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HORIZONS RESEARCH INC CLEVELAND OHIO  
SCREENING STUDY TO IDENTIFY PHASE CHANGE COOLANTS FOR PORTABLE --ETC(U)  
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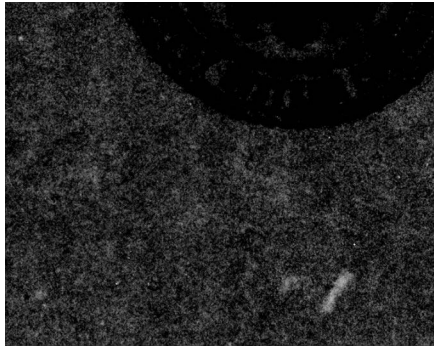
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Horizons Research Incorporated, under Contract No. N00140-76-C-6703 with the Navy Clothing & Textile Research Facility, performed a literature search to identify coolant candidates to be considered for replacing the ice-water system in a portable life support unit*. The coolants recommended for consideration are carbon dioxide, an ammonia-carbon dioxide mixture, and a salt such as potassium acid fluoride incorporated into ice. (U)		

xx CO2, an NH3-CO2 mixture, 170 550

following considerations:

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In the ~~carbon dioxide~~ <sup>CO<sub>2</sub></sup> system, solid carbon dioxide (dry ice) will sublime and the resultant gases warm to 4°C, then be expelled from the suit. The heat absorption for this process is 153.0 Kcal/kg. To achieve 504 Kcal (2000 Btu) of cooling, 3.3 Kg (7.3 lbs) of ~~Carbon dioxide~~ <sup>CO<sub>2</sub></sup> is needed. This is an 83% improvement over the heat absorption of ice melting and warming to 4°C, or a 45% reduction in the weight of ice needed. The ~~carbon dioxide~~ <sup>CO<sub>2</sub></sup> system appears to be completely safe, with reasonable logistics. (U)

In the ~~ammonia-carbon dioxide~~ <sup>NH<sub>3</sub>-CO<sub>2</sub></sup> system, the ~~carbon dioxide~~ <sup>CO<sub>2</sub></sup> will sublime, the ~~ammonia~~ <sup>NH<sub>3</sub></sup> vaporize, and the resultant gases warm to 4°C, then with mixing be expelled from the suit. This system might be flammable, so should be examined in the laboratory, as is discussed in Section 4. The heat absorption for this system is an impressive 198.5 Kcal/kg for an 0.8 mole ratio of ~~ammonia~~ <sup>NH<sub>3</sub></sup> to ~~carbon dioxide~~ <sup>CO<sub>2</sub></sup>. To achieve 504 Kcal (2000 Btu) of cooling, 2.5 Kg (5.6 lbs) of total coolant is needed. This is a 137% improvement over the heat absorption of ice melting and warming to 4°C, or a 58% reduction in the weight of ice needed. Aside from the flammability which must be examined, the logistics of the system appear reasonable. (U)

In the potassium acid fluoride-ice system, the heat of solution of the salt is added to the heat of fusion of ice. Over the temperature range of about -15 to 5°C, this system yields 121 Kcal/kg. To achieve 504 Kcal (2000 Btu) of cooling, 4.12 Kg (9.2 lbs) of total coolant is needed. This is a 45% improvement over the ice alone system, or a 31% reduction in the weight of ice needed. The salt will decompose at about 225°C. With decomposition or acids, toxic fumes result. Otherwise, the logistics of the system appear reasonable. (U)

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"SCREENING STUDY TO IDENTIFY PHASE CHANGE  
COOLANTS FOR PORTABLE LIFE SUPPORT SYSTEMS"

1.0 SUMMARY

1.1 Program Objective

The U. S. Navy Clothing and Textile Research Facility of Natick, Massachusetts, wishes to identify nontoxic, nonflammable compounds or mixtures of compounds which would produce a phase or physical change specific cooling effect greater than that produced by the heat of fusion of wet ice. The compounds or mixtures of interest shall produce this cooling effect at or near atmospheric pressure and below 5°C.

More specifically, the present ice fusion system weighing 40 pounds, with 12 pounds being due to the ice, and 4 pounds to the heat exchanger, will supply the minimal needed 504 Kcal/hr (2000 Btu/hr) for one hour, but is too heavy. The Navy would like to have as a minimum a total system which weighs less than 30 pounds, and which can supply the 504 Kcal/hr cooling for one hour.

This study was directed towards identifying coolant materials more efficient than ice which also had the additionally desired properties of safety, reasonable logistics, and reasonable costs.

1.2 Methodology Overview

Figure 1 shows the tasks addressed during this study, and their interrelationships. Categorically, the classes of coolants addressed included:

- (1) one phase change with one compound
- (2) two or more phase changes with one compound

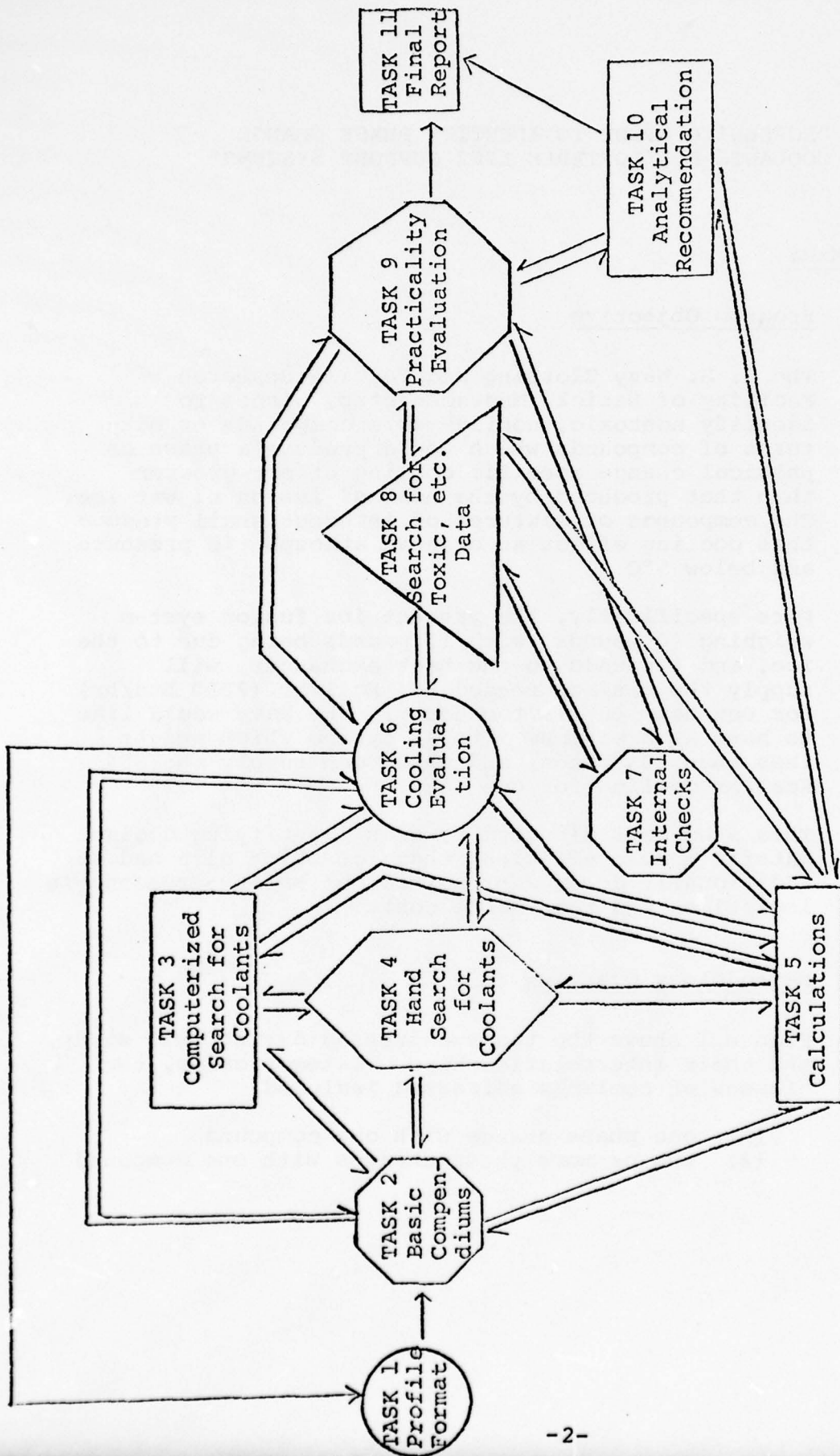


Figure 1. Schematic Diagram of Technical Approach

- (3) one phase change with each of two or more compounds
- (4) one non-phase change process with one compound
- (5) a non-phase process(es) combined with a phase change for one or more compounds.

### 1.3 Principal Results and Recommendations

The coolants recommended for consideration are carbon dioxide, an ammonia-carbon dioxide mixture, and a salt such as potassium acid fluoride incorporated into ice.

In the carbon dioxide system, solid carbon dioxide (dry ice) will sublime and the resultant gases warm to 4°C, then be expelled from the suit. The heat absorption for this process is 153.0 Kcal/kg. To achieve 504 Kcal (2000 Btu) of cooling, 3.3 Kg. (7.3 lbs) of carbon dioxide is needed. This is an 83% improvement over the heat absorption of ice melting and warming to 4°C, or a 45% reduction in the weight of ice needed. The carbon dioxide system appears to be completely safe, with reasonable logistics.

In the ammonia-carbon dioxide system, the carbon dioxide will sublime, the ammonia vaporize, and the resultant gases warm to 4°C, then with mixing be expelled from the suit. This system might be flammable, so should be examined in the laboratory, as is discussed in Section 5. The heat absorption for this system is an impressive 198.5 Kcal/kg for an 0.8 mole ratio of ammonia to carbon dioxide. To achieve 504 Kcal (2000 Btu) of cooling, 2.5 Kg (5.6 lbs) of total coolant is needed. This is a 137% improvement over the heat absorption of ice melting and warming to 4°C, or a 58% reduction in the weight of ice needed. Aside from the flammability which must be examined, the logistics of the system appear reasonable.

In the potassium acid fluoride-ice system, the heat of solution of the salt is added to the heat of fusion of ice. Over the temperature range of about -15 to 5°C, this system yields 121 Kcal/kg. To achieve 504 Kcal (2000 Btu) of cooling, 4.12 Kg (9.2 lbs) of total coolant is needed. This is a 45% improvement

over the ice alone system, or a 31% reduction in the weight of ice needed. The salt will decompose about 225°C. With decomposition or acids, toxic fumes result. Otherwise, the logistics of the system appear reasonable.

## 2.0 EXPANDED DISCUSSION OF RESULTS

### 2.1 One Phase Change With One Compound Class

Basic reference compendiums and two computer searches of relevant data banks were searched for safe compounds having either heats of fusion, heats of vaporization, or heats of sublimation great than 80 Kcal/kg (the heat fusion of ice) about or below 10°C at atmospheric pressure. Some flexibility in temperature was extended to compounds with high vapor pressures.

Only the sublimation of carbon dioxide was found to meet all of the cooling and safety requirements, and provide a 42% weight reduction in the amount of ice needed to obtain 504 Kcal or 2000 Btu of cooling for one hour.

Other compounds were found that could meet the cooling, but not the safety requirements.

A few compounds which could only partially meet the safety requirements, but which appeared to meet the cooling requirements, suggested themselves as candidates to be combined with a coolant diluent, like carbon dioxide, for increased safety. These combinations are discussed in Section 2.3 and 2.3.2.

#### 2.1.1 Cooling Obtained From Heat of Fusion

Only ammonia<sup>(3a)</sup> was found to have a heat of fusion fitting the desired cooling criteria. At -75°C, its heat of fusion is 108 Kcal/kg. Due to the uncommonness of solid ammonia and its anticipated logistical problems, it was not considered further.

### 2.1.2 Cooling Obtained From Heat of Vaporization

Twenty-three compounds were found having heats of vaporization fitting the desired cooling criteria. Of the 23, only five could, with reservation, be considered further. The remainder were not safe.

The 23 compounds are listed in Table I. Additional safety and toxicology data from Ref. 2 are in Appendix I.

The five compounds with their heat of vaporization at 0°C in Kcal/kg given in parentheses, which received reserved recommendations pending combination with a diluent for safety are: ammonia (301.6), acetone (134.8), methanol (284), ethanol (219.8) and n-propanol (193).

Carbon dioxide, also listed in Table I was identified as the possible diluent.

Of the five compounds, ammonia and/or methanol combined with carbon dioxide were the most attractive coolant combinations.

### 2.1.3 Cooling Obtained From Heat of Sublimation

A few organic compounds, listed in Table II, had attractive heats of sublimation into the temperature range of interest, but their vapor pressures at these temperatures were too low for further consideration.

Carbon dioxide has a heat of sublimation of 137 Kcal/kg at -78°C, and is safe. Table III lists the weight of solid carbon dioxide or dry ice needed to obtain cooling rates of 252 Kcal/hr. (1000 Btu/hr) or 605 Kcal/hr. (2400 Btu/hr) for 1, 2, or 4 hours.

The weight of carbon dioxide needed to produce 504 Kcal or 2000 Btu of cooling for one hour is 3.68 Kg or 8.1 lbs., a 42% decrease in the 14 pounds of ice that would be needed to achieve the same cooling.

TABLE I

## COOLING CANDIDATES FROM VAPORIZATION DATA

Compound	Formula	$\Delta H_{vap}^1$ (Kcal/Kg)	at T (°C)	B.P. (°C)	Flash <sup>2</sup> Point (°C)	Explosion <sup>2</sup> Limits (%)	Hazard <sup>2</sup>	Toxicity <sup>2</sup>	Recommendations
1. Ammonia (anhydrous)	NH <sub>3</sub>	301.6	0	-33.4		16-25	Moderate	Irritant	Reserved recommendation
2. Butane	C <sub>4</sub> H <sub>10</sub>	91.5	0	-0.5	-60	1.9-8.5	Explosive	Asphyxiant	Not recommended
3. Ethyl Acetate	CH <sub>3</sub> CO <sub>2</sub> C <sub>2</sub> H <sub>5</sub>	102	0	77.15	-4.4	2.5-9	Dangerous if exposed to heat/- flame	Irritant	" "
4. Ethyl Chloride	CH <sub>3</sub> CH <sub>2</sub> Cl	92.95	4.7	12.3	-50	3.8-15.4	Dangerous if exposed to heat/- flame	Harmful	" "
5. Ethylene- dichloride	(CH <sub>2</sub> Cl) <sub>2</sub>	85.3	0	83.5	13.3	6.2-15.9	Dangerous if exposed to heat/- flame	Severe irritant	" "
6. Hydrogen	H <sub>2</sub>	108	-252.8	-253		4.1-74.2	Explosive		" "
7. Hydrogen Chloride	HCl	98.7	-84.3	-84.8			Corrosive	Irritant	" "

TABLE I (Cont'd.)

Compound	Formula	$\Delta H_{vap}^1$ (Kcal/Kg)	at T (°C)	B.P. (°C)	Flash <sup>2</sup> Point (°C)	Explosion <sup>2</sup> Limits (%)	Hazard <sup>2</sup>	Toxicity <sup>2</sup>	Recommendation
8. Hydrogen Sulfide	H <sub>2</sub> S	131.9	-61.4	-60.4		4.3-46	Highly dangerous if exposed to heat/- flame.	Severe irritant	Not recommended
9. Isobutane	C <sub>4</sub> H <sub>10</sub>	91.5	10	-11.7		1.9-8.5	Dangerous if exposed to heat/- flame.	Asphyxiant	"
10. Methyl Acetate	CH <sub>3</sub> CO <sub>2</sub> CH <sub>3</sub>	114	0	57.8		3.1-16	Dangerous if exposed to heat/- flame.	Irritant	"
11. Methyl Chloride	CH <sub>3</sub> Cl	102.3	-23.8	-23.7	<0	10.7-17.2	Dangerous if exposed to heat/- flame.	Irritant	"
12. Propane	CH <sub>3</sub> CH <sub>2</sub> CH <sub>3</sub>	89.6	0	-41.2	-104	2.3-9.5	Highly dangerous if exposed to heat/- flame.	None	"
13. Sulfur Dioxide	SO <sub>2</sub>	94.9	-10.08	-10.0			Will react with water to produce toxic and corrosive fumes.		"

TABLE I (Cont'd.)

