, while bromine enhances their fire extinguishing qualities.

The agents selected for this evaluation were Halons 1002, 1011, 1202, and 2011B. These four were selected in particular because of:

1. Advertised rate of fire extinguishment.
2. Ability to remain in a liquid state under normal handling temperatures.
3. Ease of recharging in the field.
4. Toxicity which is less than that of carbon tetrachloride.

Table 1 defines some of their salient physical properties.

TABLE 1. Physical properties of halogenated hydrocarbon agents at one atmosphere.

Agent	Halon 1002	Halon 1011	Halon 1202	Halon 2011B
Chemical formula	CH ₂ Br ₂	CH ₂ BrCl	CBr ₂ F ₂	CH ₂ BrCH ₂ Cl
Boiling point (deg F)	209.2	154.4	77.8	163.0
Freezing point (deg F)	-64.0	-126.4	-112	-1.1
Heat of vaporization (Btu/lb)	...	99.8	141.4	100
Liquid density at 70 F (lb/gal)	20.5	15.98	19.01	14.31

The effect of the fluorine and bromine atom in the compounds is well illustrated. The presence of fluorine depresses the boiling point while the presence of bromine increases the weight. Specific gravity of Halons 1011 and 2011B is nearly twice that of water, and of Halons 1002 and 1202 nearly 2 1/2 times. Characteristic of the

Halon agents are the heavy pyrolyzed vapors that cling about the fire area with a smothering action rather than being vented off immediately with the products of combustion (see Figure 2).



Figure 2. Pyrolyzed vapors resulting from extinguishing with Halon 1011 at -65 F clinging about fire area.

A point of interest centers about the toxicity of Halon vapors and the amount required for lethal concentration. Tests have been performed by the Army Chemical Center and a partial listing of the toxic characteristics reported by it are shown in Table 2. Halons 1002 and 2011B were not tested.

TABLE 2. Approximate lethal concentrations for 15-minute exposure.

Agent	Chemical formula	Natural vapor (ppm)	Pyrolyzed vapor (ppm)
Halon 1011 (chlorobromomethane)	CH_2BrCl	64,000	4200
Halon 1202 (dibromodifluoromethane)	CBr_2F_2	55,000	1900
Halon 104 (carbon tetrachloride)	CCl_4	29,000	300

The Army Chemical Center is of the opinion that low vapor concentrations of Halon 1202 usually found in industrial and field conditions probably would not present a serious hazard to personnel. No mention was made concerning Halon 1011; however, it is assumed, since Halon 1011 is less toxic than Halon 1202, that the ACC's opinion would be the same. Of added interest is the fact that the toxicity of carbon monoxide resulting from actual fires will in most cases be greater than the pyrolyzed Halon vapors. Carbon tetrachloride is included in the table for comparative purposes.

Studies on stability and corrosion of these Halons were not made. However, the Laboratory detected no discoloring of the agent while in storage (at room temperature) and no corrosive action was apparent on the brass test extinguishers. Other agencies report the corrosion and stability about the same as carbon tetrachloride, with those Halons containing the fluorine atom having a higher stability than carbon tetrachloride.

All Halons tested are non-conductors and therefore suitable for application on Class C fires.

Water-Base Alkali-Earth-Metal-Salt Agents

The addition of any alkali-earth-metal salt to fresh water will lower the freezing point below 32 F. The extent of depression is dependent on the salt concentration. Calcium chloride, for example, has been widely used in the refrigeration field in the manufacture of ice, but concentrations required for low-temperature fire extinguishing agents are too critical for its practical use in this respect. It is conceivable that any earth-metal-salt and water solution may be used for fire extinguishment; however, certain compounds display better extinguishing efficiencies than others where concentrations for liquid phase at -65 F are less critical.

Those compounds included in this classification indicated to be best adaptable for low temperatures are the salts of zinc, calcium, lithium, and potassium. Table 3 presents some of the physical characteristics of earth-metal-salt test solutions remaining liquid at -65 F. Potassium carbonate and calcium chloride-zinc chloride

TABLE 3. Physical properties of earth-metal-salt solutions at one atmosphere.

Earth-metal-salt solution (per cent by weight)	Chemical formula	Boiling point (deg F)	Freezing point (deg F)	Density at 70 F
10% lithium chloride + 20% calcium chloride	LiCl + CaCl ₂	221	-80	10.2
24% lithium chloride	LiCl	237	-87	9.4
47% zinc chloride	ZnCl ₂	230	-69	13.2

solutions were also tested, but froze between 0 F and -65 F. It should be noted that the lowest eutectic point available for potassium carbonate is well above -65 F, but proper proportions of calcium and zinc chloride will produce a solution remaining liquid below -65 F.

Published data concerning the heat of vaporization could not be found, but it is assumed it would approximate that of fresh water, since solution evaporation is simply a distilling process.

TEST MATERIALS AND PROCEDURE

At the outset a search was made for a test method which would give reproducible results. The method specified by the Underwriters' Laboratories for a Class A vertical-burning area of wood required a panel approximately 10x10 ft constructed from over 200 individual pieces of yellow pine and fir. It had been previously estimated that NAVCERELAB tests would require over 250 panels. Although the UL method would be entirely satisfactory testwise, the abundance of materials required for NAVCERELAB tests made its use impractical. The quantity of 1 qt per test was thought to be adequate to provide valid agent evaluation. A vertical-burning frame was evolved from several trial-and-error designs which satisfied the requirement for a small standard fire. This method, then, of using 1 qt, or portion thereof, of agent to extinguish the standard test fire as shown in Figure 3 gave acceptable results of extinguishment ability. NAVCERELAB's results using this method coincided with those obtained by Engineer Research and Development Laboratories using flame-inhibition method on Halon and n-heptane vapor mixtures.



Figure 3. General test area and equipment.

Wood Frame for Burning

Figure 4 shows the dimensions and construction of the wood frame for the standard Class A fire. Construction was of rough-cut Douglas fir lath. Frames when completed were stored in a drying room for a minimum of 14 days to insure their moisture equilibrium. All frames were constructed of like material, were stored under like conditions, and were alike except for minor weight differences. For surface fires the frames were used singly and for deep-seated fires in multiples.

Hand Extinguishers

The hand extinguishers used for the tests were type A-20, 1-qt capacity, manufactured for the U.S. Air Force under specification MIL-E-5220A (USAF) 8 December 1952. This type of extinguisher does not require a cartridge to expel the fluid and can be charged and readied for reuse in a matter of minutes.

