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**CLASSIFICATION OF FLOATING CHRIS CHEMICALS  
FOR THE DEVELOPMENT OF A SPILL RESPONSE MANUAL**

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16. Abstract <p>Physico-chemical criteria were established and subjected to the chemical compounds listed in CHRIS to select those chemicals which are immiscible and float on water. This information was compiled in a menu-driven data base for easy access. As the result of this work, 294 CHRIS chemicals were found to be floaters. A literature review was conducted also to review available spill containment and recovery equipment and techniques for the application toward floating hazardous chemical spills. No single technology or equipment was found to effectively apply for the containment and recovery of spilled floating chemicals. Specific deficiencies and problems inherent in existing technologies were identified.</p> <p>A hazard and toxicity ranking system was developed and applied to the floating chemicals for groupings by degrees of flammability and toxicity hazards. These groupings include highly flammable through noncombustible and highly toxic through non-toxic and the combination of degrees of hazards.</p> <p>An attempt was made to develop a mathematical model to account for the suppression of vapors by foam. This entailed identifying the controlling mechanisms of foam vapor suppression. The literature was searched for methods to evaluate the compatibility between floating CHRIS chemicals and response equipment.</p>					
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# METRIC CONVERSION FACTORS

## Approximate Conversions to Metric Measures

Symbol	When You Know	Multiply By	To Find	Symbol
<b>LENGTH</b>				
in	inches	2.5	centimeters	cm
ft	feet	30	centimeters	cm
yd	yards	0.9	meters	m
mi	miles	1.6	kilometers	km
<b>AREA</b>				
in <sup>2</sup>	square inches	6.5	square centimeters	cm <sup>2</sup>
ft <sup>2</sup>	square feet	0.09	square meters	m <sup>2</sup>
yd <sup>2</sup>	square yards	0.8	square meters	m <sup>2</sup>
mi <sup>2</sup>	square miles	2.6	square kilometers	km <sup>2</sup>
	acres	0.4	hectares	ha
<b>MASS (WEIGHT)</b>				
oz	ounces	28	grams	g
lb	pounds	0.45	kilograms	kg
	short tons (2000 lb)	0.9	tonnes	t
<b>VOLUME</b>				
tsp	teaspoons	5	milliliters	ml
tbsp	tablespoons	15	milliliters	ml
fl oz	fluid ounces	30	milliliters	ml
c	cups	0.24	liters	l
pt	pints	0.47	liters	l
qt	quarts	0.95	liters	l
gal	gallons	3.8	liters	l
ft <sup>3</sup>	cubic feet	0.03	cubic meters	m <sup>3</sup>
yd <sup>3</sup>	cubic yards	0.76	cubic meters	m <sup>3</sup>

### TEMPERATURE (EXACT)

°F	Fahrenheit temperature	5/9 (after subtracting 32)	Celsius temperature	°C
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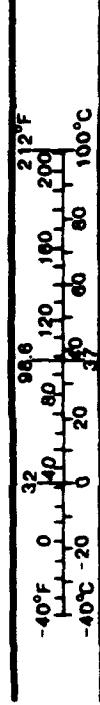
\*1 m = 2.54 (exactly) For other exact conversions and more detailed tables, see NBS Misc Publ. 286, Units of Weights and Measures Price \$2.25. SD Catalog No. C13 10 286

## Approximate Conversions from Metric Measures

Symbol	When You Know	Multiply By	To Find	Symbol
<b>LENGTH</b>				
mm	millimeters	0.04	inches	in
cm	centimeters	0.4	inches	in
m	meters	3.3	feet	ft
m	meters	1.1	yards	yd
km	kilometers	0.6	miles	mi
<b>AREA</b>				
cm <sup>2</sup>	square centimeters	0.16	square inches	in <sup>2</sup>
m <sup>2</sup>	square meters	1.2	square yards	yd <sup>2</sup>
km <sup>2</sup>	square kilometers	0.4	square miles	mi <sup>2</sup>
ha	hectares (10,000 m <sup>2</sup> )	2.5	acres	
<b>MASS (WEIGHT)</b>				
g	grams	0.035	ounces	oz
kg	kilograms	2.2	pounds	lb
t	tonnes (1000 kg)	1.1	short tons	
<b>VOLUME</b>				
ml	milliliters	0.03	fluid ounces	fl oz
l	liters	0.125	cups	c
l	liters	2.1	pints	pt
l	liters	1.08	quarts	qt
l	liters	0.26	gallons	gal
m <sup>3</sup>	cubic meters	35	cubic feet	ft <sup>3</sup>
m <sup>3</sup>	cubic meters	1.3	cubic yards	yd <sup>3</sup>

### TEMPERATURE (EXACT)

°C	Celsius temperature	9/5 (then add 32)	Fahrenheit temperature	°F
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PART I

CLASSIFICATION OF FLOATING CHRIS CHEMICALS AND  
STATE-OF-THE-ART REVIEW OF CONTAINMENT AND  
RECOVERY TECHNOLOGIES

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R. S. Moore



July 1985

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## I. INTRODUCTION

The concern for control of chemical substances has grown rapidly during the period from the late 1960's to the present as evidenced by the number of laws passed by Congress. Each law required several months of hearings and testimony serving to increase the public awareness towards chemical hazards.

The United States Coast Guard, by virtue of the Federal Water Pollution Control Act, as amended; the Comprehensive Environmental Response, Compensation, and Liability Act of 1980 (CERCLA); and the National Oil and Hazardous Substances Pollution Contingency Plan, provides the predesignated Federal On-Scene Coordinator (OSC) for response to hazardous chemical releases occurring in the coastal zone, Great Lakes waters, and specified inland ports and harbors. This responsibility includes the containment, removal, cleanup, and disposal of a large variety of hazardous chemicals which have greatly varying chemical, physical, physiological, toxicological, and ecological properties.

Most pollution control measures have emphasized removing, or to some degree reducing, the potential hazardous effects of petrochemicals on the aquatic environment. With the Coast Guard expanding its Chemical Hazards Response Information System (CHRIS), it has become evident that response techniques require modification or new development to cover the myriad of potential hazards which may be encountered by spill response personnel.

Hazardous chemicals which float on water present hazards to spill clean-up personnel not usually associated with oil spills. Many chemicals which are transported across waterways are toxic and can develop flammable vapor clouds

which could lead to a resulting explosion. In order to properly protect the personnel involved with clean-up measures and to reduce the impact on the environment, methods for treating and handling floating hazardous spills need to be developed and documented.

The objectives of this program were 1) to determine which of the CHRIS chemicals will float and require a reduction in flammability or toxicity in order to be contained and recovered safely from a waterway if spilled, 2) to evaluate the state-of-the-art of containment and recovery of floating hazardous chemicals and identify areas where improvement (i.e., reduction in flammability and/or toxicity) can be made, and 3) to propose development, test, and evaluation programs for those areas identified in the second objective where the Coast Guard's ability to reduce flammability and toxicity can be improved.

A literature review was conducted to evaluate the available spill containment and recovery methods and techniques. The purpose of this review was to determine the feasibility of applying these methods and techniques toward the containment and recovery of floating hazardous chemicals. The characteristics of the chemicals of concern were reviewed as well as the basic concepts, operational conditions and limitations of the presently available spill technologies in order to determine which techniques have the most potential for further development. Knowledge obtained through case studies, along with the expertise and experience of those personnel tasked with responding to hazardous chemical spills, were combined to evaluate all aspects necessary to assess the candidate technologies. Specific deficiencies and problems inherent in the present technologies have been identified.

Areas with deficiencies requiring more investigation include: 1) the compatibility of foams with floating hazardous chemicals; 2) the environmental effects on the effectiveness of foams on floating hazardous chemicals; 3) the compatibility of materials used in constructing spill mitigation equipment with floating hazardous chemicals; and 4) the effect of recovery equipment on the effectiveness of foams.

The remainder of Part I is organized according to the following format: Section II outlines the approach to the classification of CHRIS chemicals; Section III reviews and discusses existing clean-up technologies, procedures, and case studies; and Section IV discusses preparation of test and evaluation plans for subsequent action. The summary and conclusions are presented in Section V. A list of the physical and chemical characteristics of floating CHRIS chemicals is given in Appendix A. Groupings of these same chemicals according to degrees of toxicity and flammability are presented in Appendix B.

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## II. APPROACH

To properly assess the potential hazards and difficulties which could be encountered in combating a floating hazardous chemical, it was necessary to develop criteria to determine what constitutes a floating hazardous chemical. Three major properties -- floatability, flammability, and toxicity -- were reviewed for all of the CHRIS chemicals in order to determine if they meet the following guidelines:

### FLOATABILITY CRITERIA

The following criteria were established for determining if a particular chemical floats:

- o The chemical should have a specific gravity of 1.05 or less. This value is used to account for temperature variations and the salinity of sea water.
  
- o The chemical should be immiscible or only slightly soluble in water. If a chemical is slightly soluble, it may float, depending on the size of the spill, the size of the body of water, and the environmental conditions present in the spill area. Due to the varying methods of recording solubility data in the literature, chemicals listed as insoluble, slightly soluble, and soluble up to 25 g/100ml are included in this study.

All the CHRIS chemicals meeting both of the above criteria have been classified as floating chemicals for the purposes of this study.

## FLAMMABILITY CRITERIA

To establish criteria regarding flammability, the National Fire Protection Association's (NFPA) rating of flammability hazards was adopted. The NFPA system ranks the degree of flammability from 1 to 4 based on the chemical's susceptibility to burning, with a rating of 4 denoting the greatest flammability hazard and 0 the least hazard. A detailed description of the rating system follows.

Rating 4: A rating of 4 is given to very flammable gases and very volatile, flammable liquids. Liquid and gaseous materials which are liquids under pressure fall into this category if they have a flash point below 73°F and a boiling point below 100°F. This category includes gases, cryogenic materials, and those materials which readily form explosive mixtures in air.

Rating 3: A rating of 3 includes those liquids and solids that are ignitable under almost all ambient temperature conditions. Liquid materials with a flash point below 73°F and a boiling point at or above 100°F, and liquids with a flash point between 73°F and 100°F, are included in this rating. Also included in this category are coarse dusts which are flammable, but not explosive, in air; shredded or fibrous solid materials which burn rapidly; materials which burn with extreme rapidity, usually because of self-contained oxidizers; and materials which spontaneously ignite in air.

Rating 2: Materials with an NFPA rating of 2 must be moderately heated before ignition can occur. They may also ignite under high ambient temperatures. Liquids having a flash point between 100°F and 200°F are included in this category, as are those solids and semi-solids which release flammable vapors.



Rating 1: A rating of 1 is given to materials that must be preheated before ignition can occur. These materials will burn in air when exposed to a temperature of 1500°F for five minutes or less, and materials with a flash point above 200°F.

Rating 0: A rating of 0 is given to non-combustible materials. These chemicals will not burn when exposed to a temperature of 1500°F for five minutes.

For the purpose of this study, a chemical will be considered flammable if it has a flash point of less than 200°F. Generally, this value will encompass all chemicals with an NFPA rating of 2 or more.

#### TOXICITY CRITERIA

In order to determine criteria for toxicity, NFPA ratings of the health hazards of chemical materials along with published toxicity values were reviewed. The NFPA ranks each chemical according to the degree of health hazard from 0 to 4 under fire conditions. A rating of 4 is assigned to those chemicals representing the greatest health hazards while a rating of 0 is given to chemicals with the least health hazards. The NFPA health hazard ratings for a given chemical may be greater than one would expect from the typical measures of toxicity (Threshold Limit Values; "TLVs"; LD50 Values; etc.), because the hazardous nature of some chemicals is increased under those conditions. Fire conditions should not decrease the inherent toxicity of the material. The NFPA ratings, then, may overstate but should not understate the health hazard in non-fire conditions.

Rating 4: A health hazard rating of 4 is assigned to those substances which are very dangerous. These materials, with very short exposure, could cause death or major residual injury even with prompt medical treatment. Included in this category are materials which are too dangerous to handle without specialized protective equipment, materials which can penetrate ordinary protective clothing, and materials which release extremely toxic or corrosive vapors.

Rating 3: A rating of 3 is given to materials where short exposure could result in serious temporary or residual damage even with prompt medical treatment. Included in this category are materials with highly toxic combustion products, materials that are corrosive to living tissue or toxic via skin absorption mechanisms, and materials requiring protection from any type of bodily contact.

Rating 2: A rating of 2 is assigned to those materials which cause temporary incapacitation or possible residual injury unless prompt medical attention is received. Materials included in this category are those which give off toxic or highly irritating combustion products, and materials which require the use of protective respiratory equipment with an independent air supply.

Rating 1: A health hazard rating of 1 is given to chemicals where exposure could cause irritation but only minor residual injury even without medical treatment. Materials with irritating combustion products, chemicals which irritate but do not destroy tissue, and materials which require the use of canister-type gas masks are included in this category.

Rating 0: A rating of 0 is indicative of a material which poses no health hazard beyond that of ordinary combustible material.

The NFPA health hazard ratings of chemicals are generally not based on toxicity values obtained through laboratory studies. The NFPA health hazard ratings were determined by a group of experts, through experiences of fire fighting and through chemical knowledge. Since health hazard ratings were first introduced in 1952 (NFPA, 1984), this approach was most likely taken due to the lack of adequate toxicity information at the time. With many chemicals, the lack of toxicity data still exists; and where data are available, they are not uniform and exist as many different toxicity limits. The most frequently determined toxicity limits calculated for various exposure measurements are:

Short Term Exposure Limits - STEL

Immediately Dangerous to Life and Health Limit - IDLH

Threshold Limit Value - TLV

Toxic Concentration Low - TClO

Oral Rat LD50 - LD50

None of these most frequently determined toxicity limits are uniformly available for all of the CHRIS chemicals; indeed, for some, no measure of toxicity is available. There were some CHRIS chemicals which already had a toxicity rating assigned by NFPA. For those chemicals which did not have NFPA toxicity ratings but some other toxicity criteria such as STEL could be found, an attempt was made to statistically estimate an NFPA rating, thus increase the list of rated chemicals. A linear least squares regression analysis was performed using the NFPA Health Hazard Identification Code (HIC) as the dependent variable and the STEL values as the independent variable. Since the values of the various toxicity limits represented a wide range of concentration values ranging from 0.1 ppm to 10,000+ ppm, the logarithm of the independent variables was used.

Subsequently, linear least squares regression analyses were performed with the five toxicity criteria identified above. The same procedures were used for all five toxicity limits, except an Oral Rat LD50. Oral Rat LD50 values are often quantified by a grouping of concentrations rather than a specific numerical value. Consequently, for the LD50 regression analysis the grouping was used as the independent variable, instead of the logarithm of the calculated LD50 value.

The equations for four of the five toxicity exposure measurements with the HIC estimates, rounded to the nearest integer, are listed below. Although an equation for TCLo was also calculated, due to insufficient data, this equation is not included.

Short Term Exposure Limits

Data Points: 59  
 Regression:  $HIC = 2.79 - 0.612 * \log (STEL)$  STEL (ppm)  
 r statistic: -0.51

HIC 0	3.74 < log STEL	5500 < STEL
HIC 1	2.11 < log STEL < 3.74	130 < STEL < 5500
HIC 2	0.48 < log STEL < 2.11	3.01 < STEL < 130
HIC 3	-1.36 < log STEL < 0.48	0.07 < STEL < 3.01
HIC 4	log STEL < -1.36	STEL < 0.07

Immediately Dangerous to Life and Health Limits

Data Points: 10  
 Regression:  $HIC = 3.86 - 0.58 * \log (IDLH)$  IDLH (ppm)  
 r statistic: -0.79

HIC 0	5.76 < log IDLH	578000 < IDLH
HIC 1	4.05 < log IDLH < 5.76	112000 < IDLH < 578000
HIC 2	2.33 < log IDLH < 4.05	216 < IDLH < 11200
HIC 3	0.62 < log IDLH < 2.33	4.17 < IDLH < 216
HIC 4	log IDLH < 0.62	IDLH < 4.17

Threshold Limit Values

Data Points: 97  
 Regression:  $HIC = 2.60 - 0.660 * \log (TLV)$  TLV (ppm)  
 r statistic: -0.54

HIC 0	3.18 < log TLV	1510 < TLV
HIC 1	1.67 < log TLV < 3.18	46.3 < TLV < 1510
HIC 2	0.15 < log TLV < 1.67	1.41 < TLV < 46.3
HIC 3	-1.36 < log TLV < 0.15	0.04 < TLV < 1.41
HIC 4	log TLV < -1.36	TLV < 0.04

Oral LD50

Data Points: 15

Regression:  $HIC = 4.68 - 0.87 * \log (LD50)$

LD50 (ppm)

r statistic: -0.77

HIC 0 Grade 0: LD50 > 15000  
HIC 1 Grade 1: LD50 5000 - 15000  
HIC 2 Grade 2: LD50 500 - 5000  
HIC 3 Grade 3: LD50 50 - 500  
HIC 4 Grade 4: LD50 < 50

Based on the results of these linear regression studies, the following criteria for toxicity were developed:

- (1) STEL less than 150 ppm
- (2) IDLH less than 12000 ppm
- (3) TLV less than 50 ppm
- (4) TCLo less than 250 ppm
- (5) LDLo less than 5000 ppm, and
- (6) NFPA Health Rating of 2 or more

The information obtained from Threshold Limit Values (TLV's) and Short Term Exposure Limits (STEL's) was given first priority in the ranking process. The criteria, shown in Table II-1 are based on regression analyses and were used as a guideline in the grouping.

Table II-1. CHEMICAL RANKING GUIDELINES

Group	TLV (ppm)	STEL (ppm)
Not Toxic	1000	5500
Slightly Toxic	100	130
Moderately Toxic	5	3
Highly Toxic	0.1	0.1

Data from the OHM-TADS, LD-50's, and NFPA health codes were also considered. In some instances, it was necessary to assign a chemical to a category based on limited toxicity information. In other cases, contradictory data led to a grouping decision based on the more conservative piece of information.

Physical and chemical information for the floating CHRIS Chemicals is presented in Appendix A.

### III. REVIEW OF SPILL CLEANUP TECHNOLOGIES

Responding to a hazardous floating chemical spill requires a blend of personnel expertise and equipment utilization. The personnel involved with the spill cleanup must be able to detect, identify, and monitor the extent of the spill, as well as make progress toward reducing its environmental impact.

In order to reduce the spread of the spill with its accompanying hazards, personnel at the scene must be prepared to apply the most feasible method(s) of physical or chemical containment. To ensure that the proper means of response is chosen, the personnel directly involved should consider which technique is most effective. Although one technique may be applicable to handling a large number of hazardous substances, sometimes a specialized method for a given place, time, and chemical may need to be developed.

The technique chosen by the response team should render itself to rapid, easy deployment. This will help reduce the necessity of specialized training for the response personnel as well as help eliminate the need for stockpiling specialized equipment or chemicals.

The personnel involved in combating a spill should consider whether the technique(s) employed will present potentially harmful effects in the aquatic environment. In some cases, it may be possible to use a different counter-measure in order to reduce the chance of any hazard.

Selecting the best cleanup alternative is a decision complicated by the magnitude of information required concerning the spill and the potential hazards facing the response team. The following information is presented as a review of

the available chemical and mechanical methods which are presently available or could be developed for use at the scene of a floating hazardous chemical spill.

#### LITERATURE REVIEW

A literature review (referenced in Appendix D - Bibliography) was conducted to provide a basis for analyzing the results of previous tests of spill control agents and devices in order to compare their effectiveness. Sources of information included the final reports of American Petroleum Institute-sponsored studies, U.S. Coast Guard case histories, information from the Noyes Data Corporation, NTIS releases, technical product bulletins and personal communications with suppliers and other informed individuals. It was frequently impossible to objectively compare the agents and methods applied in previous work due to the varying test methods, differencing environmental conditions, and the lack of sufficient recorded field work concerning cleanup of hazardous floating chemicals.

#### CHEMICAL METHODS

The application of specific chemical agents on a floating hazardous chemical spill can help alleviate some of the hazards inherent in spill response procedures. The use of chemical agents such as foams and surfactant films may help reduce the vapor pressure of the hazardous chemical over the spill. The use of gelling agents can help prevent the horizontal as well as vertical spread of a hazardous chemical. Other chemical agents can effectively neutralize hazards associated with the spill materials. To effectively understand the utilization of chemical methods, the theory of the chemical mechanism as well as the method of application should be reviewed. The following section contains a discussion of vapor pressure, and the chemical methods related to its reduction.



### Overview of Vapor Pressure Reduction

Vapor pressure is a measure of the volatility of a liquid, therefore representing the ease with which a liquid is converted to a gas. It measures the tendency of molecules to escape from the liquid phase and is an indication of the intermolecular forces between molecules in a liquid.

As the temperature of a liquid increases, the kinetic energy of the molecules increases, giving molecules the energy required to break intermolecular forces. As more molecules evaporate from the liquid's surface, the vapor pressure increases.

J. S. Greer (1976) concluded that evaporation rates are controlled by five major factors: heat transfer, surface area, surface turbulence, vapor-saturated interfacial film and surface cleanliness. A discussion of each factor is presented in the paragraphs which follow.

Heat transfer and insulation properties have been thoroughly studied. There is a considerable amount of literature which discusses the theoretical and practical applications of both areas. Since evaporation is an endothermic process, anything promoting heat transfer into a spilled chemical would aid vaporization. Surface area contributes directly to the heat transfer capability of a substance. The one-dimensional steady state conduction of heat in solids is governed by the equation:

$$g = - KA \frac{dT}{dx}$$

Where  $g$  = heat transfer rate in BTU/hr.

$K$  = thermal conductivity in BTU/hr. ft. °F

$A$  = area (in ft<sup>2</sup>)

$\frac{dT}{dx}$  = temperature gradient across transfer medium

This equation can be varied to calculate the heat transfer between different phases, i.e., solid or liquid. Any process which increases the surface area of a spilled liquid should therefore allow a resulting increase in total mass of vaporized chemical per unit of time.

Surface turbulence tends to disrupt the interface between two liquids by exceeding the tension between the liquids allowing evaporation to occur more readily.

Interfacial tension corresponds to the energy required to produce a unit area of that surface when two immiscible liquids are in contact with each other. Any mechanism which aids in minimizing the effects created by the interfacial film will tend to increase the vaporization rate.

Surface cleanliness effects the parameters described above. Surface contaminants tend to disrupt the interfacial film and interfere with heat transfer.

#### **Vapor Pressure Reduction Agents**

An extensive literature review has shown five vaporization reduction agents are available for hazardous material spills. These include:

- o Thin Surfactant Films
- o Foams
- o Gelling Agents
- o Sorbents
- o Cryogens

Surfactant films reduce vaporization by generating a film which is insoluble in the liquid and acts as a barrier preventing the transfer of liquid molecules into the gaseous phase. Foams reduce the vaporization rate of hazardous floating liquids by forming a 'bubble blanket' over the liquid. This 'bubble blanket' also contributes to some vapor scrubbing as the gas

rises through the foam. The warming of the vapor by normal heat transfer and associated heat of the solution may help by making the vapor less dense and more buoyant, thereby allowing the hazardous vapor to disperse upward more quickly, away from the spill area. This would help reduce the toxic effects of the vapor that a clean-up crew could encounter from a spill. Gels reduce evaporation by forming a cover of gelled material over the spill held together by chemical and physical interactions. Surfactants and foams act to reduce the surface tension of water, allowing better wetting of organic surfaces and better penetration into material surfaces and openings. This effect aids in isolating spill surfaces from ignition sources and radiant energy effectively reducing the chances of fire from the hazardous material. Sorbents reduce vaporization by the preferential wetting and absorption of the hazardous material into a material with high surface area and activity. Cryogenics function to reduce the vaporization of hazardous material by absorbing heat energy from the spill vicinity resulting in a reduction of energy available to allow molecules to escape from the liquid phase. Each of these agents is discussed in greater detail in the succeeding paragraphs.

#### Thin Surfactant Films

Early investigations with monomolecular films demonstrated they formed a closely packaged array of molecules, vertically oriented so that their polar groups interacted with water. Vaporization reductions were attributed to the formation of a nearly impermeable film on the surface and extinction of surface waves at both interfaces. Organic chain length and both the chemical and stereochemical nature of the surfactant affected the vaporization rate of liquids through monomolecular films. Film pressure

generated from the monomolecular film considerably reduced surface turbulence and convection currents. For a film to be effective, it should:

- (1) be monomolecular and spatially oriented;
- (2) have limited solubility in the liquid; and
- (3) be uniform and continuous.

Fluorochemical surfactant foams which collapse to form a thin film over hydrocarbon liquids have been shown to reduce evaporation rates by 90 to 98%. This technique has been shown to work best on chemicals having a surface tension equal to, or greater than, 20 dyne/cm.

A technique developed by Moran et al. (1971), utilized fluorochemical surfactants to reduce evaporation of hazardous chemicals. The surfactant can be applied to the spill as an aerosol or as a foam. When applied as an aerosol, the surfactant/water solution is allowed to settle over the spill to form a thin film. The alternative method requires the fluorochemical surfactant to be incorporated into an aqueous film-forming foam which is applied over the spill surface. The foam chemistry is designed in such a way that it quickly collapses to form a surfactant film.

Assuming a spill of 100 to 100,000 gallons, 1 to 20 gallons of surfactant film solution would be required if applied as an aerosol. A nominal expansion ratio of 10 to 1 would be required to apply a low expansion foam containing the fluorochemical over the spill.

Hydraulic or pneumatic equipment could be used to apply the surfactant/water solution over the spill surface. Since hazardous chemical spills are generally small (when compared to oil spills), hydraulic

application equipment appears to be the most feasible. However, pneumatic systems could be applied to allow a larger area of dispersal of surfactant.

#### Foams

Foams can be formulated to have physical and chemical compatibility with hazardous materials. Foams offer a mechanism of applying water at a slow rate, providing dilution with a minimum amount of reaction for those substances that react violently with water. Other advantages of foams include: (1) the ability to reduce the amount of smoke and fumes; (2) the ability to aid in the removal of heat by converting water to steam; and (3) a method to build a 3-D barrier over a spill.

Foam production is aided by lowering the surface tension ( $\gamma$ ) to a foaming solution. The free energy of a surface is equivalent to the work required to produce that surface. This amount of work is equal to the product of the surface tension and the surface area of the system. Thus,  $G = \gamma A$ ; where  $G$  is the Gibbs free energy of the network of the system, and  $A$  is the total surface area of the bubbles.

Foams must have stability to be effective. For example, as a film thins when it is stretched, there must be a restoring force generated to prevent the elastic limit of the film from being exceeded, resulting in film rupture. The restoring force in foams is believed to result from the higher surface tension which an increased surface shows.

Surfactants which are good wetting agents act to reduce surface tension. Due to this, care must be taken in choosing a foam so that a defoaming mechanism does not prevent the film healing mechanism.

Foams are usually designated as low expansion (with a volume expansion of water to foam ratio of less than 20:1) or high expansion foam (with a volume expansion of water to foam ratio greater than 100:1). The gap between these two expansion ranges results from the lack of suitable equipment to generate foam in the intermediate range.

Foams can generally be formed by three mechanisms which include:

(1) mechanical agitation; (2) impaction of a spray against a screen; or (3) bubble formation through controlled orifices. Mechanical agitation generally gives an expansion of less than 80:1 with small bubble size and good stability.

Low expansion foams are generated by mechanically agitating water with the foaming agent in the dispersing nozzle system. For application in this manner, the foam is drawn into an eductor at a rate proportional to the water flow. When expansion ratios of about 5:1 are desirable, a non-air-aspirating nozzle is utilized, resulting in only the foam concentrate and water being mixed. If higher expansion ratios are desired, an aspirating nozzle allowing the introduction of air would be required. When low expansion foams are mechanically generated, they may be directed as a projectile from a range of up to 200 feet, permitting the blanketing of a large area from one or more locations somewhat distant to the spill.

High expansion foams are generated by blowing a water-surfactant solution against a screen. Impaction of a spray against a screen generally gives ratios of 100:1 to 1500:1. The expansion created will depend on the water-surfactant flow, air velocity, and screen-mesh size. The air velocity required to generate high expansion foams can be provided by fans or high pressure water sprays.

Due to its properties, the high expansion mode of foam production limits its use primarily to enclosed areas or areas with calm environmental conditions. Wind and rain present potential deleterious effects to high expansion foam generation. High expansion foams may also present a problem in enclosed areas. These foams are non-toxic but may block sight and hearing, resulting in disorientation. Work in the area is also inhibited by the presence of the foam.

Foam generation via controlled orifices utilizes a system called a flooded plate generator. This is a box-shaped compartment separated into two halves by a horizontal perforated plate. Foam solution is made to flow over the top of the plate while air flows beneath the plate. Bubble size is limited by perforation size and spacing. Due to its design, flooded plate generators have been limited in use to the generation of foam too viscous for the other types of generators.

The air required to generate high expansion foams can be achieved through several methods. In air aspirating units, the velocity of the water spray is used to create air flow into the generator. This method of generation is limited to expansion of less than 500:1. To achieve higher expansions, fans are used to create a higher air velocity. These fans may develop their mechanical driving force by water flow, electricity, gasoline, or compressed gas. Hiltz (1980) reported that electrically driven units provide the highest expansion and that water driven units are self-limiting due to the greater water flow required to develop a higher fan speed. Hiltz (1980) also stated that the water driven units are more reliable due to their independence from electrical circuitry. Two forms of water driven systems are in use -- water turbines and reaction drives.

Shaver et al. (1983) identified six major types of foaming agents. These are: (1) proteins; (2) synthetics; (3) AFFF (Aqueous Film Forming Foam); (4) fluoroproteins; (5) alcohols; and (6) polar solvents. Since foams may be used to reduce vaporization rates and to combat fires, a general description of the capabilities of the six major foam types will be described as discussed by Shaver (1983).

Protein foams have good cooling and burn back resistance. The fire knockdown capability of protein foams is not as good as AFFF. Protein foams are limited to low expansion applications.

Synthetic or detergent foams are long chain hydrocarbons with capabilities parallel to AFFF. Synthetic foams are generally used in the high expansion mode.

AFFF is a fluorocarbon-based surfactant which presents excellent fire knockdown capability but is poor for cooling a structure or maintaining a blanket of foam on the surface. AFFF is used in the low-expansion mode.

Fluoroproteins provide lower surface tension and greater fluidity than protein foams while maintaining the persistence absent in AFFF. These are primarily used in the low expansion mode.

Alcohol and polar solvent foams either precipitate or gel into an insoluble layer on the chemical surface. These could be applied to block foam degradation or to allow foam buildup. They are primarily applied as low expansion foams.

The most important factor influencing the formation of a foam cover is its chemical compatibility with the hazardous floating material. Most foams



now in use are generally compatible with nonpolar molecules and with those having a pH close to 7. (Chemical-foam interactions due to the solubility of chemicals in foams are further discussed in Part II, Section I.)

Use of nonalcohol foams with polar compounds is generally restricted to those having a dielectric constant less than 4. Gross (1982) states that nonalcohol types of foam are seriously degraded when applied to chemicals with a dielectric constant above 4. The floating hazardous chemicals reviewed in this study generally have a dielectric constant greater than 3.

For spills involving hydrocarbons or other chemicals having the property of low water solubility, rapid nozzle sweeps of low expansion foam over the spill is an effective application method. For polar solvents or other hydrophilic chemicals, gently applying an alcohol type concentrate (ATC) foam or an AFFF/ATC using an air aspirating nozzle is recommended. This method of application allows a slow buildup of the foam blanket.

Wesson and Associates, Inc., conducted a test for 3-M Company (August 1983) to determine the performance of three different low expansion foams in maintaining a foam blanket on a flammable liquid that was floated on water, then subjected to a wave producing apparatus. The foams tested were an ATC, an AFFF, and a fluoroprotein foam concentrate. The performance of the foams was judged on their capability to follow the movement of the waves and to prevent ignition of the vapor space even after several minutes of wave activity. The AFFF and ATC foams were observed to follow the movement of the waves, whereas the fluoroprotein foam did not.

The actual foam depth required to reduce the vapor concentration above a floating hazardous chemical spill to a non-hazardous level varies with the nature of the chemical involved. In general, more volatile compounds require a greater foam depth.

The application of foams to spills does not create any significant problems during cleanup activities where vacuum trucks, sorbents, skimmers, weirs, etc., are used. However, contamination of the recovered chemical in combination with the foam normally prevents reclamation of the chemical, thereby creating a disposal problem.

In general, the following conclusions can be obtained from a program conducted by Gross and Hiltz (1982).

- o High quality foams demonstrate the lowest drainage rates. This allows them to maintain their water content. These foams perform best in the reduction of vapor hazards.
- o For nonpolar liquids, any high quality foam cover, regardless of chemical type, will provide some degree of vapor release reduction.
- o Alcohol foams are the most stable agents for highly polar low molecular weight liquids. The other foam types collapse rapidly when in contact with highly polar liquids.
- o Vapor from polar liquids can be reduced with nonalcohol type low expansion foams if the volume of foam applied is several times greater than the volume of the spill. This effect can be attributed mainly to water dilution instead of the physical-chemical interaction of the foam.
- o High expansion foams with a slower rate of water addition to a reactive liquid spill provide the best control on water reactive liquids.

The application of a foaming agent to a hazardous material spill will restrict the vapor release thus ameliorating the downwind hazard resulting

from the incident. The material which may be vaporized will dissipate quickly due to heat gained as the vapors pass through the foam bubbles. Reducing the vapor concentration, even if it cannot be held below the TLV, can extend the life of canister protection and minimizes vapor hazards due to mask or hose failures.

The slow permeation through the bubble walls may result in a gas concentration in the bubbles which exceeds the lower explosive limit. High expansion foams, being more susceptible to the problem, could be ignited. However, the burn-back rate will be lower than over an uncovered surface. If ignition should occur, flame propagation should also be reduced if foam has been applied.

#### Sorption

Sorption is commonly applied in water treatment processes. Being a surface process, sorption is controlled by the physical and chemical properties of the sorbent. Sorbents are used to recover spilled materials by either: (1) adsorption, in which the material is attracted to the sorbent surface and adheres to it; or (2) absorption, in which the material penetrates into the voids of the sorbent material. Sorption is normally expressed as a capacity, mass of sorbate per unit mass of sorbent. In general, sorption applies to both liquid and vapor sorption for a chemical. Sorbents are marketed in a variety of forms including sheets, rolls, pillows, or booms.

Sorbent capacities are usually small, being in the range of 10% by weight. This lack of efficiency can be balanced by proper selection to allow the sorbent use, without modification, with all floating hazardous chemicals.

Sorption is influenced by these factors: (1) physical and chemical attraction; (2) surface geometry; (3) surface area; (4) contact time; and (5) density ratio of sorbate:sorbent. Environmental factors such as ambient temperature, pH, and salinity of the water may affect the chemical and physical interactions thus influencing sorbent capacity.