## COOLING CANDIDATES FROM VAPORIZATION DATA

Compound	Formula	$\Delta H_{vap}$ <sup>3</sup> (Kcal/kg)	at T (°C)	B.P. (°C)	Flash Point (°C)	Explosion <sup>2</sup> Limits (%)	Hazard <sup>2</sup>	Toxicity <sup>2</sup>	Recommendation <sup>2</sup>
Isopentane	C <sub>5</sub> H <sub>12</sub>	88.6	13	28	-50	1.4-7.6	Dangerous	Unknown to low.	Not recommended.
Hexene	C <sub>6</sub> H <sub>12</sub>	92.8	0	63	-30	--	Dangerous	Unknown to moderate.	"
n-hexane	C <sub>6</sub> H <sub>14</sub>	89.1	0	68.7	-22	1.2-7.5	Dangerous	Low	"
Ether	C <sub>4</sub> H <sub>10</sub> O	94 (4)	0	34.6	-45	1.8-45	Severe	Unknown to moderate.	"
Chlorine oxide	Cl <sub>2</sub> O	99.7 (4)	11	3.5	--	Explodes	Severe	--	"
Ethylene oxide	C <sub>2</sub> H <sub>4</sub> O	240 (4)	10.6	10.7	0	3.0-100	Severe	Moderate to high.	"
Acetone	C <sub>3</sub> H <sub>6</sub> O	134.8 131.9	0 20	56.5	-32	2.6-12.8	Dangerous	Low to moderate.	See text.
Methanol	CH <sub>4</sub> O	284 279.6	0 20	64.8	11	7,3-36.5	Moderately dangerous.	"	"
Ethanol	C <sub>2</sub> H <sub>6</sub> O	219.8 217.4	0 20	78.3	13	4.3-19	"	"	"
n-propanol	C <sub>3</sub> H <sub>8</sub> O	193	0	97.2	15	2.1-13.5	"	"	"
Carbon dioxide (dry ice)	CO <sub>2</sub>	87.2(1) 55.9	(-60) (0)	-78.5	None	None	None	None; local acute irritant.	"

TABLE II

## SUBLIMATION DATA FOR ORGANIC COMPOUNDS (1a)

Compound	Temp. Range (°C)	$\Delta H$ Sub. (Kcal/Kg)	Approximate Vapor Pressure (mm)
Acetic acid	-35 to 10	165.9	3.4
Acetophenone, 1-chloro	5 to 50	140.3	0.0007
Acetophenone, p-methoxy	3 to 27	123.2	0.0008
Acetone, benzoyl	5 to 26	123.5	0.0005
Benzene	-30 to 5	135.5	19.7
Cyclohexane	-5 to 5	106.4	27.6
Formic acid	-5 to 8	314.0	8.1
Methane	-194 to -184	1478.0	0
Phenol	5 to 32	172.0	.06
Thymol	0 to 40	145.4	.002

TABLE III

WEIGHT OF SOLID CARBON DIOXIDE REQUIRED TO OBTAIN  
INDICATED COOLING RATES FOR THE SPECIFIED TIME LENGTHS

Time (hrs.)	Cooling Rates	
	1000 Btu or 252 Kcal/hr. Weight of CO2 Kg lbs	2400 Btu or 605 Kcal/hr. Weight of CO2 Kg lbs
1	1.839 4.06	4.414 9.73
2	3.678 8.12	8.828 19.46
4	7.356 16.24	17.656 38.96

## 2.2 Two or More Phase Changes With One Compound Class

The objective was to find compounds which would undergo multiple phase changes within reasonable condition limits. None was found, except the coolants used in refrigeration systems. Such coolants undergo vaporization-condensation in a cyclic fashion.

Since the usual refrigeration coolants are one of the Freons, which are non-flammable and virtually non-toxic, the refrigeration industry along with government research groups, were surveyed to learn if a portable heat pump was feasible.

Neither existing units, nor combinations of available components appear capable of meeting the minimum 504 Kcal or 2000 Btu cooling with a system weighing less than 30 pounds. Some developmental systems look promising, particularly those discussed in reference 24.

### 2.2.1 Refrigeration Systems and Cooling Units

The two major components to a refrigeration unit are the cooling system (compressor, motor, condenser, fluid, pump or fan) and the power pack. Table IV lists complete refrigeration systems first, then cooling units. System No. 1 is an off-the-shelf refrigeration unit capable of supplying 1500 Btu/hr cooling and weighing 46 pounds. A significant portion of its weight is in the 22 pound inverter. The designer of this system (Ref. 6) believes System No. 1 can be refined as described in System No. 2, such that a DC, not an AC motor is used, and 1500 Btu/hr cooling rate would require a 16 pound unit. Systems numbered 3 to 5 are cooling units only, which still require power packs. System No. 5 has an AC motor, hence an inverter is needed with it. For the cooling offered by Systems 3 to 5, their weights are high.

### 2.2.2 Major Components for Refrigeration Systems

Table V lists two of the major components in a refrigeration system: the compressor (with motor)

TABLE IV

## REFRIGERATION SYSTEMS AND COOLING SYSTEMS

System No.	Components	Capabilities	Power Requirement	Weight (lbs.) 1 Hr Operation
1 (Ref.6)	Entire System	1500 BTU/hr	1330 watts	46
	Cooling Unit - Eastern Industries (O) Model RS-301B	1500 BTU/hr (400 Hz)	1000 watts	11
	Inverter - Avionics Instruments (O) Model IA-1000	1000 watts	1330 watts	22
(Ref.8)	Power Pack - LiSO <sub>2</sub> Batteries (D)	100 watt-hr/lb 100 watts/lb		13
	2 (Ref.9)	Entire System	600 watts	16
(Ref.8)	Cooling Unit - DC Motor (D)	1500 BTU/hr	600 watts	10
	Power Pack - LiSO <sub>2</sub> Batteries (D)	100 watt-hr/lb 100 watts/lb	(DC)	6
B. COOLING SYSTEMS				
3 (Ref.10)	Cooling Unit - Task Corporation (O)	400 BTU/hr	120 watts DC (12 V)	20
	4 (Ref.11)	Cooling Unit - Magnkold Inc. (O)	700 BTU/hr at 40°F	24
5 (Ref.12)	Cooling Unit - Aerotherm Corp. (N)	1000 BTU/hr	300 watts 400 Hz (110 V)	30

Status Code

O = Off shelf  
D = Developmental  
N = NASA

TABLE V  
REFRIGERATION COMPONENTS

A. COMPRESSORS		Capabilities	Power Requirements	Weight (lbs.)
Compressors				
Aircraft Refrigeration Compressor (Ref.13)	1,500 Btu/hr.	450 watts (400 Hz)	20	
Aircraft Refrigeration Compressor Model No. IC-30 (Ref.14)	2,500 Btu/hr.	250 watts (400 Hz)	20	
Household Compressor (Ref.15)	2,500 Btu/hr.	200 watts	25	
Absorption Refrigeration Unit (Ref.16)	---*	1,750 Btu/hr.	Light	
*No rating given, System sluggish to respond and must be kept reasonably level.				
B. POWER PACKS		Capabilities (watt-hr/lb.)	Weight for 500 watt-hr (lbs.)	Cost (\$)
Type of Battery	Company			
Lithium-Sulfur Dioxide	P.R. Mallory (Ref.17)	100	5	Development
Silver-Zinc	Eagle-Picher Yardney (Ref.23)	30 40	16 12	2,000.00 800.00
Lead Acid (Sealed)	Eagle-Picher Gates Research (Ref.20)	7.5 10	66 50	150.00 300.00
Nickel-Cadmium (Vented)	Eagle-Picher (Ref.21)	15	32	600.00
Thermoelectric Power Cell, U.S. Army	U.S. Army (Ref.22)	12 volts, 3 amps for 8 hrs.	--	--

and the power pack. All of the compressors are available and have AC motors, which need inverters. By combining appropriate batteries, all but one of which are available, with the various compressors, it is evident that the weight of the total systems will be too high.

### 2.3 One Phase Change With Each of Two or More Compounds Class

Two different types of systems fall into this class. The first deals with adding a water soluble salt to ice such that the cooling would be obtained from the heat of fusion of the ice, plus the heat of solution of the salt.

Seven water soluble, non-explosive salts have heats of solution ranging from 74.6 to 99.6 Kcal/kg, but of these only ammonium chloride with a heat of solution of 76.5 Kcal/kg appears completely safe. Since this value is no improvement over the heat of fusion of ice, no weight advantage is gained by its use.  $\text{NH}_4\text{HF}_2$ ,  $\text{KHF}_2$ , and  $\text{NaHF}_2$  have attractive cooling properties, especially  $\text{KHF}_2$ , but their safety is questionable. A solution of 30g  $\text{KHF}_2$  in 100 g. of water has a combined heat of fusion and heat of solution of 121 Kcal/kg.

A possible volume advantage is gained by using a salt, since the salts are more dense than ice.

The second type of system deals with pairs of compounds, in which one compound by itself possessing good cooling values is diluted by the second, completely safe compound. Such pairs examined were liquid methanol with solid carbon dioxide, and liquid ammonia with solid carbon dioxide. For each pair, it was envisioned that the liquid would vaporize, the solid carbon dioxide sublime, and the resultant gases would mix in a manner to render the mixture non-flammable and non-explosive.

The vapor pressure of methanol at the temperature of interest is too low to be practical. The ammonia-carbon dioxide system is attractive. For an

0.8 mole ratio of ammonia to carbon dioxide, the two phase changes produce 182 Kcal/kg of cooling. This translates to 2.76 Kg or 6.1 pounds total of ammonia and carbon dioxide being needed to obtain 504 Kcal or 2000 Btu of cooling, a 56% decrease in the 14 pounds of ice needed to obtain the same cooling.

### 2.3.1 Cooling Obtained From Heats of Solution

In general, heats of solution are moderate, but some compounds possess attractive heats of solution. These are listed in Table VI. Of the 15 compounds possessing heats of solution in excess of 74 Kcal/kg, five are either nitrates, nitrites, or chlorates and not recommended (Appendix II) because of their explosion and oxidizing characteristics. Of the remaining ten compounds, ammonium acid carbonate, boric acid, and potassium acid oxalate have such limited water solubility that they are not practical.

After the above eliminations, the remaining seven candidates are ammonia bifluoride ( $\Delta H=99.6$ ), sodium bifluoride ( $\Delta H=90$ ), cyanamide ( $\Delta H=84.6$ ), ammonium chloride ( $\Delta H=76.5$ ), ammonium thiocyanate ( $\Delta H=74.6$ ), ammonium oxalate hydrate ( $\Delta H=81$ ), and potassium acid fluoride ( $\Delta H=88.4$ ).

It is doubtful if the full heat of solution value is obtainable without inordinate mixing. Reference 5 gives 121 Kcal/kg over the temperature range of -12 to about 5°C as the highest fusion plus solution cooling obtained from any of the salt mixtures studied. This value was for a mixture of 30 g.  $\text{KHF}_2$  in 100 g. of water. The heat of solution of  $\text{KHF}_2$  at 30 g. was not given, but at 20 g. is 73.4 Kcal/kg. The value at 30 g. should be lower, probably about 67 Kcal/kg. This value plus 78.7 Kcal/kg for the average measured fusion of water equals about 146 Kcal/kg -- 25 Kcal/kg more than was actually obtained. However, the 121 Kcal/kg obtained is still greater than the 78.7 Kcal/kg obtained from water alone.

TABLE VI  
COOLING CANDIDATES FROM SOLUBILITY DATA

Compound	Formula	$\Delta H$ Soln. Kcal/Kg (3b)	Water Solubility g/100 ml at °C	Alcohol Solubility g/100 ml
Urea formate	$C_2H_6N_2O_3$	67.9	---	---
Urea acetate	$C_3H_8N_2O_3$	73.3	---	---
Urea nitrate	$CH_5N_3O_4$	87.8	soln. hot	S.
Urea	$CH_4N_2O$	60.1	119 <sup>25</sup>	20 <sup>20</sup>
Acetyl urea	$C_3H_6N_2O_2$	66.8	1.2 <sup>20</sup>	---
Potassium oxamate	$CH_2NO_3K$	64.4	---	---
Cyanamide	$CH_2N_2$	85.9	V.S.	V.S.
Ammonium acid carbonate	$NH_4HCO_3$	84.6 (5)	11.9° d (hot)	i
Ammonium bifluoride	$NH_4HF_2$	99.6 @10g to 100g H <sub>2</sub> O	S	---
Ammonium chloride	$NH_4Cl$	76.5	29.7°	---
Ammonium nitrate	$NH_4NO_3$	79.1	118.3°	---
Ammonium nitrite	$NH_4NO_2$	74.3	---	---
Ammonium oxalate hydrate	$NH_4HC_2O_4 \cdot H_2O$	81.0	S	---
Ammonium thiocyanate	$NH_4CNS$	74.6	128°	---
Boric acid	$H_3BO_3$	87.5	1.95°	---
Potassium chlorate	$KClO_3$	83.7	7.1°	---

TABLE VI (Cont'd.)

## COOLING CANDIDATES FROM SOLUBILITY DATA

Compound	Formula	$\Delta H$ Soln. Kcal/Kg	Water Solubility g/100 ml at °C	Alcohol Solubility g/100 ml
Potassium acid fluoride	KHF <sub>2</sub>	88.4 @10g to 100 g H <sub>2</sub> O	41 <sup>21</sup>	---
Potassium nitrate	KNO <sub>3</sub>	83.9	13.3°	---
Potassium acid oxalate	KHC <sub>2</sub> O <sub>4</sub>	74.8	2.5°	---
Potassium tetraoxalate	KHC <sub>2</sub> O <sub>4</sub> ·H <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	72.4	1.8 <sup>13</sup>	---
Sodium bifluoride	NaHF <sub>2</sub>	90.0 @5g to 100 g H <sub>2</sub> O	S	---

As an additional possible advantage of using the salt over the equivalent weight of ice is that the salt is more dense than the ice and would require less volume.

The safety of each of the seven candidates was examined. Details from reference 2 are in Appendix II. Of the seven, only ammonium chloride appears safe. Cyanamide is safe until heated to decomposition (probably 285°F) or exposed to acid when it will emit toxic fumes. Ammonium thiocyanate decomposes at 170°C and at decomposition or exposed to acid, will emit highly toxic fumes. Ammonium oxalate hydrate is corrosive and decomposes easily, emitting toxic fumes. Potassium acid fluoride is corrosive and decomposes at about 225°C instead of melting. Ammonium bifluoride melts at 125.6°C, with no boiling point given. Both of these salts, plus sodium bifluoride for which no melting or boiling points are available, will emit toxic fumes when exposed to acid, or when decomposed.

### 2.3.2 Dual Coolant Systems

The dual coolant systems examined were methanol-carbon dioxide, and ammonia-carbon dioxide.

The methanol has a 284 Kcal/kg heat of evaporation at 0°C, which is 3.5 times greater than the heat of fusion of water. However, methanol is moderately dangerous due to its flammability. Its explosion limits range from 7.3 to 36.5% by volume when mixed with air and exposed to a spark.

Ammonia has a 327.2 Kcal/kg heat of vaporization at -33.4°C, which is 4.1 times greater than the heat of fusion of water. However, ammonia is moderately dangerous due to its flammability. Its explosion limits range from 16 to 25% by volume.

Carbon dioxide has a heat of sublimation of 137 Kcal/kg at -78°C, and is safe to use. Carbon dioxide alone is an attractive substitute for ice, but combined with either methanol or ammonia is more attractive.

Methanol has a vapor pressure of only 40 mm at 5°C (Ref. 1b), so it is not practical.

Ammonia has a vapor pressure at 4.7°C of 5 atm; at -18.7°C, 2 atm; and at its boiling point of -33.4°C, a vapor pressure of 1 atm. (Ref. 1c).

Carbon dioxide has a vapor pressure at 5.9°C of 40 atm; at -18.9°C of 20 atm; at -39.5°C of 10 atm; and at -78.2°C of 1 atm. (Ref. 1d).

The cooling from various ratios of ammonia to carbon dioxide can be calculated, but the calculations are academic, since the ratios, if any, which are safe are not known. To establish a basis for cooling comparisons, a reasonable mole ratio of 0.8 for ammonia to carbon dioxide was used. This system has an effective phase change cooling of 182 Kcal/kg, found from the heat of sublimation of carbon dioxide at -78°C of 137 Kcal/kg, and the heat of vaporization of ammonia at -33.4° C of 327.2 Kcal/kg.

Table VII gives the weights of ammonia and carbon dioxide needed to achieve 252 Kcal/hr (1000 Btu/hr) or 605 Kcal/hr (2400 Btu/hr) for 1, 2 and 4 hours. For example, a total coolant weight of only 1.38 Kg or 3.05 pounds is needed to achieve 252 Kcal or 1000 Btu of cooling. This is a 56% decrease in the weight of ice needed for equivalent cooling.

The safety aspects of this ammonia-carbon dioxide mixture were examined theoretically, using a number of assumptions. Since this system appears so attractive as a coolant, the safety aspects should be laboratory checked. A brief discussion of the laboratory work needed is given in Section 5.

If the separate ammonia and carbon dioxide gas streams for the 0.8 mole ratio are permitted to mix and flow freely in a static air atmosphere, theoretically, this mixture is explosive, i.e. ignited about 18 cm from the vent port.

In doing this calculation, the following assumptions were made. The gases behaved ideally, and the conditions just outside the exit port were 1 atm pressure at 140°F (333°K). Both carbon dioxide and ammonia

TABLE VII

WEIGHT OF SOLID CARBON DIOXIDE AND LIQUID AMMONIA NEEDED TO OBTAIN INDICATED COOLING RATES INDICATED FOR SPECIFIC TIME LENGTHS WHEN THE MOLE RATIO OF AMMONIA TO CARBON DIOXIDE IS 0.8

Time (hrs.)	Cooling Rates					
	1000 Btu or 252 Kcal/hr.			2400 Btu or 605 Kcal/hr		
	Kg NH <sub>3</sub>	Kg CO <sub>2</sub>	Total Kg Lbs	Kg NH <sub>3</sub>	Kg CO <sub>2</sub>	Total Kg Lbs
1	0.327	1.056	1.383 3.050	0.785	2.534	3.319 7.318
2	0.654	2.112	2.766 6.099	1.570	5.069	6.639 14.639
4	1.308	4.224	5.532 12.198	3.139	10.138	13.277 29.276

Data used for this table was  $\Delta H_{\text{vap}} = 327.2 \text{ Kcal/kg}$  (5.572 Kcal/mole) at  $-33.4^\circ\text{C}$  for  $\text{NH}_3$

$\Delta H_{\text{sub}} = 137 \text{ Kcal/kg}$  (6.029 Kcal/mole) at  $-78^\circ\text{C}$  for  $\text{CO}_2$ .

left the exit port together at the 0.8 mole ratio and at 2 atm pressure, thus enabling them to flow easily against 1 atm of atmospheric pressure. At 4°C, the vapor pressure of ammonia is about 5 atm, and that of carbon dioxide is about 40 atm. Hence, obtaining adequate pressure for an exit flow would be possible. However, obtaining the gases at the 0.8 mole ratio when their natural mole ratio is 0.125 would require engineering skill. Both carbon dioxide and ammonia were assumed to diffuse from the exit port with a concentration gradient of  $-8 \times 10^{-7}$  mole/cm<sup>3</sup>/cm. The coolant apparatus wearer was assumed to be stationary, with no wind blowing.