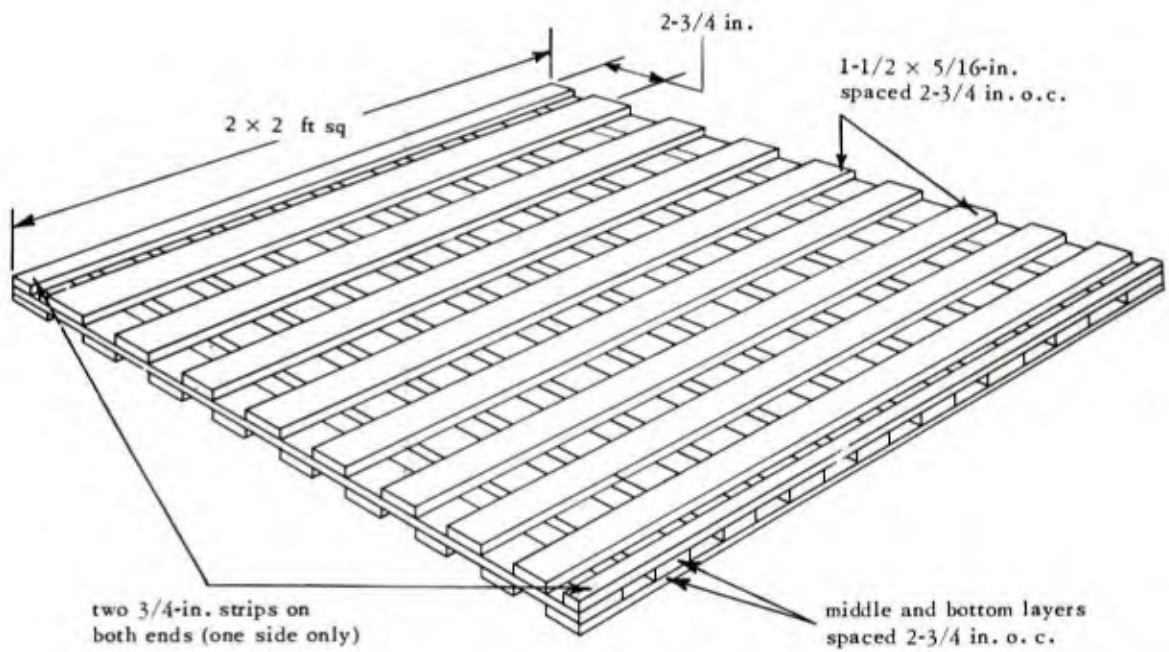


Figure 4. Wood frame for standard test fire.

Test Method for Surface Fires

The wood frame is immersed in fuel oil for approximately 30 seconds, allowed to drip, and then placed in the combustion pan. Ignition is accomplished by a small windrow of excelsior. The frame is allowed to preburn for about one minute to consume the oil and excelsior and insure an equally well established flame for each test. The agent was applied at the end of the preburn period and the weight of agent and time required to extinguish the flame was recorded. For the test area and some of the apparatus required to sustain the evaluation, see Figure 3.

The extinguishers were cold-soaked at least 24 hours for tests at 0 F and -65 F. The extinguishers were soaked with insulation about them to prevent any temperature increase from the time they were removed from the cold box until they were used. Figure 5 shows the extinguishers being cold-soaked.



Figure 5. Extinguishers being cold-soaked.

Test Method for Deep-Seated Fires

The deep-seated fires consisted of multiples of burning frames used for surface fire tests. Figure 6 shows a stack of eight.



Figure 6. Stack of eight frames for deep-seated fire.

Preparation and test routine were same as those for the surface fires except both front and back frames were dipped in fuel oil.

Extinguishment Index

The ability of a particular agent to extinguish the surface test fire is represented by its "extinguishment index." It is the product of weight and time. The weight is in pounds of agent and the time is in seconds required by the agent to extinguish the flame. Each agent earned such an index which indicates its relative effectiveness.

Appendix A contains the unabridged results obtained from the testing of NAVCERELAB standard Class A surface fires. A few individual tests were obviously incorrect and therefore not used in the averages. These, however, represent less than 5 per cent of the total number of tests made.

Abridged results of all tests on agents remaining liquid at -65 F may be found in Tables 4 and 5 and are shown graphically in Figures 7 and 8.

TABLE 4. Extinguishment index of agents remaining liquid at -65 F.

The extinguishment index is the product of the agent's extinguishing time and the quantity required to extinguish the standard fire expressed in units of pound-seconds.

Agent	Temperature		
	Ambient (70 F)	0 F	-65 F
1. Control test of			
a. water	7.0
b. carbon tetrachloride	6.3
2. Evaluation test of Halons			
a. 1002	1.9	2.2	2.1
b. 1011	2.7	2.2	2.6
c. 1202	2.1	1.7	1.9
3. Evaluation test of earth-metal salts			
a. LiCl + CaCl ₂	5.0	10.5	12.0
b. LiCl	4.6	11.6	19.2
c. ZnCl ₂	7.9	20.6	31.0

TABLE 5. Quantity of agent required to extinguish standard surface fire of agents remaining liquid at -65 F.

Figures represent pounds of agent.

Agent	Temperature		
	Ambient (70 F)	0 F	-65 F
1. Control test of			
a. water	1.0
b. carbon tetrachloride	1.0
2. Evaluation test of Halons			
a. 1002	0.8	0.7	0.8
b. 1011	0.9	0.9	0.7
c. 1202	0.7	0.6	0.7
3. Evaluation test of earth-metal salts			
a. LiCl + CaCl ₂	0.9	1.3	1.3
b. LiCl	0.8	1.1	1.2
c. ZnCl ₂	1.3	1.6	1.7