Bauer et al. (1975) identified the following materials as good sorbents: (1) activated carbon; (2) polyurethane foam; (3) macroreticular resins; (4) propylene fibers; (5) zeolite molecular sieves; (6) sorbent clays; (7) polyolefins; (8) polymethyl-methacrylates, and (9) polystyrene sulfonates. However, economics often come into play in oil spills, creating circumstances in which seaweed, leaves, corn cobs, or other similar materials are used. None of these biological components used in oil spill cleanup has the efficiency or capacity to reduce the health and flammability hazards found with floating hazardous chemicals.

Activated carbon is the most commonly used sorbent material, and its usage has been researched extensively. Activated carbons have potential application to a wide variety of hazardous chemicals but are limited in their ability to float.

Work by Mercer et al. (1973) with floating activated carbon, using the concept of subsurface injection for utilizing floating mass transfer mechanisms, was shown to be feasible in field demonstrations. Spill collection of the spent floating media in a static body of water was accomplished using existing oil spill cleanup equipment. The effectiveness of the spill treatment decreased as the spilled hazardous material became

more diluted. Mercer et al. (1973) proposed the use of weighted packages of floating media for treating hazardous material spills, whereas Dawson et al. (1977) demonstrated better recovery with free floating carbon. Fiber bag efficiency is limited by kinetic absorption considerations and may be improved with higher flow rates or contact time. The Dawson et al. (1977) report arrived at the following conclusions regarding buoyant activated carbon and porous fiber bags:

- o Buoyant carbon can be employed effectively in flowing streams without the use of ballasted packages. Buoyant carbon may be applied directly to the surface or it can be slurried and injected beneath the surface;
- o Natural turnover provides sufficient contact with contaminated water in shallow streams;
- o Floating carbon is capable of a 50% removal rate using a carbon-to-contaminant ratio of 10:1 for the flow and spill conditions studied;
- o Floating carbon recovery is generally greater than 90%;
- o Up to 25% of fiber bags were lost during the tests due to shore capture or snagging in shallow areas;
- o Buoyant carbon was superior to porous fiber bags for removal efficiency for the flow and spill conditions studies;
- o Fiber bags can be loaded, unloaded, and handled more easily than buoyant carbon;

- o Buoyant carbon will be more greatly affected in bad weather than will fiber bags; and
- o Both methods present the logistics problem of transporting large amounts of carbon.

Activated carbon can be obtained from numerous manufacturers and distributors. The price of activated carbon depends on the size of particle required and type of carbon purchased. Regeneration of the spent carbon is difficult and may not lower costs significantly or at all for those chemicals that may be hard to desorb. Thermal desorption may be too risky for flammable sorbates.

J. S. Robinson (1978) identified the following sorbents and their applicabilities. Polyurethane foam can be produced in open or closed-pore forms and in a nonporous particulate foam. Although polyurethane does not demonstrate the versatility of activated carbon, it is the best sorbent for benzene, chlorine, kerosene, naphtha:solvent, hexane, n-Butyraldehyde, dimethylsulfoxide, epichlorohydrin, and phenol. It could possibly prove feasible for most of the CHRIS list floaters. Polyurethane belts have been constructed to sorb some floating chemicals and many dissolved solutes. When laden with the absorbed chemical, polyurethane belts may be squeezed to remove the sorbate into a storage facility.

Repeated application of polyurethane may be required to sorb a spill. The sorption rate and capacity of polyurethane are dependent on the

viscosity of the spilled hazardous chemical. Polyurethane foams have been shown to pick up from 0.1 to 80 times their weight of hazardous spilled chemicals in one operation.

Polymers with a spongy structure can be produced by crosslinking linear polymers with bifunctional monomers. Two common macroreticular polymers that have been developed are poly (styrene-co-divinylbenzene) and poly (methylmethacrylate-coethylene dimethacrylate). The monomers can be developed for more versatility by substitution of polar groups. These polar groups would allow the polymer to act like an ion exchange resin.

Polypropylene, essentially a linear chain hydrocarbon, is an absorbent for covalent liquids. It has been shown to sorb benzene, kerosene, naptha:solvent, dimethyl sulfoxide, and epichlorohydrin. Polypropylene is generally less versatile than polyurethane. Lacking the crosslinking shown in polyurethane or macroreticular resins, polypropylene is more susceptible to decomposition in high-solvency liquids. The methods used for collecting and reusing polyurethane could be applied to polypropylenes.

Macroreticular resins can be developed which are more versatile than polyurethane, but they still do not possess the universal application available with activated carbon. Very little work has been done in the field of developing macroreticular resins for hazardous material cleanup.

Zeolite can sorb ions or molecules by acting as a sieve or by use of polarity. Zeolite has the disadvantage of possessing a higher affinity

for water, or ions and molecules that are naturally present in water, than the hazardous chemical. Zeolites are hydrous silicates that contain various cations. Their crystalline structure has empty channels of different dimensions. These channels give zeolite the ability to act as a sieve for a range of sizes.

Ion exchangers are probably the best sorbents to use on ammonia, concentrated sulfuric acid, sodium hydroxide, potassium cyanide, cadmium chloride, oxalic acid, ethylene diamine, sodium alkylbenzene sulfonates and phenol. They sorb polar or ionic solutes and can be used to complement polymeric sorbents for covalent nonmixers.

Polyurethane, polypropylene, macroreticular resins, zeolites, and ion exchangers serve to complement the range of hazardous chemical absorption covered by activated carbon, but in some instances one or the other may be more advantageous or more feasible for application than carbon.

Based on the range of application, the following list of high potential sorbents is provided in rank of diminishing feasibility:

- o Activated carbon
- o Polyurethane foam
- o Polypropylene fiber, polyolefin, cellulose fiber, amberlite XAD
- o Zeolite 5A
- o Poly (Methyl-co-dimethacrylate), amberlite IRA 93, amberlite IRA 900, Dowex 50WX8
- o Carbonized sawdust, zeolite F (K-Form), clinoptilolite, polyisobutylene fiber, Dowex IX10, amberlite IRA 402, DE SAL process resin, amberlite IR 252, poly (methacrylate) Floridin XXF, tonsil AC



Combinations of sorbents also present a feasible means of handling spills of certain chemicals. One sorbent presently on the market, Petro-Trap, combines a semipermeable membrane outer container with a hydrocarbon absorbing foam interior. The outer container, constructed with spun-bonded polypropylene, retards the passage of water while allowing the passage of hydrocarbon contaminants. The foam interior then absorbs the contaminant which can be recovered later using available mechanical mechanisms. Sorbing materials of this type of construction have proven feasible for ethyl ether, kerosene, n-amyl alcohol, naptha, ethyl acetate, hexane, butyraldehyde, and benzene.

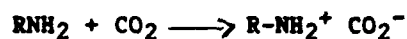
#### Gelation

Work performed by Breslin and Royer (1981) indicates that the following observations usually hold for conventional gelling agents or similar additives:

- o Introduction of gelling agents to a hazardous chemical spill enables a stable boom to contain the material at a higher current velocity or tow speed in calm water;
- o To optimize the effect of gelling agents, time for mixing and absorption must be allotted;
- o Splash over failure reduces containment ability in the presence of a .3 meter harbor chop;
- o The logistics involved in acquiring the gelling agent, transportation, distribution, separation, recycling, and disposal increase the time for cleanup;

- o Gelling agents may allow faster recovery craft speeds in some cases; and
- o Use of sorbents greatly reduces the extent of emulsification of hazardous chemicals into the water column.

Work at Lowell University by Bannister et al. (1979) concentrated on the action of carbon dioxide on a primary amine to form a zwitterionic carbamate salt:



The amine being oil soluble allows it to easily and quickly go into solution with most organics. Carbon dioxide may then be added to promote a rapid gel formation. The oil and other organic compounds can then be separated from the gelled mixture by filter pressing, centrifuging, or other chemical techniques to allow quantitative recovery of many organic materials. The conclusions drawn from this work included:

- o The optimum gelling agent is comprised of a mixture of 70% amine D (dehydroabeitylamine), 15% ethyl alcohol, and 15% Nopol, applied (to the chemical spill) in a concentration of about 15%;
- o The solubility of amine D is very low, therefore reducing the amount of emulsification which could occur;
- o Toxicities of the gelling agent are low;
- o Film thickness of the chemical spill does not appear to be a factor effecting the efficiency of gelation;
- o The optimum carbamating agent is liquid or gaseous CO<sub>2</sub>;

- o Yields of greater than 90% of the original spill material can be obtained by pressure filtration;
- o Volatilization rates may be reduced as much as 50%;
- o Most hazardous chemicals are easily gelled by this method. Important exceptions include: extremely thick and viscous materials in which solution of the amine solution is difficult to achieve; acidic compounds (which react with the basic amine) do not gel; unsaturated vegetable oils form gels of weak mechanical strength, as do some higher molecular weight naphthenic hydrocarbons often found in lubricants; and
- o Water-front protection is provided by gelling incoming spills since gelled materials do not readily soak into the sand.

An investigation conducted by Michalovic et al. (1977) for the EPA resulted in the development of a "multipurpose gelling agent" (MGA). The MGA was configured to obtain a formulation that would effectively gel a variety of spilled hazardous chemicals.

The formulation of Blend D, containing a polyacrylamide, a poly-tert-butyl-styrene, a polyacrylonitrile rubber, a poly carboxy-methyl cellulose and a fumed silica was judged to be the optimum combination based on the number of chemicals gelled with the least amount of material.

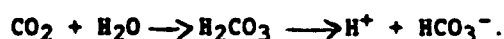
This formulation must be stored in moisture-proof containers below 122°F. It is possible to manufacture and store large amounts of MGA at distribution sites for ready use if required; however, this mixture is not commercially available.

MGA has been successfully tested with the following chemicals:  
acetone, acetone cyanohydrin, acrylonitrile, ammonium hydroxide, aniline,  
benzaldehyde, benzene, butanol, carbon disulfide, carbon tetrachloride,  
chlorine water (saturated), chloroform, cyclohexane, cyclohexanone, ethanol,  
ethyl acetate, ethylene dichloride, ethylene glycol, formaldehyde, gasoline,  
isoprene, isopropanol, kerosene, methanol, methyl ethyl ketone, octane,  
o-dichlorobenzene, petroleum ether, phenol (89%), pyridine, sulfuric acid,  
tetrahydrofuran, trichloroethylene, and xylene.

### Cryogenics

Greer (1976) reported that vapor pressures can be lowered by 40 to 95% if the temperature of a solution is lowered to its ice point; the use of cryogenics is hampered by the quantities of cryogen and the rate of dispersal required in order to treat a hazardous chemical spill.

Most refrigerants must be eliminated from the list of possible cryogenics due to their high toxicities and their extensive amount of halogenation. Carbon dioxide would tend to cause large pH changes when used in the quantities required for a spill. This pH change is caused by the reaction:



In order to obtain significant vaporization rate reductions, a homogeneous blanket of cryogen must be quickly and effectively placed over the spill. Environmental factors may significantly hamper recovery efforts by introducing a high heat load on a sunny day, while rain, wind, and waves will add to the heat load by mixing.

Greer (1976) points out that liquid CO<sub>2</sub> has been recommended over LN<sub>2</sub> based on the following critical factors:

- o CO<sub>2</sub> tanks are constructed with refrigeration cycles to reliquefy boil-off;
- o CO<sub>2</sub> storage tanks are single wall, versus the vacuum tank construction used for LN<sub>2</sub>. CO<sub>2</sub> tanks should be less costly and more mechanically resilient;
- o CO<sub>2</sub> costs less than LN<sub>2</sub> based on effective refrigeration effects; and
- o CO<sub>2</sub> dispersal is readily available by using "snow horns." Both CO<sub>2</sub> LN<sub>2</sub> would displace oxygen, creating a hazardous environment for cleanup personnel.

#### Neutralization

Organisms are extremely sensitive to environmental pH changes. They have become adapted to the environment in which they live, and any pH changes from their normal ambient range may result in deleterious effects. These effects can be observed to occur in anything from reproduction to enzymatic capabilities. Spills of hazardous chemicals which push the pH toward or out of its normal limits effect the environment in many ways. Biochemical reactions will be altered, solubilities of hazardous metals may be increased, oxygen levels may be lowered, and chemical identification systems, such as pheromones used by organisms, may be disrupted.

A good neutralizing agent should have as many of the following characteristics as possible in order to be considered for use (Akers et al., 1981).

- o It should keep the pH in the range of 6 to 9 without causing an excessive pH change toward the acid or basic side if too much neutralizing agent is used. Addition of too little of the neutralizing agent may result in the pH not returning to the 6 to 9 band. In general, overaddition of a neutralizing agent should have little adverse effect. By applying buffer type systems to the spill, such as  $\text{NaHCO}_3$  or  $\text{NaH}_2\text{PO}_4$ , serious overshoot problems should not occur.
  
- o It should be relatively nontoxic to aquatic life. Addition of neutralizing agents will generally increase the temperature of the water slightly due to heat of solution, increase the ionic strength of the water, possibly lower the amount of available oxygen, resolubilize heavy metals if the pH is lowered enough, and increase the nutrient concentration which could lead to an algae bloom.
  
- o It should have a small biological oxygen demand.
  
- o It should be safe to handle and store.
  
- o It should be low in cost and available in bulk.

The following items should be considered when neutralization is one of the methods being proposed to combat an acidic or basic spill (Akers et al. 1981).

- o Volume of the spill. With a large spill, it may not be logistically feasible to try to neutralize the entire volume. Care should be taken to neutralize, to the greatest extent, those areas that are in the most danger of biological damage.
  
- o Dilution rate. In high current areas, it may be more cost effective to allow dilution to take care of most of the spill. Any regions with low flow could then be neutralized with available chemicals.
  
- o Monitoring. The On-Scene Coordinator should have some means at his disposal to monitor pH changes. Neutralization of hazardous chemical spills in waterways should not be attempted unless proper monitoring and control of the neutralization reaction is possible.

The general mechanism for a neutralization reaction is:



Usually the salt produced is less toxic than the material being treated.

As shown by the titration curves, it is readily observed that when approaching the amount of neutralizing agent required for neutralization, the slope of the curve increases very rapidly. The ultimate pH which could be achieved by a massive overdose of a weak neutralizing agent is less toxic than that achieved by a strong agent.

Large temperature differences may occur between the region being treated and the surrounding area. If possible, this difference should be monitored to try to limit any adverse effects caused by temperature shock.

Care should be taken when applying the neutralizing agent to avoid spattering which could result in burns to the cleanup personnel. Any personnel handling neutralizing agents should wear gloves, a face shield, and an apron to protect themselves from the possible corrosive effects of the agents.

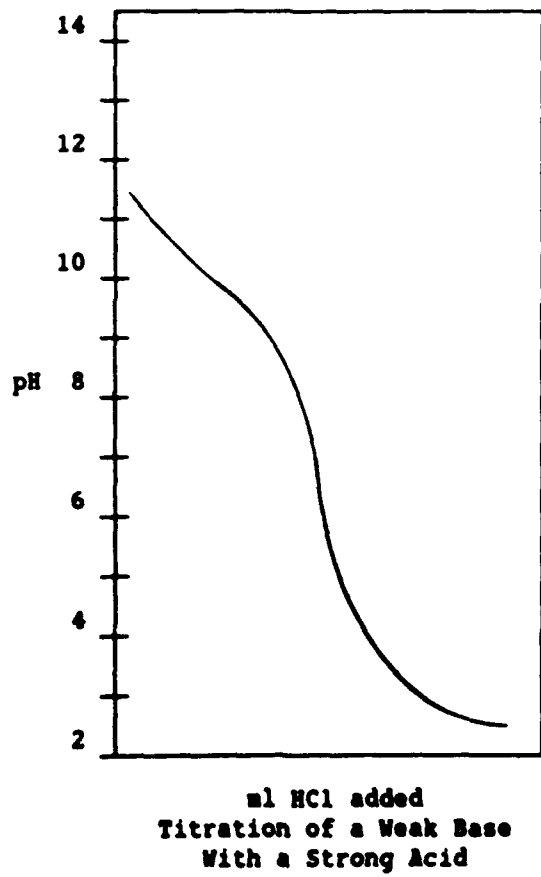
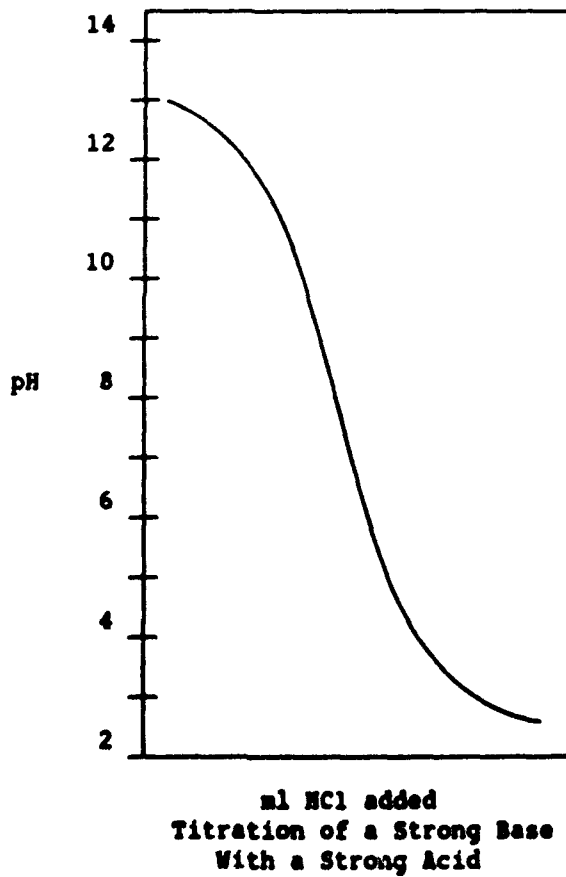
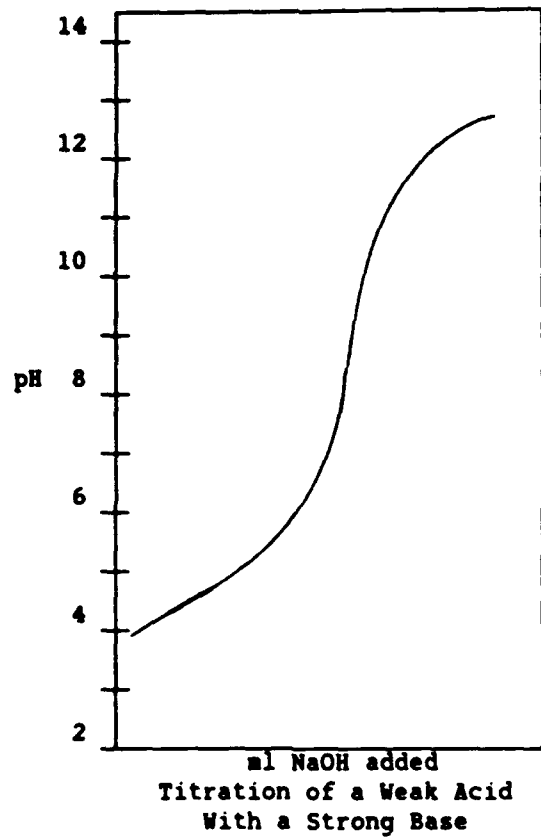
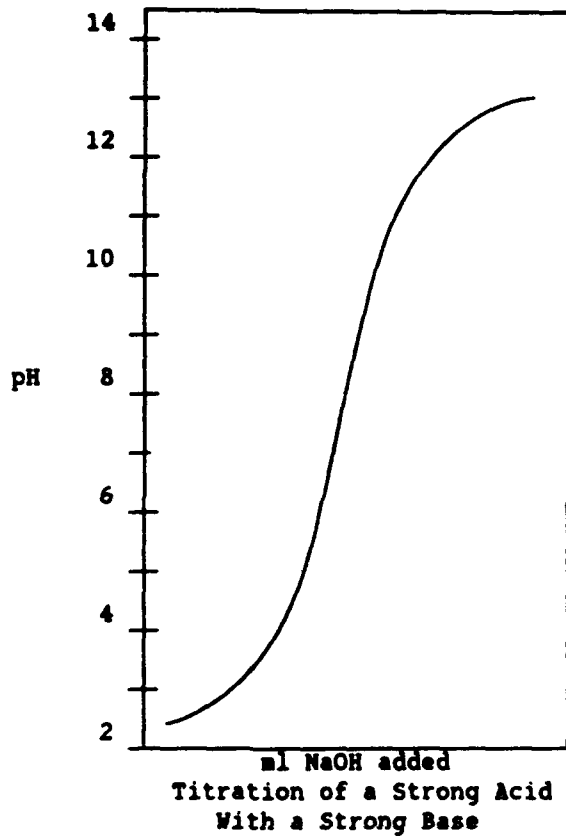
#### Precipitation

Chemical precipitation occurs when two reagents which are soluble in water react to form an insoluble compound. The solution should be supersaturated to allow precipitation. This leads to ions combining to form minute particles which serve as nuclei for the insoluble precipitate. These nuclei grow, progressing through a colloidal stage, and finally reach the final stage of large, visible, insoluble particles. These insoluble particles then precipitate as a solid in the water column.

Solubility, being an equilibrium process, can show the reverse reaction leading to dissolution. As the concentration of toxic ions in solutions decrease, the precipitate may redissolve to restore an equilibrium condition.

**Figure 1. Sample Titration Curves**

**Graphs**





In general, as temperature increases, solubility increases, and this would tend to speed up the dissolution process.

In general, a precipitation reaction would be used to remove a water-soluble chemical from the water column. Precipitation reactions usually lend themselves to metallic or ionic compounds. Since the main purpose of this study is to document methods available for removing floating hazardous chemicals, the majority of which are organics, precipitation reactions do not appear to be feasible for this use.

#### Chelation

Chelating agents are compounds or ligands (usually organics) that bind or coordinate with a metal ion in one or more positions. Precipitation reactions are exceptions to the usual condition in which a soluble complex ion, or coordination compound, is produced by the reaction of a metallic ion with one or more ligands. In coordination compounds, the metal becomes the central ion in a heterocyclic ring after reacting with the chelating agent. Binding of the metallic ion usually results in its deactivation. The metal is no longer able to react chemically, and therefore is made less toxic. As with precipitation, this method has not been developed to remove floating hazardous chemicals.

#### Biodegradation

Biodegradation has long been the method applied in water treatment systems and landfill sites. It does not have much potential as a floating hazardous chemical spill amelioration method.

Many of the floating hazardous chemicals, being organics, are susceptible to biological degradation. Chemical dispersants have been used to break up spilled oil into droplets that are dispersed through the water column in a decomposable form.

In order to allow biological degradation to occur quickly, acclimated cultures would have to be stockpiled. This would present a complex logistical and possibly a political problem. In addition, it is believed that many hazardous chemicals will resist biological degradation.

Organisms, in general, function within optimum temperature as well as optimum pH ranges. It can be observed from most enzymes that a 10° increase in temperature will double the reaction rate while inside the enzymes' functional range. Decreased metabolic rates at low temperature could seriously limit the rate of biodegradation. Similarly, pH or osmotic conditions for which bacterial cultures are not acclimated could make the use of such cultures futile.

#### Oxidation-Reduction Methods

As a spill amelioration technique, oxidation-reduction methods are more applicable to sinking hazardous chemicals than floating hazardous chemicals. In-situ oxidation has been shown to be feasible on such sinkers as: 2,4-dinitroaniline, 2,4-dinitrophenol, phenol, trichlorophenol, cresols, phthalic anhydride, and diphenylmethane diisocyanate.

Oxygen is the most important agent found in natural waters to allow oxidation of some hazardous chemicals. Use of oxygen in this reaction will

result in an increase in oxygen demand, and could result in significantly reduced dissolved oxygen levels in the water. This problem can be reduced by injecting oxygen into the reaction region.

Because of limited study in the area of oxidation of floating hazardous chemicals as a method to reduce toxicity, or to be applied in chemical cleanup, oxidation-reduction methods do not appear to be applicable or have any advantages in combating a floating hazardous chemical spill.

#### Sample Chemical Decontamination System

Work by Robert G. Sanders et al. (1975) with Industrial Bio-Test Laboratories, Inc., and R. P. Industries has resulted in the development of a "dynactor." The "dynactor" can utilize the sorption capabilities of activated carbon, without the associated problems of sinking and loss, maintaining it in an enclosed system. The "dynactor" can also be applied for aeration, ozonation, neutralization, and precipitation.

Preliminary work and studies for the "dynactor" were conducted under contract to the Environmental Protection Agency (Contract Number 68-01-0123). The feasibility study resulted in the development of a physical-chemical treatment system capable of processing contaminated water at a rate of five gallons per minute (5 GPM). The feasibility study by John S. Greer (1976) reports the further development of the system to the point that it can be used as a self-contained unit mounted in a highway trailer. This system is capable of aspirating  $5 \times 10^4$  ft.<sup>3</sup>/min of air while pumping and treating approximately 250 GPM water.

The "dynactor" is essentially a macroscopic diffusion pump. Liquid enters the system under a pressure of 40 to 100 pounds per square inch and is atomized into thin films and droplets with an average thickness or diameter of less than 1/64 inch. The liquid discharge expands into a reaction chamber entraining air or gas within the moving film and particles similar to a venturi eductor. The interior design is such that the gas-liquid turbulence is established by the time the mixed fluid exits the reaction chamber and enters into the separation reservoir.

The entering air is accelerated from low velocity and atmospheric pressure to high velocity at a vacuum as it enters the reaction chamber. This allows the "dynactor" to aspirate up to 4,800 standard volumes of gas per volume of motive liquid.

The "dynactor" has been developed in such a way that it is possible to meter liquid, gas, or powder into a flowing stream of contaminated water in stoichiometric quantities. This would allow, for example, lime, bicarbonate, or powdered carbon to be metered by aerosolization directly into the flowing contaminated liquid, resulting in decontamination by neutralization, precipitation, or absorption. Having no moving parts and no constrictions, the "dynactor" should require little maintenance.

Magnetic separation was shown capable of recovering 99 percent of the flocculated carbon. By adding 25 percent magnetic material, such as finely divided iron oxide, to the powdered carbon used to feed the "dynactor", and then adding 2 ppm of a polyelectrolyte flocculating agent at the effluent end, quantitative removal is possible.

The cost of a unit capable of handling 2500 ppm water was approximately \$400,000 in the Greer report (1976). The equipment, being mainly designed for land use, would require modifications for marine applications.

#### MECHANICAL CLEAN-UP METHODS

To minimize the environmental impact of a hazardous chemical spill, as well as facilitate its cleanup and/or disposal, it should be contained within as small an area as possible. Advantages which may be obtained by the quick response toward containing a spill include the minimization of damage to the environment, the facilitation of the on-site cleanup operations, and the prevention of the lateral spread with the corresponding dispersion of the spill into other waterways.

For those personnel directly involved in the spill, personal safety is the prime consideration. If possible, the first line of defense should be to stop the spill. Others in the area should be warned of the problem and potential hazards. The appropriate authorities should be informed, giving them as much information as possible. This could include such items as the location of the spill, time of the spill, the amount of material released, the known potential hazards of the substance, any personnel injuries, the extent of the equipment or container damage, and weather or environmental conditions. The spill area should be isolated, and restricted to only those personnel directly involved in the clean-up actions. Clean-up personnel should be made knowledgeable of any potential hazards, i.e., toxicity, flame/explosion hazards, the need of respiration equipment. The officer in charge should make it clear who he or she is, in order to ensure the smooth coordination and handling of the clean-up efforts.

For a floating hazardous chemical spill, the fundamental concern will be to prevent the lateral spread of the hazardous material. Loss of lateral control implies spreading which will result in more widespread surface damage to the environment, as well as the increased difficulty presented to the detoxification and cleanup personnel. For a floating hazardous chemical, some vertical spread may be expected in the form of droplets becoming entrained in the water column, as well as in the form of the possibility of some emulsification. This possible vertical spread increases with time, and requires quick action to limit its extent. Vertical spread can also occur via evaporation. Reducing the vaporization rate with substances such as foams, discussed elsewhere, may be important to reduce possible explosion hazards.

#### Booms

A large variety of boom devices has been developed for the containment of oil spills. In most cases, these devices could readily be applied toward the containment of floating hazardous chemicals. Several properties of a boom must be carefully analyzed before the selection is made for application in the field.

Many booms are constructed with organic material, which may be dissolved by the hazardous floating chemicals. This is due to the construction and spill materials having similar chemical and physical properties. Under these circumstances, the adage "like dissolves in like" comes into play and could seriously hinder cleanup and containment efforts. High solvency hazardous floating chemicals will remove plasticizing agents from polymeric materials over time. This action can seriously effect the elastic and tensile properties of the material being acted upon, with the final result being failure of the containment system.

Many boom systems use grommets and various other metallic fastening systems. Several systems use galvanized chain as ballast at the base of the boom skirt. Care should be taken to choose a boom system that has as little metal exposed as possible to limit a spark fire hazard in deployment.

Draft and freeboard of boom may help limit the amount of hazardous material pulled under or allowed to splash over the containment. The proper choice will significantly affect performance in high current or high wave environments.

Boom configuration and deployment significantly effect its performance. Studies by McCracken and Schwartz (1977) at OHMSETT have demonstrated head wave shedding and subsequent entrainment as the primary mode of failure for booms. This phenomenon is directly related to droplet formation and the relative velocity between the slick and the water. Test fluids of relatively high specific gravity had the tendency to become entrained via droplet formation, resulting in shedding loss occurring at lower boom-tow speeds. The OHMSETT studies indicated that the physical properties of the spill and the hydrodynamic conditions ultimately determined the maximum tow speed at which a boom could control the spill. Critical tow speeds, the speed at which either the boom fails (boom stability) or the hazardous material spill cannot be controlled by the boom, is therefore limited by:

- o Shedding - Droplet formation and entrainment of droplets under the boom;
- o Splashing - Spill is periodically heaved over the boom freeboard by waves; and

- o Washover - Large amounts of spill material are heaved over the boom by waves, combined with partial submergence and the corresponding loss of freeboard of the boom.

Critical tow speed generally demonstrates an inverse relationship with the hazardous material's specific gravity.

A study conducted by Breslin (1978) at OHMSETT came up with the following conclusions (which could be applied to hazardous materials) in applying booms to oil spills.

- o If a straight diversionary boom is deployed, parachute mooring lines are necessary. The diameter of the lines should be small, to limit generating standing waves which can entrain oil;
- o The angle of the boom in relation to the current directly affects boom performance. The more perpendicular to the current the boom is deployed, the lower the speed at which oil loss and boom stability failure occur;
- o Oil losses were predominately shedding in mechanism. The horizontal vertical action of the water, with entrained droplets passing beneath the boom skirt, tended to draw much of the entrained oil into a quiescent zone behind the boom.
- o Nozzle boom configurations appear to be better than straight diversionary techniques in minimizing oil losses. Nozzle shaped configurations have less entrainment and fewer standing vortices when compared to straight diversionary methods.

It should be mentioned, however, that nozzle configurations may be harder to deploy in actual field conditions, and some loss in performance could result.

Booms should be employed in the diversionary mode in any body of water which has an appreciable current. Skimming devices have a very limited performance capability in regions of high flow, and may be useless if the current approaches five knots. By directing the spill toward a region of less flow, skimming devices or other methods used to collect spill material will be greatly enhanced.



Skimming barriers have been developed which, in essence, are booms with integrated skimming weirs. In application, the barrier is towed along one or both sides of a vessel by lightweight outriggers. As the contaminant is collected in the skimming weirs, it is transferred to a storage facility via a pumping system and a density separating device.

#### Removal Devices

Removal devices have many mechanisms of operation. These can generally be categorized as:

- o Moving plane skimmers - the pick-up device consists of a metal or plastic sheet which descends through the spill into the water and rises back out of the water containing the adhered material, which is wiped off and drained into a reservoir while the blade continues on its cycle;
- o Belt skimmers - the pick-up element is a moving belt constructed of absorbing material. The spilled substance is absorbed on the belt and squeezed off into a containment reservoir;
- o Suction head skimmers - the spill material enters the suction head pick-up area due to flow of the spill. Suction is applied to the pick-up area of the suction head, removing the spill material to another container;
- o Weir skimmers - the spill material enters a pick-up region in the weir due to flow of the spill on the water over a lip, from which it descends into a collecting vessel. The spill material is then removed by suction with a pump or impeller; and
- o Rope skimmers - a continuous rope mop is pulled over the water surface, collecting the spilled material. The rope then enters a wringer and returns to the contaminated region to recover more liquid.

In the study by McCracken and Schwartz (1977) at the OHMSETT test facility, it was shown that stationary skimmer performance was dependent on the physical properties of the spill material and the wave conditions tested. Floating suction head skimmers and self-adjusting weir type skimmers were demonstrated to have higher efficiency with higher density hazardous materials. An oleophilic rope-type skimmer used in this test had a performance in waves optimized at close to 80% recovery efficiency.

Advancing skimmers also were shown to have a strong relationship between their performance and the physical properties of the spill material. For the Dip-1002 skimmer which was tested, the tow speed at which maximum performance occurred was dependent on the hazardous material's density. The low density Naptha used in the test was best recovered at the relatively high tow speed of 1.14 m/s. The denser dioctyl phthalate had an optimum recovery rate performance at the lower tow speed of .25 m/s.

These results can be explained as follows. The dynamic inclined belt is constructed to induce a flow velocity relative to the spill material. For fluids which tend to form large diameter droplets on breakaway, such as the dense dioctyl phthalate, and have a longer rise time, collection efficiency is increased at lower speeds, since it takes more time for the droplets to rise into the oil collection well. As the tow speed increased, the probability of the fluid droplets rising behind the collection well correspondingly increased. The reverse holds true for low density hazardous materials.

Moving plane and belt skimmers which utilize adhesion mechanisms are highly selective for contaminants; but are restricted in their ability to

remove much volume per unit time. These skimmers are generally larger, more complex, and cost more than suction head or weir skimmer devices.

Suction head and weir skimmers are capable of removing a large volume of a contaminant in rapid fashion, but may also remove a high percentage of water in the process. As more water is brought in, a storage problem may develop, restricting the effectiveness of the use of these devices.

Several skimming devices have been developed which adjust to the depth of a floating contaminant by varying the pump rate of the suction pump applied to the device. By reducing the pump rate, the weir edge will rise, resulting in less material being skimmed. Speeding up the pump causes the weir to sink and skim more of the material.

In choosing the type of removal device to employ, some of the factors used in the choice of a boom system are again worthy of thought. Those devices which utilize motors for propulsion and/or belt/blade rotation should be constructed in such a manner as to reduce the possibility of spark generation which could result in fire or an explosion. The material or device used to absorb the spill material should be compatible with the spill material and not dissolve or break up.

Again, many removal devices are available on the market which would be suitable for hazardous material applications, as long as the factors mentioned above are covered.