Table VIII shows the concentration of gases from 4.9 to 20 cm from the exit port. For the initial distance of 4.9 cm, which describes a 0.5 liter volume, the assumption was made that all of the volume was occupied by the ammonia-carbon dioxide mixture, with no air present. This is a reasonable assumption since the gases are exiting at 2 atm of pressure.

To obtain the data at the 8 cm distance, the volume percentage of ammonia and carbon dioxide after their initial concentrations were reduced by the concentration gradient, were calculated for the shell of a sphere with an inner radius of 7.9 cm and an outer radius of 8.0 cm. The unaccounted for additional volume in the shell was assumed to be 80% nitrogen and 20% oxygen.

The last column in TABLE VIII gives the volume percentage ratio of ammonia-to-oxygen. When this ratio is between 0.95 and 1.67, the mixture is explosive if ignited. This range was determined from safety data that states that 16 to 25% by volume of ammonia in air is explosive, and by assuming air to be 20% oxygen by volume. TABLE VIII indicates that around 18 cm from the vent port, a theoretically explosive ratio of ammonia-to-oxygen exists.

TABLE VIII

CONCENTRATION OF GASES AT INDICATED DISTANCES FROM EXIT PORT

Distance from Exit Port CM	Volume Percentages (Concentrations in moles/cm <sup>3</sup> )					Volume Percentage Ratio of NH <sub>3</sub> /O <sub>2</sub>
	CO <sub>2</sub>	NH <sub>3</sub>	N <sub>2</sub>	O <sub>2</sub>		
4.9	55.6% (2.034x10 <sup>-5</sup> )	44.4 (1.627x10 <sup>-5</sup> )	--	--	--	--
8	48.8 (1.787x10 <sup>-5</sup> )	37.7 (1.379x10 <sup>-5</sup> )	10.8	2.7		13.9
16	31.3 (1.146x10 <sup>-5</sup> )	20.2 (0.739x10 <sup>-5</sup> )	38.8	9.7		2.08
20	22.6 (0.826x10 <sup>-5</sup> )	11.4 (0.419x10 <sup>-5</sup> )	52.8	13.2		0.86

## 2.4 One Non-Phase Change Process

Two different non-phase change processes were considered -- the warming of a cold substance, and the expansion cooling of a gas.

The cold substances warmed from their phase change temperature to 4°C were an ammonia-carbon dioxide 0.8 mole ratio mixture, carbon dioxide, ammonia, and nitrogen. The warming alone of any of these materials is not attractive.

The gas expansions examined were for the same substances as were warmed, plus Freon-21. With expansion efficiencies of about 60%, cooling is modest.

### 2.4.1 Warming of Substances

The heat of warming between the phase change temperature and 4°C was calculated (Ref. 25) from equation (1).

$$(1) \quad \overline{\Delta H} = \int_{T_1}^{T_2} \overline{C}_p \, dt = \int_{T_1}^{T_2} (a + bT + cT^2) dt$$

where  $\overline{\Delta H}$  is the heat required to raise 1 mole of the gas from the phase change temperature  $T_1$  to 4°C,  $T_2$ ;  $\overline{C}_p$  is the molar heat capacity at constant pressure; and  $a$ ,  $b$ , and  $c$  are the heat capacity coefficients.

Table IX summarizes the warming values for each substance. None is impressive, but if the warming is combined with a phase change, it would make a nice addition.

Calculations for pure ammonia were included since the results were needed for the ammonia-carbon dioxide mixture system. Pure ammonia is not recommended as the coolant.

TABLE IX

## SUMMARY OF WARMING VALUES

Substance	$\Delta$ Warming Kcal/Kg From °C to °C	Thermodynamic Values (Ref.25)
Ammonia	18.7 From -33.4 to 4	a = 6.189 b = 7.887 x 10 <sup>-3</sup> c = -7.28 x 10 <sup>-7</sup>
Carbon Dioxide	16.0 From -78 to 4	a = 6.3957 b = 10.1933 x 10 <sup>-3</sup> c = -35.333 x 10 <sup>-7</sup>
Ammonia-Carbon Dioxide 0.8 mole ratio	16.5 From -78 to 4 for CO <sub>2</sub> From -33.4 to 4 for NH <sub>3</sub>	1 Kg at 0.8 mole ratio contains 17.36 moles CO <sub>2</sub> and 13.8 moles NH <sub>3</sub>
Nitrogen	47.7 From -195.6 to 4	a = 6.4492 b = 1.4125 x 10 <sup>-3</sup> c = -0.807 x 10 <sup>-7</sup>

#### 2.4.2 Expansion Cooling of Substances

The expansion of ammonia, carbon dioxide, ammonia-carbon dioxide at 0.8 mole ratio, nitrogen, and Freon-21 were examined. Calculations were done for pure ammonia only because the results were needed for calculations on the ammonia-carbon dioxide mixture. The most extensive calculations were for nitrogen, since it behaves as an ideal gas. Even under extreme conditions and 100% efficiency, as are discussed in detail in this section, the cooling obtained from the expansion of nitrogen is only 43 Kcal/kg. Since the efficiency of expansion is probably only about 60%, expansion of the gases results in modest additional cooling.

The cooling obtained by expanding an ideal gas, as exemplified by nitrogen, from an initial contained volume to a final contained volume, with the initial volume at pressures of 700, 1400, or 2100 psi, for various initial gas temperatures, and the final volume at 14.7 psi or 1 atm pressure was examined. The pressure of 700 psi is typical of the pressure in a small lecture sized bottle of nitrogen. The 2100 psi pressure is close to the pressure in a full sized nitrogen cylinder. Because of the possibility of obtaining the nitrogen from liquid nitrogen, initial temperatures from 4 to  $-195^{\circ}\text{C}$  were examined. All data assume 100% efficiency.

The cooling obtained from an expanding gas can be calculated from its initial and final temperature. To obtain the final temperature of the gas, the initial temperature and initial and final volumes of the gas must be known. To obtain the final volume of the gas, the initial and final pressures of the gas (which can be given as the working conditions) must be known.

The cooling obtained was first calculated for a range of initial gas temperatures at a constant initial pressure. Then the cooling obtained was calculated for a range of initial pressures at a constant initial temperature. For all calculations, the nitrogen gas was assumed to undergo reversible adiabatic expansion.

For the first set of calculations, the initial pressure was 700 psi, and the initial temperature varied. For an initial pressure of 700 psi, the initial molar volume is 0.5 liter, consistent with 100 liter of N<sub>2</sub> (STP) being contained in a 700 psi lecture bottle. Setting the final pressure at 1 atm or 14.7 psi, (actually, the final pressure should be somewhat greater than 1 atm so that the second chamber can be vented easily to the atmosphere) the final molar volume is 7.9 liters. The final volume was calculated (Ref. 25) from Equation (2).

$$(2) \quad P_1 \bar{V}_1^\gamma = P_2 \bar{V}_2^\gamma$$

where  $P_1$ ,  $P_2$  are the initial and final pressures, respectively;  $\bar{V}_1$  and  $\bar{V}_2$  are the initial and final molar volumes, respectively; and  $\gamma$  is the ratio of the molar heat capacity at constant pressure to the molar heat capacity at constant volume. For nitrogen,  $\gamma$  is 1.40. For this particular example,  $P_1 = 700$  psi = 47.6 atm;  $P_2 = 1$  atm,  $\bar{V}_1 = 0.5$  liter, and  $\bar{V}_2$  is to be determined.  $\bar{V}_2$  is 7.9 liters.

With a knowledge of  $\bar{V}_1$  and  $\bar{V}_2$ , the temperature after expansion was calculated as a function of various initial temperatures, using Equation (3).

$$(3) \quad \bar{C}_v \ln T_2/T_1 = -R \ln \bar{V}_2/\bar{V}_1$$

Where  $\bar{C}_v$  is the molar heat capacity at constant volume,  $T_2$  and  $T_1$  are the final and initial temperatures, respectively; and  $R$  is the gas constant. For nitrogen,  $\bar{C}_v$  is 4.95 cal/deg mole at 25°C. For this example,  $\bar{V}_2 = 7.9$  liters,  $\bar{V}_1 = 0.5$  liter,  $R = 1.987$  cal/deg mole;  $T_1$  was 4°C, or -50°C, or -100°C, or -195.8°C; and  $T_2$  was the unknown.

Table X shows the resultant final temperatures for the various initial temperatures.

TABLE X

COOLING OBTAINED FROM THE EXPANSION OF NITROGEN  
AT 700 PSI TO 14.7 PSI AS A FUNCTION OF VARIOUS  
INITIAL TEMPERATURES

Initial Temperature (T <sub>1</sub> ) °C	Initial Temperature (T <sub>1</sub> ) °K	Final Temperature (°C)	Final Temperature (T <sub>2</sub> ) °K	Cooling Obtained Kcal/Kg
25	298	-175	98.0	35.3
4	277	-181	91.6	32.7
-50	223	-199	73.7	26.4
-100	173	-212	57.2	20.5
-195.8	77.2	-247.5	25.5	9.1

Table X also shows the cooling obtained from the adiabatic expansion from  $T_1$  and  $T_2$  for nitrogen with an initial pressure of 700 psi, or 47.6 atm to a final pressure of 1 atm. This cooling was obtained by calculating the reversible work done in the expansion from Equation (4)

$$(4) \quad W_{\text{rev}} = - \int_{T_1}^{T_2} \bar{C}_v dt$$

Table X shows that, as the initial temperature decreases, the work obtained from the expansion, or the heat the expanding gas can absorb, decreases.

Keeping the initial temperature constant and varying the initial pressure, the following obtains. Using the condition  $T_1 = 4^\circ\text{C}$  with  $P_1 = 1400$  or  $2100$  psi,  $T_2$  and the resultant  $W_{\text{rev}}$  were calculated. Table XI summarizes the results.

As Table XI shows, increasing the initial pressure does increase the cooling obtained; but, the cooling rates are modest. Using a rather extreme case with a  $\bar{V}_2/\bar{V}_1$  ratio of 200 (at 2100 psi,  $\bar{V}_2/\bar{V}_1$  was 34 at most) and an initial temperature of  $4^\circ\text{C}$ , the cooling work obtained would be 43 Kcal/kg. Using this cooling rate, Table XII shows the weight of nitrogen required to achieve 252 Kcal (1000 Btu), or 605 Kcal (2400 Btu) of cooling for 1, 2, or 4 hours is prohibitively large.

Almost 6 Kg (13 lbs) of nitrogen is needed to obtain 252 Kcal (1000 Btu) of cooling for 1 hour.

For the other gases, the expansion work for initial conditions, generally, of  $P_1 = 47.6$  atm,  $V_1 = 0.5$  liter, and  $T_1 = 4^\circ\text{C}$ , at 100% efficiency was calculated. The exact conditions and results are given in Table XIII. For the various gases, the thermodynamic constants were obtained from references 25 and 26. For convenience, they are summarized in Appendix III. For the 0.8 mole ratio ammonia-carbon dioxide system,

TABLE XI

COOLING OBTAINED FROM THE EXPANSION OF NITROGEN  
WITH AN INITIAL TEMPERATURE OF 4°C AS A FUNCTION  
OF VARIOUS INITIAL PRESSURES

$P_1$ (psi)	$\bar{V}_1$ (Liter)	$\bar{V}_2$ (Liter)	$T_2$ (°C)	Cooling Obtained Kcal/Kg
700	0.5	7.9	-181	32.7
1400	0.25	6.5	-198	35.7
2100	0.166	5.7	-206	37.1

TABLE XII

WEIGHT OF NITROGEN REQUIRED TO ACHIEVE STATED COOLING

Time (hrs)	Cooling Rate	
	1000 Btu or 252 Kcal/Hr Kg	2400 Btu or 605 Kcal/Hr lbs Kg
1	5.86	14.06
2	11.72	28.13
4	23.44	56.26

TABLE XIII

## SUMMARY OF PARAMETERS FOR EXPANSION WORK

Substance	T <sub>1</sub> (°C)	P <sub>1</sub> (Atm)	V <sub>1</sub> (Liter)	V <sub>2</sub> (Liter)	T <sub>2</sub> (°C)	Expansion Work 100% Efficiency (Kcal/Kg)	Probable Expansion Efficiency (%)	Probable Expansion Work (Kcal/Kg)
Carbon Dioxide	4	47.6	0.5	9.95	-156	25.1	58	14.6
Ammonia	4	47.6	0.5	9.50	-161	63.7	59.9	38.2
0.8 Mole Ratio of Ammonia to Carbon Dioxide	4	47.6	0.5	--	--	34.1	59	20.1
Nitrogen	4	47.6	0.5	7.9	-181	32.7	67	21.9
Freon-21	8.9	47.6	0.5	13.17	-109.8	13.7	45	6.2

the expansion work was estimated from that of the two parent systems using the values of 21.5 Kcal/kg, or 1.10 Kcal/mole for carbon dioxide, and 63.7 Kcal/kg or 1.08 Kcal/mole for ammonia.

Table XIII also summarizes the probable efficiency of the various expansions. The probable expansion efficiencies were calculated (Ref. 26) from equation (5)

$$(5) \quad \text{Efficiency \%} = 100 \left( 1 - \frac{1}{\Delta V^\gamma} \right)$$

where  $\Delta V$  is the ratio of final to initial volume, and  $\gamma$  is the ratio of the molar heat capacity at constant pressure to that at constant volume. The initial and final volumes are given in Table XI.

To check Equation (5), it was used to calculate the efficiency in the expansion cycle of a diesel engine for an ideal gas ( $\gamma = 1.4$ ) when the volume ratio is the usual 5. The efficiency was 47.5%, or the loss was 52.5%. Perry (Ref. 28) states that the loss due to throttling from the adiabatic liquification of air is 42.9%. The two numbers are in approximate agreement. Thus, Equation (5) is probably satisfactory for an initial estimate.

The expansion cooling is modest. If expansion cooling can be coupled with a phase change, it would make a nice addition.

## 2.5 A Non-Phase Process(es) Combined With a Phase Change For One or More Compounds

The combining of a phase change with warming of the coolant to 4°C, followed by expansion cooling of the gas for five substances was examined. The substances include ammonia, carbon dioxide, an 0.8 mole ratio mixture of ammonia to carbon dioxide, nitrogen, and Freon-21.

Ammonia was included in the calculations because the results were needed for calculations on the ammonia-carbon dioxide system. A pure ammonia coolant is

not recommended because of safety hazards.

In all cases, the final expansion cooling is not weight effective.

Below is the cooling obtained from the phase change and warming to 4°C for the three systems recommended for consideration.

1. Ammonia-carbon dioxide 0.8 mole ratio of NH <sub>3</sub> /CO <sub>2</sub>	198.5 Kcal/kg
2. Carbon dioxide	153.0 Kcal/kg
3. Nitrogen	95.3 Kcal/kg

As reference, the cooling obtainable from ice melting at 0°C and the resultant water warming to 4°C is 83.73 Kcal/kg.

The ammonia-carbon dioxide system has a possible fire hazard associated with it which should be laboratory tested. Such is discussed in the final Section 5. The nitrogen system presents such a small improvement over the present system that the redesign needed to incorporate nitrogen instead of ice is probably not warranted. The carbon dioxide system is an improvement over the present ice system, and has no serious problems associated with it.

Below is the weight of coolant needed to achieve 252 Kcal or 1000 Btu of cooling for one hour.

1. Ammonia-carbon dioxide	1.27 Kg (2,80 lbs)
2. Carbon dioxide	1.65 Kg (3.64 lbs)
3. Nitrogen	2.64 Kg (5.82 lbs)
Reference Ice	3.01 Kg (6.64 lbs)

#### 2.5.1 Ammonia-Carbon Dioxide System

The 0.8 mole ratio of ammonia to carbon dioxide system will provide a heat of phase transformation and warming to 4°C of 198.5 Kcal/kg. The expansion of the gases at 4°C to obtain additional cooling is

TABLE XIV  
SUMMARY OF COOLING PARAMETERS FROM PHASE CHANGE, WARMING, AND EXPANSION

Substance	H Kcal/Kg at °C	Warming Kcal/Kg From °C to °C	Probable Expansion Work (Kcal/Kg)	Total Probable Cooling (Kcal/Kg)	Total Cooling Without Expan- sion (Kcal/Kg)	Wt. for	
						Kg	Lbs.*
Carbon Dioxide	137 @ -78	16.0 From -78 to 4	14.6	167.6	153.0	1.65	3.64
Ammonia	327 @ -33.4	18.17 From -33.4 to 4	38.2	383.6	354.4	0.74	1.57
0.8 Mole Ratio of Ammonia to Carbon Dioxide	182 CO <sub>2</sub> @ -78 NH <sub>3</sub> @ -33.4	16.5 From -78 to 4 for CO <sub>2</sub> From -33.4 to 4 for NH <sub>3</sub>	20.1	218.6	198.5	1.27	2.80
Nitrogen	47.6 @ -195.6	47.7 From -195.6 to 4	21.9	117.2	95.3	2.64	5.82
Freon-21	57.85 @ 8.9	---	6.2	64.1	57.9	4.35	9.60
Ice	79.71 @ 0	4.02 From 0 to 4	---	83.73	83.73	3.01	6.64

\*Based on total cooling without expansion.

not recommended since it would probably add only an additional 20.1 Kcal/kg, and the hardware needed would not make this increase weight effective.

For the 0.8 mole ratio system, its effective phase change cooling is 182 Kcal/kg, found from 137 Kcal/kg for the heat of sublimation of carbon dioxide at  $-78^{\circ}\text{C}$ , and 327.2 Kcal/kg for the heat of vaporization of ammonia at  $-33.4^{\circ}\text{C}$ .

The composite warming value for the 0.8 mole ratio is 16.5 Kcal/kg. This was found by knowing 1 Kg of the 0.8 mole ratio mixture will contain 17.36 moles of carbon dioxide, and 13.88 moles of ammonia, and that the heat required to raise carbon dioxide from  $-78$  to  $4^{\circ}\text{C}$  is 16 Kcal/kg, and the heat required to raise ammonia from  $-33.4$  to  $4^{\circ}\text{C}$  is 18.17 Kcal/kg.