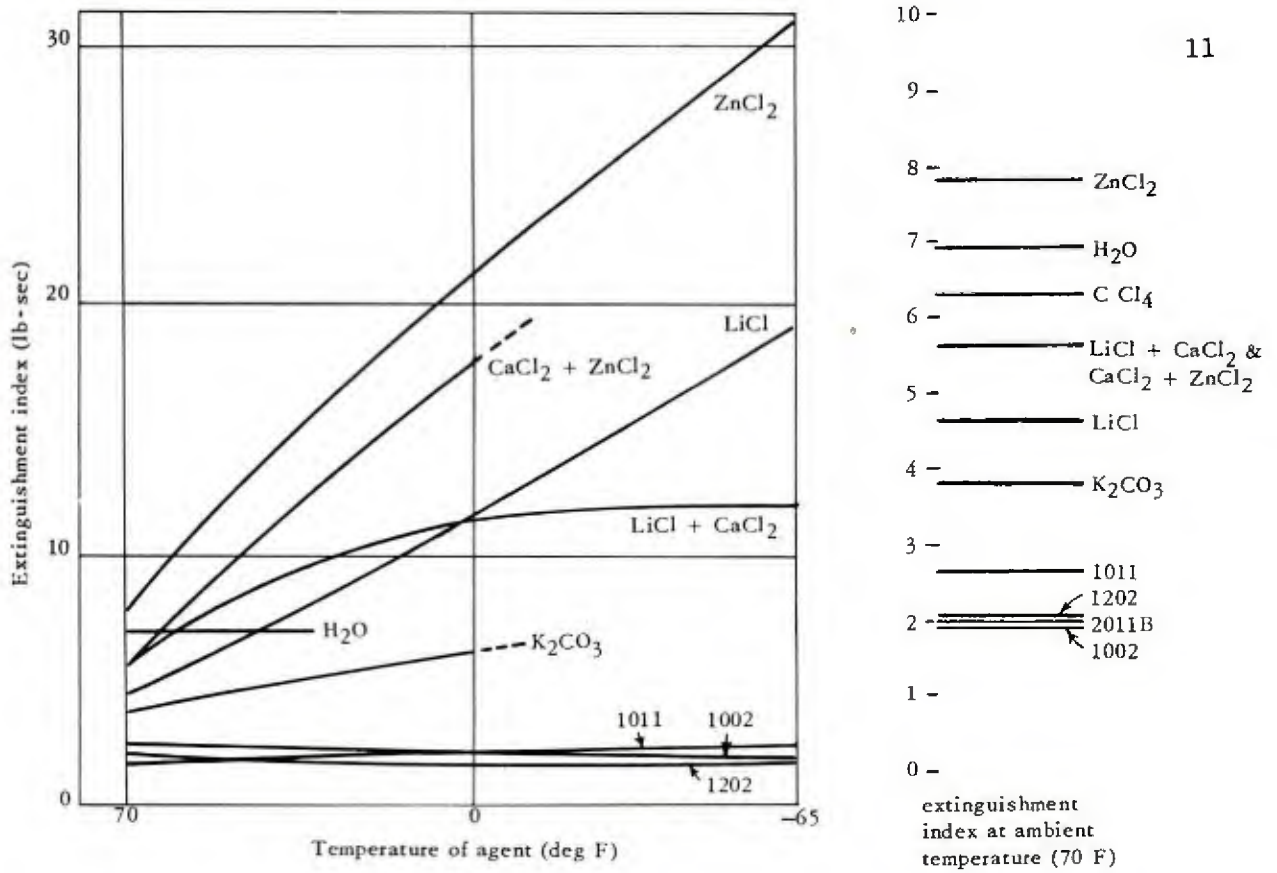


Figure 7. Extinguishment index vs temperature of agent.

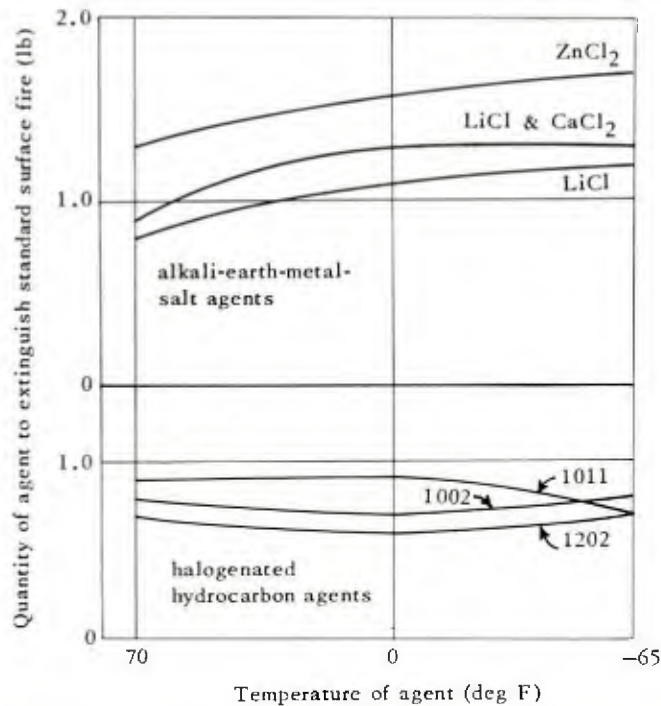


Figure 8. Quantity of agent required to extinguish standard surface fire vs temperature of agent.

Halogenated Hydrocarbon Agents

The halogenated hydrocarbon agents performed equally well over the entire temperature range of testing (ambient [70 F] to -65 F), and displayed less than 1.0 variation in their extinguishment indexes. Halon 2011B froze near 0 F, but extinguishing efficiency at ambient temperature was about equal to those of the other Halons. At ambient temperatures Halons 1002 and 2011B performed slightly better, and at -65 F Halon 1202 was the better. These results show that temperature variations do not materially affect the agent's flow characteristics or alter its viscosity.

Pyrolyzed vapors formed very quickly after applying agent to the fire. These vapors, retaining the characteristics of the heavy bromine molecule, clung about the fire area with a smothering action and were not immediately vented off with the products of combustion. This condition excluded much of the combustion-supporting oxygen and was a major contributor towards extinguishment. Figure 9 shows the formation of these vapors from Halon 1002.

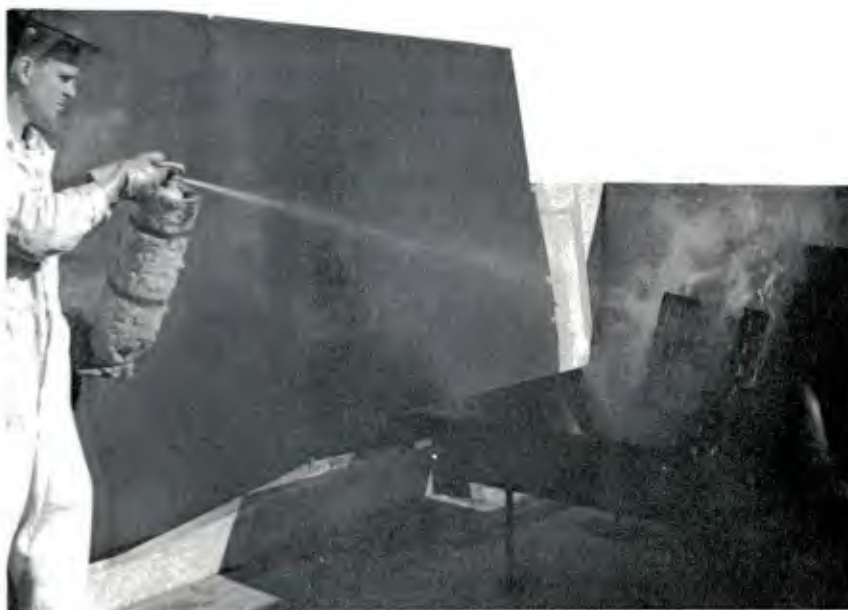


Figure 9. Formation of pyrolyzed vapors approximately three seconds after initial application of Halon 1002 at 0 F.

All Halons displayed this same characteristic. For the most part, pyrolyzed vapors from the standard test fire were not produced in quantities sufficient to affect the breathing or visibility of the operators. On a few occasions, under prolonged test periods, they did experience slight nausea.