#### Dispersion and Dilution

For the vast majority of spill occurrences, containment should be the choice of action over dispersion. Dispersion should be taken as a spill

amelioration technique only after all other possible actions have been eliminated from the list of consideration.

Dispersive methods act to spread the spill, effectively diluting it in such a manner that the concentration of the material within a small radius of the spill site is reduced to below recommended limits. Dispersion may be applicable under the following conditions:

- o A spill occurs in open water, in which case the rapid dilution of the chemical may be expected;
- o A spill occurs in a small stream flowing into a large river, in which case the greater flow would enhance quick dilution; and
- o A spill occurs at the mouth of a harbor with fast tidal currents which would hamper or defeat other methods which might be attempted to contain or recover the spill.

Numerous methods and devices are available to aid in the dispersion of floating chemicals. Water spray from a fire hose can effectively break up and enhance the dispersion of a spill. Care must be taken to limit or prevent any caustic or hazardous spill material from personnel contact. Aeration systems can be deployed to allow air bubbles to disperse the material. Propwash can be applied to push the spill downstream toward a high flow area.

Many jet blower systems are available commercially for use in this application. These systems are utilized to help remove snow from railroads or to disperse fog. The number of blowers required would depend on such factors as the nature of the natural wind, and how much vapor concentration reduction is desired and/or required.

Dispersion and dilution have the advantage of possibly lowering the vaporization rate by lowering the amount of heat transfer across the spill, and could effectively lower the vapor concentration. This would tend to reduce fire and toxicity hazards to response team personnel. Dilution could effectively combat the results of a strong acid or base spill.

#### Encapsulation

Encapsulation of a hazardous chemical spill utilizing a floating boom enclosure with an elastomeric membrane cover could be employed to contain toxic vapors with close to 100% efficiency. The methods to deploy such an apparatus quickly and safely would have to be studied further.

Many floating cover assemblies are fabricated for a variety of applications. As long as the assembly would not react chemically with the floating hazardous chemical, modifications should be minimal.

The selection of the encapsulating material and application would depend on factors such as material compatibility (mentioned above), spill size, weight, cost, availability, portability, reuse and/or disposal requirements, environmental compatibility, and interfacing with available spill removal systems. Materials such as polyethylene, polyvinyl chloride and similar plastics should be avoided due to their reactivity.

#### Close-Packed Particles

By applying small, lightweight, geometrically shaped particulates over a spill surface, it may be possible to produce a physical barrier which would reduce the vaporization rate. These particulates serve to insulate the surface, causing a reduction in the heat transfer which is required to enhance vaporization.

Greer (1976) reported that Plastic Systems, Inc., of Santa Anna, California, has developed a particulate system which is based on the geometry of a dodecahedron. One thousand particles will cover a region of  $.38 \text{ m}^2$  ( $4.12 \text{ ft}^2$ ). By forming a close packed geometry, approximately  $10^7$  particles could cover a spill of 10,000 gallons. Assuming a price of \$0.01 per particle, material costs for the spill should be about \$100,000.

To be most effective, the geometric shape should be chemically resistant to the spill material. Other than calm conditions could hamper particle distribution and the ability of the particles to form a close packed single layer.

#### Vapor Dilution

By transferring and mixing uncontaminated air with the vapors resulting from a hazardous chemical spill, dilution may lower the concentration of hazardous vapors below their TLV or LFL. Dilution of this type would be possible by applying an artificial wind. This method would be acceptable in unpopulated areas, and could serve to reduce the flammability and toxicity hazards confronting the cleanup crew.

## PERSONAL PROTECTIVE EQUIPMENT

Skin is a specialized organ composed of both living and nonliving components. Its varied functions and properties can be attributed to the arrangement of its network of different tissues, including sense organs, nerves, glands, blood vessels, connective tissue, and fat. The tissue orientation of the skin has three recognizable layers: the epidermis, the dermis, and the subcutaneous fat.

The skin has many functions associated with the maintenance and well being of an organism. The function of major concern for this study is the vital role the skin performs in protecting the internal milieu of the organism from exposure to potentially harmful materials found in the external environment.

The epidermis, being composed of keratinized resistive cells, provides the body's first line of defense against bacterial infection, mechanical injury, and chemical abuse. Most chemical substances, excluding the few such as "poison ivy" and chemical warfare agents, have long been thought to be unable to penetrate the skin. It is now known that direct contact with many chemical substances taxes the ability of the skin to protecting the organism. The result of the penetration of foreign substances into underlying tissue can result in that substance, or one of its metabolic byproducts, entering the blood system. Once the chemical is circulating in the body, it can express itself by producing severe damage to such organs as the liver and kidneys; or it may possibly lead to cancer or other delayed effects.

In order to minimize the potential hazards to spill response personnel when confronted with exposure to chemicals, chemical protective clothing should be used in conjunction with good engineering practice and carefully-planned work procedures.

## Protective Clothing Limitations

Guidelines for the Selection of Chemical Protective Clothing (Schwope, et al., 1983), a compilation of information concerning the use of protective clothing when handling hazardous chemicals, is a very informative guide from which the following material has been extracted.

The performance of Chemical Protective Clothing (CPC) as a boundary between the chemical and the worker is directly related to the materials and the quality of construction of the CPC. The majority of CPC presently available on the market today are composed of plastic and elastomeric materials. Hazardous materials interact with the plastics and elastomerics by a variety of mechanisms. Due to the different methods of interaction, no one type of material can be resistant to all chemicals. No plastic or rubber clothing can be categorized as impermeable. In fact, for certain chemicals, there is no commercially available glove or clothing that can provide more than an hour's protection following contact with the chemical.

The construction of a piece of clothing can greatly influence its performance as a barrier to a hazardous chemical. Stitched seams and fastening devices, i.e.: zippers and buttons, may present a highly penetrable route for chemical permeation if proper care is not taken to overlap the area with tape, a flap, or a coating. Pinholes may occur in plastic or rubber products due to poor manufacturing processes or poor quality control. The thickness of the clothing may also vary from point to point. Due to these problems, it may be better, in some cases, to use a multi-layer approach in clothing to help eliminate routes of entry.



The type of clothing to be used is directly related to its mode of application. One of the main factors will be the type of chemical which will come in contact with the clothing. In order to reduce possible worker injury, the clothing should be the most resistant type available to that type of chemical.

The degree of activity in which the worker will be engaged, as well as the environment, should also be considered. Light work or mild activity may allow the use of a less durable type of clothing. An environment in which there is a hazard of the clothing being punctured or torn will require a more durable piece of material.

Worker comfort is also a major factor in choosing a particular type of CPC. Clothing which is cumbersome and restrictive can hasten the onset of fatigue. If a worker is to move safely and effectively, fatigue and irritability should be reduced.

Cost is another factor which should be considered when selecting which type of clothing will be utilized for a particular application. In some cases, it may be more cost effective to use multiple changes of less expensive, less durable clothing rather than high performance, high cost clothing over an extended period. This could be an important consideration in combating a spill which has the properties of high tenacity or permeability, making the decontamination of the clothing a questionable proposal. If the multiple change route is chosen, disposal costs may become an issue of concern.

Surface contamination can often be removed by scrubbing with soap and water. Several factors should be considered when decontaminating the clothing. The effluent obtained from the soap and water scrubbing process itself may be hazardous. Care should be taken to ensure that it is properly disposed of.

Scrubbing itself could lead to a reduced performance of the clothing in its next application. Scrubbing the material can open its weave or pores, allowing easier penetration of the next chemical encountered. Scrubbing may also push some of the chemical further into the material, which may eventually diffuse to the inside surface of the clothing. Unless decontamination is rendered with proper care, the reuse of CPC, once it has been in contact with highly toxic chemicals, is not advisable.

Once the clothing has come into contact with a hazardous chemical, the diffusion of the chemical from the outside to the inside surface is a major concern. Fick's first law of diffusion states that the flux, i.e., the net amount of the solute that diffuses through a unit area per unit time, is directly proportional to the concentration gradient. This can be mathematically expressed as,

$$J = D \frac{\delta c}{\delta x(t)} \quad \text{where } \frac{\delta c}{\delta x(t)}$$

is the concentration gradient of the diffusing substance after time  $t$  of diffusion,  $D$  is the diffusion coefficient of the diffusing substance in the medium of interest, and  $J$  is the flux. Increasing the area over which a concentration gradient exists, allows more diffusion to occur.

The following generalities can be observed when considering the diffusion of substance through the protective clothing:

- o As the temperature increases, the rate of diffusion increases;
- o Permeation is inversely proportional to thickness; and
- o Breakthrough time, the elapsed time from initial contact of the chemical on the outside surface to the first detection of the chemical on the inside surface, is directly proportional to the square of the thickness of the CPC.

Once a chemical has begun to diffuse through a material, it will continue to diffuse even if the outer surface is decontaminated. This is due to the concentration gradient still present within the material.

CPC is usually classified into the following categories shown in Table III-1.

TABLE III-1. CHEMICAL PROTECTIVE CLOTHING CATEGORIES

<p>A. Head, Face, and Eyes</p> <p>Hoods Face Shields Goggles</p>	<p>D. Complete Torso</p> <p>Coveralls Full-body Encapsulating Suits</p>
<p>B. Hands and Arms</p> <p>Gloves Sleeves</p>	<p>E. Feet</p> <p>Boots Shoe Covers</p>
<p>C. Partial Torso</p> <p>Coat Jacket Pants Apron Bib Overalls</p>	

Workers responding to a spill should ensure that they are protected from the hazards associated with a particular chemical through judicious choice of the proper protective clothing from the above categories. The worker should inspect the clothing to ensure it is made of the correct material for the chemical to which it will be exposed. Care should be taken to inspect the clothing for the following items:

- o Check the clothing for punctures, rips, and tears. Pinhole punctures may be observed by holding the material up to a light. Glove integrity may be inspected by blowing it up and then applying pressure by attempting to roll the glove up. Punctures will present themselves as areas through which the air escapes.
- o Check for discoloration or stiffness present in the material. These signs may present evidence that the permeation resistance of the material is greatly reduced.
- o Check for the proper operation of all fasteners. Broken fasteners will prevent the establishment of the full integrity of that piece of clothing, as well as possibly hinder the removal of the clothing in an emergency.

Once the clothing has been inspected, it should be donned in such a manner in that the overall integrity and function of the clothing is obtained. Personnel should inspect each other to ensure that all closures are secured. The clothing should not be tight, since movement may result in tears or may limit the movement of the worker resulting in fatigue. Loose clothing may present a snag hazard or compromise the dexterity of the individual.

During the performance of the task at hand, workers should periodically inspect their clothing to ensure that tears, closure failure, or any other mechanism which might result in chemical entry has not occurred. If any piece of clothing is damaged, the worker should leave the direct vicinity of the spill and properly remove and replace the damaged clothing.

When removing clothing, workers should take care to restrict the spreading of the chemical from the work area. This objective can be reinforced by establishing an exit area that acts as a buffer between the spill scene and the surrounding area.

#### Respiratory Protective Equipment

In order to ensure the maintenance of life, the body must assimilate a large number of different substances, the most urgent being a continual supply of oxygen. Air is approximately 78% (nitrogen) by volume 21% (oxygen) by volume and less than 1% other gases by volume.

The respiratory system design provides the body with a barrier to help eliminate problems encountered with inspired air. Dust and bacteria present in inspired air are precipitated in the mucous that covers the mucosal membrane of the respiratory tract. The cilia present within the nasal passages move the entrapped particles outward. This mechanism can be overloaded as is observed by the extensive injury that results from the interaction of metal and mineral dust. The sharpness and cutting ability of this type of dust can result in the disposition of particles in the lungs, leading to conditions such as those found in black lung, often related to mining.

The olfactory capabilities of the body often warn the individual of possible hazards by detecting hazardous materials before their concentration has reached a dangerous level. However, the threshold level for detecting some substances by smell is sometimes above or very close to the level at which the substance is hazardous. In some cases, the olfactory nerves become "overloaded" and cannot sense changes in concentration of a substance.

Once a hazardous vapor has entered the gas exchange region of the lungs it can diffuse into the bloodstream. Depending on the amount inspired and the mechanism of action of that chemical in the body, tissue damage or death may occur.

Due to the variations in susceptibility and ability to detect hazardous vapors, care should be taken when approaching a hazardous chemical spill. Some substances such as carbon monoxide, will be impossible to detect by odor alone.

In order to properly confront the spill, the identity of the spilled constituent should be determined. From this information, and consultation with a health and safety professional, the OSC should be able to determine if the use of respiratory equipment will be required. Air sampling devices, such as Draeger tubes, can be used to get an idea as to the vapor concentration of the hazardous chemical above the spill. However, the use of direct reading instrumentation for emergency response applications is very limited.

#### Classification and Description of Respiratory Protective Devices

Howard H. Fawcett (1984), in his book, presents a concise discussion of respiratory equipment. Information derived from this source is presented below.

Self-contained breathing apparatus (SCBA) generally provides the maximum protection against respiratory hazards. SCBA is designed to supply complete respiratory protection to an individual. If this equipment is utilized in an environment in which vapors may present significant toxicity through the skin, complete skin protection should also be used.

Since SCBA requires no external air supply connection, it can easily be applied to emergency situations; it can also be used for entry into confined spaces. This mode of equipment could be applied where worker mobility is essential, such as those cases in which the worker is cramped for space while attempting to stop or repair a leak on a barge or ship.

Personnel donning SCBA should ensure they wear the equipment correctly. If a proper facepiece seal is not established, the hazardous substance will still have a pathway to the respiratory tract.

One of the major culprits for preventing a proper seal is facial hair. Personnel who may need to use any type of breathing apparatus should ensure that their facial hair is trimmed to the point where interference with the achievement of a proper seal is eliminated.

The open-circuit type SCBA assembly, consisting of an air cylinder, an air line and regulator, and a face mask, is the most widely used SCBA style. The air supply time is dependent on the size and pressure in the air cylinder. The positive pressure regulation is the most recommended type since it maintains a positive pressure in the face mask, reducing the chance of leakage from the external environment.

Closed-circuit SCBA assemblies which remove the exhaled carbon dioxide have been designed with a service life of up to four hours. An oxygen breathing apparatus (OBA), developed for military use, uses potassium superoxide as the oxygen source and carbon dioxide absorber. The OBA's have rated service lives of 30, 45, and 60 minutes. It should be understood that the rated lifetime of a breathing apparatus is highly dependent on the

activity level of the worker. High exertion can reduce the useful life of an OBA from 60 to 10 minutes. The heat produced by the oxygen source could be very hazardous if used in confronting some flammable spill materials.

Hose mask devices consist of a large-diameter hose connected to an uncontaminated air source and a facepiece. Positive blowers or fans may be used to force air to the facepiece. This design is considered to be a negative pressure device. It is applicable for use in areas where long-time work is important and a hose or other connection doesn't present a problem.

Air purifying devices such as canisters and gas masks can be used in instances where the air encountered is within the limits of protection for the device and an adequate amount of oxygen is present. These units are designed to protect only against specific chemicals up to certain concentrations.



### CASE STUDY SUMMARY

The following reports pertaining to hazardous material spills were reviewed in order to obtain technical information concerning present Coast Guard spill control/recovery methodologies:

- o On-Scene Coordinator (OCS) Report: Major Oil Pollution Incident Involving the M/V City of Greenville, Mile 179.0, Upper Mississippi River, on April 2, 1983
- o Summary of Incidents For Memphis Coast Guard Zone
- o New Orleans Fire Department List of Spill Incidents
- o OSC Report: Major Benzene Spill From Tank Barge NMS 1460, O. N. 57743, at Lock and Dam 26, Mile 202.9, Upper Mississippi River, on April 29, 1982
- o OSC Report: Major Acrylonitrile (ACN) Chemical Spill, From the Brazilian Tankship Quintino, at Texas City, Texas, on March 26, 1984

These reports represent all documentation received in response to letters sent to Coast Guard Zone Offices in November 1984, by The MAXIMA Corporation.

### Coast Guard Reports

The major oil pollution incident involving the M/V City of Greenville illustrates many of the problems which may arise during a hazardous material spill recovery effort. On April 2, 1983, the M/V City of Greenville, with a tow of four crude oil tank barges carrying 65,003 barrels of (Montana mix) sour crude, collided with the Poplar Street Bridge located near downtown St. Louis, Missouri. At least one of the barges exploded on impact with the bridge and

burst into flames. The fire spread quickly setting three of the barges a drift and on fire. Containing the fire and then handling the spill was, needless to say, a difficult, prolonged effort. To add to the spill clean-up difficulties, on April 25, the N/V Louis Frank and tow of eight oil barges struck the Florence Highway Bridge, mile 56.0, in the Illinois River, and discharged an additional 60,000 gallons of No. 6 fuel oil.

Constantly changing winds and water levels resulted in the necessity to use various techniques to herd the spilled oil. One skimmer was used, but proved ineffective due to the heavy amount of debris. Deflection booms combined with vacuum trucks were used to collect as much oil as possible. Much of the oil was trapped among the trees and brush, requiring methods to free it from the area before it could be recovered. The first technique attempted was to flush the oil with the propwash from outboard engines on jon boats. Wash pumps were then attempted. Both of these methods were effective for small areas, but not cost effective for large areas. Airboats were then brought in and proved to be effective at herding oil. The use of airboats was restricted to open spaces where there was no danger of catching the prop in a tree limb. By using a combination of these three methods, it was possible to bring the incident to a successful conclusion.

By May 9, 1983, of the estimated 280,000 gallons of oil released, 41, 871 gallons had been recovered; 4,201 cubic yards of oily debris had been removed to landfills; and 981 cubic yards of oil debris had been burned on site.

Other problems encountered during this clean-up effort should be considered in contingency plans, with options preplanned as to the course of action to take if the situation arises.

As in most multiple casualties, if a fire occurs it should be handled first, since it usually presents the largest hazard. In this incident, the communities surrounding the St. Louis Harbor did not have fire contingency plans designed to handle this type of incident. Had the questions concerning jurisdiction been considered prior to the incident, it is highly probable that the shoreside fires could have been brought under control sooner.

During the cleanup, a labor dispute concerning the use of personnel and equipment by the three contractors on payroll occurred. The main cause of this problem was the lack of contractor supervision at the many clean-up locations. This demonstrates the need for proper supervision and control of all clean-up activities.

The summary of incidents for the Memphis Coast Guard Zone involved discharges of styrene and vinyl acetate. All of the responses reported that no cleanup was feasible due to river current and high flow conditions. In one styrene spill incident, a sorbent boom was placed in the water around the area of the leak. The current carried the styrene around the boom resulting in no recovery of the styrene.

There has not been a Coast Guard cleanup of floating hazardous chemicals within the Captain of the Port, New Orleans Zone. Captain of the Port personnel in New Orleans have not monitored private contractor cleanups of hazardous chemicals. A copy of the New Orleans Fire Department listing of hazardous material incidents for the time period January 1, 1982 - May 23, 1983, was forwarded by the Captain of the Port, New Orleans, for

review. Of the 73 incidents reported in this time frame, 29 occurred in waterfront areas. Of these 29, 19 were due to leaks in drums. More care in handling drums and replacing old drums would help minimize the possible discharge of hazardous materials into New Orleans waterways.

On April 29, 1982, a benzene spill occurred at Lock and Dam 26, Mile 202.9, Upper Mississippi River. In this case, no efforts were made to recover any of the released benzene. The salvage team plugged the holes in the barge and partially refloated it. The remaining benzene cargo was then transferred to another barge.

One of the problems encountered during the recovery was the lack of policy concerning the authority of the OSC in a non-federal cleanup to ensure the safety of contractor personnel regarding items such as respiratory and skin protection. In some instances, the industrial toxicologist on scene and the OSC recommended response personnel wear respirators, but the recommendations were not heeded. The OSC's authority or liability concerning issues such as these should be addressed.

The prime area of improvement mentioned in this report concerned the atmospheric monitoring equipment available to Coast Guard response forces. The St. Louis MSO's atmospheric monitoring equipment included colorimetric devices and combustible gas/oxygen meters. These devices were ineffective for the type of monitoring required for a benzene spill. The OSC in the case has recommended that a HNU photoionization organic vapor monitor be purchased for each MSO.

On March 26, 1984, 63,600 gallons of acrylonitrile (ACN) were released into the waters of Texas City, Texas. Due to the volatility and solubility of the spilled product, recovery of the ACN was limited. Efforts taken to contain the spill were abandoned due to their ineffectiveness.

The major information to be derived from this report involves the use of foam to reduce vapor concentrations. Response personnel quickly applied alcohol foam to the spill. This action was taken to guard against toxic levels of vapors escaping to populated areas, and to reduce the possibility of igniting the vapor cloud. The alcohol based foam tended to absorb the ACN and a high concentration of the product was found in the foam wastes. The foam was removed by vacuum trucks to conclude clean-up efforts.

During the cleanup, water samples were taken to monitor ACN concentrations. The ACN was found to dissipate quickly from the spill location and to settle toward the bottom.

Phone conversations were conducted during the week of March 25, 1985, with Coast Guard Marine Safety Offices and Strike Teams as a follow-up to letters mailed November 16, 1984, requesting information regarding Coast Guard hazardous floating chemical spill responses. The following information is a summary of the responses to the telephone inquiries.

Generally, the Coast Guard has not responded to many floating hazardous chemical spills. Several factors contribute to the amount of action, if any, taken by the Coast Guard:

- o The ability to respond to a floating hazardous material spill is hindered or enhanced mainly by environmental factors, not the material released into the waterway. In low current areas, the Coast Guard has

successfully contained and recovered floating spills by use of booms and vacuum trucks. In currents greater than 1.5 knots, the Coast Guard has had little success in recovering floating materials. Even through the use of deflection booms, the material has not been recovered effectively in high current areas.

- o Federal regulations require that the Coast Guard be notified only of reportable quantity spills of regulated materials. As long as the material released into a waterway is below the reportable quantity, it need not be reported regardless of its toxicity or chemical characteristics.
  
- o The Coast Guard is restricted in its use of neutralizing agents for combating floating hazardous spills in fresh waters. Acid spills are usually allowed to disperse to reduce the acid strength. In some instances, lime is applied.
  
- o The Coast Guard role at a spill is to serve as the On-Scene Coordinator (OSC). The spill itself is cleaned up by the company responsible for the spill, or by a private contractor. Coast Guard training emphasizes the mechanics required for containing and recovering the spill and does not concentrate on the chemistry and toxicity of chemicals. The Coast Guard personnel rely largely on the experience of the contractors or information concerning the chemicals available from the literature or computerized data bases. Many of the descriptions of the CHRIS chemicals contain little or no information concerning their true toxicity or flammability.

### Other Case Study Reports

The following summaries illustrate some of the basic actions necessary to contain and recover hazardous chemical spills. Although the majority of these examples deal with petrochemicals, the methods utilized in the cleanup are applicable to other floating hazardous chemicals.

#### Jet Fuel Leak From Navy Terminal

A jet fuel leak was detected five miles downstream of the Point Ozol Navy Terminal. Approximately 200 gallons of fuel had leaked into the Carquinez Straits approximately three miles from the Martinez, California marina. Due to the relatively small quantity of fuel that had dispersed over a large area, considerable dilution had taken place. Clean-up personnel used an explosimeter to constantly monitor the vapor pressure of the fuel throughout the cleanup. In addition, clean-up operators were extremely careful to eliminate possible ignition sources. As much of the work as possible was accomplished upwind of the spill.

Both permanent and absorbent booms were used to surround and contain the spill. By the time the spill was controlled, the low molecular weight fractions had evaporated. The remaining fuel was absorbed by the booms which were removed from the water for disposal. The leak was found to originate from an onshore pipeline located 150 feet from the shoreline. Clean-up personnel uncovered the pipeline with a backhoe, evacuated the pipeline, and used a vacuum truck to remove the remaining product.

#### Paint Spill Into Creek

One hundred gallons of an oil-base paint residue was discharged from the stormdrain of a paint manufacturer into a local creek located 300 yards

behind their warehouse. The creek eventually emptied into the San Francisco Bay. Since paint floated on the surface of the creek, standard oil-spill control and clean-up procedures were applied. Absorbent booms were placed both upstream and downstream of the spill. The stormdrain was flushed, and a vacuum truck was used to recover the residual paint that was washed out of the line. All of the paint was effectively absorbed by the booms, which were then removed from the creek.

#### Diesel Fuel Leak Into River

A train derailment resulted in a spill of approximately 3,400 gallons of diesel fuel into the Napa River in California. Initially, absorbent booms were placed around the spill using punt boats to contain the fuel, and absorbent pads were worked within the boom area as a clean-up measure. Approximately 700 feet of permanent boom was then used to catch and divert to the shore the fuel that had escaped before containment efforts began. A vacuum truck then collected the spilled material. The boom was shifted to allow for tide changes and current. Final cleanup was accomplished with absorbent pads.

#### Jet Fuel Leak

A tank truck accident in the Knoxville, Tennessee area resulted in the release of approximately 2,600 gallons of jet fuel into a ditch that feeds Third Creek, which eventually discharges into Fort Loudon Lake. Initial responses involved the building of a dirt dike that included the placement of PVC pipe at the bottom of the dike to permit water passage. The local fire department applied AFFF low expansion foam to the floating fuel to minimize the potential for a fire. A skimmer pump was used to remove the fuel layer from the creek. Final cleanup included the use of absorbent pads. Light suits made of PVC, nitrile gloves, and PVC boots were worn by clean-up personnel.



### Drums Leaking Into River

An overturned tractor-trailer truck resulted in approximately 80 drums of a styrene-resin mixture being scattered on a river embankment. Approximately 15-20 drums were found to be leaking their contents onto the ground and into the San Joaquin River in northern California. Containment efforts included the placement of a boom at the outlet of the cove where the spill occurred to prevent further contamination of the main river channel, and placement of another boom downstream to intercept the material that had already escaped. Cleanup of the contained materials was accomplished with a vacuum truck and vacuum hose which was positioned with a punt boat. Due to the flammable nature of the spilled chemicals, only spark resistant tools were used during the clean-up activities. An on-site occupational safety and health representative identified full-face air purifying cartridge respirators and PVC gloves and boots as protective gear.

### Cleanup of PCB Contaminated Oil

An estimated 2,000 gallons of a black oil substance, suspected to contain PCBs, (as a result of field tests conducted by the U.S. Coast Guard), was discovered floating down a flood control channel which feeds the San Gabriel River in California. Emergency response measures to contain the material involved the placement of a primary permanent boom, and a secondary boom to collect material that escaped the primary boom. A boom was also positioned to protect the cooling water intake of a power generation station which was located near the released material. Booms were placed with punt boats equipped with outboard motors. Absorbent pillows were worked in the containment area to clean up the oil material.

### Gasoline Leak Into Creek

An accident involving a gasoline tank truck resulted in the release of approximately 2,400 gallons of commercial grade gasoline into a creek that flows into the Little Tennessee River. A boom was placed across the creek downstream of the spill to contain the gasoline. Absorbent pads were used in the contained area to pick up the gasoline. The gasoline was squeezed from the pads and collected in drums. An on-site occupational safety and health representative identified PVC and nitrile gloves and PVC boots as the required protective equipment.

### Feather River Oil/PCB Spill

In northern California, a rock slide at a hydroelectric plant resulted in thousands of gallons of PCB-containing oil escaping from damaged capacitors and transformers into the Feather River Canyon and the River itself. Three types of booms were used to control the extent of the spill: log, permanent plastic, and absorbent booms. They were placed using boats and punts. Booms were first placed in positions that would take advantage of both the direction of water and wind flow to effectively move the oil into the boomed area. As oil was recovered, the booms were gradually pulled in to decrease the surface area of the river covered by oil.

Once the spill was contained, two approaches were used to recover the floating oil. Vacuum trucks located at the shoreline skimmed the oil/water mixture on the river's surface. The mixture in the trucks was then decanted, after adequate settling, by draining the waste in the truck with an underdrain valve. In addition, oil mop units were used within the oil-containing area. These absorbent pompons continuously recirculated on a

rope through the oil. They selectively absorbed the oil and then passed through a wringer system located on-shore. The wringer system removed the majority of the oil prior to the pompoms passing through the oil again.

Some of the oil remained with sediments on the bottom of the reservoir. A dredging operation was undertaken to remove the oil-contaminated sediments from the reservoir. The dredged material was treated with potable water treatment polymers, settled, and the solids were passed through a mobile centrifuge to separate the sediments from the water. The concentrate, containing most of the oil, was then passed through a sand filter and MACS (Mobile Activated Carbon System) to remove suspended sediments and absorb the PCBs. The treated concentrate was returned to the river following confirmation analysis.

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#### IV. TEST PROGRAMS DISCUSSION

The review of state-of-the-art spill containment and recovery techniques, which have to date been directed primarily at crude oil spills, identified several deficiencies in response to spills of floatable chemicals. The 315 floatable chemicals identified in Section II and Appendix A collectively present potential problems in chemical compatibility with containment and recovery equipment, and in creating a toxic or otherwise hazardous atmosphere near a spill. Data exist on the compatibility of chemicals and procedures for controlling vaporization of certain spilled chemicals, but a comprehensive application of these data to floatable chemicals spill control procedures and equipment has not been done.

To arrive at a broad understanding of the appropriate response to spills of floating chemicals, a number of programs ranging from literature reviews to laboratory, pilot, and field testing will be required. Considering the large number of floatable chemicals of concern and the variety of environmental factors such as wind velocity, wave motion, temperature, etc., that can affect a spill containment and clean-up, categorization of chemicals and prioritization of factors affecting spill response should be the first task in future investigations.

The following is a list of tasks which would be appropriate to investigate and clarify the applicability of existing equipment and technology for use in the containment and recovery of floating CHRIS chemicals.

- o Investigation of the Compatibility of Foams with Floating Hazardous Chemicals

- o Investigation of the Compatibility of Containment and Recovery Device Materials with Floating Hazardous Chemicals
  
- o Investigation of the Effect of Equipment Operation on the Effectiveness of Foam in Reducing Hazards Associated with Floating Hazardous Chemicals

#### INVESTIGATION OF THE COMPATIBILITY OF FOAMS WITH FLOATING HAZARDOUS CHEMICALS

The hazard presented by the vaporization of the floatable chemicals is the major concern for response to spills of these materials. Although this investigation generally identified foams as a viable means of reducing fire and toxic hazards, specific studies may be required to establish compatibility and efficiency.

Foams have been effective in controlling the vapor release from some volatile chemicals. Foams also tend to isolate spills from ignition sources and radiant energy. Due to this ability, foams are a prime candidate for reducing the flammability risk which may be presented to personnel combating a floating hazardous chemical spill.

Gross (1982) has conducted extensive investigative studies with foams over hazardous materials (see Tables 1-3). This testing and information can serve as a guideline for further research. Areas which were not intensively covered in Gross' work include:

- o The studies did not involve hazardous chemicals floating on water, and
  
- o Environmental effects such as wave conditions, currents, temperature extremes, winds, rain, etc., and their relation to foam effectiveness were not investigated.

Gross developed a matrix which could serve as a guideline for spill clean-up personnel to use in choosing foams for application. High quality alcohol

TABLE IV-1. PRELIMINARY MATRIX OF FOAM CAPABILITIES ON THE SPILLED HAZARDOUS CHEMICALS LISTED

		Recommend	1	2	3	4	5	6
Organics-Aliphatic Acids	- Acetic Acid	ND	ND	ND	ND	ND	ND	ND
	- Caproic Acid	ND	U	ND	ND	ND	ND	ND
Alcohols	- Amyl Alcohol	ND	U	U	ND	ND	ND	ND
	- Butanol	R	E-	E-	E-	E-	A+	E-
	- Butyl Cellasolve	ND	ND	ND	U	ND	ND	ND
	- Methanol	R	E-	E-	E-	E-	A+	E-
	- Octanol	R	U	U	U	U	U	ND
	- Propanol	R	E-	E-	E-	E-	A+	E-
Aldehydes & Ketones	- Acetone	R	E-	E-	E-	E-	A+	E-
	- Methyl Butyl Ketone	R	E-	E-	U	ND	A+	ND
	- Methyl Ethyl Ketone	R	U	U	U	ND	A+	ND
Esters	- Butyl Acetate	ND	U	U	ND	ND	ND	ND
	- Ethyl Acetate	ND	U	U	U	U	ND	ND
	- Methyl Acrylate	ND	U	U	ND	U	ND	ND
	- Methyl Methacrylate	ND	U	U	ND	U	ND	ND
	- Propyl Acetate	ND	U	U	U	U	ND	ND
Halogenated	- Butyl Bromide	ND	U	U	ND	ND	ND	ND
	- Methyl Bromide	ND	U	U	ND	ND	ND	ND
	- Tetrachlorethane	ND	U	U	ND	ND	ND	ND
Hydrocarbons	- Heptane	R	C+	B+	B+	B+	A+	C+
	- Hexane	R	C+	B+	B+	B+	A+	C+
	- Octane	R	C+	B+	B+	B+	A+	C+
Nitrogen Bearing	- Dimethyl Formamide	ND	U	E-	ND	ND	ND	ND
Organics-Aromatic Hydrocarbon	- Benzene	R	C+	B+	B+	B+	A+	C+
	- Tetrahydronaphthalene	R	U	U	U	ND	ND	U
	- Toluene	R	C+	B+	B+	B+	A+	C+
Organics-Alicyclies	- Cyclohexane	R	B+	A+	B+	B+	C+	C+
Organics-Industrial	- Gasoline	R	C+	B+	B+	B+	A+	C+
	- Kerosene	R	C+	B+	B+	B+	A+	C+
	- Naptha	R	C+	B+	B+	B+	A+	C+
	- Paint Thinner	R	C+	B+	B+	B+	A+	C+
Organics-Cryogens	- Liquefied Natural Gas	R	C+	A+	E-	E-	E-	E-
Inorganics	- Silicon Tetrachloride	R	E-	A+	E-	E-	E-	E-
	- Sulfur Trioxide	R	E-	A+	E-	E-	E-	E-
Inorganics-Cryogens	- Ammonia	R	C+	A+	C+	C+	E-	C+
	- Chlorine	R	C+	C+	C+	C+	E-	E-

IDENTIFICATION OF SYMBOLS

Type of Foam:	1	2	3	4	5	6
	Surfactant Low Ex	Surfactant High Ex	Protein	Fluoroprotein	Alcohol	AFFF

- U Limited data available - capabilities uncertain
- ND No data
- R foam use recommended over spill
- A+ Best foam formulation
- B+ Next best foam formulation
- C+ Acceptable in some situations
- E- Unsuitable foam formulation

Source: S. S. Gress et al. (1982).