The probable cooling work obtainable from the expansion of this system (Section 2.4.2) is 20.1 Kcal/kg, or only 10.1% of the cooling already obtainable from the phase transitions and warming. The hardware needed to control this expansion will, in all probability make the expansion refinement weight ineffective.

Table XIV summarizes these and other data which will be referred to in this section.

#### 2.5.2 Carbon Dioxide System

The sublimation of solid carbon dioxide and the warming of the resultant gas to  $4^{\circ}\text{C}$  will yield 153 Kcal/kg of cooling. Additional expansion of the gas under proper conditions will not yield sufficient additional cooling to warrant its inclusion, even if carbon dioxide did not condense under the initial expansion conditions.

The sublimation of solid carbon dioxide yields 137 Kcal/kg, and its warming from  $-78$  to  $4^{\circ}\text{C}$  yields an additional 16 Kcal/kg.

The probable cooling obtained from expansion is 14.6 Kcal/mole. However, under the expansion

conditions suggested of  $P_1 = 47.6$  atm,  $T_1 = 4^\circ\text{C}$ , carbon dioxide is in liquid form (Ref. 29). Modifying the initial temperature and pressure conditions so that carbon dioxide is a gas decreases the expansion work. Consequently, the inclusion of expansion with the phase change and warming is not recommended.

#### 2.5.3 Nitrogen System

The cooling available from vaporizing and warming the nitrogen to  $4^\circ\text{C}$  is 95.3 Kcal/kg. The incremental cooling obtainable from expanding the nitrogen is estimated to be 21.9 Kcal/kg, and, as such, is probably not weight effective.

The probable cooling obtained by expansion is 21.9 Kcal/kg, which represents a 23% increase to the 95.3 Kcal/kg available from the vaporization and warming. As with the previous systems, this increase to the cooling from the expansion is probably not weight effective, when considering the hardware needed.

#### 2.5.4 The Ammonia System

Data for the ammonia system are presented in Table XIV for reference purposes. A pure ammonia system is not recommended because of safety reasons, even though ammonia is a most attractive coolant.

#### 2.5.5 Freon-21 System

As Table XIV shows, the cooling from Freon-21 is too low to warrant further discussion.

### 3.0 LOGISTICS OF MOST PROMISING SYSTEMS

The most promising systems are the following combining a phase change with warming:

ammonia-carbon dioxide mixture  
( $\Delta H = 198.5$  Kcal/kg) 0.8 mole ratio

pure carbon dioxide ( $\Delta H = 153$  Kcal/kg)

pure nitrogen ( $\Delta H = 95.3$  Kcal/kg)

Of these three, the first must be laboratory tested for safety. The others are safe, and all three have reasonable logistics.

A less promising system, but one which should be considered is the inclusion of a water soluble salt with ice. Of the water soluble, non-explosive salts with reasonable heats of solution, only ammonium chloride with a heat of solution of 76.5 Kcal/kg appears completely safe. Ammonium-, potassium-, and sodium-bifluoride have attractive cooling properties but their safety is questionable. The largest combined heat of fusion and heat of solution of the three is 121 Kcal/kg for potassium bifluoride.

### 3.1 Phase Change and Warming Systems

In all three systems discussed in this section, the coolant undergoes a phase change, then is warmed to 4°C. The three systems are ammonia-carbon dioxide, carbon dioxide, and nitrogen. The Freon-21 system was discarded for being too ineffective.

The logistics of the ammonia-carbon dioxide system look reasonable except for the possible fire/explosion hazard presented by the vented ammonia vapor. It is recommended that this possible hazard aspect of the system be laboratory examined. A brief outline of this examination is given in Section 4.

A pure carbon dioxide system should present no serious logistics or safety problem in that it is readily available, inexpensive, stores moderately well, can be contained by many materials, and yields no health, safety or environmental problems.

The nitrogen system should present no serious logistic problems except possibly in remote areas where liquid nitrogen may not be available.

### 3.1.1 Ammonia-Carbon Dioxide System

Both anhydrous ammonia under pressure as a saturated liquid, and solid carbon dioxide or dry ice are readily available. The pressurized ammonia can be stored for extended periods, and could either be stored in a central storage tank, or, preferably, in the suits themselves.

The cost of anhydrous ammonia (in Cleveland) in truckload quantities (4500 Kg or 10,000 lbs) is \$0.082/Kg or \$0.18/lb, and for 1-3 cylinders (68 Kg or 150 lbs each) is \$0.20/Kg or \$0.44/lb. Sometimes cylinders have initial deposit charges of \$30 to \$40, plus demurrage costs of about \$0.10/day if not returned in 30 days. Added to the cost of ammonia would be the cost to liquefy and store the ammonia for ready use.

The cost of dry ice in Cleveland is \$0.018 to \$0.027/Kg or \$0.04 to \$0.06/lb for a 23 Kg or 50 lb block and is rather insensitive to weight purchased. It is easily cut or formed to any shape, and stores rather well in an appropriate dry ice chest. Fifty to 100 pounds will keep for about one week. Its vapor pressure is 760 mm at  $-78^{\circ}\text{C}$ , 400 mm at  $-86^{\circ}\text{C}$ , 100 mm at  $-100^{\circ}\text{C}$ , and 1 mm at  $-134^{\circ}\text{C}$ . Considering its common use, it is probably routinely available at many installations.

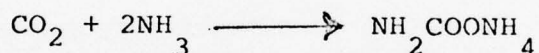
Assuming both the ammonia and dry ice are properly handled, neither should be problematic for charging the suit.

Since ammonia is irritating to the respiratory tract, eyes, and moist skin, a rip in the suit, exposing the ammonia to the wearer, could cause severe discomfort as well as a possible cold burn. Should

ammonia somehow feed into the suit wearer's breathing support system, he would suffocate. Exposure of the suit wearer to dry ice would cause a cold burn, and possible suffocation if carbon dioxide gas were fed into the breathing support system of the unit. Proper suit design should minimize the probability of these problems.

The heat exchange system must be balanced to permit the carbon dioxide and ammonia to vent in a proper and safe ratio. The ratio of 0.8 ammonia to carbon dioxide was selected because it is an attractive coolant. Some simple laboratory tests are needed to determine if this ratio is safe, or an explosion hazard, or if different blends would be even more attractive from both a cooling and a safety standpoint. The higher the ratio, the better the cooling, but probably the greater the explosion hazard. The simple laboratory tests are outlined in Section 4.

There is a chemical reaction between carbon dioxide and ammonia to form ammonium carbamate



which can be decomposed to urea and water



Industrially (Ref. 30) these reactions are used to produce urea for fertilizers. The reaction chamber is at 200 atm and 185°C. In the laboratory, the carbamate can be formed from a simple mixture of liquid ammonia with powdered dry ice (Ref. 31). The carbamate decomposes at 59°C, releasing ammonia.

In this suggested system, the liquid ammonia and dry ice reservoirs are to be separated, vaporizing into separate lines from which additional cold would be extracted until each gas reached 4°C, then vented through adjacent nozzles which would permit mixing of the gases to prevent a safety hazard. The question is whether the gases mixing in this manner will

react to form the white, powdery carbamate and possibly clog the nozzles. To answer this question, carbon dioxide gas and ammonia gas from compressed gas tanks were released in a laboratory hood at rates comparable to those coming from the proposed cooling unit in a manner to cause the two gas streams to mix. No white powder or other evidence of a reaction was visible. However, if the gas streams were trapped in a small (0.5 liter) volume, the white powder did form on the walls of the container, but the nozzles remained clear. Thus complications from the reaction of carbon dioxide with ammonia should not be expected in the venting of the gases.

The materials logistics of handling carbon dioxide as dry ice sublimating to the gas and liquid ammonia vaporizing to the gas should be reasonably straight forward. A wide range of materials can be used for the containment and handling of each. Thus materials for both thermal insulation and heat exchange needs are available.

Appendix IV summarizes chemically resistant materials for ammonia. Further detailed information for both carbon dioxide and ammonia are available in convenient form in Reference 32, with additional detailed information in various forms in Reference 33.

### 3.1.2 Carbon Dioxide System

Carbon dioxide should present no serious logistics or safety problem in that it is readily available, inexpensive, stores moderately well, can be contained by many materials, and yields no health, safety or environmental problems. The logistic details for this system were already discussed in the previous section.

### 3.1.3 Nitrogen System

Liquid nitrogen is reasonably easily handled and stored, and commonly available in industrial areas.

For 2,000 liters/month (54 Kg/day) consumption, liquid nitrogen sells for \$0.18/liter (\$0.222/Kg) in Cleveland. For larger volumes of 19,000 liters/month (510 Kg/day), the cost is \$0.16/liter (\$0.0742/Kg). The equipment rental charge for on site storage is \$180/month for the small volume and \$800/month for the large volume.

Materials (Ref. 28) that are both strong and ductile at low temperatures are copper, aluminum, nickel, most solid solution alloys of these metals, the austenitic stainless steels, teflon, mylar (a polyester), and fiber reinforced plastics.

Nitrogen presents no real safety, health, fire/-explosion or environmental danger if properly used. Liquid nitrogen is safe to handle and presents no danger if contacted by a person as long as it can roll off the body and not get lodged. If liquid nitrogen does lodge in a cupped hand, for example, it will cause a burn. Also, if excess nitrogen somehow is fed into the breathing line of the suit wearer, it can cause suffocation. Properly designed suits or packs should minimize the probability of any danger from the nitrogen.

### 3.2 Fusion Plus Solution Systems

In this system a water soluble salt is added to the ice so that a heat of solution is added to the heat of fusion. The only completely safe salt found with a reasonable heat of solution was ammonium chloride.

The inclusion of ammonium chloride in ice yields no cooling advantage over a pure water system, but does yield a volume advantage since its specific gravity is 1.95 compared to 0.917 for ice at 0 °C.

Of the three fluoride salts studied in Ref. 5, the one yielding the greatest combined heat of fusion plus heat of solution was potassium bifluoride at 121 Kcal/kg. However, this salt is corrosive, and if decomposed about 225°C or exposed to acid will emit toxic fumes. The suit wearer should not see temperatures this high, so the chemical may be given a reserved recommendation.

The other two salts, sodium-, and ammonium-bifluoride have similar safety problems. Consequently, they may be given reserved recommendations also.

All three fluoride salts are articles of commerce and available in large quantities for about \$0.40/lb. Though corrosive, containment materials are available. Containment materials for the potassium bifluoride (Ref. 32a) are stainless steels and high chrome steels; for the sodium bifluoride (Ref. 32b), copper, tin, bronze, aluminum bronze, monel, rubber, saran, and karbate; and for ammonium bifluoride (Ref. 32c), high chrome steels, stainless steels, worthite, durimet 20, monel, nickel, and inconel.

#### 4.0 RECOMMENDATIONS AND DISCUSSION

Table XV lists the coolant materials which are reasonable for consideration, and summarizes any limitations.

Of the four systems, the carbon dioxide one seems the least troublesome, and is an 83% improvement over the heat absorption of ice-water, reducing the weight of ice coolant needed by 45%.

The ammonia-carbon dioxide system has the most attractive cooling, but a laboratory check on its safety must be done. An 0.8 mole ratio of ammonia to carbon dioxide is a 137% improvement over the heat absorption of ice-water, reducing the weight of ice coolant needed by 58%.

The cooling obtained from the nitrogen system, represents only a 14% improvement over the ice-water system, reducing the weight of ice needed by only 12%. The engineering needed to change from an ice coolant to nitrogen will not be repaid by much additional cooling.

The potassium acid fluoride salt incorporated into ice will yield a 45% improvement in heat absorption over ice-water, reducing the weight of ice coolant needed by 31%. The salt will decompose at about 225°C or upon contact with acid, releasing toxic fumes.

To check the safety of the ammonium-carbon dioxide system, laboratory testing of mixtures of the gases is recommended. The gases are obtainable in convenient form at measurable pressures in cylinder tanks. With the cylinders sufficiently removed from the test area, and with proper valving precautions, the gases can be made to flow through adjacent nozzles or a burner head

TABLE XV  
COOLANTS RECOMMENDED FOR CONSIDERATION

Coolant	System	Expected Heat Absorption (Kcal/Kg)	Limitations	Wt. for	
				252 Kcal or 1000 Btu	Kg Lbs.
Carbon Dioxide	Sublimation and warming to 4°C.	153.0	None	1.65	3.64
Mixture of Ammonia with Carbon Dioxide	Vaporization/sublimation and warming to 4°C.	198.5 for 0.8 mole ratio	Possible flammability must be checked.	1.27	2.80
Nitrogen	Vaporization and warming to 4°C.	95.3	None, except for scarcity in remote locations. Small improvement over ice water system.	2.64	5.82
Potassium Acid Fluoride in Ice	Salt inclusion with ice; melting from ~-12 to 5°C.	121 30 g salt per 100 g H <sub>2</sub> O	Salt decomposes ~225°C, or with acid, releasing toxic fumes.	2.08	4.59
Ice Reference	Melting and warming to 4°C.	83.73	--	3.01	6.64

such that the gas streams mix. The ratio of the gases to each other should be controlled to vary from mole ratios of ammonia to carbon dioxide of about 0.5 to 1.5, through ranges of flow rates and pressures that can be reasonably expected to emerge from the suit. Throughout the above ranges of conditions, this mixture should be subjected to sparks and hot wire ignitors at various distances from the nozzles under static and breezy conditions to determine if a fire or explosion hazard does exist. Figure 2 shows a conceptualization of such a test setup. The test chamber is a large cylinder, open at both ends to permit a free flow of gases and air. The angle of the inlet nozzles can be changed to afford different types of mixing. The spark or ignition wire assembly is movable away from the nozzles.

Throughout this study, thought was given to how compounds with high phase change enthalpy, like the heats of vaporization of the alcohols, or water, might be useful as a coolant under the needed conditions. In the cases examined, either the phase change temperature was too high, or the compound was highly flammable or toxic.

For the compounds with inappropriate phase change temperatures, the nature of the bonds in the compounds is generally responsible for both the high phase change enthalpy, plus the inappropriate high phase change temperatures. The classic example is water with its hydrogen bonding. Modifying the compound to reduce a phase change temperature, will, in all probability, reduce its phase change enthalpy below an attractive value.

For the flammable or toxic compounds with attractive phase change enthalpy at useful temperatures, the problem becomes one of identifying why the compound is unsafe, and attempting to modify it without compromising its cooling properties. Such a study is beyond the scope of this program, but might represent the nucleus for another program.

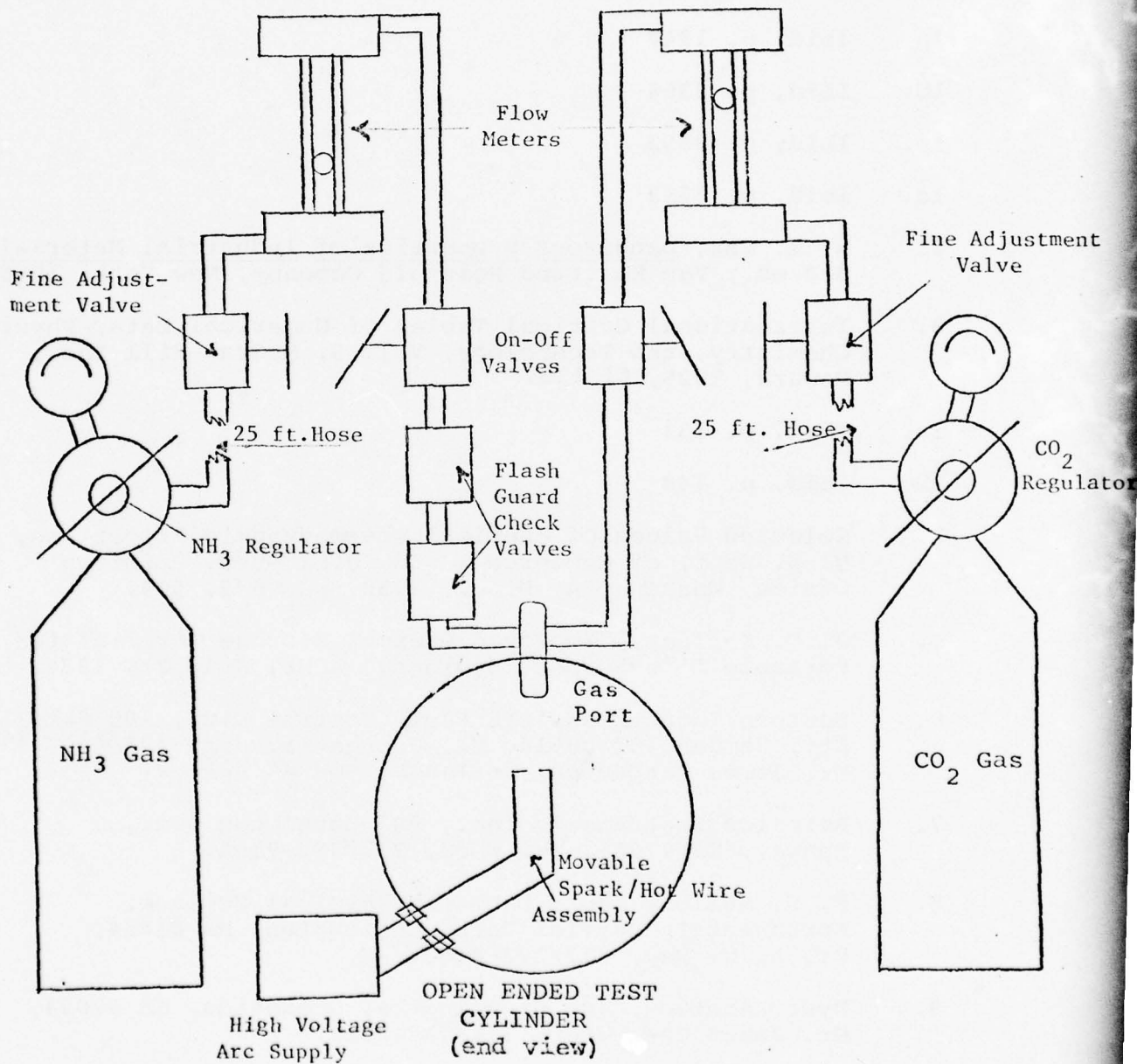


Figure 2

Ammonia-Carbon Dioxide Explosive Characteristics Test Apparatus

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11. Magnakold Inc., 17600 Monroeville Rd., Costa Mesa, CA 92626, Mr. O'Neil, 714/646-2939
12. Aerotherm Corporation, 485 Clyde Ave., Mountain View, CA 94042, Mr. William Elkins, 415/964-3200
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Mr. Manley, 313/423-8411
16. Domestic Sales Corp.  
2320 Industrial Parkway, Elkhart, IN 46514  
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17. Dr. A. N. Dey, P. R. Mallory Inc., 617/272-4100
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APPENDIX I

DETAILED SAFETY DATA ON COMPOUNDS IN TABLE I

APPENDIX I

DETAILED SAFETY DATA ON COMPOUNDS IN TABLE I

1. AMMONIA, ANHYDROUS

General Information

Synonym: Ammonia gas.