Carbon tetrachloride, or Halon 104, was tested at ambient temperature solely for control data, and its index indicates the test Halons to be approximately three times as effective. A graph of the extinguishment index at ambient temperature (70 F) shows the effectiveness of carbon tetrachloride compared to all other agents, Halons and alkali salts, participating in this evaluation (see Figure 7).

Water-Base Alkali-Earth-Metal-Salt Agents

The earth-metal-salt agents revealed a much wider variation in extinguishment indexes, approximately 26, because of a viscosity increase from a temperature decrease. A viscosity increase adversely affected the agent flow rate, thus requiring longer for the agent to flow through the fixed nozzle of the fire extinguisher and accounted for larger indexes at low temperatures (see Figure 10). The decreased flow may be overcome, for the most part, by oversizing pipes or orifices sufficiently to give the desired flow rate. Viscosity variation of potassium carbonate, lithium chloride, and lithium chloride-calcium chloride solutions was not as great as that of the solution containing zinc chloride. Of all salt solutions remaining liquid at -65 F, those of lithium chloride and lithium chloride-calcium chloride are superior to others regarding extinguishing abilities and are less viscous at low temperatures.

Pyrolyzed vapors from the earth-metal-salt agents are mostly steam with some of the solution entrained therein. Figure 11 shows vapor formation from a zinc chloride solution. Other solutions produced equal pyrolyzed vapor densities.

Toxicity from these vapors is rather moot as applied to fire fighting since their application in this field is fairly recent. Apparently nothing has been published on the subject, but participants in NAVCERELAB tests reported an occasional light-headedness from inhaling these vapors.

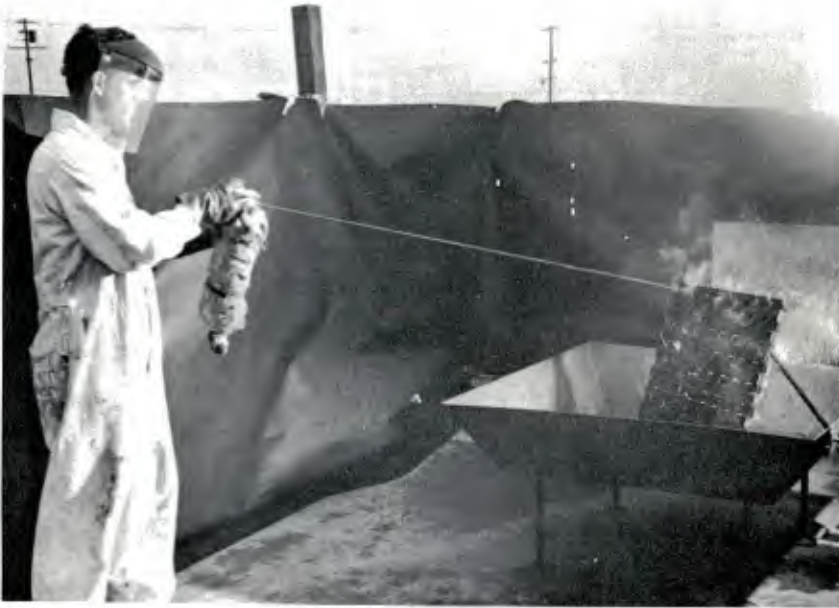


Figure 10. Extinguishing fire with zinc chloride at -65 F.
Thin stream due to increased viscosity of agent.



Figure 11. Extinguishing fire with zinc chloride at ambient temperature. Pyrolyzed vapors mostly steam.

No actual tests concerning corrosion were made; however, the handling of the aqueous solutions and observations on their corrosive action on the common metals secondary to the evaluation such as brass, iron, and steel, pointed up the need for effective inhibitors. Detailed analyses concerning corrosive action of earth-metal-salt solutions have been published by Engineer Research and Development Laboratories, Fort Belvoir, Virginia, (Final Report, "Research on Water Additives for Fire Fighting"). An analysis on zinc chloride has also been published by the Naval Research Laboratory, Washington, D. C. (Report No. 4353, "Fire Extinguishants for Arctic Use").

A search was made in NAVCERELAB technical library for material concerning hazardous properties, storage, and handling of the dry chemical involved in this evaluation, and the findings thereof appear in Appendix B.

Plain water was tested at ambient temperature to provide control data. This is shown in Figure 12. For its effectiveness compared



Figure 12. Extinguishing fire with plain water.

to all other agents participating in this evaluation, see Figure 7, graph showing the extinguishment index at ambient temperature (70 F). It is evident that the fire extinguishing abilities of plain water are enhanced by the inclusion of alkali-earth-metal salts.

Any alkali-earth-metal-salt solution is an electrolyte and therefore a conductor of electricity. If one is chosen for Class A use, all containers thereof should be clearly and boldly marked "DO NOT USE ON ELECTRICAL FIRES."

Deep-Seated Fires

Upon the suggestion of Mr. Wilbur D. Stump, Head, Fire Protection Section, Power and Utilities Branch, Bureau of Yards and Docks, the surface fire tests were enlarged to include deep-seated fires for the purpose of determining the extent of fire that could be extinguished by a fixed quantity of each class of agent.

Tests were begun by stacking frames identical to those used in surface fire tests to a depth of eight. Halon 1011 and zinc chloride were chosen to represent the two classes. Neither agent successfully extinguished the 8-stack-deep fire and the number of frames was decreased one by one until extinguishment by each agent was possible. It was found that Halon 1011 could generally extinguish a stack of 4 and zinc chloride a stack of 3 at ambient, and a stack of 3 and 2 respectively at -65 F.

Tests on deep-seated fires were not carried to completion because it became immediately evident that halogenated hydrocarbon agents were not practical on fires larger than those of the surface type. The Halon pyrolyzed vapors were so dense and heavy about the fire area that visibility was almost zero, breathing was very difficult, and to carry on the tests would have necessitated the use of respiratory apparatus (see Figures 13, 14, and 15). Because agents under this evaluation are to be used primarily for first-aid fire extinguishment, precluding the use of any respiratory equipment such as gas masks, it was concluded that Halon agents were not practical for use on structural fires and further testing was discontinued.