TABLE IV-2. MATRIX FOR POLAR AND NONPOLAR LIQUID HYDROCARBONS

	<u>Protein</u>	<u>Fluoroprotein</u>	<u>Alcohol</u>	<u>Surfactant</u>	<u>AFF</u>	<u>Surfactant High Exp.</u>
Esters	E	E	A	E	E	E
Alcohols	E	E	A	E	E	E
Ethers	E	E	A	E	E	E
Aldehydes	E	E	A	E	E	E
Ketones	E	E	A	E	E	E
Phenols	E	E	A	E	E	E
Halogenated Compounds	A	A	C(b)	C(c)	C(c)	A(a)
Alkanes	A	A	C(b)	C	C	A(a)
Alkenes	A	A	C	C	C	A(a)
Alkynes	A	A	C	C	C	A(a)
Dienes	A	A	C	C	C	A(a)
Cycloaliphatic	A	A	C	C	C	A(a)
Aromatic	A	A	C	C	C	A(a)

(a) If wind speed is less than 15 mph; also minimizes amount of water.

(b) Only satisfactory because does not flow over spill as well as other types of foam.

(c) Foam drainage and mitigation times are not as good as protein based foams.

A - Recommended

B - Satisfactory

C - Not Recommended

Source: S. S. Gross et al. (1982).



TABLE IV-3. FOAM MITIGATION TIMES - TIME FOR SIGNIFICANT VAPOR BREAKTHROUGH

Foam Agent	Cyclohexane	Benzene	Toluene	Ethyl Ether	Acetone	n-Butyl Acetate	n-Octane	Triethylamine
National 6% Regular Protein	60	60	60*	Collapsed	Collapsed	Collapsed	60	--
Larcon 6% Regular Protein	--	30 <sup>1</sup>	--	"	"	--	--	--
Larcon 3% Fluoroprotein	--	30 <sup>1</sup>	60	"	"	--	--	--
National XL-3 Fluoroprotein	60	30 <sup>1</sup>	--	"	"	60	--	--
Rockwood Alcohol	60	60	60	20	60	60	60	--
National Aer-O-Foam 99-6%	--	5	--	Collapsed	Collapsed	--	--	--
MSA Ultrafoam Low Expansion	60	15 <sup>1</sup>	55	"	"	25	--	--
Rockwood Jet-X Low Expansion	--	15	--	"	--	--	--	--
Larcon Full-Ex Low Expansion	--	35	10 <sup>1</sup>	"	Collapsed	--	--	--
National 3% AFFF	60	13	60	15 <sup>2</sup>	"	60	60	--
3M Light Water 6% AFFF	--	6	--	16 <sup>2</sup>	"	--	--	--
Rockwood Jet-X High Expansion	--	12	--	Collapsed	Collapsed	--	--	--
Larcon Full-Ex High Expansion	30	25	15 <sup>1</sup>	"	"	--	--	--
MSA Ultrafoam High Expansion	60	16	23 <sup>1</sup>	"	"	Collapsed	15 <sup>1</sup>	--
3M Light Water 6% AFFF High Expansion	--	11	--	--	--	--	--	--
National 3% AFFF High Expansion	--	10	--	--	--	--	--	--

\* Time given in minutes  
 1 Significant wind damage  
 2 Cap formed between the foam and solvent

Source: S. S. Gross et al. (1982).

foams are recommended for application to polar materials; while for nonpolar compounds a high quality low or high expansion foam is recommended.

Liquefied gases were deleted from the matrix due to the highly specific interaction of foams with liquefied gases. Counterproductive results may occur if foam is incorrectly applied to liquefied gas spills.

If a compound has several functional groups, problems may arise when using this table. For example, an aromatic may contain a polar group. Polar groups are specified to require alcohol foams, while the aromatic ring is best approached with a protein or fluoroprotein foam. Applying an alcohol foam to this compound would satisfactorily reduce the vapor pressure over the spill, while application of a protein foam could, in some instances, provide unsatisfactory results.

The matrix method also assumes that the personnel applying it have a basic knowledge of organic chemistry. This may or may not be true for O.S.C. and other personnel at the spill sight.

Based upon the recommendations given in the Gross matrix and available quantitative data regarding polarity, i.e., dielectric constants, Tables B-1 through B-13 have been developed. These thirteen tables classify the floating hazardous CHRIS chemicals by toxicity and flammability. By applying the Gross matrix and polarity data, the chemicals have been matched with what is, tentatively, the best type of foam to be used in reducing the hazards inherent to the chemical in question. To accurately assess the validity of these tables, field tests would be required.

The recommended foams for application are designated as follows:

- S: High expansion surfactant (if wind speed less than 15 mph)
- A: Alcohol type foam
- P: Protein type foam
- F: Fluoroprotein type foam

A combination of tables of flammability and toxicity ratings as defined by the criteria in Section II (pages II-2 and II-3) has been tabulated for 292 floating chemicals. The recommended foams based on the findings of Gross, et al. (1982) have also been incorporated into these tables. The resulting tables are identified below and listed in Appendix B in Tables B-1 through B-13.

<u>Table</u>	<u>Chemical Classification</u>	<u>Number of Floating Hazardous Chemicals</u>
B-1	Nontoxic, noncombustible	17
B-2	Nontoxic, highly flammable	1
B-3	Slightly toxic, noncombustible	36
B-4	Slightly toxic, combustible	33
B-5	Slightly toxic, flammable	53
B-6	Slightly toxic, highly flammable	17
B-7	Moderately toxic, noncombustible	18
B-8	Moderately toxic, combustible	44
B-9	Moderately toxic, flammable	34
B-10	Moderately toxic, highly flammable	10
B-11	Highly toxic, combustible	15
B-12	Highly toxic, flammable	11
B-13	Highly toxic, highly flammable	3
	Total	<u>292</u>

Although the sequence of these combinations should indicate a grouping of "Highly toxic, noncombustible," however, toxicity and flammability data did not produce any floating chemicals in this category.

By considering the categories for which foam usage would be most beneficial, i.e., those categories including flammable and highly flammable chemicals, the number of chemicals requiring investigation can be reduced to 153. By reducing the investigation to this number of chemicals, one can effectively reduce the amount of testing by one-half. (Incidentally, this breakdown will include 81 chemicals which are either moderately or highly toxic.)

To further reduce the number of chemicals to be tested with foams to a reasonable number, several methods could be applied:

- o A review of the Coast Guard PIRS List could be conducted to determine which chemicals are those with the highest incidence of spillage. (See Table 18)
  
- o Records of chemical transfers could be reviewed to help determine which chemicals are transported most often or in bulk on national navigable waters.
  
- o Applicable records which may be of aid in this determination include the following statistical reports:
  - Inland Waterborne Commerce Statistics Annual compiled by the U.S. Army Corps of Engineers (listed in the 1982 Statistical Reference Index); and
  
  - Waterborne Commerce of the U.S. 1981 (listed in the 1983 American Statistics Index)
  
- o Representative chemicals (based on functional groupings) could be chosen for investigation.

This reduction/elimination procedure could possibly reduce the number of chemicals to be tested with foams to a manageable number of 12-20.

TABLE IV-4. HAZARDOUS FLOATING CHEMICALS WITH A HIGH INCIDENCE OF SPILLAGE

<u>Chemical</u>	<u>Gallons Spilled+</u>	<u>Category</u>	<u>Tested*</u>
Adiponitrile	71,737	Highly toxic, combustible	
Aniline	1,010	Highly toxic, combustible	
N-Amyl Alcohol	134	Slightly toxic, flammable	X
Benzene	66,237	Highly toxic, flammable	X
N-Butyl Acetate	3,050	Moderately toxic, flammable	X
N-Butyl Acrylate	2,806	Moderately toxic, combustible	
Butyl Ether	100	Moderately toxic, flammable	
Cresols	665	Highly toxic, combustible	
Cyclohexane	214,073	Slightly toxic, flammable	X
Ethyl Acetate	71	Slightly toxic, flammable	X
Ethyl Acrylate	830	Moderately toxic, flammable	
Isoprene	200	Moderately toxic, highly flammable	
Methyl Acrylate	1	Slightly toxic, flammable	X
Methyl Isobutyl Ketone	143	Moderately toxic, flammable	
Methyl Methacrylate	4,150	Slightly toxic, flammable	X
Styrene	196,808	Moderately toxic, flammable	
Toluene	187,747	Moderately toxic, flammable	X
Turpentine	25,605	Slightly toxic, flammable	
Vinyl Acetate	22,804	Moderately toxic, flammable	
Xylene	537,107	Slightly toxic, flammable	
Ethyl Benzene	229	Moderately toxic, flammable	
Maleic Anhydride	9,700	Highly toxic, noncombustible	
Napthenic Acid	2,132	Moderately toxic, combustible	

+Information from Pollution Information Response System (PIRS) List printed March 4, 1985.

\*Gross et al. (1982).

With the number of chemicals reduced by the above methods, the remaining chemicals can be categorized further by a chemical classification technique; and a select number of floaters can be chosen for laboratory bench scale testing. The testing will involve the application of up to three different types of foams selected to have variable compatibility with polar and nonpolar organics. A layer of foam will be applied to containers with a layer of the selected chemicals floating on water. Observation of stability of the foam blanket and measurement of the collapse rate serve as indicators of compatibility of chemicals and foams.

Further bench scale testing of foams that are found to be compatible will include blanketing samples of selected chemicals that are suspended on water and monitoring the vapor space above the foam with an explosimeter to determine if this space is flammable. Other variables such as foam depth, surface turbulence (wind and waves), and temperature will be considered in developing the bench scale test program.

Additional testing of foams under simulated field conditions should also be done on a pilot scale. Test conditions should be selected based on spill scenarios. The most likely locations are harbors and rivers. Harbors should be tested because that is where most of the materials handling and transfer takes place. Rivers are likely subjects for investigation because of barge shipments and the location of other transportation modes (e.g., truck, rail) near rivers. Of major interest is the stability of foam blankets under rough water or flowing water conditions and the ability of the foams to maintain suppression of vapor release. Flammability of the vapor space above the foam should be monitored throughout the testing.

INVESTIGATION OF THE COMPATIBILITY OF CONTAINMENT AND RECOVERY DEVICE MATERIALS  
WITH FLOATING HAZARDOUS CHEMICALS

For favorable judgement to be placed on the feasibility of applying a spill amelioration device and its associated auxiliary equipment, several factors must be carefully studied. These factors may include some or all of the following:

- (1) the device or system must show some degree of efficiency and effectiveness;
- (2) the device or system must preferably provide a rapid recovery rate of the spill material;
- (3) the device or system must possess mobility to allow rapid deployment;
- and (4) the fabrication materials of the device or system should be compatible with the spilled chemical.

The following discussion will be limited to describing various construction materials which have been used with devices that have been in contact with hazardous chemicals.

Many materials have been used in the construction of spill containment devices. The following information has been extracted from J. S. Robinson's (1979) description of off-the-shelf containment devices. (See Table 19)

(Chemicals tested were pentadecanol, ethyl ether, kerosene, n-amyl alcohol, naphtha: solvent, ethyl acetate, hexane, and n-butyraldehyde.)

**TABLE IV-5. SPILL CONTAINMENT DEVICE CONSTRUCTION MATERIALS**

<u>Material</u>	<u>Chemical Compatibility</u>
Vulcanized laminated neoprene-nylon-neoprene sandwich	Resistance to solvency was good for all representative hazardous floating liquids.
Chemigum rubber-reinforced nylon fabric	Resistance to solvency was good for all representative hazardous floating liquids except for:  Ethyl acetate - which caused a weight loss of 15%, discolored the solvent, showed curling, swelling, and softening.  Ethyl ether-solvent - discolored and fabric was stiff when dry.  Butyraldehyde - solvent discoloration, marked curling, swelling, stiffening.  Naptha-solvent - discoloration, fabric stiffened. When dry, hexane and kerosene-minor effect.
Polyurethane fabric	Highly resistant to solvent action of all hazardous floating liquids.
Solvent resistant rubber-impregnated nylon fabric	Feasibility of containment high for representative floating chemicals.
Two-ply nylon fabric	No deterioration in solvent stability tests.
Neoprene	Suitable for all representative hazardous floating chemicals.
Paracril-ozo coated fabric	Solvent resistance good in all floating hazardous liquids.
Terylene fabric impregnated with chloroprene rubber	Expected to be highly solvent resistant.
Aluminum-magnesium alloy	Expected to be highly solvent resistant.



Flexible synthetic membrane liners have been applied for containing industrial wastes. These liners have demonstrated an ability to contain a variety of fluids with minimal losses from permeation and seepage, high resistance to deterioration by chemical and bacterial mechanisms, and relatively easy maintenance. Some of the membrane materials are more susceptible to ozone and ultraviolet deterioration than others. Some of the materials are more likely to demonstrate unwanted temperature effects such as cracking or stretching. Due to problems such as these, care must be taken to study the chemical and physical properties of the material before their application is justified. Table 20, which follows, is a compilation of material extracted from Fung (1980).

Due to the stability of some of these liner materials when in contact with various chemicals, it may be feasible to utilize their properties in the construction of containment devices such as booms.

**TABLE IV-6. FLEXIBLE SYNTHETIC MEMBRANE LINER MATERIALS**

<u>Material</u>	<u>Properties</u>
Polyvinyl chloride	Contain 30-50% of one or more plasticizers (subject to attack by high solvency chemicals) to make film flexible and rubber-like, 2% chemical stabilizer, and various amounts of fillers.
Neoprene	Chlorine containing synthetic rubber; superior to natural rubber in resisting oils, weathering, ozone, and ultraviolet radiation; extremely resistant to puncture, abrasion, and mechanical damage; relatively expensive compared to other liners.
Polyethylene	Tough, highly flexible, inert in solvents, excellent low temperature qualities; poor puncture resistance and weatherability if formulated without carbon black or UV absorbers; low cost.
Butyl rubber	Copolymer consisting of 97% isobutylene and a small amount of isoprene to allow unsaturation for vulcanization; excellent resistance to permeation and swelling in water; poor resistance to hydrocarbon, some ozone cracking possible.
Chlorinated polyethylene	Produced by a reaction between chlorine and polyethylene; not susceptible to ozone attack, excellent crack resistance at low temperature, good tensile and elongation strength, excellent resistance to atmospheric deterioration, limited range of tolerance for chemicals, oils, and acids.
Ethylene-propylene rubber (EPDM)	Terpolymer of ethylene, propylene and a diene monomer to introduce unsaturation (to allow vulcanization); resistant to dilute (10%) acids, alkalis, silicates, phosphates, and brine; excellent resistance to water absorption and permeation, relatively poor resistance to some hydrocarbons, is not recommended for petroleum solvents, aromatics, or halogenated solvents.
Chlorosulfonated polyethylene	Made by chlorosulfonation of polyethylene; can be used in vulcanized or non-vulcanized compounds; good puncture resistance, excellent resistance to weathering, age, oil, and bacteria; high cost, low tensile strength.

Of the materials briefly discussed above, the following appear to be most resistant, i.e., compatible with the largest range of hazardous chemicals: vulcanized laminated neoprene-nylon-neoprene material, polyurethane fabrics, solvent resistant rubber impregnated nylon fabric, two-ply nylon fabric, neoprene, paracrill-ozo coated fabric, terylene fabric impregnated with chloroprene rubber, aluminum-magnesium alloy, and polypropylene. All of these materials are commercially manufactured and available. An in-depth literature review should be conducted to add to and refine this list of materials to ensure completeness and present state-of-the-art knowledge.

The floatable chemicals will be categorized by chemical class for determining chemical compatibility with containment and cleanup equipment. If deficiencies in compatibility data are found, simple laboratory tests will be conducted to determine compatibility of selected chemicals with the fabrication materials of commercially available response equipment. The tests would involve placement of small samples of various materials in selected chemicals and observation by means of simple measurements of the effects on the materials with time. Pitting, softening, signs of dissolving, and weight loss are typical of the types of observations and tests to be made.

INVESTIGATION OF THE EFFECT OF EQUIPMENT OPERATION ON THE EFFECTIVENESS OF FOAM IN REDUCING HAZARDS ASSOCIATED WITH FLOATING HAZARDOUS CHEMICALS

Consideration should be given in the test program definition to the impact that the type of collection equipment used in a spill cleanup would have on the flammability protection provided by the foam. Skimming devices such as weir skimmers appear to have a high degree of adaptability to cleanup of floating chemicals. The action of the skimming/transfer device on the foam blanket

protection may require testing to verify the protective efficacy of foam systems. Use of a full-scale test facility such as OHMSETT may represent the best way to test this potential problem.

The following Table IV-7 is an idealized outline of a minimum testing effort inclusive of laboratory, bench, pilot and simulated field tests with selected foams and a limited number of hazardous chemicals. The initial number of chemicals should be selected based on frequency and quantity of shipments, frequency of spills on waterways, and fire and toxicity hazards. The fire and toxicity criteria should be selected to include high flammability and toxicity ratings but without excessive hazards to testing personnel and without difficult waste disposal problems.

**TABLE IV-7. OUTLINE OF A MINIMUM TESTING EFFORT  
OF FOAM AND MATERIAL COMPATIBILITY**

The following is an estimated level of effort for conducting the tests described in the outline of development testing. This estimate does not include an estimated level of effort for conducting further literature reviews and technical reviews.

	<u>Level of Effort Man-Weeks</u>
A. Preparation of Detailed Plan	4
B. Chemical/Foam Compatibility Tests	
assume 20 chemicals	
3 foams	
<u>60 tests</u>	8
Waste Disposal	
C. Vapor Suppression Tests	
1. Bench Scale Vapor Suppression Tests	
assume 10 chemicals	
3 foams	
2 foam depth	
2 temperatures	
2 water types	
1 turbulence condition	
(quiescent)	
<u>240 tests</u>	20
Waste Disposal	
2. Pilot Scale Vapor Suppression Tests	
assume 4 chemicals	
2 foams	
3 turbulence conditions	
(quiescent, flowing, waves)	
<u>24 tests</u>	40
Waste Disposal	
Equipment	
3. Full Scale Tests at OHMSETT	
D. Compatibility Testing of Equipment	
Materials and Chemicals	
assume 6 materials	
10 chemicals	
<u>60 tests</u>	10
Waste Disposal	

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## V. SUMMARY AND CONCLUSIONS

This project was divided into three major tasks -- A review and classification of chemicals contained in the Coast Guard Chemical Hazards Response Information System (CHRIS), a state-of-the-art review of technologies for the containment and recovery of floating hazardous chemicals, and general recommendations for testing of foam and material efficiencies and compatibilities. As a result of this project, specific deficiencies and problems inherent in present technology have been identified.

The identification and evaluation of state-of-the-art techniques for the containment and recovery of floating hazardous chemicals must include the consideration of the operative mechanisms of the techniques involved and the physical and chemical properties of the spilled chemicals. Containment and recovery techniques serve to limit the horizontal as well as vertical spread of spilled hazardous chemicals. Each of these techniques will have an effect on, and be effected by the physical chemistry of the spill, the mass transfer of the spilled chemicals, as well as conditions at the spill site, such as wind, waves, and temperature. By understanding the techniques and chemical properties and their inter-relationships, problem areas or developmental needs in improving the applicability of state-of-the-art techniques can be readily identified.

CHRIS is designed to provide Coast Guard spill response personnel with the decision-making information required in their response to emergencies that occur during the water transport of hazardous chemicals. This system contains information such as fire hazards, health hazards, shipping information, chemical reactivity and the physical and chemical properties of over 1100 chemicals. To properly assess the potential hazards and difficulties which could be encountered

in combating a floating hazardous chemical, it was necessary to develop criteria to determine what constituted a floating hazardous chemical. Three major properties--floatability, flammability, and toxicity--were reviewed for all of the CHRIS chemicals against criteria that were established. The application of these criteria resulted in the identification of 330 floating hazardous chemicals from the CHRIS list of chemicals.

A literature review was then conducted to identify state-of-the-art techniques for the containment and recovery of the floating hazardous chemicals. Of major concern during the review were those areas such as flammability and toxicity reduction which would improve personnel safety. Through this review a basis for analyzing the results of previous tests of spill control agents and devices was possible.

Surfactant films, foams, and, to some extent, sorbents appear feasible for reducing vaporization rates of floating hazardous chemicals. By reducing the vaporization rate, these methods should also contribute to reducing the flammability and toxicity hazards presented to spill response personnel.

One major point of concern for the addition of any substance to a spill is that this addition will most likely result in more waste material. Any material added to a spill becomes at least partially contaminated and will introduce an added liquid or solid disposal and cost problem. Personnel who have handled hazardous floating chemical spills have indicated that, in many instances, they would rather attempt containment and recovery of a spill without the application of foams or other vapor pressure reducing materials.

Surfactant films, in theory, have high promise for reducing flammability or toxicity hazards associated with vapor pressure over a spill. These films, when



applied in a mist or aerosol form, would form a thin uniform layer over the surface of the spill, effectively decreasing the risk of vertical spread into the atmosphere through evaporation. Fluorochemical surfactant foams which collapse to form a thin cover over hydrocarbon liquids have been shown to reduce evaporation rates by up to 90 to 98%. This technique has been shown to work best on chemicals having a surface tension equal to or greater than 20 dyne/cm.

The application of surfactant films in the form of Aqueous Film Forming Foam (AFFF) has been studied. This study showed that AFFF will follow the movement of waves, a major concern when choosing a method of vapor rate reduction.

Hydraulic or pneumatic equipment could be used to apply the surfactant/water solution over a spill surface. Since hazardous chemical spills are generally small (in comparison to oil spills) hydraulic application would be most feasible.

To ensure that the vapor suppression provided by the generation of thin films is maintained, the film should be removed with the hazardous chemical. Weirs and skimmers should be compatible with this goal, but testing should be conducted to determine the best method of removal while retaining the film protection.

Another factor which could effect the choice of surfactant films is the question of the introduction of environmental pollutants. Surfactant films, being composed of fluorinated chemicals, may introduce an added burden upon the ecosystem due to the inability of many organisms to biologically decompose halogenated substances. Investigation into this question should also be addressed.

Foams have demonstrated a proven effectiveness in controlling the vapor release from some volatile chemicals. Foams also tend to isolate spills from

ignition sources and radiant energy. The availability of foams, the wider applicability of newer foams, and on-going research and development help make foams one of the more feasible means of lowering evaporation rates of floating hazardous chemicals.

Extensive studies have been conducted to investigate the use of foams over a variety of hazardous chemicals. As a result of this research, guidelines have been developed which allow the determination of the compatibility of foams with the functional groupings of chemicals.

The major deficiency still inherent in the use of foams is the degradation which occurs when they are applied to chemicals with a dielectric constant above 3. Further investigation and testing should be conducted in this area to improve the applicability of foams to polar hazardous chemicals.

Due to the density of the material, low expansion foams perform better than high expansion in rough weather. The higher density of low expansion foams allows them to be delivered from a greater distance, a factor which may be of benefit to cleanup personnel. When used as a means to reduce flammability risks, it has been shown that volume expansions to foam ratios of less than 10:1 are most effective.

High expansion foams, while not performing as well under difficult environmental conditions, have proven to be the most effective for maintaining the vapor concentration over a spill less than TLV. This is due to the entrapment of the evaporating material in the bubbles of the foam. Although this absorption may result in a liquid-air gas mixture that may be hazardous, the flammability risk can be reduced by blowing the foam with an inert gas during its formation.

For spills involving hydrocarbons or other chemicals with low water solubility, rapid sweeps of low expansion foam over the spill from a nozzle represent an effective application method. For polar solvents or other hydrophilic chemicals, gently applying an alcohol type concentrate (ATC) foam or an AFFF/ATC using an air-aspirating nozzle is recommended. This method of application allows a slow buildup of the foam blanket.

Tests that have been conducted with foams in wave conditions have shown that AFFF and ATC follow the movement of waves, whereas fluoroprotein foams do not. Further research should be conducted to establish what effect environmental factors and solvation have on foams. Research should also be conducted to determine the layer-thickness of foam required to effectively reduce the vapor concentration over the floating hazardous chemical and determine the best methods for obtaining that thickness.

Due to the mechanisms involved for reducing the vaporization rate over a floating hazardous chemical, foam stability and durability should be greater than that provided by surfactant films. Foams should also be more durable during recovery operations, providing more protection for response personnel. Testing should be conducted to evaluate the best means of chemical removal when a foam has been applied.

A large variety of sorbent materials have been developed for responses to spills of petrochemicals. Recently, development of sorbents for application to hazardous chemicals has begun.

Sorbents reduce vaporization by the preferential wetting and absorption of the hazardous material into a material with high surface area and activity.

Sorption is influenced by factors such as surface geometry, physical and chemical attraction, contact time, and the density ratio of sorbent/sorbate. By judicious choice of sorbent, this response technique is applicable toward a wide range of hazardous chemicals. Hazardous materials may be readily accumulated and removed from the spill site.

The evaporation reduction capability and uncertainty as to the extent of protection that sorbents provide are based upon the fact that, as a sorbent becomes saturated, a larger surface area is provided for evaporation. Sorptive capacity and buoyancy may be limiting, with the resultant overloading reducing the effectiveness of the sorbent. Further testing should be conducted to investigate methods of improving the buoyancy of effective sorbents and improving the efficiency of their removal.

Encapsulation directly localizes the spill and its accompanying vapor hazards. While being highly effective over small regions, the ability to apply an encapsulation membrane over a large area of open water could be extremely difficult. Some plastics which may be used for encapsulation may dissolve when exposed to high solvency chemicals. The ability to seal individual covers may also prove difficult in an open water environment.

The application of solid or liquid carbon dioxide or nitrogen will effectively reduce the vapor concentration over spill. The feasibility of transporting the large storage vessels, and the resulting high cost, detract from the use of cryogenics. Another factor serving to reduce the feasibility of this method is that the displacement of oxygen by the cryogenics may present a personnel hazard.

Gelation has been demonstrated to reduce the vaporization rate by as much as 50%. While being effective to some extent as a vapor reduction measure, gelations largest promise appears to be its application in helping to contain spills in high current areas, as well as possibly serving as a base for foam application. Further work involving the combined action of gels and foams may prove useful.

Dilution augments the existing air movement available for removing hazardous vapors over a spill. While this method may lower flammability hazards, it does not reduce vapor concentrations below TLV. This technique requires the movement of increased volumes of air with large blowers. Use of dilution would be applicable only in sparsely populated areas.

Foams appear to be the most promising method for reducing vaporization and vapor flammabilities of hazardous chemicals that float on water. Foams have demonstrated their effectiveness in reducing the flammability hazards present above a hazardous chemical. While not able to keep the vapor concentration below TLV, foams may have some effectiveness in reducing the toxicity hazard above a hazardous spill.

Factors which contribute to the selection of a containment or recovery system or device include its effectiveness and efficiency, its recovery rate of the spill material, its safety features, its transportability to allow rapid deployment, and the compatibility of the materials used to construct the containment or recovery device with the spilled hazardous chemical.

None of the containment devices reviewed could function effectively in choppy water or in currents greater than about 4 knots. Extensive research has been conducted to investigate the different modes of failure of these devices. Based upon this research, it can be concluded that to be effective, barriers

should be erected to deflect the spilled material to a region of slower currents and calmer water to allow adequate containment and recovery of the hazardous chemical. To facilitate containment and recovery procedures in areas not presenting nominal conditions, research should be conducted to investigate the feasibility of applying gels in combination with containment configurations.

Most of the skimming devices which have been developed are meant to be used with petrochemicals. The effectiveness of the devices that have been developed for response to hazardous chemicals is greatly influenced by environmental factors and the density of the hazardous chemical. To be effective, these devices should nominally be used in low current or calm waters. Some of the devices reviewed were limited in their range of applicability to floating hazardous chemicals. Work should be conducted to improve the effectiveness of these devices in rough water and to extend their range of use.

A major factor to be considered in choosing a containment or removal device is the compatibility of its material of construction with the hazardous chemical agent. Many materials presently utilized in constructing spill response equipment contain plasticizing agents. High solvency chemicals will quickly destroy the effectiveness of such materials. By properly choosing construction materials which are compatible with the spill material, the lifetime of the equipment may be extended, equipment failure may be reduced or prevented, and the release of more chemicals into the environment may be prevented. This area should be more thoroughly investigated.

Upon completion of the state-of-the-art review, the CHRIS chemicals were placed into categories based on flammability and toxicity information accumulated during the first part of this program. A discussion concerning two methods of categorizing the floating CHRIS chemicals is presented in Appendix B.

Using this classification method, spill mitigation technologies were investigated to determine which technologies showed the greatest promise of being areas in which further research would contribute significantly toward increasing spill response effectiveness.

The review of state-of-the-art spill containment and recovery techniques, which have to date been directed primarily at crude oil spills, identified several deficiencies in response procedures to spills of floatable chemicals. The 315 floatable chemicals that were identified during the first part of the program collectively present potential problems in chemical compatibility with containment and recovery equipment and in the creation of a toxic or otherwise hazardous atmosphere near a spill. Data exist on the compatibility of chemicals and procedures for controlling vaporization of spilled chemicals, but a comprehensive application of this data to floatable chemicals' spill control procedures and equipment has not been done.

To arrive at a broad understanding of the appropriate response to spills of hazardous floatable chemicals, a number of programs ranging from literature reviews to laboratory, pilot, and field testing would be required. Considering the large number of floatable chemicals of concern, and the variety of environmental factors such as wind velocity, wave motion, temperature, etc., that can affect spill containment and clean-up, categorization of chemicals and prioritization of factors affecting spill response would be an important aspect of further work.

The following areas are proposed for further study:

1. Investigation of the compatibility of foams with floating hazardous chemicals;

- 2) Investigation of environmental effects on the effectiveness of the use of foams with floating hazardous chemicals;
- 3) Investigation of the compatibility of containment and recovery device construction materials with floating hazardous chemicals; and
- 4) Investigation of the effect of collection equipment operation on foam protection.



**APPENDIX A**  
**PHYSICAL-CHEMICAL CHARACTERISTICS OF FLOATING CHRIS CHEMICALS**

**TABLE A-1. Floatability/Flammability/Toxicity Characteristics**

To properly assess the potential hazards and difficulties which could be encountered in combating a hazardous floating chemical, it was necessary to develop criteria to determine what constitutes a floating hazardous chemical. Three major properties -- floatability, flammability, and toxicity -- were determined as those that would factor significantly in assessing the risk involved in attempting to mitigate a floating hazardous chemical spill. A discussion of the criteria developed for determining the floatability, flammability, and toxicity of the chemicals reviewed for this study is presented in the Approach section.

Floatability: The chemicals are noted as being floatable (yes) or floatable under various environmental conditions such as high salinity (yes\*).

Flammability: The flammability data was based primarily on NFPA ratings and secondarily on the material's respective flash point.

Noncombustible: Materials having an NFPA rating of 1 or 0 and/or those having a flash point greater than 200F.

Combustible: Materials having an NFPA rating of 2 and/or those having a flash point of 100-200F.

Flammable: Materials having an NFPA rating of 3 and/or having a flash point of less than 100F.

Highly Flammable: Materials having an NFPA rating of 4.

Toxicity: Information obtained from Threshold Limit Values (TLV's) and Short Term Exposure Limits (STEL's) was given first priority in the ranking process. The following criteria, which are based on regression analyses, were used as a guideline in the grouping.

<u>Group</u>	<u>TLV (ppm)</u>	<u>STEL (ppm)</u>
Not Toxic	1000	5500
Slightly Toxic	100	130
Moderately Toxic	5	3
Highly Toxic	0.1	0.1

Data from the OEHM-TADS, LD-50's, and NFPA health codes were also considered. In some instances, it was necessary to assign a chemical to a category based on limited toxicity information. In other cases, contradictory data led to a grouping decision based on the more conservative piece of information.

Not Toxic: Indicates that the material poses no health hazard.

Slightly Toxic: Indicates chemicals which on exposure would cause irritation but only minor residual injury even without medical treatment. Chemicals which irritate, but do not destroy tissue, and materials which require the use of canister-type gas masks are included in this category.

Moderately Toxic: Indicates those materials which cause temporary incapacitation or possible residual injury unless prompt medical attention is given. Materials included in this category require the use of protective respiratory equipment with independent air supply.

Highly toxic: Indicates materials which on short exposure could cause serious temporary or residual damage (possibly death) even with prompt medical attention. Materials that are corrosive to living tissue or toxic by skin adsorption, and materials requiring protection from all bodily contact are included in this category.