Description: Colorless gas, extremely pungent odor, liquefied by compression.

Formula:  $\text{NH}_3$ .

Constants: Mol wt: 17.03, mp:  $-77.7^\circ\text{C}$ , bp:  $-33.35^\circ\text{C}$ , lcl: 16%, ucl: 25%, d: 0.771 g/liter at  $0^\circ\text{C}$ , 0.817 g/ml at  $-79^\circ\text{C}$ , autoign temp:  $1204^\circ\text{F}$ , vap press: 10 atm at  $25.7^\circ\text{C}$ , vap d: 0.6.

Hazard Analysis

Toxic Hazard Rating:

Acute Local: Irritant 3; Ingestion 3; Inhalation 3.

Acute Systemic: U.

Chronic Local: Irritant 1.

Chronic Systemic: U.

TLV: ACGIH (recommended) 50 parts per million in air; 35 milligrams per cubic meter of air.

Toxicology: Irritating to eyes and mucous membranes of respiratory tract. Signs and symptoms of exposure are irritation of the eyes, conjunctivitis, swelling of the eyelids, irritation of the nose and throat, coughing, dyspnoea and vomiting. Irritation of the skin may be experienced, especially if it is moist. Corneal ulcers have been reported following splashing of ammonia water in the eye (Section 1). A common air contaminant (Section 4).

Fire Hazard: Moderate, when exposed to heat or flame.

Spontaneous Heating: No. Requires high concentrations in air before it catches fire.

Explosion Hazard: Moderate, when exposed to flame. Forms explosive compounds in contact with silver or mercury (Section 7).

Disaster Hazard: Moderately dangerous; exposed to heat, it emits toxic fumes.

Countermeasures

Ventilation Control: Section 2.

To Fight Fire: Stop flow of gas, carbon dioxide, dry chemical or water spray (Section 6).

Personnel Protection: Section 3.

Personal Hygiene: Section 3.

First Aid: Section 1.

Storage and Handling: Section 7.

Shipping Regulations: Section 11.

I.C.C.: Nonflammable gas; green label, 300 pounds.

Coast Guard Classification: Nonflammable gas; green gas label.

MCA warning label.

IATA: Nonflammable gas, green label, not acceptable (passenger), 140 kilograms (cargo).

2. BUTANE

General Information

Synonyms: N-Butane; methylethylmethane; butyl hydride.

Description: Colorless gas.

Formula:  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$ .

Constants: Mol wt: 58.1, bp:  $-0.5^\circ\text{C}$ , fp:  $-138.6^\circ\text{C}$ , lcl: 1.9%, ucl: 8.5%, flash p:  $-76^\circ\text{F}$  (C.C.), d: 0.599, autoign. temp:  $761^\circ\text{F}$ , vap. press.: 2 atm at  $18.8^\circ\text{C}$ , vap. d.: 2.046.

Hazard Analysis

Toxic Hazard Rating:

Acute Local: 0.

Acute Systemic: Inhalation 2.

Chronic Local: U.

Chronic Systemic: Inhalation 1.

A general purpose food additive (Section 10).

Caution: Produces drowsiness. Simple asphyxiant.

Fire Hazard: Dangerous; when exposed to heat or flame.

Spontaneous Heating: No.

Explosion Hazard: Moderate, when exposed to flame (Section 7).

Disaster Hazard: Moderately dangerous; when heated it emits acid fumes; can react with oxidizing materials.

Countermeasures

Ventilation Control: Section 2.

To Fight Fire: Carbon dioxide, dry chemical or water spray (Section 6).

Storage and Handling: Section 7.

Shipping Regulations: Section 11.

I.C.C.: Flammable gas; red gas label, 300 pounds.

IATA: Flammable gas, red label, not acceptable (passenger), 140 kilograms (cargo).

BUTANE

Butane mixtures, and mixtures having similar properties contained in lighters, candles, heating devices, refill containers and similar devices each *not* exceeding 65 grams (2.3ozs)

Shipping Regulations: Section 11.

IATA: Flammable gas, red label, 0.6 kilogram (passenger), 12 kilograms (cargo).

TOXIC HAZARD RATING CODE (For detailed discussion, see Section 1.)

0 NONE: (a) No harm under any conditions; (b) Harmful only under unusual conditions or overwhelming dosage.

1 SLIGHT: Causes readily reversible changes which disappear after end of exposure.

2 MODERATE: May involve both irreversible and reversible changes, not severe enough to cause death or permanent injury.

3 HIGH: May cause death or permanent injury after very short exposure to small quantities.

U UNKNOWN: No information on humans considered valid by authors.

APPENDIX I (Cont'd.)

3. ETHYL ACETATE

General Information

Synonym: Acetic ether; ethyl ester; ethyl ethanoate.

Description: Colorless liquid; fragrant odor.

Formula:  $\text{CH}_3\text{COOC}_2\text{H}_5$ .

Constants: Mol wt: 88.10, mp:  $-83.6^\circ\text{C}$ , bp:  $77.15^\circ\text{C}$ , ul: 85-90, lel: 2.5%, uel: 9%, flash p:  $24^\circ\text{F}$ , d: 0.8946 at  $25^\circ\text{C}$ , autoign. temp.:  $800^\circ\text{F}$ , vap. press.: 100 mm at  $27.0^\circ\text{C}$ , vap. d.: 3.04.

Hazard Analysis

Toxic Hazard Rating:

Acute Local: Irritant 1.

Acute Systemic: Ingestion 2; Inhalation 2; Skin Absorption 2.

Chronic Local: Irritant 1.

Chronic Systemic: Ingestion 1; Inhalation 1; Skin Absorption 1.

TLV: ACGIH (recommended): 400 parts per million in air; 1400 milligrams per cubic meter of air.

Toxicology: Ethyl acetate is irritating to mucous surfaces, particularly the eyes, gums, and respiratory passages

and is also mildly narcotic. On repeated or prolonged exposures, it causes conjunctival irritation and corneal clouding. It can cause dermatitis. High concentrations have a narcotic effect and can cause congestion of the liver and kidneys. Chronic poisoning has been described as producing secondary anemia, leucocytosis and cloudy swelling, and fatty degeneration of the viscera. Note: Used as a synthetic flavoring substance and adjuvant (Section 10).

Fire Hazard: Dangerous, when exposed to heat or flame; can react vigorously with oxidizing materials.

Spontaneous Heating: No.

Explosion Hazard: Moderate, when exposed to flame.

Disaster Hazard: Dangerous, upon exposure to heat or flame.

Countermeasures

Ventilation Control: Section 2.

To Fight Fire: Carbon dioxide, dry chemical or carbon tetrachloride (Section 6).

Personnel Protection: Section 3.

Storage and Handling: Section 7.

Shipping Regulations: Section 11.

I.C.C.: Flammable liquid; red label, 10 gallons.

Coast Guard Classification: Inflammable liquid; red label.

MCA warning label.

IATA: Flammable liquid, red label, 1 liter (passenger), 40 liters (cargo).

4. ETHYL CHLORIDE

General Information

Synonyms: Chloroethane; hydrochloric ether; muriatic ether.

Description: Colorless liquid or gas; ether-like odor, burning taste.

Formula:  $\text{CH}_3\text{CH}_2\text{Cl}$ .

Constants: Mol wt: 64.52, bp:  $12.3^\circ\text{C}$ , lel: 3.8%, uel: 15.4%, sp:  $-139^\circ\text{C}$ , flash p:  $-58^\circ\text{F}$  (C.C.), d: 0.9214 at  $0^\circ/4^\circ\text{C}$ , autoign. temp.:  $966^\circ\text{F}$ , vap. press.: 1000 mm at  $20^\circ\text{C}$ , vap. d.: 2.22.

Hazard Analysis

Toxic Hazard Rating:

Acute Local: Irritant 1; Ingestion 2; Inhalation 2.

Acute Systemic: Ingestion 2; Inhalation 2.

Chronic Local: U.

Chronic Systemic: U.

TLV: ACGIH (recommended): 1000 ppm in air 2600 milligrams per cubic meter of air.

Toxicology: The liquid is harmful to the eyes and can cause some irritation. In the case of guinea pigs, the symptoms attending exposure are similar to those caused by methyl chloride, except that the signs of lung irritation are not as pronounced. It gives some warning of its presence because it is irritating, but it is possible to tolerate exposure to it until one becomes unconscious. It is the least toxic of all of the chlorinated hydrocarbons. It can cause narcosis, although the effects are usually transient. Animal experiments show some evidence of kidney irritation and accumulation of fat due to this material in the kidneys, cardiac muscles and liver.

Fire Hazard: Highly dangerous, when exposed to heat or flame.

Spontaneous Heating: No.

Explosion Hazard: Severe, when exposed to flame.

Disaster Hazard: Highly dangerous! Keep away from heat and open flame; forms phosgene on combustion; reacts with water or steam to produce toxic and corrosive fumes; can react vigorously with oxidizing materials.

Countermeasures

Ventilation Control: Section 2.

To Fight Fire: Carbon dioxide, dry chemical or carbon tetrachloride (Section 6).

Personnel Protection: Section 3.

Storage and Handling: Section 7.

Shipping Regulations: Section 11.

I.C.C.: Flammable liquid; red label, 300 pounds in cylinders, 15 pounds in other containers.

Coast Guard Classification: Inflammable liquid; red label.

MCA warning label.

IATA: Flammable liquid, red label, not acceptable (passenger), 140 kilograms (cargo).

APPENDIX I (Cont'd.)

5. ETHYLENE DICHLORIDE

General Information

Synonyms: Ethylene chloride; 1,2-dichloroethane.

Description: Colorless liquid.

Formula:  $\text{CH}_2\text{ClCH}_2\text{Cl}$ .

Constants: Mol wt: 99.0, bp: 83.5°C, ulc: 60-70, lel: 6.2%, uel: 15.9%, fp: -35.7°C, flash p: 56°F, d: 1.257 at 20°/4°C, autoign. temp.: 775°F, vap. press.: 100 mm at 29.4°C, vap. d.: 3.35.

Hazard Analysis

Toxic Hazard Rating:

Acute Local: Irritant 3; Ingestion 3; Inhalation 3.

Acute Systemic: Ingestion 3; Inhalation 3.

Chronic Local: Irritant 2.

Chronic Systemic: Ingestion 3; Inhalation 3; Skin Absorption 2.

TLV: ACGIH (recommended) 50 ppm of air; 200 milligrams per cubic meter of air.

Toxicology: Ethylene dichloride has a distinctive odor and strong local irritating effects, which give warning of its presence in relatively safe concentrations. There is irritation of the eyes and upper respiratory passages. Ethylene dichloride has a specific effect on the cornea. Exposure to the vapor, or, in animals, injection under the skin, produces a clouding which may progress to endothelial necrosis and infiltration of the cornea by lymphocytes and connective tissue cells. The narcotic action of the compound is strong, probably of the same order as chloroform. Its toxic effects upon the liver and kidneys are less than that of carbon tetrachloride, but animal experiments indicate that these organs may show congestion and fatty degeneration. Edema of the lungs has also been reported in animals. Dermatitis in man has been observed (Section 9).

In short exposures to high concentrations, the picture is one of irritation of the eyes, nose and throat, followed by dizziness, nausea, vomiting, increasing stupor, cyanosis, rapid pulse, and loss of consciousness.

Chronic poisoning, where exposure has occurred over a period of several months, may cause loss of appetite, nausea and vomiting, epigastric distress, tremors, nystagmus, leucocytosis, low blood sugar levels, and possibly dermatitis if there has been skin contact. A soil fumigant. Used as a food additive permitted in food for human consumption.

Fire Hazard: Dangerous, if exposed to heat or flame.

Spontaneous Heating: No.

Explosion Hazard: Moderate, in the form of vapor when exposed to flame (Section 7).

Disaster Hazard: Dangerous; when heated to decomposition, it emits highly toxic fumes of phosgene; can react vigorously with oxidizing materials.

Countermeasures

Ventilation Control: Section 2.

To Fight Fire: Water, foam, carbon dioxide, dry chemical or carbon tetrachloride (Section 6).

Personnel Protection: Section 3.

First Aid: Section 1.

Storage and Handling: Section 7.

Shipping Regulations: Section 11.

I.C.C.: Flammable liquid; red label, 10 gallons.

Coast Guard Classification: Inflammable liquid; red label.

MCA warning label.

IATA: Flammable liquid, red label, 1 liter (passenger), 40 liters (cargo).

6. HYDROGEN

General Information

Description: Colorless gas.

Formula:  $\text{H}_2$ .

Constants: Mol wt: 2.0162, mp: -259.18°C, bp: -252.8°C, lel: 4.1%, uel: 74.2%, d: 0.0899 g/liter, autoign. temp. 1085°F, vap. d.: 0.069.

Hazard Analysis

Toxic Hazard Rating:

Acute Local: 0.

Acute Systemic: Inhalation 1.

Chronic Local: 0.

Chronic Systemic: 0.

Radiation Hazard: Section 5. For permissible levels, see Table 000.

Artificial and natural isotope  $^3\text{H}$  (tritium), half life 12.3 y. Decays to stable  $^3\text{He}$  by emitting beta particles of 0.018 MeV. Tritium occurs naturally as a result of cosmic ray bombardment of deuterium.

Fire Hazard: Highly dangerous; when exposed to heat or flame.

Explosion Hazard: Severe, when exposed to heat or flame. Explosive Range: 4.1-74.2%.

Disaster Hazard: Dangerous; can react vigorously with oxidizing materials.

Countermeasures

Ventilation Control: Section 2.

Storage and Handling: Section 7.

To Fight Fire: Carbon dioxide or dry chemical (Section 6).

Shipping Regulations: Section 11.

I.C.C.: Flammable gas; red gas label, 300 pounds.

I.C.C.: (Liquefied) not accepted.

Coast Guard Classification: Inflammable gas; red gas label.

Coast Guard Classification: (Liquefied) not permitted.

IATA: Flammable gas, red label, not acceptable (passenger), 140 kilograms (cargo).

APPENDIX I (Cont'd.)

7. **HYDROGEN CHLORIDE.** See hydrochloric acid.  
Shipping Regulations: Section 11.

I.C.C.: Nonflammable gas; green label, 300 pounds.  
Coast Guard Classification: Nonflammable gas; green gas label.  
MCA warning label.  
IATA: Nonflammable gas, green label, not acceptable (passenger), 140 kilograms (cargo).

**HYDROCHLORIC ACID**

**General Information**

Synonyms: Muriatic acid; chlorohydric acid; hydrogen chloride.

Description: Colorless gas or colorless, fuming liquid; strongly corrosive.

Formula: HCl.

Constants: Mol wt: 36.47, mp:  $-114.3^{\circ}\text{C}$ , bp:  $-84.8^{\circ}\text{C}$ , d: 1.639 g/liter (gas) at  $0^{\circ}\text{C}$ ; 1.194 at  $-36^{\circ}\text{C}$  (liquid), vap. press.: 4.0 atm at  $17.8^{\circ}\text{C}$ .

**Hazard Analysis**

**Toxic Hazard Rating:**

Acute Local: Irritant 3; Ingestion 3; Inhalation 3.

Acute Systemic: U.

Chronic Local: Irritant 2.

Chronic Systemic: U.

TLV: ACGIH (recommended); 5 parts per million in air; 7 milligrams per cubic meter of air.

Toxicology: Hydrochloric acid is an irritant to the mucous membranes of the eyes and respiratory tract, and a concentration of 35 ppm causes irritation of the throat after short exposure. Concentrations of 50 to 100 ppm are tolerable for 1 hour. More severe exposures result in pulmonary edema, and often laryngeal spasm. Concentrations of 1,000 to 2,000 ppm are dangerous, even for brief exposures. Mists of hydrochloric acid are considered less harmful than the anhydrous hydrogen chloride, since the droplets have no dehydrating action. In general, hydrochloric acid causes little trouble in industry, other than from accidental splashes and burns. It is used as a general purpose food additive (Section 10). It is a common air contaminant (Section 10).

Disaster Hazard: Dangerous; see chlorides; will react with water or steam to produce toxic and corrosive fumes.

**Countermeasures**

Ventilation Control: Section 2.

Personnel Protection: Section 3.

Storage and Handling: Section 7.

First Aid: Section 1.

Shipping Regulations: Section 11.

I.C.C.: Corrosive liquid; white label, 10 pints.

Coast Guard Classification: Corrosive liquid; white label.

Coast Guard (anhydrous) Classification: Nonflammable gas; green gas label.

MCA warning label.

IATA: Corrosive liquid, white label, 1 liter (passenger), 5 liters (cargo).

8. **HYDROGEN SULFIDE**

**General Information**

Synonym: Sulfuretted hydrogen.

Description: Colorless; flammable gas, offensive odor.

Formula:  $\text{H}_2\text{S}$ .