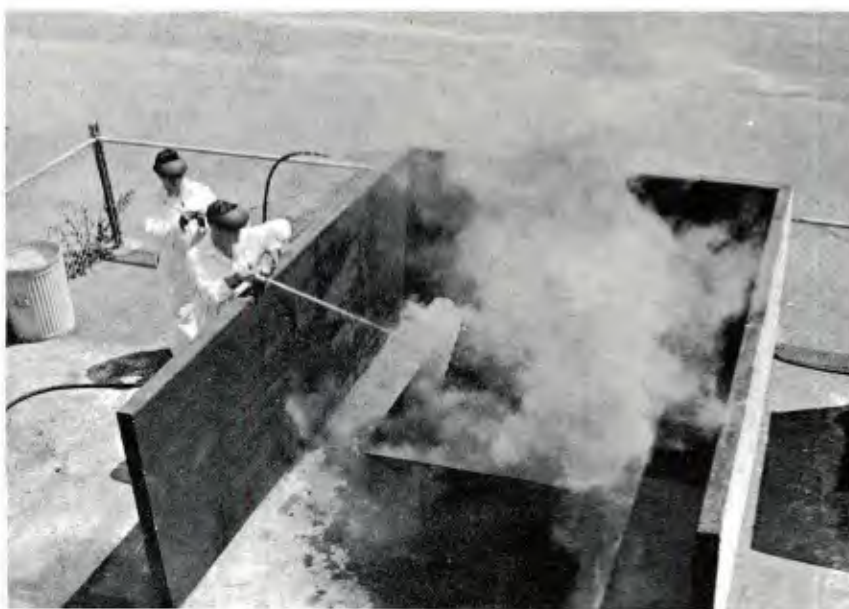


Figure 13. Deep-seated fire test with formation of heavy hydrolyzed vapors resulting from extinguishing with Halon 1011 at ambient temperature. A few seconds later this observation point was completely enveloped by vapor (see Figure 14).



Figure 14. Maximum vapor density resulting from test shown in Figure 13. Test area completely shrouded.



Figure 15. Deep-seated fire test with pyrolyzed vapors resulting from extinguishing with zinc chloride at -65 F. Vapors are not nearly as dense as those when Halon 1011 was used.

Table 4 lists halogenated hydrocarbon agents as outperforming alkali-earth-metal-salt agents approximately 2.5 to 1 at ambient temperature and 15 to 1 at -65 F. The superiority of the Halons is due mostly to the higher viscosity of the earth-metal-salt agents at low temperatures. However, in Table 5 which gives pounds of agent needed to extinguish the fire the amount is approximately equal at ambient temperature and varies less than 2 to 1 at -65 F. The fact that Halons required about one-half the time for extinguishment accounted for the extinguishment index differential.

Curves shown in Figures 7 and 8 were constructed from the data appearing in these tables.

CONCLUSIONS

1. At ambient temperature each class of chemical agent required the same weight of agent to extinguish the surface fire. The halogenated hydrocarbon class accomplished extinguishment in one-half the time required by the alkali-earth-metal-salt class.

2. The alkali-earth-metal-salt class is much more sensitive to low temperatures because of viscosity increase, but can be compensated for by oversized piping, nozzles, and/or orifices large enough to achieve desired flow rate.

3. Fire extinguishing abilities of plain water are improved by the inclusion of alkali-earth-metal salts.

4. In this class of agent, solutions containing lithium chloride are superior in their extinguishment abilities and are less viscous at low temperatures.

5. The halogenated hydrocarbon agents, notwithstanding their superior extinguishment abilities, are not practical as first-aid fire extinguishing agents because of the toxicity and density of their pyrolyzed vapors.

RECOMMENDATIONS

It is recommended that water solutions of lithium chloride and lithium chloride-calcium chloride be considered for Class A first-aid fire extinguishers. It is further recommended that effective inhibitors be sought or developed compatible to the selected agent, and that the agent be given thorough toxicity tests by the Navy Bureau of Medicine.

APPENDIXES

Appendix A. Test Results of Halogenated Hydrocarbon and Alkali-Earth-Metal-Salt Fire Extinguishing Agents on Standard Class A Surface Fires

Appendix B. Hazardous Properties, Storage, and Handling of Dry Alkali-Earth-Metal-Salt Chemicals

APPENDIX A

Test Results from Extinguishing Surface Fires by Halogenated Hydrocarbon Agents at Ambient (70 F) Temperature.

Agent	Test no.	Air pressure (psig)	Wt of agent used (lb)	Extinguishing time (sec)	Extinguishment index (lb · sec)	Remarks
Halon 1002 (dibromomethane)	1	150	1.0625	3.5	3.72	
	2	150	0.6875	2.2	1.51	
	3	150	0.7500	2.4	1.80	
	4	150	0.7188	2.2	1.58	
	5	150	0.9063	2.2	1.99	
	6	150	0.8125	2.4	1.95	
	7	150	0.5940	2.2	1.31	
	8	150	0.7500	2.4	1.80	
	9	150	0.9375	2.0	1.88	
Average			0.80	2.39	1.91	
Halon 1011 (chlorobromo- methane)	10	150	0.8125	4.2	3.41	
	11	150	1.0625	3.5	3.72	
	12	150	0.8125	2.9	2.36	
	13	150	0.8125	3.0	2.44	
	14	150	0.8750	3.5	3.06	
	15	150	0.8125	3.0	2.44	
	16	150	1.0625	3.0	3.19	
	17	150	0.7500	2.5	1.88	
	18	150	0.7500	2.1	1.58	
Average			0.86	3.08	2.65	
Halon 1202 (dibromodifluoro- methane)	19	150	0.8750	3.6	3.15	
	20	150	0.7500	2.8	2.10	
	21	150	0.6250	2.4	1.50	
	22	150	0.6250	2.6	1.63	
	23	150	0.3750	2.4	0.90	low - not used in average
	24	150	0.6250	2.6	1.63	
	25	150	0.7500	2.6	1.95	
	26	150	0.8750	3.6	3.15	
	27	150	0.7500	2.4	1.80	
Average			0.73	2.83	2.07	

APPENDIX A (contd p. 2)

Test Results from Extinguishing Surface Fires by Halogenated Hydrocarbon Agents at Ambient (70 F) Temperature (contd).

Agent	Test no.	Air pressure (psig)	Wt of agent used (lb)	Extinguishing time (sec)	Extinguishment index (lb-sec)	Remarks
Halon 2011B (1-bromo-2-chloro-ethane)	28	150	0.6875	2.5	1.72	low - not used in average
	29	150	0.6875	3.0	2.06	
	30	150	0.3750	2.1	.79	
	31	150	0.7500	2.9	2.18	
	32	150	0.7500	4.0	3.00	
	33	150	0.7500	2.5	1.88	
	34	150	0.8125	2.7	2.19	
	35	150	0.6250	2.8	1.75	
	36	150	0.6250	2.2	1.38	
Average			0.71	2.83	2.01	
Halon 104 (carbon tetra-chloride)	37	140	1.5625	11.0	17.2	high - not used in average
	38	145	1.1250	6.4	7.2	
	39	125	0.9375	5.9	5.5	
	40	145	0.8750	5.6	4.9	
	41	125	1.1250	6.9	7.8	
Average			1.02	6.20	6.32	

APPENDIX A (contd p. 3)

Test Results from Extinguishing Surface Fires by Halogenated Hydrocarbon Agents at 0 F.