CHEMICAL	FLOATABILITY	FLAMMABILITY	TOXICITY
ACETOPHENONE	YES*	COMBUSTIBLE	MODERATELY
ACETYL ACETONE	YES*	COMBUSTIBLE	MODERATELY
ACETYLENE	YES*	HIGHLY	NOT TOXIC
ADIPONITRILE	YES*	COMBUSTIBLE	HIGHLY
ALLYL CHLORIDE	YES	FLAMMABLE	HIGHLY
n-AMYL ACETATE	YES*	FLAMMABLE	SLIGHTLY
sec-AMYL ACETATE	YES*	FLAMMABLE	SLIGHTLY
tert-AMYL ACETATE	YES*	FLAMMABLE	SLIGHTLY
n-AMYL ALCOHOL	YES*	FLAMMABLE	SLIGHTLY
n-AMYL CHLORIDE	YES	FLAMMABLE	SLIGHTLY
n-AMYL MERCAPTAN	YES	FLAMMABLE	MODERATELY
n-AMYL METHYL KETONE	YES	COMBUSTIBLE	MODERATELY
n-AMYL NITRATE	YES	COMBUSTIBLE	MODERATELY
iso-AMYL NITRITE	YES*	FLAMMABLE	MODERATELY
AMYL PHTHALATE	YES	NON-COMBUS.	SLIGHTLY
ANILINE	YES*	COMBUSTIBLE	HIGHLY
ASPHALT	YES*	FLAMMABLE	MODERATELY
BENZALDEHYDE	YES*	COMBUSTIBLE	MODERATELY
BENZENE	YES	FLAMMABLE	HIGHLY
BENZONITRILE	YES*	COMBUSTIBLE	MODERATELY
BENZYL ALCOHOL	YES*	NON-COMBUS.	MODERATELY
BUTADIENE	YES	HIGHLY	SLIGHTLY
BUTANE	YES	HIGHLY	SLIGHTLY
n-BUTYL ACETATE	YES*	FLAMMABLE	MODERATELY
sec-BUTYL ACETATE	YES*	FLAMMABLE	MODERATELY
tert-BUTYL ACETATE	YES	FLAMMABLE	SLIGHTLY
iso-BUTYL ACRYLATE	YES*	FLAMMABLE	MODERATELY
n-BUTYL ACRYLATE	YES	COMBUSTIBLE	MODERATELY
BUTYL BUTYRATE	YES*	COMBUSTIBLE	MODERATELY
BUTYL/DECYL/CETYL-ESTER METHACRYLATE	YES	COMBUSTIBLE	MODERATELY
BUTYLENE	YES	HIGHLY	SLIGHTLY
n-BUTYL ETHER	YES	FLAMMABLE	MODERATELY
tert-BUTYL HYDROPEROXIDE	YES*	HIGHLY	MODERATELY
n-BUTYL MERCAPTAN	YES*	FLAMMABLE	HIGHLY
iso-BUTYL METHACRYLATE	YES	COMBUSTIBLE	NO DATA
n-BUTYL METHACRYLATE	YES*	COMBUSTIBLE	SLIGHTLY
p-tert-BUTYLPHENOL	YES*	NON-COMBUS.	SLIGHTLY
iso-BUTYRALDEHYDE	YES*	FLAMMABLE	MODERATELY
n-BUTYRALDEHYDE	YES	FLAMMABLE	MODERATELY
CAMPHENE	YES	FLAMMABLE	NO DATA
CAMPOR (OIL)	YES	COMBUSTIBLE	MODERATELY
CARBOIC OIL	YES*	COMBUSTIBLE	HIGHLY
CARBON MONOXIDE	YES	HIGHLY	MODERATELY
CARSOL	YES	COMBUSTIBLE	MODERATELY
CETYL ESTER METHACRYLATE	YES	NO DATA	NO DATA
CHLOROPRENE	YES*	FLAMMABLE	SLIGHTLY
COLLOIDION	YES	HIGHLY	SLIGHTLY
COPPER NAPHTHATE(1:1) COPPER(II)NAPTH	YES*	COMBUSTIBLE	SLIGHTLY
CRUDE OIL, COAL TAR	YES*	COMBUSTIBLE	MODERATELY

CHEMICAL	FLOATABILITY	FLAMMABILITY	TOXICITY
m-CRESOL	YES*	NON-COMBUS.	HIGHLY
p-CRESOL	YES*	NON-COMBUS.	HIGHLY
CRESOLS	YES*	COMBUSTIBLE	HIGHLY
CRESYLATE SPENT CAUSTIC	NO DATA	NO DATA	NO DATA
CROTONALDEHYDE	YES*	FLAMMABLE	HIGHLY
CUMENE	YES	FLAMMABLE	MODERATELY
CUMENE HYDROPEROXIDE	YES*	COMBUSTIBLE	MODERATELY
CYCLOHEXANE	YES	FLAMMABLE	SLIGHTLY
CYCLOHEXANONE	YES*	COMBUSTIBLE	MODERATELY
CYCLOHEXANONE PEROXIDE	YES*	COMBUSTIBLE	MODERATELY
CYCLOHEXENE	YES	FLAMMABLE	SLIGHTLY
CYCLOPENTANE	YES	FLAMMABLE	SLIGHTLY
CYCLOPROPANE	YES*	HIGHLY	SLIGHTLY
p-CYNEHE	YES	COMBUSTIBLE	MODERATELY
DECABORANE	YES*	COMBUSTIBLE	HIGHLY
DECANTHRONAPHTHALENE	YES*	COMBUSTIBLE	MODERATELY
n-DECALDEHYDE	YES	COMBUSTIBLE	MODERATELY
1-DECENE	YES	COMBUSTIBLE	SLIGHTLY
n-DECYL ACRYLATE	YES	NON-COMBUS.	MODERATELY
n-DECYL ALCOHOL	YES	COMBUSTIBLE	MODERATELY
n-DECYLBENZENE	YES	NON-COMBUS.	MODERATELY
DI-n-AMYL PHTHALATE	YES	NON-COMBUS.	MODERATELY
DIBENZYL ETHER	YES	NON-COMBUS.	MODERATELY
DI-n-BUTYLAMINE	YES*	COMBUSTIBLE	HIGHLY
DI-n-BUTYL ETHER	YES	FLAMMABLE	MODERATELY
DI-n-BUTYL KETONE	YES	COMBUSTIBLE	HIGHLY
DIBUTYLPHENOL	YES	NON-COMBUS.	MODERATELY
DIBUTYL PHTHALATE	YES*	NON-COMBUS.	MODERATELY
4,4-DICHLORO-DI-TRICHLOROMETHYLBENZENE	YES	FLAMMABLE	MODERATELY
DICYCLOPENTADIENE	YES	FLAMMABLE	MODERATELY
DIETHYLBENZENE	YES*	COMBUSTIBLE	MODERATELY
DIETHYL CARBONATE	YES	FLAMMABLE	MODERATELY
DIETHYLENE GLYCOL MONOBUTYL ETHER ACETATE	YES*	NON-COMBUS.	SLIGHTLY
DI-(2-ETHYLBENZYL)PHOSPHORIC ACID	YES	NON-COMBUS.	MODERATELY
DIETHYL KETONE	YES*	FLAMMABLE	SLIGHTLY
1,1-DIFLUOROETHANE	YES	FLAMMABLE	NO DATA
DINEPTYL PHTHALATE	YES	FLAMMABLE	NO DATA
DIISOBUTYLAMINE	YES*	FLAMMABLE	HIGHLY
DIISOBUTYLALCOHOL	YES	COMBUSTIBLE	SLIGHTLY
DIISOBUTYLENE	YES	FLAMMABLE	SLIGHTLY
DIISOBUTYL KETONE	YES	COMBUSTIBLE	MODERATELY
DIISOBUTYL PHTHALATE	YES*	NON-COMBUS.	SLIGHTLY
DIISODECYL PHTHALATE	YES	NON-COMBUS.	SLIGHTLY
DIISONONYL PHTHALATE	YES	FLAMMABLE	NO DATA
DIISOOCTYL PHTHALATE	YES	NON-COMBUS.	SLIGHTLY
DIISOPROPYLAMINE	YES	FLAMMABLE	HIGHLY
2,2-DIETHYL OCTANOIC ACID	YES*	FLAMMABLE	NO DATA
DINETHYLPOLYSILOXANE	YES	NON-COMBUS.	MODERATELY
DINETHYL SULFIDE	YES	HIGHLY	MODERATELY

CHEMICAL	FLATABILITY	FLAMMABILITY	TOXICITY
DIOCTYL ADIPATE	YES	NON-COMBUS.	SLIGHTLY
DIOCTYL PHTHALATE	YES	NON-COMBUS.	SLIGHTLY
DIPENTENE	YES	COMBUSTIBLE	SLIGHTLY
DI-n-PROPYLAMINE	YES	FLAMMABLE	HIGHLY
DISTILLATES: FLASHED FEED STOCKS	YES	COMBUSTIBLE	MODERATELY
DISTILLATES: STRAIGHT RUN	YES	COMBUSTIBLE	MODERATELY
DIUNDECYL PHTHALATE	NO DATA	FLAMMABLE	NO DATA
DODECANOL	YES	NON-COMBUS.	SLIGHTLY
DODECENE	YES	COMBUSTIBLE	SLIGHTLY
1-DODECENE	YES	COMBUSTIBLE	SLIGHTLY
DODECYLBENZENE	YES	NON-COMBUS.	SLIGHTLY
DODECYLDIPHENYL OXIDE DISULFONATE	NO DATA	NO DATA	HIGHLY
DODECYLMETHACRYLATE	YES	FLAMMABLE	NO DATA
DODECYL PENTA DECYL METHACRYLATE	NO DATA	NO DATA	NO DATA
EPOXIDIZED VEGETABLE OILS	YES	NON-COMBUS.	NOT TOXIC
ETHANE	YES	HIGHLY	SLIGHTLY
ETHOXYDINHYDROPIRAN	YES*	COMBUSTIBLE	MODERATELY
ETHOXYLATED DODECANOL	YES*	FLAMMABLE	SLIGHTLY
ETHOXYLATED PENTADECANOL	YES*	FLAMMABLE	NO DATA
ETHOXYLATED TETRADECANOL	YES*	FLAMMABLE	NO DATA
ETHOXYLATED TRIDECANOL	YES*	FLAMMABLE	MODERATELY
ETHYL ACETATE	YES*	FLAMMABLE	SLIGHTLY
ETHYL ACETOACETATE	YES*	COMBUSTIBLE	MODERATELY
ETHYL ACRYLATE	YES*	FLAMMABLE	MODERATELY
ETHYLBENZENE	YES	FLAMMABLE	MODERATELY
ETHYL BUTANOL	YES	COMBUSTIBLE	SLIGHTLY
n-ETHYL-n-BUTYLAMINE	YES	FLAMMABLE	HIGHLY
ETHYL BUTYRATE	YES	FLAMMABLE	SLIGHTLY
ETHYL CHLORIDE	YES*	HIGHLY	MODERATELY
ETHYL CYCLODIANE	YES	FLAMMABLE	SLIGHTLY
n-ETHYL CYCLOHEXYLAMINE	YES*	FLAMMABLE	HIGHLY
ETHYLENE GLYCOL DIETHYL ETHER	YES*	FLAMMABLE	MODERATELY
ETHYLENE GLYCOL MONOBUTYL ETHER ACETATE	YES	COMBUSTIBLE	MODERATELY
ETHYL ETHER	YES*	HIGHLY	MODERATELY
ETHYL FORMATE	YES	FLAMMABLE	MODERATELY
ETHYLNITRALBENZYDE	YES*	COMBUSTIBLE	MODERATELY
2-ETHYL NDIANOL	YES*	COMBUSTIBLE	MODERATELY
2-ETHYLNEXYL ACRYLATE	YES*	COMBUSTIBLE	MODERATELY
ETHYLNEXYL TALLATE	YES	NON-COMBUS.	NO DATA
ETHYLBENENORBORNENE	YES	FLAMMABLE	MODERATELY
ETHYL MERCAPTAN	YES	HIGHLY	HIGHLY
ETHYL METHACRYLATE	YES	FLAMMABLE	SLIGHTLY
ETHYL NITRITE	YES	HIGHLY	MODERATELY
2-ETHYL-3-PROPYLACROLEIN	YES	COMBUSTIBLE	MODERATELY
ETHYL TOLUENE	YES	COMBUSTIBLE	HIGHLY
GAS OIL: CRACKED	YES	FLAMMABLE	SLIGHTLY
GASOLINE: AUTOMOTIVE (4.236 Pb/GAL)	YES	FLAMMABLE	SLIGHTLY
GASOLINE: AVIATION (4.066 Pb/GAL)	YES	FLAMMABLE	SLIGHTLY
GASOLINE BLENDING STOCKS: ALKYLATES	YES	FLAMMABLE	SLIGHTLY

CHEMICAL	FLOATABILITY	FLAMMABILITY	TOXICITY
GASOLINE BLENDING STOCKS: REFORMATES	YES	FLAMMABLE	SLIGHTLY
GASOLINE: CASINGHEAD	YES	FLAMMABLE	SLIGHTLY
GASOLINE: POLYMER	YES	FLAMMABLE	SLIGHTLY
GASOLINE: STRAIGHT RUN	YES	FLAMMABLE	SLIGHTLY
HEPTANE	YES	FLAMMABLE	SLIGHTLY
HEPTANOIC ACID	YES*	FLAMMABLE	SLIGHTLY
HEPTANOL	YES*	COMBUSTIBLE	SLIGHTLY
1-HEPTENE	YES	FLAMMABLE	SLIGHTLY
HEXADECYLTRIMETHYL AMMONIUM CHLORIDE	YES*	FLAMMABLE	HIGHLY
n-HEXALDEHYDE	YES	FLAMMABLE	MODERATELY
HEXAMETHYLENEMINE	YES*	FLAMMABLE	HIGHLY
HEXANE	YES	FLAMMABLE	SLIGHTLY
HEXANOL	YES*	COMBUSTIBLE	SLIGHTLY
1-HEXENE	YES	FLAMMABLE	SLIGHTLY
HYDROGEN, LIQUIFIED	YES*	HIGHLY	SLIGHTLY
HYDROGEN SULFIDE	YES*	HIGHLY	HIGHLY
ISOBUTYL ACETATE	YES*	FLAMMABLE	SLIGHTLY
ISOBUTYL ALCOHOL	YES*	COMBUSTIBLE	SLIGHTLY
ISOBUTANE	YES	HIGHLY	SLIGHTLY
ISOBUTYL ACETATE	YES	FLAMMABLE	SLIGHTLY
ISOBUTYLENE	YES	HIGHLY	SLIGHTLY
ISOBUTYRONITRILE	YES*	FLAMMABLE	HIGHLY
ISODECALDENE	YES	COMBUSTIBLE	MODERATELY
ISODECYL ACRYLATE	YES	NON-COMBUS.	SLIGHTLY
ISODECYL ALCOHOL	YES	COMBUSTIBLE	SLIGHTLY
ISOHEXANE	YES	FLAMMABLE	SLIGHTLY
ISOOCTALDEHYDE	YES	FLAMMABLE	SLIGHTLY
ISOOCTANE	YES	FLAMMABLE	SLIGHTLY
ISOOCTYL ALCOHOL	YES	COMBUSTIBLE	MODERATELY
ISOPENTANE	YES	HIGHLY	SLIGHTLY
ISOPHORONE	YES*	COMBUSTIBLE	HIGHLY
ISOPHORONE DIAMINE	YES	COMBUSTIBLE	HIGHLY
ISOPHORONE DIISOCYANATE	YES	COMBUSTIBLE	HIGHLY
ISOPRENE	YES	HIGHLY	MODERATELY
ISOPROPYL ACETATE	YES*	FLAMMABLE	SLIGHTLY
ISOPROPYL CYCLOHEXANE	YES	FLAMMABLE	SLIGHTLY
ISOPROPYL ETHER	YES	FLAMMABLE	MODERATELY
ISOPROPYL MERCAPTAN	YES*	FLAMMABLE	HIGHLY
ISOVALERALDEHYDE	YES*	FLAMMABLE	MODERATELY
JET FUEL: JP-1 (KEROSENE)	YES	COMBUSTIBLE	SLIGHTLY
JET FUEL: JP-3	YES	COMBUSTIBLE	SLIGHTLY
JET FUEL: JP-4	YES	FLAMMABLE	SLIGHTLY
JET FUEL: JP-5 (KEROSENE, HEAVY)	YES	COMBUSTIBLE	SLIGHTLY
KEROSENE	YES	COMBUSTIBLE	SLIGHTLY
LAURYL PEROXIDE	YES	COMBUSTIBLE	HIGHLY
LAURYL MERCAPTAN	YES	NON-COMBUS.	MODERATELY
LINEAR ALCOHOLS (12-15 CARBONS)	YES	COMBUSTIBLE	SLIGHTLY
LIQUIFIED PETROLEUM GAS	YES	HIGHLY	SLIGHTLY
MALEIC ANHYDRIDE	YES*	NON-COMBUS.	HIGHLY

CHEMICAL	FLOATABILITY	FLAMMABILITY	TOXICITY
METHYL OXIDE	YES*	FLAMMABLE	MODERATELY
METHALLYL CHLORIDE	YES	FLAMMABLE	MODERATELY
METHANE	YES*	HIGHLY	SLIGHTLY
METHYL ACETYLENE, PROPADIENE MIXTURE	YES	HIGHLY	SLIGHTLY
METHYLACRYLATE	YES*	FLAMMABLE	SLIGHTLY
METHYL AMYL ACETATE	YES	COMBUSTIBLE	MODERATELY
METHYL AMYL ALCOHOL	YES*	COMBUSTIBLE	HIGHLY
N-METHYLANILINE	YES*	COMBUSTIBLE	HIGHLY
METHYL-t-BUTYL ETHER	YES	FLAMMABLE	NO DATA
METHYL-n-BUTYL KETONE	YES*	FLAMMABLE	MODERATELY
METHYLCYCLOPENTANE	YES	FLAMMABLE	SLIGHTLY
2-METHYL-6-ETHYL ANILINE	YES*	FLAMMABLE	MODERATELY
2-METHYL-5-ETHYLPRYDINE	YES*	COMBUSTIBLE	MODERATELY
METHYL HYDRAZINE	YES*	FLAMMABLE	HIGHLY
METHYL ISOBUTYL CARBINOL	YES*	COMBUSTIBLE	MODERATELY
METHYL ISOBUTYL KETONE	YES*	FLAMMABLE	MODERATELY
METHYL METHACRYLATE	YES	FLAMMABLE	SLIGHTLY
METHYL NAPHTHALENE	YES*	COMBUSTIBLE	MODERATELY
2-METHYL PENTENE	YES	FLAMMABLE	SLIGHTLY
METHYL STYRENE, ALPHA	YES	COMBUSTIBLE	MODERATELY
METHYL VINYL KETONE	YES*	FLAMMABLE	HIGHLY
MINERAL SPIRITS	YES	COMBUSTIBLE	SLIGHTLY
NAPTHA:COAL TAR	YES	COMBUSTIBLE	MODERATELY
NAPTHA:SOLVENT	YES	COMBUSTIBLE	MODERATELY
NAPTHA:STODDARD SOLVENT	YES	COMBUSTIBLE	MODERATELY
NAPTHA:VM & P (75% NAPTHA)	YES	FLAMMABLE	SLIGHTLY
NAPHTHIC ACID	YES	NON-COMBUS.	MODERATELY
NEOHEXANE	YES	FLAMMABLE	SLIGHTLY
NITROGEN, LIQUIFIED	YES*	FLAMMABLE	NO DATA
1-NITROPROPANE	YES*	FLAMMABLE	MODERATELY
2-NITROPROPANE	YES*	FLAMMABLE	MODERATELY
NONANE	YES	FLAMMABLE	MODERATELY
NONANOL	YES	COMBUSTIBLE	SLIGHTLY
NONENE	YES	FLAMMABLE	SLIGHTLY
1-NONENE	YES	FLAMMABLE	SLIGHTLY
NONYL PHENOL	YES*	NON-COMBUS.	MODERATELY
OCTANE	YES	FLAMMABLE	SLIGHTLY
OCTANOL	YES	COMBUSTIBLE	SLIGHTLY
1-OCTENE	YES	FLAMMABLE	SLIGHTLY
OCTYL EPOXYTALLATE	YES*	NON-COMBUS.	SLIGHTLY
OIL: CLARIFIED	YES	NO DATA	SLIGHTLY
OIL: CRUDE	YES	FLAMMABLE	SLIGHTLY
OIL: DIESEL	YES	COMBUSTIBLE	SLIGHTLY
OIL, EDIBLE: CASTOR	YES	NON-COMBUS.	NOT TOXIC
OIL, EDIBLE: COCONUT	YES	NON-COMBUS.	NOT TOXIC
OIL, EDIBLE: COTTONSEED	YES	NON-COMBUS.	SLIGHTLY
OIL, EDIBLE: FISH	YES	NON-COMBUS.	NOT TOXIC
OIL, EDIBLE: LARD	YES	NON-COMBUS.	NOT TOXIC
OIL, EDIBLE: OLIVE	YES	NON-COMBUS.	NOT TOXIC

CHEMICAL	FLOATABILITY	FLAMMABILITY	TOXICITY
OIL, EDIBLE: PALM	YES	NON-COMBUS.	NOT TOXIC
OIL, EDIBLE: PEANUT	YES	NON-COMBUS.	NOT TOXIC
OIL, EDIBLE: SAFFLOWER	YES	NON-COMBUS.	NOT TOXIC
OIL, EDIBLE: SOYA BEAN	YES	NON-COMBUS.	NOT TOXIC
OIL, EDIBLE: TUCUM	YES	NON-COMBUS.	NOT TOXIC
OIL, EDIBLE: VEGETABLE	YES	NON-COMBUS.	NOT TOXIC
OIL, FUEL: NO. 1 (KEROSENE)	YES	NON-COMBUS.	SLIGHTLY
OIL, FUEL: NO. 1-D	YES	COMBUSTIBLE	SLIGHTLY
OIL, FUEL: NO. 2	YES*	COMBUSTIBLE	SLIGHTLY
OIL, FUEL: NO. 2-D	YES	COMBUSTIBLE	SLIGHTLY
OIL, FUEL: NO. 4	YES	COMBUSTIBLE	SLIGHTLY
OIL, FUEL: NO. 5	YES	COMBUSTIBLE	SLIGHTLY
OIL, FUEL: NO. 6	YES	COMBUSTIBLE	SLIGHTLY
OIL, MISC: ABSORPTION	YES	NON-COMBUS.	MODERATELY
OIL, MISC: CASHEW NUT SHELL (UNTREATED)	YES	NO DATA	SLIGHTLY
OIL, MISC: COAL TAR	YES	FLAMMABLE	SLIGHTLY
OIL, MISC: CROTON	YES	NO DATA	SLIGHTLY
OIL, MISC: LINSEED	YES	NON-COMBUS.	NOT TOXIC
OIL, MISC: LUBRICATING	YES	NON-COMBUS.	SLIGHTLY
OIL, MISC: MINERAL	YES	NON-COMBUS.	SLIGHTLY
OIL, MISC: MINERAL SEAL	YES	COMBUSTIBLE	SLIGHTLY
OIL, MISC: MOTOR	YES	NON-COMBUS.	SLIGHTLY
OIL, MISC: HEATSPOOT	YES	NON-COMBUS.	SLIGHTLY
OIL, MISC: PENETRATING	YES	NON-COMBUS.	SLIGHTLY
OIL, MISC: RANGE	YES	NON-COMBUS.	SLIGHTLY
OIL, MISC: RESIN	YES	NON-COMBUS.	SLIGHTLY
OIL, MISC: ROAD	YES	NON-COMBUS.	SLIGHTLY
OIL, MISC: ROSIN	YES	NON-COMBUS.	SLIGHTLY
OIL, MISC: SPERM	YES	NON-COMBUS.	SLIGHTLY
OIL, MISC: SPINDLE	YES	COMBUSTIBLE	SLIGHTLY
OIL, MISC: SPRAY	YES	COMBUSTIBLE	SLIGHTLY
OIL, MISC: TALL	YES	NON-COMBUS.	SLIGHTLY
OIL, MISC: TANNER'S	YES	NON-COMBUS.	SLIGHTLY
OIL, MISC: TRANSFORMER	YES	NON-COMBUS.	MODERATELY
OIL, MISC: TURBINE	YES	NON-COMBUS.	SLIGHTLY
OLEIC ACID	YES	NON-COMBUS.	NOT TOXIC
PENTADECANOL	YES	NON-COMBUS.	NO DATA
1,3-PENTADIENE	YES	HIGHLY	SLIGHTLY
1,4-PENTADIENE	YES	HIGHLY	SLIGHTLY
n-PENTANE	YES	HIGHLY	SLIGHTLY
1-PENTENE	YES	HIGHLY	MODERATELY
PETROLATUM	YES	NON-COMBUS.	NOT TOXIC
PETROLEUM NAPHTHA	YES	HIGHLY	SLIGHTLY
POLYBUTENE	YES	NON-COMBUS.	SLIGHTLY
POLYETHYLENE POLYAMINES	NO DATA	NO DATA	HIGHLY
POLYPROPYLENE	YES	NO DATA	NO DATA
POLYPROPYLENE GLYCOL	YES*	NON-COMBUS.	SLIGHTLY
n-PROPYL ACETATE	YES*	FLAMMABLE	MODERATELY
PROPYLENE BUTYLENE POLYMER	YES	FLAMMABLE	NO DATA



CHEMICAL	FLOATABILITY	FLAMMABILITY	TOXICITY
PROPYLENE TETRAMER	YES	COMBUSTIBLE	SLIGHTLY
n-PROPYL ETHER	YES*	FLAMMABLE	MODERATELY
PYRETHRINS	YES	NO DATA	MODERATELY
STEARIC ACID	YES	NON-COMBUS.	SLIGHTLY
STYRENE	YES	FLAMMABLE	MODERATELY
TALLOW	YES	NON-COMBUS.	SLIGHTLY
TALLOW FATTY ALCOHOL	YES	NON-COMBUS.	SLIGHTLY
TETRADECANOL	YES	NON-COMBUS.	SLIGHTLY
1-TETRADECENE	YES	NON-COMBUS.	SLIGHTLY
TETRADECYLBENZENE	YES	NON-COMBUS.	NO DATA
TETRAHYDRONAPHTHALENE	YES	COMBUSTIBLE	MODERATELY
TOLUENE	YES	FLAMMABLE	MODERATELY
o-TOLUIDINE	YES*	COMBUSTIBLE	HIGHLY
TRIDECANOL	YES	NON-COMBUS.	SLIGHTLY
1-TRIDECENE	YES	COMBUSTIBLE	SLIGHTLY
TRIETHYLAMINE	YES	FLAMMABLE	HIGHLY
TRIETHYLBENZENE	YES	COMBUSTIBLE	MODERATELY
TRIMETHYLACETIC ACID	YES	COMBUSTIBLE	MODERATELY
TURPENTINE	YES	FLAMMABLE	SLIGHTLY
UNDECANOL	YES	NON-COMBUS.	SLIGHTLY
1-UNDECENE	YES	COMBUSTIBLE	NO DATA
n-UNDECYLBENZENE	YES	NON-COMBUS.	NO DATA
n-VALERALDEHYDE	YES	FLAMMABLE	MODERATELY
VINYL ACETATE	YES	FLAMMABLE	MODERATELY
VINYL CHLORIDE	YES	HIGHLY	HIGHLY
VINYL ETNYL ETHER	YES*	HIGHLY	MODERATELY
VINYL FLUORIDE	YES*	HIGHLY	MODERATELY
VINYL METHYL ETHER	YES*	HIGHLY	MODERATELY
VINYL NODDECANATE	YES*	NO DATA	HIGHLY
VINYL TOLUENE	YES*	COMBUSTIBLE	MODERATELY
WAX: CARNAUBA	YES	NON-COMBUS.	NOT TOXIC
WAX: PARAFFIN	YES	NON-COMBUS.	NOT TOXIC
m-XYLENE	YES	FLAMMABLE	SLIGHTLY
o-XYLENE	YES	FLAMMABLE	SLIGHTLY
p-XYLENE	YES	FLAMMABLE	SLIGHTLY
XYLENOL	YES*	NON-COMBUS.	MODERATELY

## TABLE A-2. Physical-Chemical Characteristics of Floating Hazardous Chemicals

The Specific Gravity of a solid or liquid is the ratio of the weight of the substance to the weight of an equal volume of water at a specified temperature.

The Dielectric Constant of a medium is defined by  $D$  in the Coulomb equation,  $F = \frac{Q Q'}{R^2 D}$ , where  $F$  = the force of attraction between two charges,  $Q$  and  $Q'$ , separated by a distance  $R$ .

Polarity: Although a molecule may be neutral and have no net charge, it can be polarized resulting in a separation of charge within the molecule. Polarization may exist permanently in a molecule or it may be induced by the approach of another molecule which itself has a charge.

Surface Tension: Two fluids in contact exhibit various properties due to molecular attractions which appear to arise from a tension in the surface of separation. Generally, the higher the surface tension of a substance, the more the substance adheres to itself.

Solubility Rating: There is a lack of uniformity in the literature concerning the method of reporting water solubility. Numerical data concerning water solubility scarcely appears in the literature. Based on available quantitative and qualitative data, the chemicals in this table are listed as immiscible (IM), slightly soluble (SL), soluble (SO), and very soluble (YS) in water.

CHEMICAL	SPECIFIC GRAVITY	DIELECTRIC CONSTANT	POLARITY	SURFACE TENSION (dynes/cm)	SOLUBILITY RATING (in water)
ACETOPHENONE	1.028	17.4	POLAR	39.5	SL
ACETYL ACETONE	0.976	2.5	NONPOLAR	31.2	SL
ACETYLENE	0.002	25.1...	POLAR		SL
ADIPONITRILE	0.950		POLAR		IM
ALLYL CHLORIDE	0.900	8.2	POLAR	28.9	SL
n-AMYL ACETATE	0.900		SLIGHTLY	12.0	SL
sec-AMYL ACETATE	0.900		SLIGHTLY		SL
tert-AMYL ACETATE	0.874		SLIGHTLY		SL
n-AMYL ALCOHOL	0.800	13.9	POLAR	25.6	IM
n-AMYL CHLORIDE	0.900	6.6	POLAR	23.6	IM
n-AMYL MERCAPTAN	0.857		SLIGHTLY	26.8	IM
n-AMYL METHYL KETONE	0.821		POLAR		IM
n-AMYL NITRATE	1.000		POLAR		SL
iso-AMYL NITRITE	0.876		POLAR	2.0	IM
AMYL PHTHALATE	1.000		POLAR		SL
ANILINE	1.022	6.8	POLAR	42.7	IM
ASPHALT	1.100		NONPOLAR		SL
BENZALDEHYDE	1.100	17.8	POLAR	40.0	IM
BENZENE	0.900	2.2	NONPOLAR	28.9	IM
BENZONITRILE	1.010	25.2	POLAR	39.4	SL
BENZYL ALCOHOL	1.050	13.5	POLAR	40.0	IM
BUTADIENE	0.834		NONPOLAR	16.6	IM
BUTANE	0.600	1.7	NONPOLAR	12.5	SL
n-BUTYL ACETATE	0.900	5.0	SLIGHTLY	25.2	SL
sec-BUTYL ACETATE	0.865	5.0	SLIGHTLY	23.6	IM
tert-BUTYL ACETATE	0.896		SLIGHTLY	24.1	SL
iso-BUTYL ACRYLATE	0.889		NONPOLAR	2.5	IM
n-BUTYL ACRYLATE	0.900		NONPOLAR	20.0	SL
BUTYL BUTYRATE	0.900		SLIGHTLY		IM
BUTYL/DECYL/CETYL-EICOSYL METHACRYLATE	0.890		NONPOLAR		IM
BUTYLENE	0.595		NONPOLAR		IM
n-BUTYL ETHER	0.800	3.1	NONPOLAR	12.5	IM
tert-BUTYL HYDROPEROXIDE	0.900		SLIGHTLY	22.9	SL
n-BUTYL MERCAPTAN	0.834	5.7	POLAR	20.9	SL
			SLIGHTLY		IM

CHEMICAL	SPECIFIC GRAVITY	DIELECTRIC CONSTANT	POLARITY	SURFACE TENSION (dynes/cm)	SOLUBILITY RATING (in water)
iso-BUTYL METHACRYLATE	0.886		NONPOLAR		SL
n-BUTYL METHACRYLATE	0.900		NONPOLAR	3.0	IM
p-tert-BUTYLPHENOL	1.037		POLAR		SL
iso-BUTYRALDEHYDE	0.794		SLIGHTLY	22.0	IM
n-BUTYRALDEHYDE	0.800		SLIGHTLY	24.8	IM
CAMPHENE	0.870	2.3	NONPOLAR		IM
CAMPHOR (OIL)	0.900	11.4	POLAR		IM
CARBOLIC OIL	1.040		NONPOLAR	41.0	IM
CARBON MONOXIDE	0.001		POLAR	11.4	IM
CARENE	0.860		NONPOLAR		IM
CEXYL ECOSYL METHACRYLATE	0.900		NONPOLAR		SL
CHLOROPRENE	0.954		SLIGHTLY		IM
COLLODION	0.772		POLAR		IM
COPPER NAPHTHATE(IC) COPPER(II)NAPTH	1.020		SLIGHTLY	20.0	IM
CREOSOTE, COAL TAR	1.050		NONPOLAR		SL
n-CRESOL	1.034	11.8	POLAR	35.7	SL
p-CRESOL	1.000	9.9	POLAR	34.9	IM
CRESOLS	1.030		POLAR		IM
CRESYLATE SPENT CAUSTIC			SLIGHTLY		SL
CROTONALDEHYDE	0.900		SLIGHTLY		IM
CUMENE	0.864	2.3	NONPOLAR	28.2	SL
CUMENE HYDROPEROXIDE	1.030		POLAR	25.0	IM
CYCLOHEXANE	0.779		NONPOLAR	25.0	SL
CYCLOHEXANONE	0.997		POLAR	34.5	IM
CYCLOHEXANONE PEROXIDE	1.050		POLAR	30.0	IM
CYCLOHEXENE	0.811	2.2	NONPOLAR	26.8	IM
CYCLOPENTANE	0.751	1.9	NONPOLAR	22.6	SL
CYCLOPROPANE	0.720		NONPOLAR	22.0	IM
p-CYMENE	0.857	2.2	NONPOLAR	29.4	SL
DECABORANE	0.900		NONPOLAR		SL
DECAHYDRONAPHTHALENE	0.897	20.1	POLAR	29.9	IM
n-DECALDEHYDE	0.830		SLIGHTLY	28.0	IM
1-DECENE	0.748		NONPOLAR	24.0	IM
n-DECYL ACRYLATE	0.900		NONPOLAR		IM

CHEMICAL	SPECIFIC GRAVITY	DIELECTRIC CONSTANT	POLARITY	SURFACE TENSION (dynes/cm)	SOLUBILITY RATING (in water)
n-DECYL ALCOHOL	0.829	8.1	POLAR	28.9	IM
n-DECYLBENZENE	0.900		NONPOLAR	29.9	IM
DI-n-ANYL PHTHALATE	1.000		POLAR		IM
DIBENZYL ETHER	1.000		NONPOLAR		SL
DI-n-BUTYLAMINE	0.800		SLIGHTLY	24.6	IM
DI-n-BUTYL ETHER	0.800	3.1	NONPOLAR	22.4	IM
DI-n-BUTYL KETONE	0.822		POLAR	26.6	IM
DIBUTYLPHENOL	0.914		NONPOLAR		IM
n-BUTYL PHTHALATE	1.049	6.4	POLAR	34.0	IM
4,4-DICHLORO- <i>o</i> -1-TRICHLOROMETHYLBENZYLHYDRO	0.900		POLAR		IM
DICYCLOPENTADIENE	0.976		NONPOLAR		SL
DIETHYLBENZENE	0.860		NONPOLAR	32.1	IM
DIETHYL CARBONATE	0.975	2.8	NONPOLAR	26.4	SL
DIETHYLENE GLYCOL MONOBUTYL ETHER ACETAT	0.985		POLAR	22.0	IM
DI-(2-ETHYLHEXYL) PHOSPHORIC ACID	0.977		POLAR	30.0	SL
DIETHYL KETONE	0.800	17.0	POLAR	25.7	IM
1,1-DIFLOROETHANE	0.909		POLAR	11.2	IM
DIDEPHYL PHTHALATE	1.000		POLAR		SL
DIISOBUTYLAMINE	0.746		SLIGHTLY	22.2	IM
DIISOBUTYL CARBINOL	0.800		POLAR		IM
DIISOBUTYLENE	0.715		NONPOLAR	20.7	IM
DIISOBUTYL KETONE	0.800		SLIGHTLY	23.9	IM
DIISOBUTYL PHTHALATE	1.049		SLIGHTLY		IM
DIISODECYL PHTHALATE	0.967		SLIGHTLY		IM
DIISOMONYL PHTHALATE	1.000		SLIGHTLY		IM
DIISOCTYL PHTHALATE	1.000		SLIGHTLY		SO
DIISOPROPYLAMINE	0.722	2.9	NONPOLAR	19.6	SL
2,2-DIMETHYL OCTANOIC ACID	0.910		SLIGHTLY		IM
DIMETHYLPOLYSILOXANE	0.980		NONPOLAR	19.0	IM
DIMETHYL SULFIDE	0.846		POLAR	26.5	IM
DIOCTYL ADIPATE	0.900		SLIGHTLY	15.0	IM
DIOCTYL PHTHALATE	0.986		SLIGHTLY	15.0	IM
DIPENTENE	0.840	2.3	NONPOLAR	27.1	IM
DI-n-PROPYLAMINE	0.738		POLAR		IM