Constants: Mol wt: 34.08, mp:  $-85.5^{\circ}\text{C}$ , bp:  $-60.4^{\circ}\text{C}$ , lcl: 4.3%, ucl: 46%, autoign. temp.:  $500^{\circ}\text{F}$ , d: 1.539 g/liter at  $0^{\circ}\text{C}$ , vap. press.: 20 atm at  $25.5^{\circ}\text{C}$ , vap. d.: 1.189.

**Hazard Analysis**

**Toxic Hazard Rating**

Acute Local: Irritant 3; Inhalation 3.

Acute Systemic: Inhalation 3.

Chronic Local: Irritant 3.

Chronic Systemic: Inhalation 3.

TLV: ACGIH (recommended) 10 parts per million of air; 15 milligrams per cubic meter of air.

Toxicology: Hydrogen sulfide is both an irritant and an asphyxiant. Low concentrations of from 20 to 150 ppm cause irritation of the eyes; slightly higher concentrations may cause irritation of the upper respiratory tract, and if exposure is prolonged, pulmonary edema may result. The irritant action has been explained on the basis that  $\text{H}_2\text{S}$  combines with the alkali present in moist surface tissues to form sodium sulfide, a caustic.

With higher concentrations the action of the gas on the nervous system becomes more prominent, and a 30-minute exposure to 500 ppm results in headache, dizziness, excitement, staggering gait, diarrhea and dysuria, followed sometimes by bronchitis or bronchopneumonia. The action on the nervous system is, with small amounts, one of depression; in larger amounts, it stimulates, and with very high amounts the respiratory center is paralyzed. Exposures of 800 to 1000 ppm may be fatal in 30 minutes, and high concentrations are instantly fatal. Fatal hydrogen sulfide poisoning may occur even more rapidly than that following exposure to a similar concentration of hydrogen cyanide.  $\text{H}_2\text{S}$  does not combine with the hemoglobin of the blood, its asphyxiant action is due to paralysis of the respiratory center.

With repeated exposures to low concentrations, conjunctivitis, photophobia, corneal bullae, tearing, pain and blurred vision are the commonest findings. High concentrations may cause rhinitis, bronchitis, and occasionally pulmonary edema. Exposure to very high concentrations results in immediate death. Chronic poisoning results in headache, inflammation of the conjunctivae and eyelids, digestive disturbances, loss of weight and general debility. It is a common air contaminant (Section 4).

Fire Hazard: Dangerous, when exposed to heat or flame.

Explosion Hazard: Moderate, when exposed to heat or flame.

Disaster Hazard: Highly dangerous; when heated to decomposition, it emits highly toxic fumes of oxides of sulfur; can react vigorously with oxidizing materials.

**Countermeasures**

Ventilation Control: Section 2.

Personnel Protection: Section 3.

Storage and Handling: Section 7.

To Fight Fire: Carbon dioxide, dry chemical or water spray (Section 6).

Shipping Regulations: Section 11.

I.C.C.: Flammable gas; red gas label, 300 pounds.

Coast Guard Classification: Inflammable gas; red gas label.

MCA warning label.

IATA: Flammable gas, red label, not acceptable (passenger), 140 kilograms (cargo).

APPENDIX I (Cont'd.)

9. ISOBUTANE

General Information

Synonyms: 2-Methyl propane; trimethyl methane.

Description: Colorless gas.

Formula:  $C_4H_{10}$ .

Constants: Mol wt: 58.12, bp:  $-11.7^\circ C$ , lcl: 1.9%, ucl: 8.5%, fp:  $-160^\circ C$ , d: 0.5572 at  $20^\circ C$ , autoign. temp.:  $864^\circ F$ , vap. d.: 2.01.

Hazard Analysis

Toxic Hazard Rating:

Acute Local: 0.

Acute Systemic: Inhalation 1.

Chronic Local: 0.

Chronic Systemic: U.

Caution: An asphyxiant. A common air contaminant.

Fire Hazard: Dangerous, when exposed to heat or flame (Section 6).

Explosion Hazard: Severe, when exposed to heat or flame.

Disaster Hazard: Dangerous; on contact with oxidizing materials, it can react vigorously.

Countermeasures

Ventilation Control: Section 2.

To Fight Fire: Carbon dioxide, dry chemical or water spray (Section 6).

10. METHYL ACETATE

General Information

Description: Colorless, volatile liquid.

Formula:  $CH_3CO_2CH_3$ .

Constants: Mol wt: 74.08, mp:  $-98.7^\circ C$ , lcl: 3.1%, ucl: 16%, bp:  $57.8^\circ C$ , ulc: 85-90, flash p:  $14^\circ F$ , d: 0.92438, autoign. temp.:  $935^\circ F$ , vap. press.: 100 mm at  $9.4^\circ C$ , vap. d.: 2.55.

Hazard Analysis

Toxic Hazard Rating:

Acute Local: Irritant 1.

Acute Systemic: Ingestion 2; Inhalation 2; Skin Absorption 2.

Chronic Local: U.

Chronic Systemic: Ingestion 2; Inhalation 2; Skin Absorption 2.

TLV: ACGIH (recommended); 200 parts per million in air; 610 milligrams per cubic meter of air.

Toxicology: Methyl acetate is narcotic, but is less so than the higher members of the acetate series. It has an irritating effect upon the mucous membranes of the eyes and upper respiratory tract, and in this respect its action is stronger than that of the higher members of the series. The irritant concentration is about 10,000 ppm.

Signs and symptoms are irritation and burning of the eyes, lachrymation, dyspnea, palpitation of the heart, and complaints of depression or dizziness.

Fire Hazard: Dangerous, when exposed to heat or flame.

Spontaneous Heating: No.

Explosion Hazard: Moderate, when exposed to heat or flame.

Disaster Hazard: Dangerous, upon exposure to heat or flame; can react vigorously with oxidizing materials.

Countermeasures

Ventilation Control: Section 2.

To Fight Fire: Alcohol foam, carbon dioxide, dry chemical or carbon tetrachloride (Section 6).

Personnel Protection: Section 3.

Storage and Handling: Section 7.

Shipping Regulations: Section 11.

I.C.C.: Flammable liquid; red label, 10 gallons.

Coast Guard Classification: Inflammable liquid; red label.

IATA: Flammable liquid, red label, 1 liter (passenger), 40 liters (cargo).

11. METHYL CHLORIDE

General Information

Synonyms: Chloromethane.

Description: Colorless gas.

Formula:  $CH_3Cl$ .

Constants: Mol wt: 50.49, bp:  $-23.7^\circ C$ , lcl: 10.7% ucl: 17.2%, fp:  $-97.7^\circ C$ , flash p:  $< 32^\circ F$  (O.C.), d: 0.918 at  $20^\circ C$ , autoign. temp.:  $1170^\circ F$ , vap. d.: 1.78.

Hazard Analysis

Toxic Hazard Rating:

Acute Local: Irritant 1; Inhalation 1.

Acute Systemic: Ingestion 3; Inhalation 3.

Chronic Local: U.

Chronic Systemic: Ingestion 2; Inhalation 2.

TLV: ACGIH (recommended); 100 parts per million in air; 209 milligrams per cubic meter of air.

Toxicology: Methyl chloride has very slight irritant properties and may be inhaled without noticeable discomfort. It has some narcotic action, but this effect is weaker than that of chloroform. Acute poisoning, characterized by the narcotic effect, is rare in industry. Repeated exposure to low concentrations causes damage to the central nervous system, and, less frequently, to the liver, kidneys, bone marrow and cardiovascular system. Hemorrhages into the lungs, intestinal tract and dura have been reported. Sprayed on the skin, methyl chloride produces anesthesia through freezing of the tissue as it evaporates.

In exposures to high concentrations, dizziness, drowsiness, incoordination, confusion, nausea and vomiting, abdominal pains, hiccoughs, diplopia and dimness of vision are followed by delirium, convulsions and coma. Death may be immediate, but if the exposure is not fatal, recovery is usually slow, and degenerative changes in the central nervous system are not uncommon. The liver, kidneys, and bone marrow may be affected, with resulting acute nephritis and anemia. Death may occur several days after exposure, resulting from degenerative changes in the heart, liver and especially the kidneys. In repeated exposures to lower concentrations there is usually fatigue, loss of appetite, muscular weakness, drowsiness, and dimness of vision.

After effects are commonly the result of damage to the central nervous system, with visual changes and attacks of depression and other psychic disturbances being reported.

Note: Used as a food additive permitted in food for human consumption.

Fire Hazard: Dangerous, when exposed to heat or flame.

Spontaneous Heating: No.

Explosion Hazard: Moderate, when exposed to heat or flame.

Disaster Hazard: Dangerous; when heated to decomposition, it emits highly toxic fumes of chlorides; can react vigorously with oxidizing materials.

Countermeasures

Ventilation Control: Section 2.

To Fight Fire: Stop flow of gas, carbon dioxide, dry chemical or water spray (Section 6).

Personal Hygiene: Section 3.

Storage and Handling: Section 7.

Shipping Regulations: Section 11.

I.C.C.: Flammable gas; red gas label, 300 pounds.

Coast Guard Classification: Inflammable gas; red gas label.

MCA warning label.

IATA: Flammable gas, red label, not acceptable (passenger), 140 kilograms (cargo).

APPENDIX I (Cont'd.)

12. PROPANE

General Information

Synonym: Dimethylmethane.

Description: Colorless gas.

Formula:  $\text{CH}_3\text{CH}_2\text{CH}_3$ .

Constants: Mol wt: 44.09, bp:  $-42.1^\circ\text{C}$ , lcl: 2.3% uel: 9.5%, fp:  $-187.1^\circ\text{C}$ , flash p:  $-156^\circ\text{F}$ , d: 0.5852 at  $-44.5^\circ/4^\circ\text{C}$ , autoign. temp.:  $874^\circ\text{F}$ , vap. d.: 1.56.

Hazard Analysis

Toxic Hazard Rating:

Acute Local: 0.

Acute Systemic: Inhalation 1.

Chronic Local: 0.

Chronic Systemic: U.

TLV: ACGIH (recommended); 1000 parts per million of air, 1800 milligrams per cubic meter of air.

Toxicity: A general purpose food additive (Section 10).

Fire Hazard: Highly dangerous when exposed to heat or flame.

Spontaneous Heating: No.

Explosion Hazard: Severe, when exposed to flame.

Disaster Hazard: Dangerous; can react vigorously with oxidizing materials.

Countermeasures

Ventilation Control: Section 2.

To Fight Fire: Carbon dioxide, dry chemical or water spray (Section 6).

Storage and Handling: Section 7.

13. SULFUR DIOXIDE

General Information

Synonym: Sulfurous acid anhydride.

Description: Colorless gas or liquid; pungent odor.

Formula:  $\text{SO}_2$ .

Constants: Mol wt: 64.06, mp:  $-75.5^\circ\text{C}$ , bp:  $-10.0^\circ\text{C}$ , d liq: 1.434 at  $0^\circ\text{C}$ , vap d: 2.264 at  $0^\circ\text{C}$ , vap. press 2538 mm at  $21.1^\circ\text{C}$ .

Hazard Analysis

Toxic Hazard Rating:

Acute Local: Irritant 3; Ingestion 3; Inhalation 3.

Acute Systemic: U.

Chronic Local: Irritant 2; Inhalation 2.

Chronic Systemic: U.

TLV: ACGIH (recommended); 5 parts per million in air; 13 milligrams per cubic meter of air.

Toxicology: This gas is dangerous to the eyes, as it causes irritation and inflammation of the conjunctiva. It has a suffocating odor and is a corrosive and poisonous material. In moist air or fogs, it combines with water to form sulfurous acid, but is only very slowly oxidized to sulfuric acid (Section 4). Concentrations of 6 to 12 ppm cause immediate irritation of the nose and throat, while 0.3 to 1 ppm can be detected by the average individual possibly by taste rather than by the sense of smell. 3 ppm has an easily noticeable odor and 20 ppm is the least amount which is irritating to the eyes. 10,000 ppm is an irritant to moist areas of the skin within a few minutes of exposure.

It chiefly affects the upper respiratory tract and the bronchi. It may cause edema of the lungs or glottis, and can produce respiratory paralysis. Concentrations of  $< 1$  ppm are believed to be injurious to plant foliage.

This material is so irritating that it provides its own warning of toxic concentrations. 400 to 500 ppm is immediately dangerous to life and 50 to 100 ppm is considered to be the maximum permissible concentration for exposures of 30 to 60 minutes. Excessive exposures to high enough concentrations of this material can be fatal. Its toxicity is comparable to that of hydrogen chloride. However, less than fatal concentrations can be borne for fair periods of time with no apparent permanent damage. It is used as a fumigant, insecticide and fungicide, and a chemical preservative food additive (Section 10). It is a common air contaminant (Section 4).

Disaster Hazard: Dangerous; will react with water or steam to produce toxic and corrosive fumes.

Countermeasures

Ventilation Control: Section 2.

Treatment and Antidotes: Personnel who have shown toxic symptoms when exposed to this material should immediately be removed to fresh air. If the eyes are involved, they should be irrigated with copious quantities of warm water. If the symptoms persist, call a physician.

Storage and Handling: Section 7.

Shipping Regulations: Section 11.

I.C.C.: Nonflammable gas; green label, 300 pounds.

Coast Guard Classification: Nonflammable gas; green gas label.

IATA: Nonflammable gas, green label, not acceptable (passenger), 140 kilograms (cargo).

APPENDIX I (Cont'd.)

14. **ISOPENTANE**  
**General Information**  
 Synonyms: 2-Methyl butane, isoamyl hydride.  
 Description: Colorless liquid with pleasant odor.  
 Formula:  $CH_3CH(CH_3)CH_2CH_3$   
 Constants: Mol wt: 72.15, bp: 27.8°C, fp: -160.5°C, flash p: < -60°F (C.C.), d: 0.621 at 20°/4°C, autoign. temp.: 788°F, vap. press.: 595 mm at 21.1°C, vap. d.: 2.48, lel: 1.4%, uel: 7.6%.  
**Hazard Analysis**  
 Toxicity: See pentane.  
 Fire Hazard: Highly dangerous when exposed to heat or flame.  
 Explosion Hazard: Unknown.  
 Disaster Hazard: Dangerous. Keep away from sparks, heat or open flame; can react vigorously with oxidizing materials.  
**Countermeasures**  
 Ventilation Control: Section 2.  
 To Fight Fire: Foam, carbon dioxide, dry chemical or carbon tetrachloride (Section 6).  
 Storage and Handling: Section 7.  
 Shipping Regulations: Section 11.  
 I.C.C.: Flammable liquid, red label, 10 gallons.  
 Coast Guard Classification: Inflammable liquid, red label.  
 IATA: Flammable liquid, red label, 1 liter (passenger), 40 liters (cargo).

**n-PENTANE**  
**General Information**  
 Synonym: Amyl hydride.  
 Description: Colorless liquid.  
 Formula:  $CH_3(CH_2)_4CH_3$   
 Constants: Mol wt: 72.15, bp: 36.1°C, flash p: < -40°F, fp: -129.8°C, d: 0.626 at 20°/4°C, autoign. temp.: 588°F, vap. press.: 400 mm at 18.5°C, vap. d.: 2.48, lel: 1.5%, uel: 7.8%.  
**Hazard Analysis**  
 Toxic Hazard Rating:  
 Acute Local: U.  
 Acute Systemic: Inhalation 1.  
 Chronic Local: U.  
 Chronic Systemic: U.  
 Toxicology: Narcotic in high concentrations.  
 TLV: ACGIH (recommended); 1000 parts per million; 2950 milligrams per cubic meter of air.  
 Fire Hazard: Highly dangerous, when exposed to heat or flame.  
 Spontaneous Heating: No.  
 Explosion Hazard: Severe, when exposed to heat or flame.  
 Explosive Range: 1.4-8.0%.  
 Disaster Hazard: Highly dangerous, keep away from heat,

sparks or open flame; shock can shatter metal containers and release contents.  
**Countermeasures**  
 Ventilation Control: Section 2.  
 To Fight Fire: Foam, carbon dioxide, dry chemical or carbon tetrachloride (Section 6).  
 Storage and Handling: Section 7.  
 Shipping Regulations: Section 11.  
 I.C.C.: Flammable liquid, red label, 10 gallons.  
 Coast Guard Classification: Inflammable liquid, red label.  
 IATA: Flammable liquid, red label, 1 liter (passenger), 40 liters (cargo).

15. **HEXENE-1**  
**General Information**  
 Synonyms: Hexene, butylethylene, hexylene.  
 Description: Colorless liquid.  
 Formula:  $CH_3CH(CH_3)CH=CH_2$   
 Constants: Mol wt: 84.16, mp: -98.5°C, bp: 63.5°C, fp: -139.9°C, flash p: < 20°F, d: 0.6732 at 20°/4°C, vap. press.: 310 mm at 38°C, vap. d.: 3.0.  
**Hazard Analysis**  
 Toxic Hazard Rating:  
 Acute Local: Irritant 2; Ingestion 2; Inhalation 2.  
 Acute Systemic: Inhalation 2.  
 Chronic Local: U.  
 Chronic Systemic: U.  
 Fire Hazard: Dangerous, when exposed to heat or flame (Section 6).  
 Disaster Hazard: Dangerous, upon exposure to heat or flame; can react vigorously with oxidizing materials.  
**Countermeasures**  
 Ventilation Control: Section 2.  
 Personnel Protection: Section 3.  
 Storage and Handling: Section 7.