Agent	Test no.	Air pressure (psig)	Wt of agent used (lb)	Extinguishing time (sec)	Extinguishment index (lb-sec)	Remarks
Halon 1002 (dibromomethane)	42	90	0.6250	3.3	2.06	
	43	95	0.8750	3.5	3.06	
	44	89	0.5000	2.3	1.15	
	45	118	0.7500	2.7	2.02	
	46	95	0.7500	3.6	2.70	
	47	90	0.8125	2.6	2.11	
	48	132	0.7500	2.7	2.02	
	49	130	0.8750	2.5	2.19	
	50	108	0.6250	2.4	1.50	
	Average			0.73	2.84	2.07
Halon 1011 (chlorobromo- methane)	51	110	1.0000	2.4	2.40	
	52	110	1.0625	2.0	2.13	
	53	112	0.8750	2.2	1.93	
	54	147	0.6250	2.6	1.63	
	55	142	1.2500	2.5	3.13	
	56	147	0.7500	2.8	2.10	
	57	100	0.7500	2.6	1.95	
	58	100	0.7500	2.4	1.80	
	59	100	1.0625	2.7	2.87	
	Average			0.90	2.47	2.22
Halon 1202 (dibromodifluoro- methane)	60	90	0.8750	3.0	2.63	
	61	90	0.5000	3.4	1.70	
	62	90	0.6250	2.6	1.63	
	63	120	0.6250	2.1	1.31	
	64	125	0.5000	2.2	1.10	
	65	138	0.8750	3.4	2.98	
	66	83	0.6250	2.2	1.38	
	67	90	0.6250	2.7	1.69	
	68	65	0.5000	2.8	1.40	
	Average			0.64	2.71	1.73

APPENDIX A (contd p. 4)

Test Results from Extinguishing Surface Fires by Halogenated Hydrocarbon Agents at -65 F.

Agent	Test no.	Air pressure (psig)	Wt of agent used (lb)	Extinguishing time (sec)	Extinguishment index (lb-sec)	Remarks
Halon 1002 (dibromomethane)	69	130	0.7500	2.3	1.73	extinguisher valve would not close
	70	140	0.7500	2.7	2.03	
	71	140	0.5000	2.4	1.20	
	72	110	0.8750	3.1	2.71	
	73	100	1.0000	3.2	3.20	
	74	100	...	4.8	...	
	75	100	0.7500	2.6	1.95	
	76	90	0.7500	2.6	1.95	
	77	100	0.7500	2.4	1.80	
	Average			0.77	2.66	
Halon 1011 (chlorobromo- methane)	78	100	1.1250	6.4	...	frame fell
	79	60	0.7500	5.2	3.90	
	80	100	0.6250	3.7	2.31	
	81	90	0.5625	3.6	2.03	
	82	87	0.6250	3.6	2.25	
	83	130	0.7500	2.8	2.10	
	84	125	0.7500	3.3	2.47	
	85	140	0.8750	3.6	3.15	
	86	105	0.8675	3.0	2.60	
Average			0.73	3.60	2.63	
Halon 1202 (dibromodifluoro- methane)	87	105	0.6250	2.4	1.50	extinguisher valve would not close
	88	100	0.7500	2.9	2.18	
	89	100	
	90	95	0.6875	2.7	1.86	
	91	100	0.7500	3.6	2.70	
	92	85	0.6875	2.6	1.79	
	93	100	0.6250	2.5	1.56	
	94	105	0.6250	2.3	1.44	
	95	108	0.6125	3.2	1.96	
	Average			0.67	2.77	

APPENDIX A (contd p. 5)

Test Results from Extinguishing Surface Fires by Water-Base
Alkali-Earth-Metal-Salt Agents at Ambient (70 F) Temperature.

Agent	Test no.	Air pressure (psig)	Wt of agent used (lb)	Extinguishing time (sec)	Extinguishment index (lb-sec)	Remarks
Water	1	150	1.0250	6.3	6.46	
	2	155	0.8750	5.2	4.55	
	3	140	1.1250	9.5	10.69	
	4	145	1.1250	7.0	7.88	
	5	148	1.0625	5.9	6.27	
	6	162	0.7500	4.6	3.45	
	7	90	0.8750	9.7	8.49	
	8	155	0.9375	7.7	7.22	
	9	155	0.7500	10.0	7.50	
Average			0.95	7.32	6.95	
47 per cent zinc chloride + 53 per cent water	10	155	1.0000	5.6	5.60	high - not used in average
	11	155	1.5000	6.3	9.45	
	12	165	0.9375	4.4	4.13	
	13	148	2.0000	7.9	15.80	
	14	160	1.5625	7.4	11.56	
	15	150	1.0000	4.4	4.40	
	16	82	1.2500	6.4	8.00	
	17	150	1.5000	7.6	11.40	
	18	150	1.3125	7.8	10.24	
Average			1.26	6.24	7.86	
23 per cent potassium carbonate + 77 per cent water	19	170	0.8750	4.2	3.67	
	20	170	0.8125	4.5	3.66	
	21	160	0.8125	4.8	3.90	
	22	160	0.9375	4.0	3.75	
	23	150	0.7500	4.8	3.60	
	24	85	0.6875	4.7	3.23	
	25	85	0.8750	5.4	4.73	
	26	90	0.8375	4.9	4.10	
	27	92	0.8125	4.7	3.82	
Average			0.82	4.67	3.83	

APPENDIX A (contd p. 6)

Test Results from Extinguishing Surface Fires by Water-Base
Alkali-Earth-Metal-Salt Agents at Ambient (70 F) Temperature (contd).

Agent	Test no.	Air pressure (psig)	Wt of agent used (lb)	Extinguishing time (sec)	Extinguishment index (lb-sec)	Remarks
24 per cent lithium chloride + 76 per cent water	28	155	0.7500	4.4	3.30	
	29	170	0.7500	5.7	4.28	
	30	150	0.6250	4.1	2.56	
	31	150	0.6875	8.5	5.84	
	32	170	0.8750	5.0	4.38	
	33	150	1.0000	5.7	5.70	
	34	155	0.7500	4.9	3.68	
	35	150	0.7500	5.0	3.75	
	36	150	1.0000	8.9	8.90	
Average			0.80	5.8	4.64	
10 per cent lithium chloride + 20 per cent calcium chloride + 70 per cent water	37	150	0.8750	5.0	4.37	
	38	145	0.7500	5.1	3.83	
	39	150	0.8750	6.4	5.60	
	40	170	0.8125	5.1	4.14	
	41	150	0.8750	5.0	4.37	
	42	170	0.6875	4.5	3.09	
	43	170	1.0000	8.2	8.20	
	44	150	0.7500	6.3	4.72	
	45	150	1.1250	6.6	7.43	
Average			0.86	5.8	4.99	
30 per cent calcium chloride + 22 per cent zinc chloride + 48 per cent water	46	155	1.1875	6.6	7.84	
	47	155	1.0000	5.3	5.30	
	48	155	1.2500	6.8	8.50	
	49	165	0.9375	6.0	5.63	
	50	150	1.1250	6.4	7.20	
	51	150	0.8750	3.9	3.41	
	52	150	0.8750	5.3	4.64	
	53	150	0.8750	5.2	4.55	
	54	150	0.9375	5.0	4.69	
Average			1.01	5.6	5.66	

APPENDIX A (contd p. 7)

Test Results from Extinguishing Surface Fires by Water-Base
Alkali-Earth-Metal-Salt Agents at 0 F.