CHEMICAL	SPECIFIC GRAVITY	DIELECTRIC CONSTANT	POLARITY	SURFACE TENSION (dynes/cm)	SOLUBILITY RATING (in water)
DISTILLATES: FLASHED FEED STOCKS	0.710			19.0	IM
DISTILLATES: STRAIGHT RUN	0.731			19.0	IM
DIUNDECYL FTHALATE	1.050	5.1	POLAR		IM
DODECANOL	0.835		SLIGHTLY	29.4	IM
DODECENE	0.770		NONPOLAR	25.0	IM
1-DODECENE	0.758		NONPOLAR		IM
DODECYLBENZENE	0.900		NONPOLAR		IM
DODECYLDIPHENYL OXIDE DISULFONATE	0.910		POLAR		IM
DODECYLMETHACRYLATE					IM
DODECYL PENTA DECYL METHACRYLATE					IM
EPOXIDIZED VEGETABLE OILS				1.1	IM
ETHANE	1.000		SLIGHTLY		IM
ETHOXYDIHYDROPYRAN	0.572		NONPOLAR		IM
ETHOXYLATED DODECANOL	1.000		NONPOLAR		SL
ETHOXYLATED DODECANOL	1.020		POLAR		SL
ETHOXYLATED PENTADECANOL	1.007		SLIGHTLY		SL
ETHOXYLATED TETRADECANOL	1.007		SLIGHTLY		SL
ETHOXYLATED TRIDECANOL	1.000		SLIGHTLY		SL
ETHYL ACETATE	0.900	6.0	SLIGHTLY	23.7	SL
ETHYL ACETOACETATE	1.028	15.7	POLAR		SL
ETHYL ACRYLATE	0.900		NONPOLAR		IM
ETHYLENE	0.900	2.4	NONPOLAR	29.2	IM
ETHYL BENZENE	0.800	6.1	SLIGHTLY		IM
ETHYL BUTANOL					IM
N-ETHYL-n-BUTYLAMINE	0.700		SLIGHTLY		IM
ETHYL BUTYRATE	0.900	5.1	SLIGHTLY		SL
ETHYL CHLORIDE	0.900	9.4	POLAR	20.6	IM
ETHYL CYCLOHEXANE	0.788	2.0	NONPOLAR		SL
N-ETHYL CYCLOHEXYLAMINE	0.800		SLIGHTLY		SL
ETHYLENE GLYCOL DIETHYL ETHER	0.848		POLAR		IM
ETHYLENE GLYCOL MONOBUTYL ETHER ACETATE	0.900		POLAR		SL
ETHYL ETHER	0.713	4.2	SLIGHTLY	16.6	IM
ETHYL FORMATE	0.917		SLIGHTLY		SL
ETHYLHEXALDEHYDE	0.900		NONPOLAR		SL
2-ETHYL HEXANOL	0.800	4.4	SLIGHTLY		SL
2-ETHYLHEXYL ACRYLATE	0.887		NONPOLAR		IM

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CHEMICAL	SPECIFIC GRAVITY	DIELECTRIC CONSTANT	POLARITY	SURFACE TENSION (dynes/cm)	SOLUBILITY RATING (in water)
ETHYLHEXYL TALLATE	0.950		NONPOLAR		IM
ETHYLIDENEBORNORBIENE	0.896		SLIGHTLY	23.5	IM
ETHYL MERCAPTAN	0.800		NONPOLAR		IM
ETHYL METHACRYLATE	0.900		POLAR		IM
ETHYL NITRITE	0.903		NONPOLAR		IM
2-ETHYL-3-PROPYLACROLEIN	0.848		NONPOLAR		IM
ETHYL TOLUENE	0.880		NONPOLAR		IM
GAS OIL: CRACKED	0.848		NONPOLAR		IM
GASOLINE: AUTOMOTIVE (4.23G Pb/GAL)	0.800		NONPOLAR		IM
GASOLINE: AVIATION (4.86G Pb/GAL)	0.711		NONPOLAR		IM
GASOLINE BLENDING STOCKS: ALKYLATES	0.710		NONPOLAR		IM
GASOLINE BLENDING STOCKS: REFORMATES	0.793		NONPOLAR		IM
GASOLINE: CASINGHEAD	0.671		NONPOLAR		IM
GASOLINE: POLYMER	0.710		NONPOLAR		IM
GASOLINE: STRAIGHT RUN	0.710		NONPOLAR		IM
HEPTANE	0.700	1.9	NONPOLAR	20.1	SL
HEPTANOIC ACID	0.919		SLIGHTLY	28.2	SL
HEPTANOL	0.819	12.1	POLAR		IM
1-HEPTENE	0.700	2.0	NONPOLAR	20.3	SL
HEXADECYLTRIMETHYL AMMONIUM CHLORIDE	0.900		POLAR		IM
n-HEXALDEHYDE	0.800		NONPOLAR		SL
HEXAMETHYLENEAMINE	0.880		POLAR		IM
HEXANE	0.660	1.8	NONPOLAR	18.4	SL
HEXANOL	0.815	13.7	POLAR	25.8	IM
1-HEXENE	0.673	2.0	NONPOLAR	18.4	SL
HYDROGEN, LIQUIFIED	0.070		NONPOLAR		SL
HYDROGEN SULFIDE	0.916	5.9	SLIGHTLY		SL
ISOAMYL ACETATE	0.900	4.8	SLIGHTLY		SL
ISOAMYL ALCOHOL	0.800	14.7	POLAR		IM
ISOBUTANE	0.557	1.7	NONPOLAR	15.3	IM
ISOBUTYL ACETATE	0.900	5.2	SLIGHTLY	23.7	IM
ISOPENTYLENE	0.590		NONPOLAR		SL
ISOBUTYRONITRILE	0.761		POLAR		IM
ISODECALDEHYDE	0.800	20.4	NONPOLAR		IM

CHEMICAL	SPECIFIC GRAVITY	DIELECTRIC CONSTANT	POLARITY	SURFACE TENSION (dynes/cm)	SOLUBILITY RATING (in water)
ISODECYL ACRYLATE	0.885		NONPOLAR		IM
ISODECYL ALCOHOL	0.849		SLIGHTLY		IM
ISOMEXANE	0.700	1.8	NONPOLAR	17.3	IM
ISOCTALDENYDE	0.818		NONPOLAR		IM
ISOCTANE	0.700		NONPOLAR	19.3	IM
ISOCTYL ALCOHOL	0.800		SLIGHTLY		IM
ISOPENTANE	0.600	1.8	NONPOLAR	14.8	SL
ISOPHORONE	0.923		POLAR		IM
ISOPHORONE DIAMINE	0.930		POLAR		IM
ISOPHORONE DIISOCYANATE	0.930		POLAR		IM
ISOPRENE	0.700	2.1	NONPOLAR		SL
ISOPROPYL ACETATE	0.900	5.2	SLIGHTLY	22.2	IM
ISOPROPYL CYCLOHEXANE	0.800		NONPOLAR		IM
ISOPROPYL ETHER	0.726	3.9	SLIGHTLY		SL
ISOPROPYL MERCAPTAN	0.808		NONPOLAR		SL
ISOVALERALDENYDE	0.803		SLIGHTLY	23.7	IM
JET FUEL: JP-1 (KEROSENE)	0.800		NONPOLAR		IM
JET FUEL: JP-3	0.800		NONPOLAR		IM
JET FUEL: JP-4	0.760		NONPOLAR		IM
JET FUEL: JP-5 (KEROSENE, HEAVY)	0.810		NONPOLAR		IM
KEROSENE	0.800		NONPOLAR		IM
LAUROYL PEROXIDE	0.910		POLAR		IM
LAURYL MERCAPTAN	0.800		NONPOLAR		IM
LINEAR ALCOHOLS (12-15 CARBONS)	0.800		SLIGHTLY		IM
LIQUPIED PETROLEUM GAS	0.510		NONPOLAR		SL
MALIC ANHYDRIDE	0.900		SLIGHTLY		SL
MESITYL OXIDE	0.900	15.4	POLAR		IM
METHALLYL CHLORIDE	0.900		POLAR		SL
METHANE	0.415		NONPOLAR		IM
METHYL ACETYLENE, PROPADIENE MIXTURE	0.576		NONPOLAR		SL
METHYLACRYLATE	0.956		NONPOLAR		IM
METHYL ANYL ACETATE	0.900		SLIGHTLY		SL
METHYL ANYL ALCOHOL	0.800		POLAR		SL
N-METHYLANILINE	1.000		SLIGHTLY		IM



CHEMICAL	SPECIFIC GRAVITY	DIELECTRIC CONSTANT	POLARITY	SURFACE TENSION (dynes/cm)	SOLUBILITY RATING (in water)
METHYL-t-BUTYL ETHER	0.744		SLIGHTLY		SL
METHYL-n-BUTYL KETONE	0.800	12.2	POLAR	25.4	IM
METHYLCYCLOPENTANE	0.800		NONPOLAR	21.6	SL
2-METHYL-6-ETHYL ANILINE	1.020		POLAR		SL
2-METHYL-5-ETHYLPRYDINE	0.918		POLAR		SL
METHYL HYDRAZINE	0.874		POLAR		SL
METHYL ISOBUTYL CARBINOL	0.800	13.1	POLAR	23.6	IM
METHYL ISOBUTYL KETONE	0.800	2.9	NONPOLAR		IM
METHYL METHACRYLATE	0.900	2.7	NONPOLAR	40.7	IM
METHYL NAPHTHALENE	1.029		NONPOLAR	18.8	IM
2-METHYL PENTENE	0.700		NONPOLAR	33.9	SL
METHYL STYRENE, ALPHA	0.914	2.2	POLAR		IM
METHYL VINYL KETONE	0.864		NONPOLAR		IM
MINERAL SPIRITS	0.800		NONPOLAR		IM
NAPHTHA:COAL TAR	0.880		NONPOLAR		IM
NAPHTHA:SOLVENT	0.800		NONPOLAR		IM
NAPHTHA:STANDARD SOLVENT	0.800		NONPOLAR		IM
NAPHTHA:W & P (75% NAPHTHA)	0.750		NONPOLAR		IM
NAFTHENIC ACID	0.982		POLAR		IM
NEOHEXANE	0.600	1.8	NONPOLAR	16.2	SL
NITROGEN, LIQUIFIED	0.800	1.5	NONPOLAR		SL
1-NITROPROPANE	1.022	23.2	POLAR	30.0	SL
2-NITROPROPANE	0.982	25.5	POLAR	30.0	IM
NONANE	0.718	1.9	NONPOLAR	22.9	IM
NONANOL	0.827		POLAR	28.3	IM
NONENE	0.700		NONPOLAR	23.0	IM
1-NONENE	0.729		NONPOLAR		SL
NOYL PHENOL	0.950		SLIGHTLY		IM
OCTANE	0.700	1.9	NONPOLAR	21.8	IM
OCTANOL	0.800	10.3	POLAR	27.5	IM
1-OCTENE	0.710	2.0	NONPOLAR	21.8	IM
OCTYL EPOXYTAILATE	1.002		NONPOLAR		IM
OIL: CLARIFIED	0.850		NONPOLAR		IM
OIL: CRUDE	0.700		NONPOLAR		IM

CHEMICAL	SPECIFIC GRAVITY	DIELECTRIC CONSTANT	POLARITY	SURFACE TENSION (dynes/cm)	SOLUBILITY RATING (in water)
OIL: DIESEL	0.841		NONPOLAR		IM
OIL: EDIBLE: CASTOR	0.900		NONPOLAR		IM
OIL: EDIBLE: COCONUT	0.900		NONPOLAR		IM
OIL: EDIBLE: COTTONSEED	0.900		NONPOLAR		IM
OIL: EDIBLE: FISH	0.930		NONPOLAR		IM
OIL: EDIBLE: LARD	0.900		NONPOLAR		IM
OIL: EDIBLE: OLIVE	0.900		NONPOLAR		IM
OIL: EDIBLE: PALM	0.900		NONPOLAR		IM
OIL: EDIBLE: PEANUT	0.900		NONPOLAR		IM
OIL: EDIBLE: SAFFLOWER	0.923		NONPOLAR		IM
OIL: EDIBLE: SOYA BEAN	0.900		NONPOLAR		IM
OIL: EDIBLE: TUCUM	0.908		NONPOLAR		IM
OIL: EDIBLE: VEGETABLE	0.923		NONPOLAR		IM
OIL: FUEL: NO. 1 (KEROSENE)	0.810		NONPOLAR		IM
OIL: FUEL: NO. 1-D	0.810		NONPOLAR		IM
OIL: FUEL: NO. 2	0.850		NONPOLAR		SL
OIL: FUEL: NO. 2-D	0.856		NONPOLAR		IM
OIL: FUEL: NO. 4	0.904		NONPOLAR		IM
OIL: FUEL: NO. 5	0.916		NONPOLAR		IM
OIL: FUEL: NO. 6	0.967		NONPOLAR		IM
OIL: MISC: ABSORPTION	0.850		NONPOLAR		IM
OIL: MISC: CASHEW NUT SHELL (UNTREATED)	0.800		NONPOLAR		IM
OIL: MISC: COAL TAR	0.900		NONPOLAR		IM
OIL: MISC: CROTON	0.946		NONPOLAR		IM
OIL: MISC: LINSKED	0.900		NONPOLAR		IM
OIL: MISC: LUBRICATING	0.902		NONPOLAR		IM
OIL: MISC: MINERAL	0.822		NONPOLAR		IM
OIL: MISC: MINERAL SEAL	0.800		NONPOLAR		IM
OIL: MISC: MOTOR	0.840		NONPOLAR		IM
OIL: MISC: HEATSFOOT	0.900		NONPOLAR		IM
OIL: MISC: PENETRATING	0.896		NONPOLAR		IM
OIL: MISC: RANGE	0.800		NONPOLAR		IM
OIL: MISC: RESIN	0.960		NONPOLAR		IM
OIL: MISC: ROAD	1.000		NONPOLAR		IM

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CHEMICAL	SPECIFIC GRAVITY	DIELECTRIC CONSTANT	POLARITY	SURFACE TENSION (dynes/cm)	SOLUBILITY RATING (in water)
OIL, MISC: ROBIN	0.960		NONPOLAR		IM
OIL, MISC: SPERM	0.900		NONPOLAR		IM
OIL, MISC: SPINDLE	0.881		NONPOLAR		IM
OIL, MISC: SPRAY	0.820		NONPOLAR		IM
OIL, MISC: TALL	0.951		NONPOLAR		IM
OIL, MISC: TAMER'S	0.850		NONPOLAR		IM
OIL, MISC: TRANSFORMER	0.900		NONPOLAR		IM
OIL, MISC: TURBINE	0.870		NONPOLAR		IM
OLEIC ACID	0.851	2.4	NONPOLAR		IM
PENTADECANOL	0.829		SLIGHTLY		IM
1,3-PENTADIENE	0.700	2.3	NONPOLAR	17.8	IM
1,4-PENTADIENE	0.659	1.9	NONPOLAR	16.1	IM
n-PENTANE	0.626	1.8	NONPOLAR	16.0	IM
1-PENTENE	0.641	2.1	NONPOLAR	16.0	IM
PETROLATUM	0.865		NONPOLAR		IM
PETROLEUM NAPHTHA	0.600		NONPOLAR		IM
POLYBUTENE	0.810	2.2	NONPOLAR		SL
POLYETHYLENE POLYAMINES			SLIGHTLY		IM
POLYPROPYLENE	0.900	2.2	NONPOLAR		IM
POLYPROPYLENE GLYCOL	1.004		SLIGHTLY		SL
n-PROPYL ACETATE	0.887	5.6	SLIGHTLY	24.6	IM
PROPYLENE BUTYLENE POLYMER	0.910		NONPOLAR		IM
PROPYLENE TETRAMER	0.770		NONPOLAR		SL
n-PROPYL ETHER	0.736	3.4	SLIGHTLY	20.0	IM
PYRTHRINS	0.830				IM
STEARIC ACID	0.800	2.2	NONPOLAR		IM
STYRENE	0.909	2.4	NONPOLAR	32.2	IM
TALLOW	0.900		NONPOLAR		IM
TALLOW FATTY ALCOHOL	0.800		NONPOLAR		IM
TETRADECANOL	0.824		NONPOLAR		IM
1-TETRADECENE	0.775		SLIGHTLY		IM
TETRADECYLBENZENE	0.856	2.1	NONPOLAR	26.8	IM
TETRAHYDRONAPHTHALENE	0.973		NONPOLAR	35.5	IM
TOLUENE	0.866	2.3	NONPOLAR	26.5	SL

CHEMICAL	SPECIFIC GRAVITY	DIELECTRIC CONSTANT	POLARITY	SURFACE TENSION (dynes/cm)	SOLUBILITY RATING (in water)
O-TOLUIDINE	0.999	6.3	POLAR	40.7	IM
TRIDECANOL	0.800		SLIGHTLY		IM
1-TRIDECENE	0.766		NONPOLAR	26.2	YS
TRISTYLANINE	0.729	2.4	NONPOLAR	20.7	IM
TRISTYLBENZENE	0.874		NONPOLAR		IM
TRIMETHYLACETIC ACID	0.905		SLIGHTLY		IM
TURPENTINE	0.860		NONPOLAR		IM
UNDECANOL	0.800		POLAR		IM
1-UNDECENE	0.763		NONPOLAR	24.9	IM
n-UNDECYLBENZENE	0.855		NONPOLAR		IM
n-VALERALDEHYDE	0.800		SLIGHTLY	25.9	SO
VINYL ACETATE	0.900		SLIGHTLY		IM
VINYL CHLORIDE	0.910		POLAR	20.9	SL
VINYL ETHYL ETHER	0.800	6.2	NONPOLAR		SL
VINYL FLUORIDE	0.707		POLAR		SL
VINYL METHYL ETHER	0.777		NONPOLAR		SL
VINYL NEODECANATE	0.800		NONPOLAR		SL
VINYL TOLUENE	0.890		NONPOLAR		IM
WAX: CANAUBA	0.996		NONPOLAR		IM
WAX: PARAFFIN	0.900		NONPOLAR		IM
n-XYLENE	0.868	2.3	NONPOLAR	29.0	IM
o-XYLENE	0.880	2.5	NONPOLAR	30.3	IM
p-XYLENE	0.900	2.2	NONPOLAR	28.6	SL
XYLENOL	1.010		SLIGHTLY		

### TABLE A-3. Flammability Data for Floating Hazardous Chemicals

NFPA Flammability Ratings: The National Fire Protection Association (NFPA) ranks chemical flammability hazards on a scale of 0 to 4, with a rating of 4 being the greatest flammability hazard and 0 the least hazard. The rating system is described in detail in the Approach section.

Flammable (Explosive) Limits: For vapors or gases which form flammable mixtures with air or oxygen, there will exist a minimum concentration of vapor in air or oxygen below which propagation of flame does not occur on contact with a source of ignition. For a gas or vapor there also exists a maximum percentage in air or oxygen above which the propagation of a flame will not occur. These lower and upper concentration percentages are known as the Lower and Upper Flammability Limit, respectively.

Vapor Pressure is the pressure exerted when a solid or liquid is in equilibrium with its own vapor. The vapor pressure is a direct function of the substance and the temperature.

The flash point of a substance is the minimum temperature at which it gives off sufficient vapor to form an ignitable mixture with the air near the surface of the liquid or within the vessel used. An ignitable mixture is a mixture with a concentration between the upper and lower flammable limits that is able to propagate a flame away from the source of ignition when ignited.

CHEMICAL	NFPA FLAMMAB. RATING	LOWER FLAMMAB. LIMIT	UPPER FLAMMAB. LIMIT	VAPOR PRESSURE (mm Hg)	FLASH POINT (Deg F)
ACETOPHENONE	2				170
ACETYL ACETONE	2	2.4	11.6	10.0	93
ACETYLENE	4	2.5	80.0	39.5	64
ADIPONITRILE	2			996.9	199
ALLYL CHLORIDE	3	2.9	11.1	360.0	-25
n-AMYL ACETATE	3	1.1	7.5	5.0	71
sec-AMYL ACETATE	3	1.0	7.5	9.0	89
tert-AMYL ACETATE	3	1.1		380.0	25
n-AMYL ALCOHOL	3	1.2	10.0	2.8	91
n-AMYL CHLORIDE	3	1.6	8.6	4.3	55
n-AMYL MERCAPTAN	3				64
n-AMYL METHYL KETONE		1.1		2.0	120
n-AMYL NITRATE	2				118
iso-AMYL NITRITE					50
AMYL PHTHALATE					245
ANILINE	1				158
ASPHALT	2	1.3	11.0	15.0	400
BENZALDEHYDE	3				145
BENZENE	2			75.0	12
BENZONITRILE	3	1.3	7.1	74.7	167
BENZYL ALCOHOL				3.5	200
BUTADIENE	1			105.8	-103
BUTANE	4	2.0	11.5	2.4	-76
n-BUTYL ACETATE	4	1.9	8.5	1500.0	
sec-BUTYL ACETATE	3	1.7	7.6	15.0	72
tert-BUTYL ACETATE	3	1.7	9.8	10.0	91
iso-BUTYL ACRYLATE	3	1.7		16.3	88
n-BUTYL ACRYLATE				5.0	49
BUTYL BUTYRATE	2	1.5	9.9	5.0	120
BUTYL/DECYL/CETYL-EICOSYL METHACRYLATE	2			65.0	128
BUTYLENE	4	1.7			-112
n-BUTYL ETHER	3	1.5	7.6	3480.0	77
tert-BUTYL HYDROPEROXIDE	4			4.8	100
n-BUTYL MERC/PTAN	3			35.6	35

CHEMICAL	NFPA FLAMMAB. RATING	LOWER FLAMMAB. LIMIT	UPPER FLAMMAB. LIMIT	VAPOR PRESSURE (mm Hg)	FLASH POINT (Deg F)
iso-BUTYL METHACRYLATE	2				126
n-BUTYL METHACRYLATE					126
p-tert-BUTYLPHENOL	3	1.6	10.6	1.0	205
iso-BUTYRALDEHYDE	3			71.0	-40
n-BUTYRALDEHYDE				20.0	20
CAMPRENE				0.6	90
CAMPOR (OIL)	2	0.6	3.5	1.0	117
CARBOLIC OIL	2	1.3			60
CARBON MONOXIDE	4	12.0		0.0	0
CARENE				0.3	120
CETYL DICOXYL METHACRYLATE	3	4.0	20.0	215.0	-4
CHLOROPRENE	4				-80
COLLODION					100
COPPER NAPHTHENATE(1C) COPPER(II)NAPTH	2	0.8	5.0		165
CREOSOTE, COAL TAR					187
n-CRESOL	1	1.1	1.4	4.0	187
p-CRESOL	1	1.1	1.4	4.0	187
CRESOLS	2	1.3			202
CRESYLATE SPENT CAUSTIC					
CROTONALDEHYDE	3	2.1	15.5	19.0	55
CUMENE	3	0.9	6.5	10.0	111
CUMENE HYDROPEROXIDE	2				175
CYCLOHEXANE	3	1.3	8.0	-5.0	-4
CYCLOHEXANONE	2	1.0	9.4	5.0	111
CYCLOHEXANONE PEROXIDE					111
CYCLOHEXENE	3	1.1		4.0	20
CYCLOPENTANE	3	1.5		-30.1	20
CYCLOPROPANE	4	2.4	10.4	4636.0	-160
p-CYMENE	2	0.7	5.6	2.0	117
DECABORANE	2	0.8	98.0		176
DECAHYDRONAPHTHALENE	2	0.7	4.9	2.0	136
n-DECALDEHYDE				3.1	186
1-DECENE	2			100.0	131
n-DECYL ACRYLATE	1				441

CHEMICAL	NFPA FLAMMAB. RATING	LOWER FLAMMAB. LIMIT	UPPER FLAMMAB. LIMIT	VAPOR PRESSURE (mm Hg)	FLASH POINT (Deg F)
n-DECYL ALCOHOL	2			1.0	180
n-DECYLBENZENE	1				225
DI-n-AMYL PHTHALATE	1			0.0	245
DIBENZYL ETHER	1				275
DI-n-BUTYLAMINE	2	1.1		2.0	117
DI-n-BUTYL ETHER	3	1.5	7.6	0.8	77
DI-n-BUTYL KETONE				0.1	135
DIETHYLPHENOL					200
DIETHYL PHTHALATE	1	0.5		7.8	315
4,4-DICHLORO-a1-TRICHLOROMETHYLBENZENE					70
DICYCLOPENTADIENE	3			10.0	90
DIETHYLBENZENE	2			0.0	132
DIETHYL CARBONATE	3			8.0	77
DIETHYLENE GLYCOL MONOBUTYL ETHER ACETAT	1	0.8	10.7	0.0	240
DI-(2-ETHYLHEXYL) PHOSPHORIC ACID					385
DIETHYL KETONE	3	1.6	18.0	27.9	55
1,1-DIFLUOROETHANE		5.1		4020.0	-60
DINEPTYL PHTHALATE					65
DIISOBUTYLAMINE	3			5.1	85
DIISOBUTYL CARBINOL	2	0.8	6.1	0.0	165
DIISOBUTYLENE	3	0.8	4.8		23
DIISOBUTYL KETONE	2	0.8	6.2	2.0	140
DIISOBUTYL PHTHALATE	1				365
DIISODECYL PHTHALATE	1	0.3			450
DIISOMONYL PHTHALATE					75
DIISOCTYL PHTHALATE	1				380
DIISOPROPYLAMINE	3	1.1	7.1	70.0	30
2,2-DIMETHYL OCTANOIC ACID					80
DIMETHYLPOLYSILOXANE					275
DIMETHYL SULFIDE	4	2.2	19.7	395.0	-1
DIOCTYL ADIPATE	1	0.4			402
DIOCTYL PHTHALATE	1	0.3			424
DIPENTENE	2	0.7	6.1	1.2	113
DI-n-PROPYLAMINE	3				63



CHEMICAL	NFPA FLAMMAB. RATING	LOWER FLAMMAB. LIMIT	UPPER FLAMMAB. LIMIT	VAPOR PRESSURE (mm Hg)	FLASH POINT (Deg F)
DISTILLATES: FLASHED FEED STOCKS					141
DISTILLATES: STRAIGHT RUN					141
DIUNDECYL PHTHALATE					20
DODECANOL	1			1.0	260
DODECENE	2			1.0	120
1-DODECENE				0.0	174
DODECYLBENZENE	1			0.0	285
DODECYLDIPHENYL OXIDE DISULFONATE					-30
DODECYLMETHACRYLATE					
DODECYL PENTA DECYL METHACRYLATE					
EPOXIDISED VEGETABLE OILS					
ETHANE	4	3.0	12.5	*****	585
ETHOXYDINHYDROPIRAN	2				275
ETHOXYLATED DODECANOL					111
ETHOXYLATED PENTADECANOL					35
ETHOXYLATED TETRADECANOL					80
ETHOXYLATED TRIDECANOL					45
ETHYL ACETATE	3	2.2	11.0	100.0	-30
ETHYL ACETOACETATE	2	1.4	9.5	0.8	24
ETHYL ACRYLATE	3	1.8	14.0	30.0	135
ETHYLENE	3	1.0	6.7	9.0	60
ETHYL BUTANOL	2			6.8	59
N-ETHYL-n-BUTYLAMINE	3				135
ETHYL BUTYRATE	3			27.8	64
ETHYL CHLORIDE	4	3.8	15.4	539.0	75
ETHYL CYCLOHEXANE	3	0.9	6.6	10.0	58
N-ETHYL CYCLOHEXYLAMINE	3				95
ETHYLENE GLYCOL DIETHYL ETHER	3				86
ETHYLENE GLYCOL MONOBUTYL ETHER ACETATE	2	0.8	8.5	0.3	95
ETHYL ETHER	4	1.9	48.0	442.0	160
ETHYL FORMATE	3	2.8	16.0	200.0	-192
ETHYLHEXALDEHYDE	2	0.9	7.2		32
2-ETHYL HEXANOL	2	0.9	9.7		112
2-ETHYLHEXYL ACRYLATE	2			1.0	164
					180

CHEMICAL	NFPA FLAMMAB. RATING	LOWER FLAMMAB. LIMIT	UPPER FLAMMAB. LIMIT	VAPOR PRESSURE (mm Hg)	FLASH POINT (Deg F)
ETHYLHEXYL TALLATE					395
ETHYLIDENEBORBORNE	4	2.8	18.1	436.4	90
ETHYL MERCAPTAN	3				80
ETHYL METHACRYLATE	4	4.0	50.0		68
ETHYL NITRITE	4				-31
2-ETHYL-3-PROPYLACROLEIN	2				155
ETHYL TOLUENE	2	6.0	3.0		110
GAS OIL: CRACKED	3				150
GASOLINE: AUTOMOTIVE (4.23G Pb/GAL)	3				-49
GASOLINE: AVIATION (4.86G Pb/GAL)	3				-50
GASOLINE BLENDING STOCKS: ALKYLATES	3				73
GASOLINE BLENDING STOCKS: REFORMATES	3				73
GASOLINE: CASINGHEAD	3				0
GASOLINE: POLYMER	3				73
GASOLINE: STRAIGHT RUN	3				73
NEPTANE	3	1.1	6.7	150.0	25
NEPTANOIC ACID					40
NEPTANOL	2			0.7	160
1-HEPTENE	3			44.2	32
HEXADECYLTRIMETHYL AMMONIUM CHLORIDE					-30
n-HEXALDEHYDE	3				90
HEXAMETHYLENEIMINE					75
HEXANE	3	1.2	7.5	120.0	32
HEXANOL	2			0.5	145
1-HEXENE	3	1.2	6.9	100.0	20
HYDROGEN, LIQUIFIED	4	4.0			0
HYDROGEN SULFIDE	4	4.3		*****	-180
ISOMYL ACETATE	3	1.0	7.5	6.0	77
ISOMYL ALCOHOL	2	1.2	9.0	4.0	67
ISOBUTANE	4	1.8	8.4	3734.0	-117
ISOBUTYL ACETATE	3	2.4	10.5	20.0	64
ISOBUTYLENE	4	1.8	9.6	3279.0	-105
ISOBUTYRONITRILE	3				47
ISODECALDEHYDE	2				185

CHEMICAL	NFPA FLAMMAB. RATING	LOWER FLAMMAB. LIMIT	UPPER FLAMMAB. LIMIT	VAPOR PRESSURE (mm Hg)	FLASH POINT (Deg F)
ISODECYL ACRYLATE					240
ISODECYL ALCOHOL					170
ISOHEXANE	3	1.0	7.0		-20
ISOOCTALDEHYDE	3				95
ISOOCTANE	2				40
ISOOCTYL ALCOHOL	4	1.4	7.6	598.0	180
ISOPENTANE	2	0.8	3.8	0.4	-60
ISOPHORONE	4	1.5	8.9	496.3	184
ISOPHORONE DIISOCYANATE	3	1.8	8.0	47.0	180
ISOPRENE	4	1.4	21.0	150.0	163
ISOPROPYL ACETATE	3			226.1	-65
ISOPROPYL CYCLOHEXANE	3				40
ISOPROPYL ETHER	3				96
ISOPROPYL MERCAPTAN	2	1.2	6.0		-18
ISOVALERALDEHYDE	2				-10
JET FUEL: JP-1 (KEROSENE)	2	0.7	5.0	30.0	40
JET FUEL: JP-3	2				149
JET FUEL: JP-4	3				110
JET FUEL: JP-5 (KEROSENE, HEAVY)	2				-10
KEROSENE	2				140
LAURYL PEROXIDE	2				100
LAURYL MERCAPTAN	1				262
LINEAR ALCOHOLS (12-15 CARBONS)	4				180
LIQUIFIED PETROLEUM GAS	1				-200
MALEIC ANHYDRIDE	3	1.4	7.2	10.0	14
MESITYL OXIDE	3	3.2	8.1		87
METHALLYL CHLORIDE	4	5.0	15.0	0.0	11
METHANE	4	1.7	25.0	3876.0	-306
METHYL ACETYLENE, PROPADIENE MIXTURE	3	2.8	25.0	65.0	0
METHYLACRYLATE	2	1.0	5.5	3.8	27
METHYL AMYL ACETATE	2			3.6	113
METHYL AMYL ALCOHOL	2			3.6	106
N-METHYLANILINE	2			0.3	185

CHEMICAL	NFPA FLAMMAB. RATING	LOWER FLAMMAB. LIMIT	UPPER FLAMMAB. LIMIT	VAPOR PRESSURE (mm Hg)	FLASH POINT (Deg F)
METHYL-t-BUTYL ETHER					90
METHYL -n-BUTYL KETONE	3	1.2	8.0	50.0	77
METHYLCYCLOPENTANE	3	1.0	8.4	110.2	20
2-METHYL-6-ETHYL ANILINE	2	1.1	6.6		45
2-METHYL-5-ETHYLPRYDINE	3	2.5	92.0	49.6	165
METHYL HYDRAZINE	3	1.0	5.5	10.0	47
METHYL ISOBUTYL CARBIMOL	2	1.7	8.2	24.5	106
METHYL ISOBUTYL KETONE	3			13.0	73
METHYL METHACRYLATE	3			0.0	50
METHYL NAPHTHALENE	2			128.5	200
2-METHYL PENTENE	3			2.0	-15
METHYL STYRENE, ALPHA	2	1.9	6.1		129
METHYL VINYL KETONE	3	2.1	15.6		20
MINERAL SPIRITS	2	0.8	6.0	80.0	104
NAPHTHA(COAL TAR	2				100
NAPHTHA(SOLVENT	2	0.8			138
NAPHTHA(STANDARD SOLVENT	2			8.0	100
NAPHTHA(VN & P (75% NAPHTHA)	3	0.9	6.7	0.1	50
NAPHTHIC ACID					300
NEOHEXANE	3	1.2	7.0		-54
NITROGEN, LIQUIFIED					0
1-NITROPROPANE	3	2.2		8.0	120
2-NITROPROPANE	3	2.6	11.0	13.0	103
NONANE	3	0.8	2.9	3.2	88
NONANOL		0.8	61.0	0.3	165
NONENE	3				78
1-NONENE	3			0.0	115
NONYL PHENOL	1				285
OCTANE	3	1.0	6.5	11.0	56
OCTANOL	2			0.4	178
1-OCTENE	3			13.8	70
OCTYL EPOXYTALLATE					450
OIL: CLARIFIED					
OIL: CRUDE	3				