16. **n-HEXANE**  
**General Information**  
 Synonym: Hexyl hydride.  
 Description: Colorless liquid.  
 Formula:  $CH_3(CH_2)_5CH_3$   
 Constants: Mol wt: 86.17, bp: 68.7°C, ulc: 90-95, lel: 1.2%, uel: 7.5%, fp: -95.6°C, flash p: -7°F, d: 0.6603 at 20°/4°C, autoign. temp.: 500°F, vap. press.: 100 mm at 15.8°C, vap. d.: 2.97.  
**Hazard Analysis**  
 Toxic Hazard Rating:  
 Acute Local: Irritant 1.  
 Acute Systemic: Ingestion 1; Inhalation 1.  
 Chronic Local: Irritant 1.  
 Chronic Systemic: U.  
 Note: Use as a food additive permitted in food for human consumption (Section 10).  
 TLV: ACGIH (recommended); 500 parts per million in air; 1760 milligrams per cubic meter of air.  
 Fire Hazard: Dangerous, when exposed to heat or flame.  
 Spontaneous Heating: No.  
 Explosion Hazard: Moderate, when exposed to heat or flame.  
 Disaster Hazard: Dangerous, when heated or exposed to flame; can react vigorously with oxidizing materials.  
**Countermeasures**  
 Ventilation Control: Section 2.  
 To Fight Fire: Carbon dioxide, dry chemical or carbon tetrachloride (Section 6).  
 Personal Hygiene: Section 3.  
 Storage and Handling: Section 7.  
 Shipping Regulations: Section 11.  
 I.C.C.: Flammable liquid, red label, 10 gallons.  
 Coast Guard Classification: Inflammable liquid, red label.  
 IATA: Flammable liquid, red label, 1 liter (passenger), 40 liters (cargo).

APPENDIX I (Cont'd.)

17. ETHYL ETHER

General Information

Synonyms: Sulfuric ether; anesthesia ether; ether; ethyl oxide.

Description: A clear, volatile liquid.

Formula:  $C_2H_5OC_2H_5$ .

Constants: Mol wt: 74.12, mp:  $-116.2^{\circ}C$ , bp:  $34.6^{\circ}C$ , ulc: 100, lcl: 1.85%, ucl: 48%, flash p:  $-49^{\circ}F$ , d: 0.7135 at  $20^{\circ}/4^{\circ}C$ , autoign. temp.:  $356^{\circ}F$ , vap. press.: 442 mm at  $20^{\circ}C$ , vap. d.: 2.56.

Hazard Analysis

Toxic Hazard Rating:

Acute Local: Ingestion 2; Inhalation 1.  
Acute Systemic: Inhalation 2; Skin Absorption 2.  
Chronic Local: U.  
Chronic Systemic: U.

TLV: ACGIH (recommended): 400 parts per million in air; 1212 milligrams per cubic meter of air.

Toxicology: Ether is not corrosive or dangerously reactive. However, it must not be considered safe for individuals to inhale or ingest. It is not toxic in the sense of being a poison. It is, however, a depressant of the central nervous system and is capable of producing intoxication, drowsiness, stupor, and unconsciousness. Death

due to respiratory failure may result from severe and continued exposure.

Fire Hazard: Dangerous, when exposed to heat or flame; can react vigorously with oxidizing materials. See ethers.

Explosion Hazard: Severe, when exposed to heat or flame.

Disaster Hazard: Highly dangerous, in the presence of heat or flame. See ethers.

Countermeasures

Ventilation Control: Section 2.

To Fight Fire: Alcohol foam, carbon dioxide, dry chemical or carbon tetrachloride (Section 6).

Treatment and Antidote: Removal from exposure almost always produces rapid and complete recovery.

Personal Hygiene: Section 3.

Storage and Handling: Section 7.

Shipping Regulations: Section 11.

I.C.C.: Flammable liquid; red label, 10 gallons.

Coast Guard Classification: Inflammable liquid; red label.

MCA warning label.

IATA: Flammable liquid, red label, 1 liter (passenger), 40 liters (cargo).

19. ETHYLENE OXIDE

General Information

Synonyms: 1,2-Epoxyethane; oxirane.

Description: Colorless gas at room temperature.

Formula:  $(CH_2)_2O$ .

Constants: Mol wt: 44.05, mp:  $-111.3^{\circ}C$ , bp:  $10.7^{\circ}C$ , ulc: 100, lcl: 3.0%, ucl: 100%, flash p:  $<0^{\circ}F$ , d: 0.8711 at  $20^{\circ}/20^{\circ}C$ , autoign. temp.:  $804^{\circ}F$ , vap. press.: 1095 mm at  $20^{\circ}C$ , vap. d.: 1.52.

Hazard Analysis

Toxic Hazard Rating:

Acute Local: Irritant 3; Inhalation 2.  
Acute Systemic: Inhalation 2.  
Chronic Local: Irritant 2.  
Chronic Systemic: U.

Toxicology: Irritating to eyes and mucous membranes of respiratory tract. High concentrations can cause pulmonary edema.

TLV: ACGIH (recommended): 50 parts per million in air; 90 milligrams per cubic meter of air.

Fire Hazard: Dangerous, when exposed to heat or flame; can react with oxidizing materials.

Spontaneous Heating: No.

Explosion Hazard: Severe, when exposed to flame.

Disaster Hazard: Highly dangerous, upon exposure to heat or flame.

Countermeasures

Ventilation Control: Section 2.

To Fight Fire: Alcohol foam, carbon dioxide, dry chemical or carbon tetrachloride (section 6).

Personnel Protection: Section 3.

Storage and Handling: Section 7.

Shipping Regulations: Section 11.

I.C.C.: Flammable liquid, red label, 300 pounds in cylinder, 15 pounds in other containers.

Coast Guard Classification: Inflammable liquid, red label, MCA warning label.

IATA: Flammable liquid, red label, not acceptable (passenger), 140 kilograms (cargo).

APPENDIX I (Cont'd.)

20. ACETONE

**General Information**

Synonyms: Dimethyl ketone; ketone propane; propanone.  
Description: Colorless liquid; fragrant mintlike odor.  
Formula:  $CH_3COCH_3$   
Constants: Mol. wt. 58.08, mp:  $-94.6^\circ C$ , bp:  $56.48^\circ C$ ,  
ule = 90, flash p.  $0^\circ F$  (C. C.), lcl = 2.6%, ucl = 12.8%, d  
0.7972 at  $15^\circ C$ , autoign. temp.: 1000 F, vap. press.:  
400 mm at  $39.5^\circ C$ , vap. d.: 2.00.

**Hazard Analysis**

**Toxic Hazard Rating:**

Acute Local: Irritant 1; Ingestion 2; Inhalation 2.  
Acute Systemic: Ingestion 2; Inhalation 2; Skin Absorption 2.  
Chronic Local: Irritant 1.  
Chronic Systemic: Ingestion 1; Inhalation 1; Skin Absorption 1.

TLV: ACGIH, 1000 parts per million in air; 2400 milligrams per cubic meter of air.

Toxicology: Acetone is narcotic in high concentrations. In industry, no injurious effects from its use have been reported, other than the occurrence of skin irritations resulting from its de-fating action or headache from prolonged inhalation. A food additive permitted in food for human consumption (Section 10). A common air contaminant. See Section 4.

Fire Hazard: Dangerous, when exposed to heat or flame.

Explosion Hazard: Moderate, when vapor is exposed to flame.

Disaster Hazard: Dangerous, due to fire and explosion hazard; can react vigorously with oxidizing materials.

**Countermeasures**

Ventilation Control: Section 2.

To Fight Fire: Carbon dioxide, dry chemical, alcohol foam or carbon tetrachloride (Section 6).

Personnel Protection: Section 3.

Storage and Handling: Section 7.

Shipping Regulations: Section 11.

I. C. C.: Flammable liquid, red label, 10 gallons.

Coast Guard Classification: Inflammable liquid; red label, MCA warning label.

IATA: Flammable liquid, red label, 1 liter (passenger), 40 liters (cargo).

21. METHYL ALCOHOL

**General Information**

**Synonyms:** Methanol

Description: Clear colorless very mobile liquid.

Formula:  $CH_3OH$ .

Constants: Mol. wt. 32.04, bp:  $64.8^\circ C$ , lcl 7.3%, ucl 36.5%,  
fp:  $-97.8^\circ C$ , flash p.:  $52^\circ F$ , d 0.7913 at  $20^\circ/4^\circ C$ ,  
autoign. temp.:  $867^\circ F$ , vap. press.: 100 mm at  $21.2^\circ C$ ,  
vap. d.: 1.11.

**Hazard Analysis**

**Toxic Hazard Rating:**

Acute Local: Irritant 1; Inhalation 1.  
Acute Systemic: Ingestion 3; Inhalation 2; Skin Absorption 2.  
Chronic Local: Irritant 1; Inhalation 1.  
Chronic Systemic: Ingestion 2; Inhalation 2; Skin Absorption 2.

TLV: ACGIH (recommended); 200 parts per million in air; 262 milligrams per cubic meter of air.

Toxicology: Methyl alcohol possesses distinct narcotic properties. It is also a slight irritant to the mucous membranes. Its main toxic effect is exerted upon the nervous system, particularly the optic nerves and possibly the retinae. The effect upon the eyes has been attributed to optic neuritis, which subsides but is followed by atrophy of the optic nerve. Once absorbed, methyl alcohol is only very slowly eliminated. Coma resulting from massive exposures may last as long as 2 to 4 days. In the body the products formed by its oxidation are formaldehyde and formic acid, both of which are toxic. Because of the slowness with which it is eliminated, methyl alcohol should be regarded as a cumulative poison. Though single exposures to fumes may cause no harmful effect, daily exposure may result in the accumulation of sufficient methyl alcohol in the body to cause illness.

Severe exposures may cause dizziness, unconsciousness, sighing respiration, cardiac depression, and eventually death. Where the exposure is less severe, the first symptoms may be blurring of vision, photophobia and conjunctivitis, followed by the development of definite eye lesions. There may be headache, gastrointestinal disturbances, dizziness and a feeling of intoxication. The visual symptoms may clear temporarily, only to recur later and progress to actual blindness. Irritation of the mucous membranes of the throat and respiratory tract, peripheral neuritis, and occasionally, symptoms referable to other lesions of the nervous system have been reported. The skin may become dry and cracked due to the solvent action of methyl alcohol.

Methyl alcohol is a common air contaminant (Section 4). It is used as a food additive permitted in foods for human consumption. Section 10.

Fire Hazard: Dangerous, when exposed to heat or flame.

Spontaneous Heating: No.

Explosion Hazard: Moderate, when exposed to flame.

Disaster Hazard: Dangerous, upon exposure to heat or flame; can react vigorously with oxidizing materials.

**Countermeasures**

Ventilation Control: Section 2.

To Fight Fire: Carbon dioxide, dry chemical, or carbon tetrachloride (Section 6).

Personnel Protection: Section 3.

Storage and Handling: Section 7.

Shipping Regulations: Section 11.

I. C. C.: Flammable liquid, red label, 10 gallons.

Coast Guard Classification: Inflammable liquid; red label.

MCA warning label.

IATA: See Alcohol, N.O.S.

APPENDIX I (Cont'd.)

22. ETHYL ALCOHOL

**General Information**

Synonyms: Ethanol, methyl carbinol, spirit of wine.

Description: Clear, colorless, fragrant liquid.

Formula:  $\text{C}_2\text{H}_5\text{OH}$

Constants: Mol wt: 46.07, bp: 78.32°C, ulc: 70, lcl: 4.3%, uel: 19%, fp: -114.1°C, flash p: 55°F, d: 0.7893 at 20/4°C, autoign. temp.: 793°F, vap. press.: 40 mm at 19°C, vap. d.: 1.59.

**Hazard Analysis**

**Toxic Hazard Rating**

Acute Local: Irritant 1.

Acute Systemic: Ingestion 2, Inhalation 2, Skin Absorption 1.

Chronic Local: Irritant 1.

Chronic Systemic: Ingestion 1, Inhalation 1, Skin Absorption 1.

TLV: ACGIH (recommended): 1000 parts per million in air; 1880 milligrams per cubic meter of air.

**Toxicology:** The systemic effect of ethyl alcohol differs from that of methyl alcohol. Ethyl alcohol is rapidly oxidized in the body to carbon dioxide and water, and in contrast to methyl alcohol, no cumulative effect occurs. Though ethyl alcohol possesses narcotic properties, concentrations sufficient to produce this effect are not reached in industry. Exposure to concentrations of 5,000 to 10,000 ppm results in irritation of the eyes and mucous membranes of the upper respiratory tract. If continued for an hour, stupor and drowsiness may result. Concentrations below 1,000 ppm usually produce no signs of intoxication. There is no concrete evidence that repeated exposure to ethyl alcohol vapor results in cirrhosis of the liver. The main effect of ethyl alcohol is due to its irritant action on the mucous membranes of the eyes and upper respiratory tract.

Exposure to concentrations of over 1,000 ppm may cause headache, irritation of the eyes, nose and throat, and, if long continued, drowsiness and lassitude, loss of appetite and inability to concentrate.

**Fire Hazard:** Dangerous, when exposed to heat or flame; can react vigorously with oxidizing materials.

**Disaster Hazard:** Dangerous, when exposed to heat or flame.

**Spontaneous Heating:** No.

**Explosion Hazard:** Moderate, when exposed to flame.

**Countermeasures**

**Ventilation Control:** Section 2.

**To Fight Fire:** Alcohol foam, carbon dioxide, dry chemical or carbon tetrachloride (Section 6).

**Storage and Handling:** Section 7.

**Shipping Regulations:** Section 11.

U.C.C.: Flammable liquid, red label, 10 gallons.

Coast Guard Classification: Inflammable liquid, red label.

MCA warning label.

23. n-PROPYL ALCOHOL

**General Information**

Synonym: 1-Propanol, ethyl carbinol.

Description: Clear, odorless liquid; alcohol-like odor.

Constants: Mol wt: 60.1, mp: -127°C, bp: 97.19°C, flash p: 59°F (C.C.), ulc: 55-60, d: 0.8044 at 20/4°C, lcl: 2.1%, uel: 13.5%, autoign. temp.: 700°F, vap. press.: 10 mm at 14.7°C, vap. d.: 2.07.

**Hazard Analysis**

**Toxic Hazard Rating**

Acute Local: Irritant 1; Ingestion 1; Inhalation 1.

Acute Systemic: Inhalation 1.

Chronic Local: U.

Chronic Systemic: Inhalation 1.

TLV: ACGIH (tentative): 200 parts per million; 310 milligrams per cubic meter of air.

**Fire Hazard:** Dangerous, when exposed to heat or flame.

**Spontaneous Heating:** No.

**Explosion Hazard:** Moderate, when exposed to flame.

**Disaster Hazard:** Dangerous, upon exposure to heat or flame; can react vigorously with oxidizing materials.

**Countermeasures**

**Personnel Protection:** Section 3.

**Ventilation Control:** Section 2.

**To Fight Fire:** Alcohol foam, carbon dioxide, dry chemical or carbon tetrachloride (Section 6).

**Storage and Handling:** Section 7.

APPENDIX II

ADDITIONAL SAFETY DATA ON COMPOUNDS LISTED IN TABLE VI

## APPENDIX II

### ADDITIONAL SAFETY DATA ON COMPOUNDS LISTED IN TABLE VI

#### NITRATES, N.O.S.

##### General Information

**Description:** Organic nitrates are usually termed nitro compounds. These compounds are a combination of the nitro ( $\text{NO}_2$ ) group and an organic radical. However, this term is often used to denote nitric acid esters of an organic material. Inorganic nitrates are compounds of metals which are combined with the mono-valent  $\text{-NO}_2$  radical.

##### Hazard Analysis

###### Toxic Hazard Rating:

Acute Local: U.

Acute Systemic: Ingestion 2; Inhalation 2.

Chronic Local: U.

Chronic Systemic: Ingestion 2; Inhalation 2.

**Toxicology:** Large amounts taken by mouth may have serious or even fatal effects. The symptoms are dizziness, abdominal cramps, vomiting, bloody diarrhea, weakness, convulsions and collapse. Small, repeated doses may lead to weakness, general depression, headache and mental impairment.

**Fire Hazard:** Moderate, by spontaneous chemical reaction; practically all nitrates are powerful oxidizing agents (Section 6).

**Explosion Hazard:** Nitrates may explode when shocked, exposed to heat or flame or by spontaneous chemical reaction (See also explosives, high). All the inorganic nitrates act as oxygen carriers; under proper conditions these can give up their oxygen to other materials, which may in turn detonate. For example, potassium or barium nitrate are added to double-base powders for the purpose of reducing flash and rendering the powder more ignitable. A further use for these materials is to mix them with a smokeless powder which is not completely colloided, for the purpose of granulation. An example of such a powder is "E. C. Powder," used for loading blank cartridges and hand grenades. Sodium and potassium nitrate are also used in black powder as the oxygen carrier to support the combustion of the sulfur and the charcoal.

Ammonium nitrate has all the properties of the other nitrates, but is also able to detonate by itself under certain conditions. It is therefore a high explosive, although very insensitive to impact and difficult to detonate. In the pure state, it requires a combination of an initiator and a high explosive. This combination is known as a reinforced detonator. Ammonium nitrate in combination with nitro compounds (such, perhaps, as trinitrotoluene) forms one of the major high explosives for military use. Ammonium nitrate is widely used also as the chief component of "ammonia permissibles," and of "ammonia dynamites"; as a component of many pyrotechnic mixtures; and in combination with smokeless powder, as a granular blasting explosive. It is a relatively safe high explosive which, however, must be stored in a cool, ventilated place, away from acute fire hazards and easily oxidized materials. Ammonium nitrate must not be confined, because if a fire should start, confinement can cause detonation with extremely violent results.

**Disaster Hazard:** Dangerous, due to fire and explosion hazard. On decomposition they emit toxic fumes. They are powerful oxidizing agents which may cause violent reaction with reducing materials. Nitrates should be protected carefully as discussed in detail in Section 7.

##### Countermeasures

Ventilation Control: Section 2.

Personal Hygiene: Section 3.

Storage and Handling: Section 7.

Shipping Regulations: Section 11.

I.C.C.: Oxidizing material, yellow label, 100 pounds.

Coast Guard Classification: Oxidizing material.

IATA: Oxidizing material, yellow label, 12 kilograms (passenger), 45 kilograms (cargo).

#### CHLORATES, N.O.S.

##### General Information

**Description:** Chlorates are a combination of a metal or hydrogen and  $\text{ClO}_2$  monovalent radical. They are crystalline and somewhat deliquescent.

##### Hazard Analysis

###### Toxic Hazard Rating:

Acute Local: Irritant 1.