Agent	Test no.	Air pressure (psig)	Wt of agent used (lb)	Extinguishing time (sec)	Extinguishment index (lb - sec)	Remarks
47 per cent zinc chloride + 53 per cent water	55	112	2.8750	17.5	50.31	high - not used in average
	56	118	1.6250	10.6	17.23	
	57	115	2.0000	16.3	32.60	
	58	102	2.0000	17.2	34.40	
	59	97	1.9375	11.3	21.89	
	60	118	1.2500	11.4	14.25	
	61	120	1.5000	10.0	15.00	
	62	115	1.3875	11.0	15.26	
	63	120	1.5000	12.2	18.30	
	Average			1.65	12.50	
23 per cent potassium carbonate + 77 per cent water	64	120	0.8750	12.0	10.50	
	65	128	0.8750	9.3	8.14	
	66	115	0.7500	3.5	2.63	
	67	115	0.7500	3.0	2.25	
	68	115	0.7500	6.0	4.50	
	69	125	0.7500	4.3	3.22	
	70	122	1.1250	6.3	7.09	
	71	128	1.3125	11.0	14.44	
Average			0.90	6.93	6.24	
24 per cent lithium chloride + 76 per cent water	72	140	0.8750	9.0	7.88	
	73	110	0.6875	6.0	4.13	
	74	125	1.2500	9.7	12.13	
	75	125	0.6250	6.6	4.13	
	76	130	1.3750	10.6	14.58	
	77	130	1.6250	16.0	26.00	
	78	110	1.1250	13.2	14.85	
	79	110	1.2500	9.7	12.13	
	80	115	1.3750	11.9	16.36	
	Average			1.13	10.30	11.64
10 per cent lithium chloride + 20 per cent calcium chloride + 70 per cent water	81	115	1.2500	7.4	9.25	
	82	115	1.2500	7.6	9.50	
	83	115	1.3125	8.1	10.63	
	84	118	1.3750	8.7	11.96	
	85	115	1.3750	8.3	11.41	
Average			1.31	8.02	10.51	

APPENDIX A (contd p. 8)

Test Results from Extinguishing Surface Fires by Water-Base
Alkali-Earth-Metal-Salt Agents at 0 F (contd).

Agent	Test no.	Air pressure (psig)	Wt of agent used (lb)	Extinguishing time (sec)	Extinguishment index (lb - sec)	Remarks
30 per cent calcium chloride + 22 per cent zinc chloride + 48 per cent water	86	115	1.6875	12.0	20.25	low - not used in average
	87	120	1.7500	16.0	28.00	
	88	140	1.1875	10.0	11.88	
	89	155	1.6875	13.3	22.44	
	90	115	1.1250	11.7	13.16	
	91	115	0.8750	6.6	5.77	
	92	135	1.6875	13.3	22.44	
	93	110	0.8125	14.0	11.38	
	94	165	1.3750	9.8	13.47	
Average			1.41	12.51	17.64	

APPENDIX A (contd p. 9)

Test Results from Extinguishing Surface Fires by Water-Base
Alkali-Earth-Metal-Salt Agents at -65 F.

Agent	Test no.	Air pressure (psig)	Wt of agent used (lb)	Extinguishing time (sec)	Extinguishment index (lb-sec)	Remarks
47 per cent zinc chloride + 53 per cent water	95	100	1.4375	18.0	25.87	
	96	105	1.9375	22.0	42.62	
	97	105	1.5000	17.0	25.50	
	98	105	1.2125	16.5	20.00	
	99	100	1.6250	19.4	31.52	
	100	105	1.8750	20.0	37.50	
	101	110	1.7500	18.6	32.55	
	102	110	1.7500	20.1	35.17	
	103	115	1.8750	16.4	30.75	
	Average			1.66	18.67	30.99
24 per cent lithium chloride + 76 per cent water	104	150	1.8750	27.5	51.56	
	105	105	0.8750	10.0	8.75	
	106	100	1.1250	21.5	24.19	
	107	130	1.2500	12.2	15.25	
	108	100	1.7500	23.9	41.83	
	109	140	1.2500	15.9	19.88	
	110	125	1.1250	11.5	12.94	
	111	140	0.8750	9.2	8.05	
	112	100	0.7500	10.9	8.18	
	Average			1.21	15.84	19.17
10 per cent lithium chloride + 20 per cent calcium chloride + 70 per cent water	113	140	1.5000	10.6	15.90	
	114	145	1.1250	8.2	9.23	
	115	125	1.1250	7.2	8.10	
	116	145	1.5625	11.2	17.50	
	117	125	1.1875	8.8	10.45	
Average			1.30	9.2	11.96	

APPENDIX B

Hazardous Properties, Storage, and Handling of Dry-Alkali-Earth-Metal-Salt Chemicals

- A. The following quotations are from the Handbook of Dangerous Materials by N. Irving Sax, Reinhold Publishing Corporation, New York 18, N. Y. (1951).

1. CALCIUM

Hazardous Properties: Metallic calcium reacts with moisture or acids to liberate large quantities of hydrogen and can develop enough pressure in the containers in which it is being kept to explode. Therefore, it is a dangerous fire hazard. See Hydrogen. When exposed to air, it turns to calcium hydroxide, which is caustic in action and can cause burns. Finally, it can ignite spontaneously in the presence of oxygen and some moisture. The fumes evolved are irritating to skin, eyes, and mucous membranes as well as upper respiratory tract.

Treatment and Antidotes: Any calcium residue left on the body or clothing should be brushed off and the area washed with water to prevent skin burns due to the calcium oxide which will be left there.

Storage and Handling: Metallic calcium should be stored under kerosene toluene or some other inert, oxygen-free liquid. It should not be stored in water or dry. When calcium catches fire and personnel must be exposed to the fumes, protective equipment should be worn, such as chemical safety goggles and a respirator, since the fumes are caustic. Calcium containers should be plainly labelled. Personnel should be cautioned against careless handling. Store in a cool place away from acute fire hazards, away from possible high temperatures, and away from pipes which might condense moisture and then drip on it.