CHEMICAL	NFPA FLAMMAB. RATING	LOWER FLAMMAB. LIMIT	UPPER FLAMMAB. LIMIT	VAPOR PRESSURE (mm Hg)	FLASH POINT (Deg F)
OIL, DIESEL	2				100
OIL, EDIBLE: CASTOR	1				445
OIL, EDIBLE: COCONUT	1				420
OIL, EDIBLE: COTTONSEED	1				486
OIL, EDIBLE: FISH	1				420
OIL, EDIBLE: LARD	1				395
OIL, EDIBLE: OLIVE	1				437
OIL, EDIBLE: PALM	1				421
OIL, EDIBLE: PEANUT	1				540
OIL, EDIBLE: SAFFLOWER	1				540
OIL, EDIBLE: SOYA BEAN	1				540
OIL, EDIBLE: TUCUM	1				398
OIL, EDIBLE: VEGETABLE	1				610
OIL, FUEL: NO. 1 (KEROSENE)	0	0.7	5.0		100
OIL, FUEL: NO. 1-D	2				100
OIL, FUEL: NO. 2	2				100
OIL, FUEL: NO. 2-D	2				126
OIL, FUEL: NO. 4	2				129
OIL, FUEL: NO. 5	2				129
OIL, FUEL: NO. 6	2				150
OIL, MISC: ABSORPTION					255
OIL, MISC: CASHEN NUT SHELL (UNTREATED)	3	1.3			60
OIL, MISC: COAL TAR					
OIL, MISC: CROTON					
OIL, MISC: LINSEED	1				432
OIL, MISC: LUBRICATING	1				300
OIL, MISC: MINERAL	1				380
OIL, MISC: MINERAL SEAL	2				275
OIL, MISC: MOTOR					300
OIL, MISC: NEATSFOOT	1				470
OIL, MISC: PENETRATING					295
OIL, MISC: RANGE	0	0.7	5.0		100
OIL, MISC: RESIN	0				255
OIL, MISC: ROAD	1				225

CHEMICAL	NFPA FLAMMAB. RATING	LOWER FLAMMAB. LIMIT	UPPER FLAMMAB. LIMIT	VAPOR PRESSURE (mm Hg)	FLASH POINT (Deg F)
OIL, MISC: ROSIN	1				266
OIL, MISC: SPERM	1				428
OIL, MISC: SPINDLE	2				169
OIL, MISC: SPRAY	2				140
OIL, MISC: TALL	1				380
OIL, MISC: TANNER'S	1				295
OIL, MISC: TRANSFORMER	1				400
OIL, MISC: TURBINE	1				372
OLEIC ACID	1		1.0		250
PENTADECANOL	4			335.0	-20
1,3-PENTADIENE	4			600.0	-180
1,4-PENTADIENE	4	1.5	7.8	400.0	-40
n-PENTANE	4	1.5	8.7	550.0	0
1-PENTENE	4	1.1	5.9		360
PETROLATUM	4				-50
PETROLEUM NAPHTHA	1				215
POLYBUTENE					
POLYETHYLENE POLYAMINES					
POLYPROPYLENE	1				381
POLYPROPYLENE GLYCOL	3	2.0	8.0	25.0	58
n-PROPYL ACETATE					10
PROPYLENE BUTYLENE POLYMER	2				125
PROPYLENE TETRAMER	3	1.3	7.0		70
n-PROPYL ETHER					
PYRETHRINS	1			1.0	385
SEBACIC ACID	3	1.1	6.1	5.0	90
STYRENE	1				509
TALLOW					492
TALLOW FATTY ALCOHOL	1				285
TETRADECANOL	1			0.0	230
1-TETRADECENE	1			0.0	310
TETRADECYLBENZENE	2	0.8	5.0	93.8	160
TETRAHYDROMAPHTHALENE	3	1.2	7.1	284.0	40
TOLUENE					

**APPENDIX B  
METHODS OF GROUPING FLOATING CHRIS CHEMICALS**

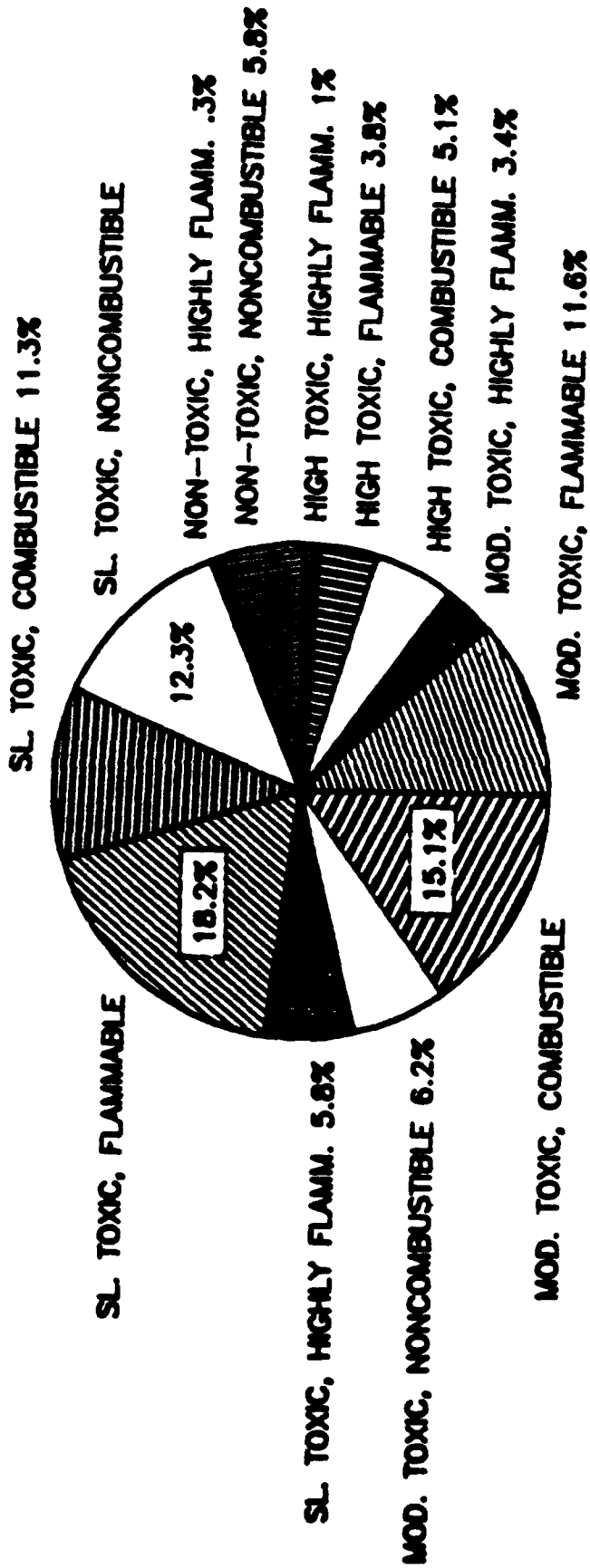
Several methods of categorizing the floating CHRIS chemicals have been investigated to serve as a guide toward directing which spill mitigation technology should be utilized and to warn the spill response team of possible toxicity or flammability hazards. The method which seems to be most feasible is one which involves a table containing an alphabetical listing of all the floating CHRIS chemicals. Through this table, the spill response personnel can identify the chemical(s) of interest and be referred to a table giving information concerning the toxic or flammability hazards of that chemical. Thirteen tables have been developed which group chemicals from not toxic and not combustible through highly toxic and highly flammable. The percent distribution of the 292 floating chemicals according to these groupings is depicted in Figure B-1, and the groupings are listed in Tables B-1 through B-13. These tables also indicate the type of foams recommended for vapor suppression. The proposed grouping of chemicals as well as definitions of each group is given below. The toxicity characteristics were used to group the chemicals into one of four categories based on the NFPA guidelines:

- |                       |   |
|-----------------------|---|
| <b>Not Toxic</b>      | Indicates that the material poses no health hazard.   |
| <b>Slightly Toxic</b> | Indicates chemicals which on exposure would cause irritation but only minor residual injury even without medical treatment. Chemicals which irritate, but do not destroy tissue, and materials which require the use of cannister-type gas masks are included in this category. |

**Moderately Toxic** Indicates those materials which cause temporary incapacitation or possible residual injury unless prompt medical attention is given. Materials included in this category require the use of protective respiratory equipment with independent air supply.

**Highly Toxic** Indicates materials which on short exposure could cause serious temporary or residual damage (possibly death) even with prompt medical attention. Materials that are corrosive to living tissue or toxic by skin adsorption, and materials requiring protection from all bodily contact are included in this category.





**Legend**  
 SL = Slightly  
 MOD = Moderately  
 HIGH = Highly

**Figure B-1. Percentage Distribution of Floating Chemicals in Reference to Flammability and Toxicity Grouping.**

**TABLE B-1. Non-Toxic, Noncombustible**

**EPOXIDIZED VEGETABLE OILS**

**OIL, EDIBLE: CASTOR**

**OIL, EDIBLE: COCONUT**

**OIL, EDIBLE: FISH**

**OIL, EDIBLE: LARD**

**OIL, EDIBLE: OLIVE**

**OIL, EDIBLE: PALM**

**OIL, EDIBLE: PEANUT**

**OIL, EDIBLE: SAFFLOWER**

**OIL, EDIBLE: SOYA BEAN**

**OIL, EDIBLE: TUCUM**

**OIL, EDIBLE: VEGETABLE**

**OIL, MISC: LINSEED**

**OLEIC ACID**

**PETROLATUM**

**WAX: CARNAUBA**

**WAX: PARAFFIN**

**TABLE B-2. Non-Toxic, Highly Flammable**

**ACETYLENE**

TABLE B-3. Slightly Toxic, Noncombustible

1-TETRADECENE  
AMYL PHTHALATE  
DIETHYLENE GLYCOL MONOBUTYL ETHER ACETAT  
DIISOBUTYL PHTHALATE  
DIISODECYL PHTHALATE  
DIISOCTYL PHTHALATE  
DIOCTYL ADIPATE  
DIOCTYL PHTHALATE  
DODECANOL  
DODECYLBENZENE  
ETHOXYLATED DODECANOL  
ISODECYL ACRYLATE  
OCTYL EPOXY TALLATE  
OIL, EDIBLE: COTTONSEED  
OIL, MISC: LUBRICATING  
OIL, MISC: MINERAL  
OIL, MISC: MOTOR  
OIL, MISC: NEATSFOOT  
OIL, MISC: PENETRATING  
OIL, MISC: RANGE  
OIL, MISC: RESIN  
OIL, MISC: ROAD  
OIL, MISC: ROSIN  
OIL, MISC: SPERM  
OIL, MISC: TALL  
OIL, MISC: TANNER'S  
OIL, MISC: TURBINE  
POLYBUTENE  
POLYPROPYLENE GLYCOL  
STEARIC ACID  
TALLOW  
TALLOW FATTY ALCOHOL  
TETRADECANOL  
TRIDECANOL  
UNDECANOL  
p-tert-BUTYLPHENOL

**TABLE B-4. Slightly Toxic, Combustible**

1-DECENE  
1-DODECENE  
1-TRIDECENE  
COPPER NAPHTHENATE (IC) COPPER (II) NAPTH  
DIISOBUTYLCARBINOL  
DIPENTENE  
DODECENE  
ETHYL BUTANOL  
HEPTANOL  
HEXANOL  
ISOAMYL ALCOHOL  
ISODECYL ALCOHOL  
JET FUEL: JP-1 (KEROSENE)  
JET FUEL: JP-3  
JET FUEL: JP-5 (KEROSENE, HEAVY)  
KEROSENE  
LINEAR ALCOHOLS (12-15 CARBONS)  
MINERAL SPIRITS  
NONANOL  
OCTANOL  
OIL, FUEL: NO. 1 (KEROSENE)  
OIL, FUEL: NO. 1-D  
OIL, FUEL: NO. 2  
OIL, FUEL: NO. 2-D  
OIL, FUEL: NO. 4  
OIL, FUEL: NO. 5  
OIL, FUEL: NO. 6  
OIL, MISC: MINERAL SEAL  
OIL, MISC: SPINDLE  
OIL, MISC: SPRAY  
OIL: DIESEL  
PROPYLENE TETRAMER  
n-BUTYL METHACRYLATE

TABLE B-5. Slightly Toxic, Flammable

1-HEPTENE  
1-HEXENE  
1-NONENE  
1-OCTENE  
2-METHYL PENTENE  
CHLOROPRENE  
CYCLOHEXANE  
CYCLOHEXENE  
CYCLOPENTANE  
DIETHYL KETONE  
DIISOBUTYLENE  
ETHYL ACETATE  
ETHYL BUTYRATE  
ETHYL CYCLOHEXANE  
ETHYL METHACRYLATE  
GAS OIL: CRACKED  
GASOLINE BLENDING STOCKS: ALKYLATES  
GASOLINE BLENDING STOCKS: REFORMATES  
GASOLINE: AUTOMOTIVE (4.23G Pb/GAL)  
GASOLINE: AVIATION (4.86G Pb/GAL)  
GASOLINE: CASINGHEAD  
GASOLINE: POLYMER  
GASOLINE: STRAIGHT RUN  
HEPTANE  
HEPTANOIC ACID  
HEXANE  
ISOAMYL ACETATE  
ISOBUTYL ACETATE  
ISOHEXANE  
ISOOCTALDEHYDE  
ISOOCTANE  
ISOPROPYL ACETATE  
ISOPROPYL CYCLOHEXANE  
JET FUEL: JP-4  
METHYL METHACRYLATE  
METHYLACRYLATE  
METHYLCYCLOPENTANE  
NAPHTHA: VM & P (75% NAPHTHA)  
NEOHEXANE  
NONENE  
OCTANE  
OIL, MISC: COAL TAR  
OIL: CRUDE  
TURPENTINE  
m-XYLENE  
n-AMYL ACETATE  
n-AMYL ALCOHOL  
n-AMYL CHLORIDE  
o-XYLENE  
p-XYLENE  
sec-AMYL ACETATE  
tert-AMYL ACETATE  
tert-BUTYL ACETATE

**TABLE B-6. Slightly Toxic, Highly Flammable**

**1,3-PENTADIENE  
1,4-PENTADIENE  
BUTADIENE  
BUTANE  
BUTYLENE  
COLLODION  
CYCLOPROPANE  
ETHANE  
HYDROGEN, LIQUIFIED  
ISOBUTANE  
ISOBUTYLENE  
ISOPENTANE  
LIQUIFIED PETROLEUM GAS  
METHANE  
METHYL ACETYLENE, PROPADIENE MIXTURE  
PETROLEUM NAPHTHA  
n-PENTANE**

**TABLE B-7. Moderately Toxic, Noncombustible**

**ASPHALT**  
**BENZYL ALCOHOL**  
**DI-(2-ETHYLHEXYL) PHOSPHORIC ACID**  
**DI-n-AMYL PHTHALATE**  
**DIBENZYL ETHER**  
**DIBUTYL PHTHALATE**  
**DIBUTYLPHENOL**  
**DIMETHYLPOLYSILOXANE**  
**DIMETHYLPOLYSILOXANE**  
**ETHOXYLATED TRIDECANOL**  
**LAURYL MERCAPTAN**  
**NAPHTHENIC ACID**  
**NONYL PHENOL**  
**OIL, MISC: ABSORPTION**  
**OIL, MISC: TRANSFORMER**  
**XYLENOL**  
**n-DECYL ACRYLATE**  
**n-DECYLBENZENE**



TABLE B-8. Moderately Toxic, Combustible

2-ETHYL HEXANOL  
2-ETHYL-3-PROPYLACROLEIN  
2-ETHYLHEXYL ACRYLATE  
2-METHYL-5-ETHYLPYRIDINE  
ACETOPHENONE  
ACETYL ACETONE  
BENZALDEHYDE  
BENZONITRILE  
BUTYL BUTYRATE  
CAMPHOR OIL  
CARENE  
CREOSOTE, COAL TAR  
CUMENE  
CUMENE HYDROPEROXIDE  
CYCLOHEXANONE  
CYCLOHEXANONE PEROXIDE  
DECAHYDRONAPHTHALENE  
DIETHYLBENZENE  
DIISOBUTYL KETONE  
DISTILLATES: FLASHED FEED STOCKS  
DISTILLATES: STRAIGHT RUN  
ETHOXYDIHYDROPYRAN  
ETHYL ACETOACETATE  
ETHYLENE GLYCOL MONOBUTYL ETHER ACETATE  
ETHYLHEXALDEHYDE  
ISODECALDEHYDE  
ISOOCTYL ALCOHOL  
METHYL AMYL ACETATE  
METHYL ISOBUTYL CARBINOL  
METHYL NAPHTHALENE  
METHYL STYRENE, ALPHA  
NAPHTHA:COAL TAR  
NAPHTHA:SOLVENT  
NAPHTHA:STODDARD SOLVENT  
TETRAHYDRONAPHTHALENE  
TRIETHYLBENZENE  
TRIMETHYLACETIC ACID  
VINYL TOLUENE  
n-AMYL METHYL KETONE  
n-AMYL NITRATE  
n-BUTYL ACRYLATE  
n-DECALDEHYDE  
n-DECYL ALCOHOL  
p-CYME

TABLE B-9. Moderately Toxic, Flammable

1-NITROPROPANE  
2-METHYL-6-ETHYL ANILINE  
2-NITROPROPANE  
4,4-DICHLORO- $\alpha$ -TRICHLOROMETHYLBENZYLHYDRO  
DI-n-BUTYL ETHER  
DICYCLOPENTADIENE  
DIETHYL CARBONATE  
ETHYL ACRYLATE  
ETHYL FORMATE  
ETHYLBENZENE  
ETHYLENE GLYCOL DIETHYL ETHER  
ETHYLIDENENORBORNENE  
ISOPROPYL ETHER  
ISOVALERALDEHYDE  
MESITYL OXIDE  
METHALLYL CHLORIDE  
METHYL -n-BUTYL KETONE  
METHYL ISOBUTYL KETONE  
NONANE  
STYRENE  
TOLUENE  
VINYL ACETATE  
iso-AMYL NITRITE  
iso-BUTYL ACRYLATE  
iso-BUTYRALDEHYDE  
n-AMYL MERCAPTAN  
n-BUTYL ACETATE  
n-BUTYRALDEHYDE  
n-HEXALDEHYDE  
n-PROPYL ACETATE  
n-PROPYL MERCAPTAN  
n-VALERALDEHYDE  
sec-BUTYL ACETATE  
tert-BUTYL HYDROPEROXIDE

**TABLE B-10. Moderately Toxic, Highly Flammable**

**1-PENTENE  
CARBON MONOXIDE  
DIMETHYL SULFIDE  
ETHYL CHLORIDE  
ETHYL ETHER  
ETHYL NITRITE  
ISOPRENE  
VINYL ETHYL ETHER  
VINYL FLUORIDE  
VINYL METHYL ETHER**

**TABLE B-11. Highly Toxic, Combustible**

**ADIPONITRILE  
ANILINE  
CRESOLS  
DECABORANE  
DI-n-BUTYL KETONE  
DI-n-BUTYLAMINE  
ETHYL TOLUENE  
ISOPHORONE  
ISOPHORONE DIAMINE  
ISOPHORONE DIISOCYANATE  
LAUROYL PEROXIDE  
METHYL AMYL ALCOHOL  
n-METHYLANILINE  
o-TOLUIDINE  
p-CRESOL**

**TABLE B-12. Highly Toxic, Flammable**

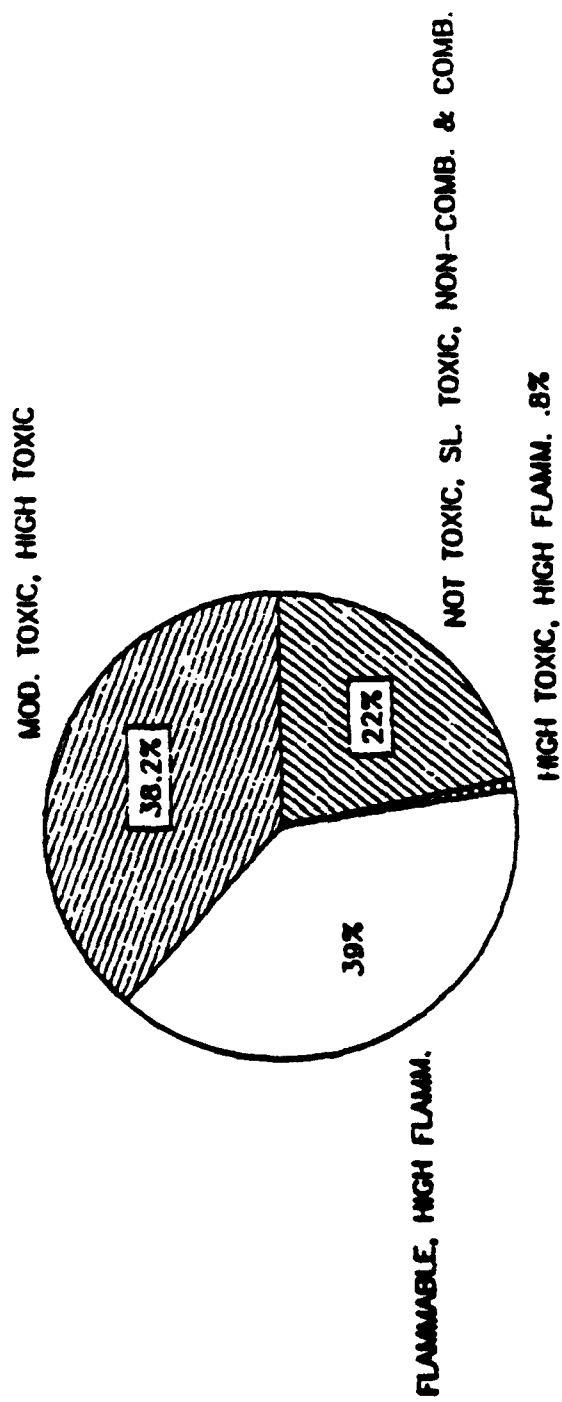
**ALLYL CHLORIDE  
BENZENE  
CROTONALDEHYDE  
DI-n-PROPYLAMINE  
DIISOBUTYLAMINE  
HEXAMETHYLENEIMINE  
ISOBUTYRONITRILE  
TRIETHYLAMINE  
n-BUTYL MERCAPTAN  
n-ETHYL CYCLOHEXYLAMINE  
n-ETHYL-n-BUTYLAMINE**

**TABLE B-13. Highly Toxic, Highly Flammable**

**ETHYL MERCAPTAN  
HYDROGEN SULFIDE  
VINYL CHLORIDE**

Another means by which the floating CHRIS chemicals may be grouped is according to the degree of hazard that they present. By this system, chemicals determined to be both highly toxic and highly flammable would form one group; those found to be either moderately toxic or highly toxic would form another group; a third group would contain those chemicals that are flammable or highly flammable; and the fourth group would be comprised of the remainder of the chemicals. The advantage of such an arrangement is that attention is focused toward the hazardous nature of the chemicals. The disadvantage of this system lies in the large size of the fourth group which masks the characteristics of each chemical.

The first grouping of highly toxic, highly flammable is already listed in Table B-13. The percent distribution of the 292 floating chemicals according to these groupings is depicted in Figure B-2, and the remainder of the groupings is listed in Tables B-14 through B-16.



Legend

SL = Slightly  
 MOD = Moderately  
 HIGH = Highly  
 FLAMM. = Flammable

**Figure D-2. Percentage Distribution of 315 Floating Chemicals in Reference to Flammability and Toxicity Rating.**



TABLE B-14. Moderately Toxic, Highly Toxic

ACETOPHENONE  
ADIPONITRILE  
ALLYL CHLORIDE  
n-AMYL METHYL KETONE  
n-AMYL MERCAPTAN  
iso-AMYL NITRITE  
ANILINE  
n-AMYL NITRATE  
ASPHALT  
ACETYL ACETONE  
iso-BUTYRALDEHYDE  
iso-BUTYL ACRYLATE  
BENZYL ALCOHOL  
n-BUTYL ACETATE  
tert-BUTYL HYDROPEROXIDE  
BENZENE  
sec-BUTYL ACETATE  
n-BUTYL ACRYLATE  
n-BUTYL MERCAPTAN  
n-BUTYRALDEHYDE  
BUTYL BUTYRATE  
BENZALDEHYDE  
BENZONITRILE  
CARENE  
CYCLOHEXANONE  
CREOSOTE, COAL TAR  
CYCLOHEXANONE PEROXIDE  
CUMENE HYDROPEROXIDE  
CARBON MONOXIDE  
p-CYMENE  
CAMPHOR OIL  
CRESOLS  
p-CRESOL  
CROTONALDEHYDE  
CUMENE  
n-DECALDEHYDE  
n-DECYL ALCOHOL  
DI-n-AMYL PHTHALATE  
n-DECYL ACRYLATE  
DI-n-BUTYLAMINE  
DI-n-BUTYL ETHER  
DI-n-BUTYL KETONE  
DIBENZYL ETHER  
DECABORANE  
DIBUTYLPHENOL  
DIISOBUTYLAMINE  
n-DECYLBENZENE  
DIETHYLBENZENE  
DIETHYL CARBONATE  
DI-(2-ETHYLHEXYL) PHOSPHORIC ACID  
DISTILLATES: FLASHED FEED STOCKS  
DECAHYDRONAPHTHALENE  
DIISOBUTYL KETONE

TABLE B-14. Moderately Toxic, Highly Toxic, con'd.

DIMETHYLPOLYSILOXANE  
DIMETHYLPOLYSILOXANE  
DI-n-PROPYLAMINE  
DODECYLDIPHENYL OXIDE DISULFONATE  
DIBUTYL PHTHALATE  
DICYCLOPENTADIENE  
DIMETHYL SULFIDE  
DISTILLATES: STRAIGHT RUN  
4,4-DICHLORO-*o*-TRICHLOROMETHYLBENZYLHYDRO  
ETHYL ACETOACETATE  
ETHYL ACRYLATE  
2-ETHYLHEXYL ACRYLATE  
n-ETHYL-n-BUTYLAMINE  
n-ETHYL CYCLOHEXYLAMINE  
ETHYL CHLORIDE  
ETHYLENE GLYCOL DIETHYL ETHER  
ETHYL ETHER  
ETHYL FORMATE  
ETHYLHEXALDEHYDE  
ETHOXYDIHYDROPYRAN  
2-ETHYL HEXANOL  
ETHYLENE GLYCOL MONOBUTYL ETHER ACETATE  
ETHYL MERCAPTAN  
ETHYLIDENENORBORNENE  
2-ETHYL-3-PROPYLACROLEIN  
ETHYLBENZENE  
ETHOXYLATED TRIDECANOL  
ETHYL TOLUENE  
ETHYL NITRITE  
n-HEXALDEHYDE  
HYDROGEN SULFIDE  
HEXAMETHYLENEIMINE  
ISOBUTYRONITRILE  
ISODECALDEHYDE  
ISOCTYL ALCOHOL  
ISOPHORONE DIISOCYANATE  
ISOPROPYL ETHER  
ISOPHORONE  
ISOPHORONE DIAMINE  
ISOPRENE  
ISOVALERALDEHYDE  
LAUROYL PEROXIDE  
LAURYL MERCAPTAN  
METHYL AMYL ALCOHOL  
METHYL AMYL ACETATE  
n-METHYLANILINE  
METHYL -n-BUTYL KETONE  
METHALLYL CHLORIDE  
2-METHYL-6-ETHYL ANILINE  
2-METHYL-5-ETHYLPYRIDINE  
METHYL ISOBUTYL CARBINOL  
METHYL ISOBUTYL KETONE  
METHYL NAPHTHALENE

TABLE B-14. Moderately Toxic, Highly Toxic, con'd.

MESITYL OXIDE  
METHYL STYRENE, ALPHA  
NONANE  
NAPHTHA:COAL TAR  
NONYL PHENOL  
1-NITROPROPANE  
2-NITROPROPANE  
NAPHTHA:STODDARD SOLVENT  
NAPHTHA:SOLVENT  
NAPHTHENIC ACID  
OIL, MISC: ABSORPTION  
OIL, MISC: TRANSFORMER  
n-PROPYL ACETATE  
POLYETHYLENE POLYAMINES  
n-PROPYL MERCAPTAN  
PYRETHRINS  
1-PENTENE  
STYRENE  
TRIMETHYLACETIC ACID  
TRIETHYLBENZENE  
TRIETHYLAMINE  
TETRAHYDRONAPHTHALENE  
o-TOLUIDINE  
TOLUENE  
n-VALERALDEHYDE  
VINYL ACETATE  
VINYL CHLORIDE  
VINYL ETHYL ETHER  
VINYL FLUORIDE  
VINYL METHYL ETHER  
VINYL NEODECANATE  
VINYL TOLUENE  
XYLENOL

TABLE B-15. Flammable, Highly Flammable

n-AMYL ALCOHOL  
sec-AMYL ACETATE  
ACETYLENE  
ALLYL CHLORIDE  
n-AMYL ACETATE  
n-AMYL MERCAPTAN  
n-AMYL CHLORIDE  
iso-AMYL NITRITE  
tert-AMYL ACETATE  
iso-BUTYRALDEHYDE  
iso-BUTYL ACRYLATE  
n-BUTYL ACETATE  
BUTADIENE  
tert-BUTYL HYDROPEROXIDE  
BENZENE  
sec-BUTYL ACETATE  
n-BUTYL MERCAPTAN  
BUTYLENE  
n-BUTYRALDEHYDE  
BUTANE  
tert-BUTYL ACETATE  
CYCLOHEXANE  
COLLODION  
CARBON MONOXIDE  
CAMPHENE  
CYCLOPROPANE  
CHLOROPRENE  
CROTONALDEHYDE  
CYCLOHEXENE  
CYCLOPENTANE  
DI-n-BUTYL ETHER  
DIISOBUTYLENE  
DIISOBUTYLAMINE  
DODECYLMETHACRYLATE  
DIETHYL CARBONATE  
DIETHYL KETONE  
1,1-DIFLUOROETHANE  
DIHEPTYL PHTHALATE  
DIISONONYL PHTHALATE  
2,2-DIMETHYL OCTANOIC ACID  
DI-n-PROPYLAMINE  
DICYCLOPENTADIENE  
DIMETHYL SULFIDE  
4,4-DICHLORO- $\alpha$ -1-TRICHLOROMETHYLBENZYLHYDRO  
DIUNDECYL PHTHALATE  
ETHYL ACRYLATE  
n-ETHYL-n-BUTYLAMINE  
ETHYL BUTYRATE  
n-ETHYL CYCLOHEXYLAMINE  
ETHYL CHLORIDE  
ETHYL CYCLOHEXANE  
ETHYLENE GLYCOL DIETHYL ETHER  
ETHYL ETHER

TABLE B-15. Flammable, Highly Flammable, con'd.

ETHYL FORMATE  
ETHYL MERCAPTAN  
ETHYLIDENENORBORNENE  
ETHYL ACETATE  
ETHYLBENZENE  
ETHANE  
ETHYL METHACRYLATE  
ETHYL NITRITE  
GASOLINE BLENDING STOCKS: ALKYLATES  
GASOLINE: AUTOMOTIVE (4.23G Pb/GAL)  
GASOLINE: AVIATION (4.86G Pb/GAL)  
GASOLINE: CASINGHEAD  
GAS OIL: CRACKED  
GASOLINE: POLYMER  
GASOLINE BLENDING STOCKS: REFORMATES  
GASOLINE: STRAIGHT RUN  
n-HEXALDEHYDE  
HYDROGEN SULFIDE  
HEPTANOIC ACID  
HEXAMETHYLENEIMINE  
HEPTANE  
1-HEPTENE  
HEXANE  
1-HEXENE  
HYDROGEN, LIQUIFIED  
ISOPROPYL ACETATE  
ISOAMYL ACETATE  
ISOBUTYL ACETATE  
ISOBUTYLENE  
ISOBUTYRONITRILE  
ISOBUTANE  
ISOHEXANE  
ISOOCTALDEHYDE  
ISOOCTANE  
ISOPROPYL ETHER  
ISOPRENE  
ISOPENTANE  
ISOPROPYL CYLCOHEXANE  
ISOVALERALDEHYDE  
JET FUEL: JP-4  
LIQUIFIED PETROLEUM GAS  
METHYLACRYLATE  
METHYL ACETYLENE, PROPADIENE MIXTURE  
METHYL-t-BUTYL ETHER  
METHYL -n-BUTYL KETONE  
METHALLYL CHLORIDE  
METHYLCYCLOPENTANE  
2-METHYL-6-ETHYL ANILINE  
METHYL ISOBUTYL KETONE  
METHYL METHACRYLATE  
2-METHYL PENTENE  
MESITYL OXIDE  
METHANE

TABLE B-15. Flammable, Highly Flammable, con'd.

NONANE  
NEOHEXANE  
1-NONENE  
NONENE  
1-NITROPROPANE  
2-NITROPROPANE  
NAPTHA:VM & P (75% NAPTHA)  
OCTANE  
OIL, MISC: COAL TAR  
OIL: CRUDE  
1-OCTENE  
n-PROPYL ACETATE  
1,3-PENTADIENE  
1,4-PENTADIENE  
n-PROPYL MERCAPTAN  
n-PENTANE  
1-PENTENE  
PETROLEUM NAPHTHA  
STYRENE  
TRIETHYLAMINE  
TOLUENE  
TURPENTINE  
n-VALERALDEHYDE  
VINYL ACETATE  
VINYL CHLORIDE  
VINYL ETHYL ETHER  
VINYL FLUORIDE  
VINYL METHYL ETHER  
m-XYLENE  
o-XYLENE  
p-XYLENE

TABLE B-16. Non-Toxic, Slightly Toxic, Noncombustible,  
Combustible

n-AMYL ALCOHOL  
sec-AMYL ACETATE  
ACETYLENE  
ACETOPHENONE  
ADIPONITRILE  
n-AMYL METHYL KETONE  
n-AMYL ACETATE  
n-AMYL CHLORIDE  
ANILINE  
n-AMYL NITRATE  
ASPHALT  
ACETYL ACETONE  
AMYL PHTHALATE  
tert-AMYL ACETATE  
BENZYL ALCOHOL  
BUTADIENE  
iso-BUTYL METHACRYLATE  
n-BUTYL METHACRYLATE  
n-BUTYL ACRYLATE  
BUTYLENE  
p-tert-BUTYLPHENOL  
BUTYL BUTYRATE  
BUTANE  
tert-BUTYL ACETATE  
BENZALDEHYDE  
BENZONITRILE  
CARENE  
CYCLOHEXANONE  
CREOSOTE, COAL TAR  
CYCLOHEXANONE PEROXIDE  
CYCLOHEXANE  
COLLODION  
CUMENE HYDROPEROXIDE  
p-CYMENE  
COPPER NAPHTHENATE (IC) COPPER (II) NAPTH  
CAMPHOR OIL  
CYCLOPROPANE  
CHLOROPRENE  
CRESOLS  
p-CRESOL  
CUMENE  
CYCLOHEXENE  
CYCLOPENTANE  
n-DECALDEHYDE  
n-DECYL ALCOHOL  
DI-n-AMYL PHTHALATE  
n-DECYL ACRYLATE  
DI-n-BUTYLAMINE  
DIISOBUTYL CARBINOL  
DI-n-BUTYL KETONE  
DIISOBUTYLENE  
DIBENZYL ETHER  
DECABORANE

TABLE B-16. Non-Toxic, Slightly Toxic, Noncombustible,  
Combustible, con'd.