Acute Systemic: Ingestion 2.

Chronic Local: Irritant 1.

Chronic Systemic: Ingestion 2.

**Toxicology:** The principal toxic effects of chlorates are the production of methemoglobin in the blood and destruc-

tion of red blood corpuscles. The latter may lead to irritation of the kidneys. Damage to heart muscle has been reported.

**Fire Hazard:** Moderate, in contact with flammable matter.

When contaminated with oxidizable materials, they are particularly sensitive to friction, heat and shock; they are powerful oxidizing agents (Section 6).

**Explosion Hazard:** Moderate, when shocked, exposed to heat or rubbed, particularly when contaminated with sugar, charcoal, shellac, sulfur, starch, sawdust, sulfuric acid, ammonium compounds, cyanides, phosphorus or antimony sulfide.

Chlorates when mixed with combustible materials may form explosive mixtures. For instance, potassium chlorate, when mixed with sulfur or with other combustible substances explodes on friction. Pure chlorates which have been spilled on the floor, or mixed with small amounts of impurities, become very sensitive to shock and friction. Water is considered the best agent for fighting fires involving chlorates. In the explosive industry, chlorates are used as oxidizing agents in the primer caps in combination with mercury fulminates, phosphorus, antimony sulfide and other combustible substances. They are used in pyrotechnic mixtures, as a component of airplane flares and aerial bombs. They are also used as a component of permissible explosives. Chlorates are used extensively in the manufacture of chlorate explosives. The chief constituent of such an explosive is from 60 to 80 percent chlorate. This can be the chlorate of ammonium, sodium or potassium. The other ingredients in such a mixture are combustible materials, such as metallic powders, powdered sulfur, powdered charcoal or possibly mixtures of organic matter. Nitro derivatives of benzene, toluene, and other aromatic compounds are also added. Paraffin may be added as a desensitizer. Recently, similar mixtures were used in Europe but with the addition of small amounts of nitroglycerin or collodion cotton. Chlorate explosives are more sensitive than modern permissible explosives, and therefore not as safe as for instance the perchlorate explosives, or the permissibles. Plastic mixtures of chlorate explosives (containing nitroglycerin) are somewhat less sensitive to shock and friction, in spite of the nitroglycerin present, than the dryer explosives with no nitroglycerin. In this case the nitroglycerin or "explosive oil," as it is known, serves to wet the rest of the mixture. Barium chlorate is shipped and stored in wooden boxes, barrels, or kegs. It should have isolated storage in a cool, ventilated place, away from acute fire hazards and should not be stored in the same building with combustible materials, acids, sulfur, powdered magnesium or powdered aluminum. Examples of chlorates used in the explosive industry, would be potassium chlorate, sodium chlorate and barium chlorate.

**Disaster Hazard:** Moderate, shock will explode them, when heated to decomposition, they can emit toxic fumes and explode; can react with reducing materials.

##### Countermeasures

Personal Hygiene: Section 3.

Storage and Handling: Section 7.

Shipping Regulations: Section 11.

I.C.C.: Oxidizing material, yellow label, 200 pounds.

IATA: Oxidizing material, yellow label, 12 kilograms (passenger), 45 kilograms (cargo).

APPENDIX II (Cont.d.)

ADDITIONAL SAFETY DATA ON COMPOUNDS LISTED IN TABLE VI

NITRITES

**Hazard Analysis**  
**Toxic Hazard Rating:**  
 Acute Local: U.  
 Acute Systemic: Ingestion 3; Inhalation 3.  
 Chronic Local: U.  
 Chronic Systemic: Ingestion 1; Inhalation 1.  
**Toxicology:** Large amounts taken by mouth may produce nausea, vomiting, cyanosis (due to methemoglobin formation) collapse and coma. Repeated small doses cause a fall in blood pressure, rapid pulse, headache and visual disturbances.  
**Fire Hazard:** Details unknown. They are generally powerful oxidizers. In contact with readily oxidized materials, a violent reaction such as a fire or explosion may ensue.  
**Explosion Hazard:** Details unknown. Organic nitrites may decompose violently.  
**Disaster Hazard:** Dangerous; shock may explode them; when heated to decomposition, they emit highly toxic fumes of oxides of nitrogen; can react vigorously with reducing materials.  
**Countermeasures**  
 Ventilation Control: Section 2.  
 Personnel Protection: Section 3.  
 First Aid: Section 1.  
 Storage and Handling: Section 7.

AMMONIUM CHLORIDE

**General Information**  
 Synonym: Sal ammonia.  
 Description: White crystals.  
 Formula:  $\text{NH}_4\text{Cl}$ .  
 Constants: Mol wt. 53.50, mp: 520°C, bp: 337.8°C, d: 1.520, vap. press.: 1 mm at 160.4°C (sublimes).  
**Hazard Analysis**  
**Toxic Hazard Rating:**  
 Acute Local: Irritant 1; Ingestion 1; Inhalation 1.  
 Acute Systemic: U.  
 Chronic Local: Irritant 1.  
 Chronic Systemic: Ingestion 1.  
**Toxicology:** A substance migrating to food from packaging materials. Large doses cause nausea, vomiting and acidosis.  
**Countermeasures**  
 Ventilation Control: Section 2.  
 Personal Hygiene: Section 3.

AMMONIUM THIOCYANATE

**General Information**  
 Synonym: Ammonium sulfocyanate.  
 Description: Colorless solid.  
 Formula:  $\text{NH}_4\text{SCN}$ .  
 Constants: Mol wt: 76.1, mp: 149.6°C, bp: decomposes at 170°C, d: 1.305.  
**Hazard Analysis**  
 Toxicity: A herbicide. See thiocyanates.  
 Disaster Hazard: See thiocyanates.  
**Countermeasures**  
 Storage and Handling: Section 7.

THIOCYANATES

**Hazard Analysis**  
 Toxicity: Variable. Thiocyanates are not normally dissociated into cyanide; they have a low acute toxicity. Prolonged absorption may produce various skin eruptions, running nose, and occasionally dizziness, cramps, nausea, vomiting and mild or severe disturbances of the nervous system.  
 Disaster Hazard: Dangerous; when heated to decomposition or on contact with acid or acid fumes, they emit highly toxic fumes of cyanides.  
**Countermeasures**  
 Storage and Handling: Section 7.

**TOXIC HAZARD RATING CODE** (For detailed discussion, see Section 1.)

- |  |   |
|--|---|
| <p><b>0 NONE:</b> (a) No harm under any conditions, (b) Harmful only under unusual conditions or overwhelming dosage.</p> <p><b>1 SLIGHT:</b> Causes readily reversible changes which disappear after end of exposure.</p> | <p><b>2 MODERATE:</b> May involve both irreversible and reversible changes; not severe enough to cause death or permanent injury.</p> <p><b>3 HIGH:</b> May cause death or permanent injury after very short exposure to small quantities.</p> <p><b>U UNKNOWN:</b> No information on humans considered valid by authors.</p> |
|--|---|

APPENDIX II (Cont'd.)

ADDITIONAL SAFETY DATA ON COMPOUNDS LISTED IN TABLE VI

AMMONIUM BIFLUORIDE

General Information

Synonym: Ammonium hydrogen fluoride.

Description: White crystals.

Formula:  $\text{NH}_4\text{HF}_2$ .

Constants: Mol wt: 57.05, d: 1.21 at 12°C/12°C (liquid).

Hazard Analysis

Toxicity: See fluorides.

Disaster Hazard: See fluorides.

Countermeasures

Storage and Handling: Section 7.

IATA: Other restricted articles, class B, no label required, no limit (passenger), no limit (cargo).

SODIUM DIFLUORIDE

General Information

Description: White powder.

Formula:  $\text{NaF} \cdot \text{HF}$ .

Hazard Analysis and Countermeasures

See fluorides and hydrofluoric acid.

SODIUM DI-HYDROGEN o-ARSENATE

General Information

Description: Rhombic or monoclinic, colorless crystals.

Formula:  $\text{NaH}_2\text{AsO}_4 \cdot \text{H}_2\text{O}$ .

Constants: Mol wt: 181.94, mp:  $-\text{H}_2\text{O}$  at 100-130°C,

bp: decomposes at 200-280°C, d: 2.53.

Hazard Analysis and Countermeasures

See arsenic compounds.

FLUORIDES

Hazard Analysis

Toxic Hazard Rating:

Acute Local: Irritant 3; Ingestion 3; Inhalation 3.

Acute Systemic: Ingestion 3.

Chronic Local: Irritant 1.

Chronic Systemic: Ingestion 3; Inhalation 3.

TLV: ACGIH (recommended); 2.5 milligrams per cubic meter of air.

Toxicology: Inorganic fluorides are generally highly irritant and toxic. Acute effects resulting from exposure to fluorine compounds are due to hydrogen fluoride. Chronic fluorine poisoning, or "fluorosis," occurs among miners of cryolite, and consists of a sclerosis of the bones, caused by fixation of the calcium by the fluorine. There may also be some calcification of the ligaments. The teeth are mottled, and there is osteosclerosis and osteomalacia. The bony and ligamentous changes are demonstrable by x-ray.

Loss of weight, anorexia, anemia, wasting and cachexia, and dental defects are among the common findings in chronic fluorine poisoning. There may be an eosinophilia, and impairment of growth in young workers.

Organic fluorides are generally less toxic than other halogenated hydrocarbons.

Common air contaminants (Section 4).

Disaster Hazard: Dangerous; when heated to decomposition or on contact with acid or acid fumes, they emit highly toxic fumes.

Countermeasures

Ventilation Control: Section 2.

Personnel Protection: Section 3.

First Aid: Section 1.

Storage and Handling: Section 7.

POTASSIUM BIFLUORIDE

General Information

Synonyms: Potassium acid fluoride; Fremy's salt.

Description: Colorless crystals.

Formula:  $\text{KHF}_2$ .

Constants: Mol wt: 78.10, mp: decomposes.

Hazard Analysis and Countermeasures

See fluorides.

Shipping Regulations: Section 11.

IATA (solid): Poison B, poison label, 25 kilograms (passenger), 95 kilograms (cargo).

(solution): Corrosive liquid, white label, 1 liter (passenger), 20 liters (cargo).

HYDROFLUORIC ACID

General Information

Synonyms: Hydrogen fluoride; fluorhydric acid.

Description: Clear, colorless, fuming corrosive liquid or gas.

Formula:  $\text{HF}$ .

Constants: Mol wt: 20.01, mp:  $-92.3^\circ\text{C}$ , bp:  $19.4^\circ\text{C}$ , d: 0.921 g/liter (gas); 0.987 (liquid), vap. press: 400 mm at  $2.5^\circ\text{C}$ .

Hazard Analysis

Toxic Hazard Rating:

Acute Local: Irritant 3; Ingestion 3; Inhalation 3.

Acute Systemic: Ingestion 3; Inhalation 3.

Chronic Local: Irritant 2.

Chronic Systemic: Ingestion 2; Inhalation 2.

TLV: ACGIH (recommended); 3 parts per million in air, 2 milligrams per cubic meter of air.

Toxicology: It is extremely irritating and corrosive to the skin and mucous membranes. Inhalation of the vapor may cause ulcers of the upper respiratory tract. Concentrations at 50 to 250 ppm are dangerous, even for brief exposures. Hydrofluoric acid produces severe skin burns which are slow in healing. The subcutaneous tissues may be affected, becoming blanched and bloodless. Gangrene of the affected areas may follow. See also fluorides. It is a common air contaminant. (Section 4).

Disaster Hazard: Dangerous; when heated, it emits highly corrosive fumes of fluorides; will react with water or steam to produce toxic and corrosive fumes.

Countermeasures

Ventilation Control: Section 2.

Personnel Protection: Section 3.

First Aid: Section 1.

Storage and Handling: Section 7.

Shipping Regulations: Section 11.

I.C.C.: Corrosive liquid, white label, 10 pints.

Coast Guard Classification: Corrosive liquid, white label.

MCA warning label.

IATA: Corrosive liquid, white label, 1 liter (passenger), 5 liters (cargo).

APPENDIX II. (Cont'd.)

ADDITIONAL SAFETY DATA ON COMPOUNDS LISTED IN TABLE VI

**CYANAMIDE**

General Information

Synonyms: Carbodiimide; cyanogenamide.

Description: Deliquescent crystals.

Formula: HNCNH.

Constants: Mol wt: 42.05, mp: 42°C, bp: 260°C, flash p:  
285°F, d: 1.073, vap. d.: 1.45.

Hazard Analysis

Toxic Hazard Rating:

Acute Local: U.

Acute Systemic: Ingestion 2; Inhalation 2.

Chronic Local: U.

Chronic Systemic: Ingestion 1; Inhalation 1.

Toxicology: Does not contain free cyanide. Causes increase in respiration and pulse rate, lowered blood pressure and dizziness. There may be a flushed appearance of the face.

Fire Hazard: Slight, when exposed to heat or flame.

Disaster Hazard: Moderately dangerous; when heated to decomposition or on contact with acid or acid fumes, it emits toxic fumes.

Countermeasures

Ventilation Control: Section 2.

To Fight Fire: Carbon dioxide, dry chemical or carbon tetrachloride (Section 6).

Personal Hygiene: Section 3.

Storage and Handling: Section 7.

**OXALATES**

General Information

Formula: Salts of oxalic acid.

Hazard Analysis

Toxic Hazard Rating:

Acute Local: Irritant 3; Ingestion 3.

Acute Systemic: Ingestion 3.

Chronic Local: Irritant 1.

Chronic Systemic: Ingestion 1.

Toxicology: Oxalates are corrosive and produce local irritation. When taken by mouth they have a caustic effect on the mouth, esophagus and stomach. The soluble oxalates are readily absorbed from the gastro-intestinal tract and can cause severe damage to the kidneys.

Disaster Hazard: Dangerous; when heated to decomposition, they emit toxic fumes.

Countermeasures

Personnel Protection: Section 3.

Ventilation Control: Section 2.

Storage and Handling: Section 7.

APPENDIX III

SUMMARY OF THERMODYNAMIC CONSTANTS USED IN EXPANSION  
COOLING CALCULATIONS OF SECTION 2.4.2

Substance	$C_v$ (cal/deg mole at 25°C)	Gamma
Nitrogen	4.95	1.40
Carbon dioxide	6.92	1.27
Ammonia	6.57	1.31
Freon-21	11.898 at 16°C	1.180

## APPENDIX IV

### MATERIALS FOR AMMONIA

H.H. Uhlig, The Corrosion Handbook, The Electrochemical Society, Inc., New York, 1948, p. 799.

TABLE 12. AMMONIA GROUP

*Types of Material*

(See p. 753 for sub-groups and further details of composition.)

- |   |                            |                                     |
|---|----------------------------|-------------------------------------|
| 1. Al and Al-Base Alloys                | 10. Nickel                 | 19. Silver                          |
| 2. Iron and Steel                       | 11. Ni-Cr-Fe Alloy         | 20. Noble Metals and Tantalum       |
| 3. High-Si Cast Irons                   | 12. Ni-Cu Alloys (>50% Ni) | 21. Mg and Mg-Base Alloys           |
| 4. High-Ni Cast Irons                   | 13. Ni-Mo-Fe-(Cr) Alloys   | 22. Ceramic Materials               |
| 5. 4 to 10% Chromium Steels             | 14. Ni-Cr-Cu-Mo Alloy      | 23. Carbon and Graphite             |
| 6. Stainless Steels (Martensitic)       | 15. Ni-Si Alloy            | 24. Plastics                        |
| 7. Stainless Steels (Ferritic)          | 16. Cu-Ni Alloys (>50% Cu) | 25. Rubber and Synthetic Elastomers |
| 8. Stainless Steels (Austenitic)        | 17. Cu and Cu-Base Alloys  |                                     |
| 9. Special Fe-Cr-Ni Alloys (Austenitic) | 18. Lead                   |                                     |

Ammonia and Ammoniumhydroxide, Ammonia Liquors	Class A Materials	Class B Materials	Class C Materials
Compressed liquid and gas (Note 1) anhydrous	1; 2; 3A, B; 4B, C; 5; 6; 7; 8; 9 (Note 1); 10; 11; 13A, B, C; 14A; 15; 18; 19 (Note 2); 20A, B, C; 21; 23A, B, C, D		1A; 12; 16; 17
Moist vapors Ammonium hydroxide	1; 4B*, C up to 70° C (160° F); 8; 9; 11; 13C; 14A; 20A, B, C; 21; 23A, B, C, D up to b.p. 24E and all Type 25 materials up to 65° C (150° F)	2; 3A, B; 5; 6; 7; 4B*, C above 70° C (160° F) up to b.p.; 19 (Note 2); 24B at room temp.	1A, B; 10; 12; 15; 16; 17; 19, (Note 2); 24A above 30° C (85° F) with up to 10%; at all temperatures with concentrated grade. 24B above 30° C (85° F).
Ammonium carbonate Ammonium phosphate (tribasic)	In general, the ratings for ammonium hydroxide apply here. All materials which are Class A or Class C with ammonium hydroxide are similarly rated with solutions of these salts. Materials which are Class B with ammonium hydroxide may approach Class A with solutions of these salts.		
Ammonia liquors (mixtures of ammonium hydroxide, ammonium salts, and other components)	All materials which are Class C with ammonium hydroxide are Class C with ammonia liquors. The A and B ratings for ammonium hydroxide and ammonium salts will usually apply also, but they should be used cautiously, depending upon the other components.		

\* Preferably Cu-free grade.

† Cu-bearing grade.

Note 1. All the ratings in this Table are based on the assumption that the temperature is below that at which dissociation of the gas and nitriding of the metal occur.

Note 2. Silver alloys containing copper are always Class C. Pure silver resists dry gas and air-free aqueous solutions well, but is attacked vigorously by aerated solutions and by hot moist vapors.

**Class A:** Suitable for critical parts where very little dimensional change can be tolerated.

**Class B:** Common use for non-critical parts where some corrosion can be tolerated.

**Class C:** Not ordinarily considered suitable.