2. CALCIUM CHLORIDE

Hazardous Properties: If this material comes in contact with the eyes, it will cause lachrymation and conjunctivitis.

Treatment and Antidotes: Eyes so exposed should be washed with plenty of warm water and the irritation will stop. If it is severe, consult a physician.

Storage and Handling: Personnel exposed to this material in the form of a fine dust should wear chemical safety goggles.

3. LITHIUM

Hazardous Properties: Lithium is a dangerous fire hazard because it reacts very vigorously with acids and water to liberate hydrogen, which can accumulate to form explosions or fires. See Hydrogen. There is controversy regarding the effect of lithium salts in the diet. There is, in fact, some feeling that lithium chloride could not be substituted safely for sodium chloride.

Storage and Handling: This material should be stored in an inert, oxygen-free solvent, such as kerosene or toluene. It should be kept away from water, because it reacts violently with it to liberate hydrogen. It should be stored away from acids or acid fumes, in a cool, well ventilated place away from areas of acute fire hazards. Containers should be kept closed and plainly labelled.

4. ZINC

Maximum Allowable Concentration in Air: 15 mg/cu. meter

Hazardous Properties: Zinc is not inherently an extremely toxic element. However, when heated, it evolves a fume of freshly formed zinc oxide which, upon inhalation, can cause a disease known as "brass founders' ague," "brass chills," etc. which has the property of causing habituation, that is, it is possible for people to become immune to it. However, this immunity can be broken by a cessation of exposure of only a few days. Zinc oxide dust which is not freshly formed

is virtually innocuous. There is no cumulative effect to the inhalation of zinc fumes. Fatalities, however, have resulted from lung damage caused by the inhalation of high concentrations of zinc chloride fumes. Soluble salts of zinc have a harsh metallic taste; small doses can cause nausea and vomiting, while larger doses cause violent vomiting and purging. So far as can be determined, the continued administration of zinc salts in small doses has no effects in man except those of disordered digestion and constipation. Exposure to zinc chloride fumes can cause damage to the mucous membrane of the nasopharynx and respiratory tract and give rise to a pale gray cyanosis.

It has been stated that zinc oxide dust can block the ducts of the sebaceous glands and give rise to a papular, pustular eczema in men engaged in packing this compound into barrels. Sensitivity to zinc oxide in man is extremely rare. Zinc chloride, because of its caustic action, can cause ulceration of the fingers, hands and forearms of those who use it as a flux in soldering. This condition has even been observed in men who handle railway ties which have been impregnated with this material. It is the opinion of some who work with it that it is carcinogenic.

Finely divided zinc powder is a dangerous fire hazard in that it can spontaneously ignite in air. Also in laboratory experiments, it has been found that zinc residues of reduction experiments can spontaneously ignite and cause fires when they are discarded along with papers and other combustible materials.

5. ZINC CHLORIDE

Hazardous Properties: This is one of the most dangerous compounds of zinc. It is very toxic. See Zinc. By contact it can cause reddened conjunctiva, and burns of the cornea. Upon ingestion it can cause dilation of the pupils (6). It attacks skin and mucous membranes wherever it comes in contact with the body.

(6) "Toxic Eye Hazards," Publication 494, National Society Prevention of Blindness, Inc.

- Storage and Handling: Personnel exposed to this material should wear chemical safety goggles for protection of the eyes. A respirator is also advised to avoid inhalation of the material, and protective clothing should be worn to avoid skin contact. See Zinc.

- B. The following quotations are from "Chemistry of Industrial Toxicology," by Harvey B. Elkins, Ph. D., John Wiley and Sons, Inc., New York, N. Y. (1950), page 34.

Fundamentally, zinc is not a highly toxic element; and zinc oxide dust, for example, is virtually innocuous. The inhalation of freshly formed zinc fumes caused by the volatilization of burning of zinc, however, causes a peculiar disease known variously as zinc-fume fever, metal-fume fever, brass-founders' ague, zinc chills, and galvo.

This ailment is characterized by a fever and chills occurring a few hours after exposure. The patient usually recovers within 36 hours and if the exposure is repeated daily an immunity is developed. This immunity is lost when exposure ceases for a few days, even over a week-end. Ordinarily there are no aftereffects. According to Johnstone²⁰, fatal cases have been reported, but these are rare.

Occupations in which zinc chills are common include welding of galvanized metal, and melting and casting of brass or bronze. Casting of zinc and galvanizing apparently do not produce a heavy exposure to zinc fumes.

Other metal fumes, such as magnesium, iron, and cadmium fumes, are said to produce similar effects, but zinc is by far the commonest offender, in this respect.

Fatalities have resulted from lung damage caused by the inhalation of high concentrations of zinc chloride fumes²¹.

20. Johnstone, R. T., "Occupational Diseases", W. B. Saunders Co. (1941)

21. Evans, E. H. "The Lancet", 6369, 368 (1945)

- C. The following is an excerpt from the *Journal of Industrial and Engineering Chemistry* (December 1951), page 2644.

Lithium chloride is extremely corrosive, especially in the presence of water. Since it is also very hygroscopic, it presents serious corrosion problems.

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1	Factory Insurance Association, Los Angeles, Attn: Mr. R. W. Fuller
1	Fire Chief, U. S. Naval Air Station, San Diego, Attn: Mr. A. L. Hatley
1	Fire Chief, U. S. Naval Air Station, Los Alamitos, Attn: Mr. Harry V. Jordon

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1 Cylpro Company, Attn: Mr. Floyd J. Lee

1 Fire Chief, Naval Supply Center, Oakland, Attn: Mr. G. H. Matthews

1 Deputy Chief, Milwaukee Fire Department, Attn: Mr. James Moher

1 District Fire Marshal, 4th Naval District, Attn: Mr. R. L. Noyes

1 Fire Chief, Woodland Fire Department, Attn: Mr. Everett H. Runkle

1 Chief, Stockton Fire Department, Attn: Mr. J. L. Stevenson

1 Fire Chief, Davis Fire Department, Attn: Mr. Henry Sullivan

1 Factory Mutual Engineering Division, Los Angeles, Attn: Mr. A. W. Swanson

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1 Chief, Fire Protection and Aircraft Rescue Branch, Headquarters USAF, Attn: Mr. G. T. Cook

1 Bureau of Aeronautics, SE 743, Attn: Mr. Carl Dreesen

1 District Fire Marshal, 14th Naval District, Attn: Mr. Laurence Duhrkoop

1 Engineer Research and Development Laboratories, Fort Belvoir, Attn: Mr. T. B. Edwards

1 Office of the Chief of Naval Operations, Attn: Mr. Orville Emory

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1 National Bureau of Standards, Attn: Mr. A. F. Robertson

1 National Fire Protection Association, Boston, Attn: Mr. George Tryon

1 Naval Research Laboratories, Attn: Mr. R. L. Tuve

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