DIBUTYLPHENOL  
n-DECYLBENZENE  
1-DECENE  
DODECYLBENZENE  
1-DODECENE  
DODECANOL  
DIETHYLBENZENE  
DIETHYL KETONE  
DIETHYLENE GLYCOL MONOBUTYL ETHER ACETAT  
DI-(2-ETHYLHEXYL)PHOSPHORIC ACID  
DISTILLATES: FLASHED FEED STOCKS  
DECAHYDRONAPHTHALENE  
DIISODECYL PHTHALATE  
DIISOBUTYL KETONE  
DIISOCTYL PHTHALATE  
DIISOBUTYL PHTHALATE  
DIMETHYLPOLYSILOXANE  
DIMETHYLPOLYSILOXANE  
DIOCTYL ADIPATE  
DODECENE  
DIOCTYL PHTHALATE  
DIBUTYL PHTHALATE  
DIPENTENE  
DISTILLATES: STRAIGHT RUN  
ETHYL ACETOACETATE  
2-ETHYLHEXYL ACRYLATE  
ETHYL BUTYRATE  
ETHYL BUTANOL  
ETHYL CYCLOHEXANE  
ETHYLHEXALDEHYDE  
ETHOXYDIHYDROPYRAN  
ETHYLHEXYL TALLATE  
2-ETHYL HEXANOL  
ETHYLENE GLYCOL MONOBUTYL ETHER ACETATE  
ETHOXYLATED DODECANOL  
ETHOXYLATED PENTADECANOL  
ETHOXYLATED TETRADECANOL  
2-ETHYL-3-PROPYLACROLEIN  
ETHYL ACETATE  
ETHOXYLATED TRIDECANOL  
ETHYL TOLUENE  
ETHANE  
ETHYL METHACRYLATE  
EPOXIDIZED VEGETABLE OILS  
GASOLINE BLENDING STOCKS: ALKYLATES  
GASOLINE: AUTOMOTIVE (4.23G Pb/GAL)  
GASOLINE: AVIATION (4.86G Pb/GAL)  
GASOLINE: CASINGHEAD  
GAS OIL: CRACKED  
GASOLINE: POLYMER  
GASOLINE BLENDING STOCKS: REFORMATES  
GASOLINE: STRAIGHT RUN  
HEPTANOIC ACID



TABLE B-16. Non-Toxic, Slightly Toxic, Noncombustible,  
Combustible, con'd.

HEPTANE  
1-HEPTENE  
HEPTANOL  
HEXANE  
1-HEXENE  
HEXANOL  
HYDROGEN, LIQUIFIED  
ISOAMYL ALCOHOL  
ISOPROPYL ACETATE  
ISODECYL ACRYLATE  
ISOAMYL ACETATE  
ISOBUTYL ACETATE  
ISOBUTYLENE  
ISOBUTANE  
ISODECALDEHYDE  
ISOHEXANE  
ISOOCTYL ALCOHOL  
ISOOCTALDEHYDE  
ISOOCTANE  
ISOPHORONE DIISOCYANATE  
ISOPHORONE  
ISOPHORONE DIAMINE  
ISOPENTANE  
ISOPROPYL CYCLOHEXANE  
ISODECYL ALCOHOL  
JET FUEL: JP-4  
JET FUEL: JP-1 (KEROSENE)  
JET FUEL: JP-3  
JET FUEL: JP-5 (KEROSENE, HEAVY)  
KEROSENE  
LINEAR ALCOHOLS (12-15 CARBONS)  
LIQUIFIED PETROLEUM GAS  
LAUROYL PEROXIDE  
LAURYL MERCAPTAN  
METHYL AMYL ALCOHOL  
METHYL AMYL ACETATE  
METHYLACRYLATE  
n-METHYLANILINE  
METHYL ACETYLENE, PROPADIENE MIXTURE  
METHYLCYCLOPENTANE  
2-METHYL-5-ETHYLPRYIDINE  
METHYL ISOBUTYL CARBINOL  
METHYL METHACRYLATE  
METHYL NAPHTHALENE  
MINERAL SPIRITS  
2-METHYL PENTENE  
METHYL STYRENE, ALPHA  
METHANE  
NAPHTHA:COAL TAR  
NEOHXANE  
1-NONENE  
NONANOL  
NONYL PHENOL

TABLE B-16. Non-Toxic, Slightly Toxic, Noncombustible,  
Combustible, con'd.

NONENE  
NAPTHA:STODDARD SOLVENT  
NAPTHA:SOLVENT  
NAPHTHENIC ACID  
NAPTHA:VM & P (75% NAPTHA)  
NITROGEN, LIQUIFIED  
OCTANE  
OIL, MISC: ABSORPTION  
OIL, EDIBLE: CASTOR  
OIL, EDIBLE: COCONUT  
OIL: CLARIFIED  
OIL, MISC: CASHEW NUT SHELL (UNTREATED)  
OIL, MISC: CROTON  
OIL, EDIBLE: COTTONSEED  
OIL, MISC: COAL TAR  
OIL: DIESEL  
OCTYL EPOXY TALLATE  
OIL, FUEL: NO. 4  
OIL, EDIBLE: FISH  
OIL, FUEL: NO. 5  
OIL: CRUDE  
OLEIC ACID  
OIL, MISC: LUBRICATING  
OIL, EDIBLE: LARD  
OIL, MISC: LINSEED  
OIL, MISC: MINERAL  
OIL, MISC: MINERAL SEAL  
OIL, MISC: MOTOR  
OIL, MISC: NEATSFOOT  
OIL, FUEL: NO. 1-D  
OIL, EDIBLE: OLIVE  
OIL, FUEL: NO. 1 (KEROSENE)  
OIL, EDIBLE: PALM  
OIL, EDIBLE: PEANUT  
OIL, MISC: PENETRATING  
OIL, MISC: ROAD  
OIL, MISC: RANGE  
OIL, MISC: ROSIN  
OIL, MISC: RESIN  
OIL, EDIBLE: SOYA BEAN  
OIL, MISC: SPINDLE  
OIL, EDIBLE: SAFFLOWER  
OIL, MISC: SPERM  
OIL, FUEL: NO. 6  
OIL, MISC: SPRAY  
OCTANOL  
OIL, MISC: TURBINE  
OIL, EDIBLE: TUCUM  
OIL, FUEL: NO. 2-D  
1-OCTENE  
OIL, MISC: TRANSFORMER  
OIL, MISC: TALL  
OIL, MISC: TANNER'S

TABLE B-16. Non-Toxic, Slightly Toxic, Noncombustible,  
Combustible, con'd.

OIL, FUEL: NO. 2  
OIL, EDIBLE: VEGETABLE  
PENTADECANOL  
1,3-PENTADIENE  
1,4-PENTADIENE  
POLYPROPYLENE GLYCOL  
POLYBUTENE  
n-PENTANE  
PETROLATUM  
PETROLEUM NAPHTHA  
PROPYLENE TETRAMER  
STEARIC ACID  
TRIMETHYLACETIC ACID  
TETRADECYLBENZENE  
1-TRIDECENE  
TRIDECANOL  
TRIETHYLBENZENE  
TALLOW FATTY ALCOHOL  
TETRAHYDRONAPHTHALENE  
o-TOLUIDINE  
TALLOW  
TURPENTINE  
1-TETRADECENE  
TETRADECANOL  
n-UNDECYLBENZENE  
1-UNDECENE  
UNDECANOL  
VINYL TOLUENE  
WAX: CARNAUBA  
WAX: PARAFFIN  
m-XYLENE  
o-XYLENE  
p-XYLENE  
XYLENOL

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## APPENDIX C

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## APPENDIX D

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PART II

EVALUATION OF FOAM VAPOR SUPPRESSION AND OF  
COMPATIBILES BETWEEN SPILLED CHEMICALS  
AND RESPONSE EQUIPMENT

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## I. CHARACTERISTICS AND MECHANISMS OF VAPOR SUPPRESSION OF FOAM INTRODUCTION

In recent years the federal government has promulgated regulations which designate responsibility for responses to spills of hazardous chemicals. The U.S. Coast Guard has been delegated the responsibility for responses to spills of hazardous chemicals affecting navigable waterways. One major concern associated with the release of hazardous chemicals is the production of vapors which could adversely affect the population or the environment. The hazards can stem from vapors which are toxic or flammable. From previous investigation, the most plausible response method for the mitigation of hazardous vapors is the application of an aqueous foam.

Current response methods are not well formulated to cover the myriad of potential hazards and behaviors which may be encountered by spill response personnel. The development of an updated response manual is needed to inform response personnel of new response technologies. To assist in predicting foam behavior for the response manual, a mathematical analysis of the vapor-suppression mechanisms is being conducted in an attempt to predict the efficiency of vapor suppression by foam. Pertinent information hoped to be obtained from such an analysis includes thickness of foam needed to reduce vapor concentration below the lower explosive level and reapplication time.

### BACKGROUND

Aqueous foams have been a source of interest for centuries and have been studied scientifically since the 17th century. Examples of aqueous foams can be found everywhere. In nature, several insects protect themselves during the pupa stage by enveloping their bodies in a secreted foam which later hardens. Natural waters have the ability to foam with the proper agitation. The head of beer is an aqueous foam caused by the entrainment of carbon dioxide.

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Foams are an agglomeration of air and water with a small amount of impurity. Typical foams are 95 percent air and 5 percent water. An impurity in these solutions causes them to foam. Because of the chemical nature of the impurity, it has the ability to lower the surface tension of the water to accommodate the large surface area of foams. Impurities with the ability to lower surface tensions are called surfactants or surface-active agents.

Early scientific investigation of foams was on the actual mechanism of foaming. The interest was on the intermolecular interactions which resulted in the lowering of the surface tension. More recent studies focused on engineered foams to accomplish specified tasks. Some of these applications are industrial separation processes, secondary oil recovery, fire fighting, and, more recently, vapor suppression of hazardous materials.

Early investigations of foams have given explanations for the stability of these highly energetic systems. Foams must overcome the destructive forces of surface tension to maintain their large interfacial surface areas. This is accomplished by the lowering of the surface tension.

The mechanism of the surface-active agents lowering surface tension is dependent on solubility differences in the surfactant chain. Surfactant molecules, usually alcohols or polymers, are made up of two chemical groups which differ greatly in their solubility in water. The hydrophilic group is very soluble in water and is typically OH, CO<sub>2</sub>Na, or SO<sub>3</sub>K. The highly insoluble, or hydrophobic, group is a long hydrocarbon chain. The surfactant's surface activity is dependent on its solubility and length.



Surfactant molecules orient themselves in a particular fashion in the bubble wall. The hydrophilic group has affinity for the water and is submerged in the bubble wall or lamellae. The hydrophobic group prefers the air-water interface, and probably a portion of the hydrocarbon chain is located in the internal gas of the bubble. This position of the surfactant molecule is more energetically favorable than that of water molecules, and consequently the surface tension is lowered.

Foams are, in general, unstable. They begin to collapse as soon as they are generated. Foam collapse can be accounted for by two mechanisms. The first mechanism is foam drainage. Gravitational effects cause excess water from the foam to drain through a system of interconnected lamellae called Plateau borders, which were named after the 19th century physicist who first discovered them. Plateau borders are always the product of the intersection of three bubbles. This drainage causes instability because the lamellae are thinned to the point where they can be easily ruptured by vibrations, by disturbances from diffusing chemicals, or because the lamellae have thinned beyond the physical limitations of the system. Mathematical attempts to predict foam drainage were successful when modeled as the drainage of liquid between two parallel plates. Equation 1 is an example of a two-parameter drainage equation.

$$R = a (bt + 1)^{-1.667} \quad (1)$$

This expression is representative of drainage characteristics of simple foam solutions that drain quickly. However, they are not applicable to the modern-day engineered foams that contain additives to extend foam life. In this case, drainage equations would have to predict the equilibrium between intermolecular forces and the effects of gravity and viscosity. Presently, no equations of this type are available.

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The second mechanism of foam collapse is caused by the diffusion of air between adjacent bubbles. The internal pressure of a bubble is inversely proportional to the bubble radius. Smaller bubbles have higher pressures than larger ones. Generated foams have a normal distribution of bubble sizes. Pressure differences between adjacent bubbles create a driving force for the diffusion of gas between bubbles in an attempt to equalize their pressures. As the gas from the smaller bubble diffuses to the larger bubble, the radius of the smaller bubble decreases and its pressure increases: this creates a larger driving force. This can continue until the smaller bubble disappears. The result is a foam with a lowered total surface area. This mechanism was first proposed by de Vries (1957) and later extensively studied by Cheng and Lemlich (1985). The results from their studies are a collection of theoretical equations for predicting changes with time in the distribution of bubble sizes.

Foam lifetime is a key parameter in the development of engineered foam. Early studies by Marangoni and Gibbs identified a mechanism of foam stability for simple foams (Bikerman, 1973). These simple foams are water and a small amount of surface active agents agitated to entrain air. As the bubbles stretch, the concentration of surface-active agents decreases and thus causes an increase in the surface tension. With an increase in the surface tension, the bubble wall will try to contract. This will oppose the initial stretching. Shortly after the bubble wall contracts, surfactant molecules will diffuse to the newly contracted film because of the lowered concentration due to the initial stretch. As the concentration of surface-active agents increases, the surface tension decreases and the film equilibrates.

Studies by Bikerman (1973) identified that additives can aid in foam stability. These additives have the ability to increase the surface and bulk viscosity which slows drainage. These additives may also interfere with steric forces to prolong foam life. Additives range from proteins to metal stearates. Although the factors of foam stability are generally known, no quantitative relationship exists that correlates the effects of additives to foam lifetime. Modern-day foams have taken advantage of the qualitative work done by Bikerman and others to engineer foams which are very persistent.

#### VAPOR SUPPRESSION

In the 1970's, it was noticed that foams used for fire fighting when applied to a volatile chemical could suppress vapors. With the increase of concern for developing response techniques for responsible federal agencies, vapor-suppression capabilities of foams have become an area of increased interest. Early studies (Moran, et al, 1971; Friel, 1973; Greer, 1976; and others) were concerned with the feasibility of using foam for the suppression of vapor. Later, studies attempted to identify the variables that are pertinent for the suppression (Gross and Hiltz, 1982).

To understand the mechanisms of vapor suppression, one must begin with the structure of the foam. Foam applied to the surface of a vaporizing chemical offers a medium less favorable for diffusion than air. The foam forms a barrier with a high resistance to both convective and molecular diffusion as well as an ability to absorb vapors. Collectively, this results in a reduction in the concentration of the diffusing component in the vapor space above the foam.

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Two of the most important variables related to the efficiency of vapor suppression are the vapor pressure and the solubility in water of the vaporizing chemical. Vapor pressure is important because it is a measure of the amount of vapor to be suppressed by the foam. Water solubility is important because in early foam life the bubble walls are approximately 95 percent water. It is proposed, on the basis of similar situations of diffusion of gas into bubbles, that the controlling step in the suppression of vapor is the diffusion of the gas through the bubble wall. For convenience, chemicals will be divided into two categories - soluble and insoluble in water.

The characteristics of insoluble chemicals will be discussed first. In early foam life, the primary barrier to gas permeation is the foam lamellae which are predominately water. The ability of gas to permeate is proportional to the product of its solubility and diffusivity in the lamellae. Foam concentrates are generally proportioned with water between 2 and 10 percent to produce foam. The concentrates are typically made up of around 40 percent organic solvents and around 40 percent surface-active agents. The organic solvents are usually glycol ethers, such as butyl ethoxy ethanol. The surface-active agents can be any of many chemicals, which include sodium laryl sulfonates, proteins, or synthetic fluorinated hydrocarbons. The remaining 20 percent of the foam concentrate consists of a variety of additives for foam stability, foam protection, and optically determining foam concentration. As the foam drains (drainage is proposed to be mostly water), the concentration of the surface-active agents and solvents increases. This results in a mixture which is more favorable for permeation. The greatest resistance to diffusion is offered at the chemical/foam interface because the foam there is the last to drain to the more desirable concentration for diffusion. Therefore, a semi-permeable barrier is produced. The persistence of this barrier is proportional to the drainage rate of the foam.

For chemicals which are soluble in water, foam behavior is much the same as above. The only two differences are that the chemical is more permeable through the lamellae during early foam life and the physical characteristics of soluble chemicals may affect the stabilizing forces in the foam.

Another important factor in determining the efficiency of vapor suppression is the compatibility of the foam and the chemical. A previous study (Gross and Hiltz, 1982) indicates that chemicals which can cause shifts in the pH of the foam or which have the ability to form hydrogen bonds with water degrade foam. Foams cannot tolerate large changes in pH. Manufacturers' specifications will indicate the range of pH suitable for use. Chemicals which are able to form hydrogen bonds degrade foam by actually removing water from the bubble wall or interfering with stabilizing forces in the bubble wall and thus cause the foam to collapse. An example of this type of behavior is offered in a MSA report (Gross and Hiltz, 1982). Triethylamine, which collapsed 11 of 16 foams applied for vapor suppression, has the ability to form strong hydrogen bonds with water.

Foam manufacturers have engineered foams applicable to chemicals which form hydrogen bonds or are polar (dielectric constants greater than 2.5). These are referred to as alcohol type foams (ATF). They consist of a fluorocarbon, regular protein, or fluoroprotein surface active agents with metal stearate additives for foam stability. One foam concentrate known as ATF/AFFF has a polysaccharide additive which forms a polymeric membrane between the chemical and foam. The draining water from this foam is rich in the polysaccharide additive. Since the diffusing chemical has an affinity for water, the water is removed, and a polymeric membrane is left to protect the foam from the destructive action of the chemical (DiMeio and Norman, 1986).

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To address the problem of pH changes, special engineered foams have been developed which are applicable to acidic or alkali chemicals. These foams have the ability to tolerate a wide band of pH on either the acidic or alkaline end of the pH scale, depending on the foam concentrate considered. These foams have been developed for the suppression of vapor and are not applicable for extinguishing fires.

The quality of the foam is also important in the efficiency of the vapor suppression. The quality of foam refers to the distribution of bubble sizes and the mixing of the foam concentrate with the water. Foams with a broad distribution of bubble sizes are less stable. The reason for this stems from considerations of foam collapse by Cheng and Lemlich (1985) discussed in the background section. Because of the diffusion of gas between bubbles to equalize internal pressures, larger bubbles cannibalize smaller bubbles and therefore reduce the interfacial area of the foam. Since the interfacial area offers the resistance for diffusion of gas through the foam, the resistance is lowered.

Foam is generated with regular fire-fighting equipment with special air aspiration nozzles or foam generating equipment. For good quality foam, the foam concentrate and the water need to be mixed to form a homogeneous solution. If this is not accomplished, the resulting foam will have a poor bubble distribution which will affect the efficiency of the vapor suppression.

Foams also have the ability to insulate a spilled chemical from solar radiation or convective heat transfer from the ambient air. As a chemical vaporizes, the temperature of the chemical pool is lowered adiabatically. This results in a reduction of vaporization. If the spill is on land, the ground will initially serve as a heat source.

The ground will quickly cool as the temperature of the chemical pool decreases and then aid in insulating the pool against the addition of heat from the ground. With the application of foam, the pool is further insulated by blocking solar radiation and convective heat transfer from the surroundings. Consequently vaporization is reduced. For chemicals that float on the water surface, the water body will be a heat source due to a constant renewal of warm water at the chemical/water interface. This is not necessarily true for cryogen, which may form an ice layer at the chemical/water interface, which will aid in insulating the chemical pool. The probability of this happening is related to the spill size. If the spill volume is large enough for the pool to persist for an extended period of time, the ice layer may form.

#### MATHEMATICAL TREATMENT

In an attempt to mathematically predict the efficiency of vapor suppression by foam, one must be able to account for a number of complex intermolecular phenomena. The intermolecular phenomena include the equilibrium of steric forces to account for foam drainage and the permeability of the diffusing chemical through a lamellae with a changing composition. Thermodynamic treatment of a foam/chemical system requires definitive information about the composition of the foam concentrate. Thermodynamic relationships attempt to account for physical interaction forces between molecules which constitute the solution to predict thermodynamic properties. For this reason, the specific functional groups which constitute the chemicals present in the solution need to be known. To date, only one foam manufacturer has expressed a willingness to cooperate in an exchange of information about the foam concentrate makeup.

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Presently, there are no foam drainage equations which can account for drainage from engineered fire-fighting or vapor-suppression foams. To account for drainage from these foams, a polynomial or exponential equation will have to be fitted for the drainage characteristics of the foam under investigation. This will enable estimations to be made on the composition of the lamellae in the foam. It is these lamellae which offer the resistance to permeation of gas through the foam.

### Lag Time

Results from MSA's report (Gross and Hiltz, 1982) on the feasibility of foam as a vapor suppressant support the concept that a lag or dead time was present during initial foam suppression (See Figure 1). This lag time was especially evident for high-expansion foams. It is proposed that the water draining from the foam was responsible for lag times. The proposed mechanism is that the draining water actually washed the diffusing vapor down to the bottom of the foam, hindering the migration of vapor through the foam.

An attempt was made to verify the proposed mechanism by using a calculational scheme to predict the lag time. The equations for foam drainage are valid for fast-draining foams. From Eq. 1, a volumetric flow rate can be calculated for the draining of water from the foam. A velocity component for the water,  $V_1$ , can be obtained since the area of the foam and the expansion ratio are known.

A velocity component for the vaporizing chemical,  $V_g$ , is needed. This can be accomplished from a correlation supplied by Matsak (1963) for chemicals with boiling points near or above room temperature.

$$S = (5.38 + 4.1 V) P M^{\frac{1}{2}} \quad (2)$$



A. MSA Ultrafoam 2%

1. Cyclohexane
2. Benzene
3. Toluene
4. Ethyl Benzene

B. Lorcon Full-Ex 2%

1. Cyclohexane
2. Benzene
3. Toluene
4. Ethyl Benzene

C. Emulsiflame 2%

1. Cyclohexane
2. Benzene
3. Toluene
4. Ethyl Benzene

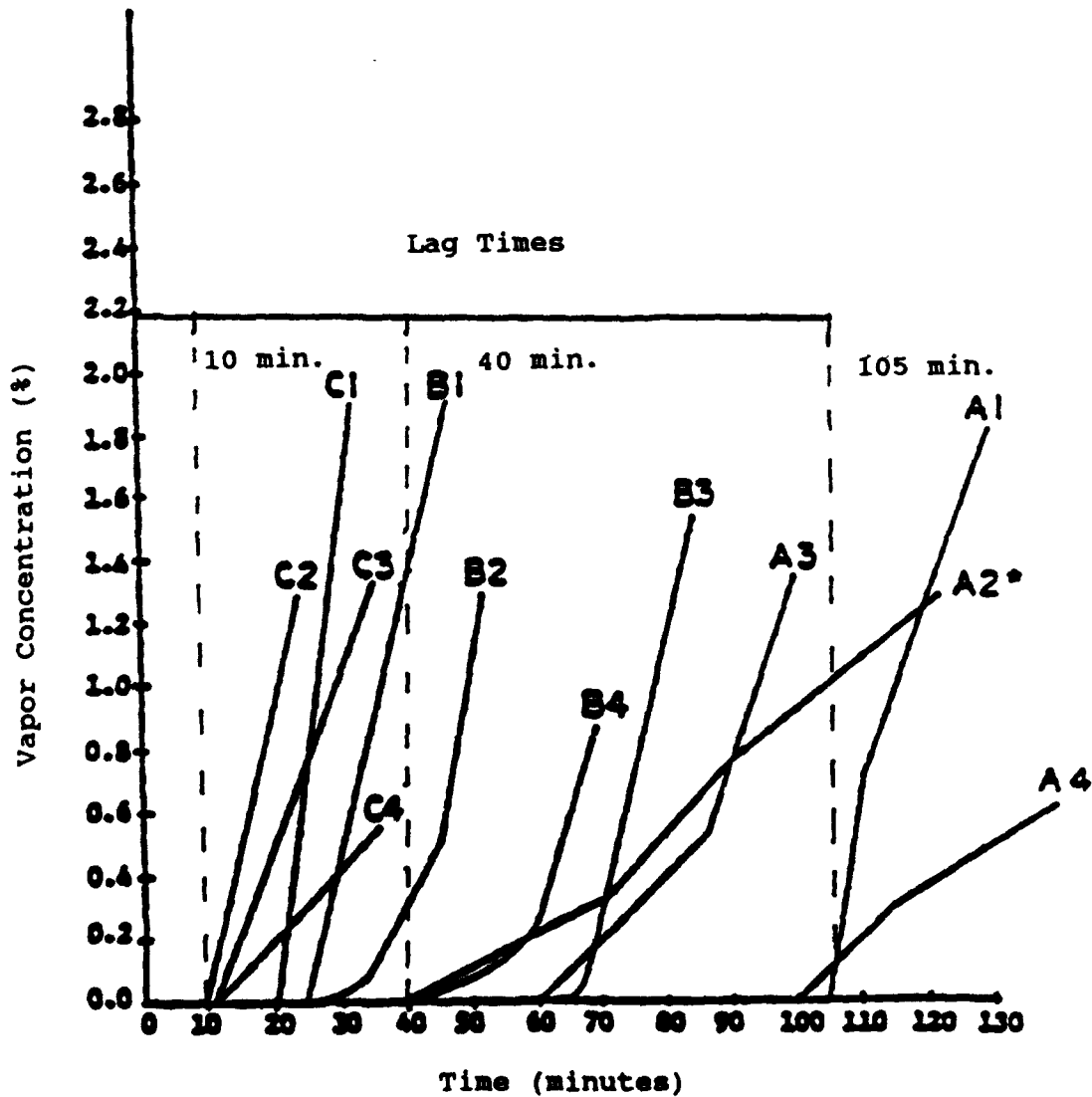


Figure 1. High-expansion foams with nonpolar hydrocarbons (initial foam height was 20 in.)

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Vaporization rates from this equation are in units of mass area-time. From the geometry of the test container, the velocity component for the vaporizing chemical can be determined. This treatment of the situation is similar to that of gas absorption in agitated tanks. The velocity components are summed with the water velocity component having a negative sign and the vapor velocity component a positive sign. The summed value is referred to as a slip velocity and is a measure of the magnitude and direction of the bulk fluid (gas or liquid) motion. In early foam application, the slip velocity is negative; this reflects that the vapor has been washed down to the water/chemical interface. A positive slip velocity is an indication that the vapor from the chemical has begun migrating through the foam.

Results on lag times for fast-draining foams from this mathematical treatment were compared with those from the MSA report (Gross and Hiltz, 1982) and were found to be similar. For slow-draining foams, the drainage equations are no longer valid. A detailed sample calculation using the aforementioned mathematical treatment is given in Appendix A.

On the basis of the results, the calculational scheme has some merit, but when the actual mechanisms the equations reflect are considered, the proposed mechanism appears questionable. For the example in Appendix A, the high-expansion foam drains around 70 cubic centimeters of water. The volume of the vaporizing chemical is around 1500 cubic centimeters. It seems unlikely that this amount of water could wash this amount of vapor. However, this proposed mechanism of vapor is analogous to flooding in countercurrent mass transfer operations in packed towers.

In the treatment of flooding, mathematical correlations involve the ratio of the gas and liquid mass flow rates per hour per cross-sectional area. The following ratio becomes the ratio of interest instead of the ratio of the volumes of gas and liquid:

$$\frac{G_x}{G_y} = \frac{V_l \rho_l}{V_g \rho_g} \quad (3)$$

where  $G_x$  and  $G_y$  are the liquid and gas mass velocities, respectively, and  $\rho_l$  and  $\rho_g$  are the densities of liquid and gas, respectively. For the example given in Appendix A, the mass velocity ratio is 1,271 after 1 minute and 170 after 10 minutes. On the basis of these considerations, the proposed mechanism becomes more acceptable.

#### Mass Transport Effects

The above calculational scheme can be used to account for the observed lag time in foam vapor-suppression tests. The next step is to construct a method to account for the transport of the chemical through the foam. Since the controlling step for the transport of vapor through the foam is the diffusion of gas through the bubble wall, mathematical expressions are needed to describe the solubility of gas in the bubble wall. As stated earlier in the Vapor-Suppression Section, the concentrations of the bubble wall change during drainage to a composition more favorable for diffusion. The thickness of the bubble walls and their geometry also change during drainage. In early foam life, bubbles are spherical and the bubble walls are relatively thick. As the foam drains, the bubble walls thin and the shape of the bubbles change from spherical to polyhedral. Together the lowering in the concentration of water and the thinning of the bubble walls create a system which is favorable for mass transfer of the chemical through the foam.

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The proposed mathematical treatment of the mechanism incorporates a method outlined by Prausnitz (1969). The system is characterized as gas solubility in mixed solvents. Henry's law states that the concentration of the solubilizing chemical in the liquid phase is proportional to that in the gas phase.

$$f_i = \phi_i Y_i P = H_{i,\text{solvent}} x_i \quad (4)$$

The gas phase fugacity coefficient,  $\phi$ , at low pressures is equal to unity.

The Henry constant for the mixture can be calculated from the following equation derived by O'Connell and Prausnitz (1964):

$$\ln(H_{2,m}) = \sum x_i \ln(H_{2,j}) - \sum \sum a_{ij} x_i Y_k \quad (5)$$

The constant  $a_{ij}$  can be calculated from the following derived equation to account for polar solvents:

$$a_{ij} = \frac{(v_i + v_j) * x_i \omega/kT}{2 v_j \phi^2} \quad (6)$$

where

$$\phi_i = \frac{x_i v_i}{\sum x_i v_i} \quad (7)$$

$v_i$  is the liquid molar volume, and  $\omega$  is the interchange energy, which will be discussed later. The liquid molar volume can be estimated by a method given in The Properties of Gases and Liquid (Reid et al., 1977). This method utilizes empirical parameters based on the structure of the molecule.

After the solubility of the chemical into the bubble wall is determined, the diffusion of chemical through the foam can be calculated by the equation commonly used for mass-transfer operations:

$$N = k_x a(x_b - x_i) \quad (8)$$

where  $N$  = number of moles of chemical absorbed by unit volume per unit time

$k_x$  = mass transfer coefficient

$a$  = interfacial area

$x$  = concentration of the diffusing chemical in the bulk solution and at the interface

The mass-transfer coefficient can be calculated from a equation derived by Cheng and Lemlich (1985):

$$P = \frac{H_{2,m} D_{r3,2}}{3 D(1-D')} \quad (9)$$

where  $D_{r3,2}$  is the sauter-mean bubble radius,  $D$  is the diffusivity, and  $D'$  is the volume of foam that is liquid. This equation is based on the diffusion of gas between bubbles. The result from Eq. 9 is in units of centimeters per second. For the proper units for a mass-transfer coefficient,  $P$  must be multiplied by the ratio of the interfacial area/molecular weight. To obtain the initial reduction of vapors, the interfacial concentration will be set to zero. A detailed outline of the proposed calculational scheme is given in Appendix B.

The above calculational scheme reduces the problem to a single overall resistance due to the application of foam. This resistance is based on the proposed rate-controlling step of the diffusion of vapor through the bubble lamellae. For variances over time, the calculational scheme will take advantage of the fitted drainage equation to account for the drained water from the foam. If the volume drained is known, a new expansion ratio of the foam can be calculated from Eq. 9. The interfacial concentration in Eq. 7, which is initially assumed to be zero, can be increased over the foam life to account for the saturation of the foam by the diffusing gas.

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An attempt to account for the foam lifetime (Reapplication Time) can be made by using results from de Vries (1957). de Vries combined the classical law of Laplace and Young with a form of Fick's law of diffusion to yield the following equation:

$$\tau = \frac{P_a r^2}{2 R T J} \quad (10)$$

where  $P_a$  = surrounding pressure

$r$  = bubble radius

$\gamma$  = surface tension

$J$  =  $1/P$

$T$  = absolute temperature

$R$  = the gas constant

Eq. 10 estimates the lifetime of a small spherical bubble based on the diffusion of gas between bubbles. As the vapor from the chemical spill saturates the foam, Eq. 10 can be recalculated to yield the estimated bubble lifetime. Also, from the drainage equation, the concentrations of solvent, surface active agents, and water will change over time. The solubility of the diffusing gas in this mixture can be adjusted by Eqs. 4 and 5 to account for the changing composition of the lamellae.

As presented, the calculational scheme treats the foam layer as a single bulk phase resistance. This method, although capable of providing gross estimates of vapor flux, may provide underestimates of the active quantity of diffusion species. Comparison of output from the proposed model with experimental data will yield conclusions concerning the tendency of this method to underestimate flux.

Two methods which rely on a calculational scheme similar to the proposed model may provide closer agreement between experimental and predicted diffusion

rates of the chemical species. The first method is a rigorous calculation of the serial resistance present in the foam blanket. The first resistance is viewed as permeation through or across a bubble wall, as is currently developed in the above proposed calculational scheme.

The second resistance is the resistance to mass transfer offered by the air contained within the bubble. This resistance may be quantified by a Fick's law expression for unicomponent diffusion:

$$\frac{N/A}{B_t} = D \rho_m \ln(1-y/1-y_i) \quad (11)$$

where

$N/A$  = moles transferred area

$\rho_m$  = molar density of diffusion species

$y_i$  = interface concentration

$y$  = predicted concentration

$B_t$  = thickness of air space species diffuses across

$D$  = diffusivity

Since a flux known from the original permeation equations and  $y_i$  is related to this, the unknowns from the proposed scheme are  $D$ ,  $\rho_m$ , and  $B_t$ . Generally,  $\rho_m$  may be found or estimated, and many diffusivities in air are tabulated.

Eq. 12 can be used to predict air diffusivity:

$$D = \frac{0.01498 T^{1.81} (1/M_a + 1/M_b)}{P(T_{ca} T_{cb})^{0.1405} (v_{ca} + v_{cb})} \quad (12)$$

The quantity  $B_t$  is related to bubble diameter; therefore the thickness of air space that resists transport is known. This calculation predicts the concentration of diffusing species at the inside upper surface of a bubble available for permeation into the succeeding layer of bubbles above the first layer.

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The third resistance is that offered by the upper bubble wall surface and the lower surface of the bubble immediately above it. If concentration effects due to drainage are ignored, this resistance may be quantified as approximately twice that predicted for the lower bubble surface adjacent to the chemical foam interface (the output from the above proposed scheme). Summation of this series of calculations across the entire foam layer should yield a closer approximation of the flux chemical from the foams.

This rigorous scheme is hindered in application by two limitations. First, the rigorous approach will require thousands of successive approximations in predicting flux from bubble layer to bubble layer. If, for a foam layer of 6 in. with an average bubble size of 6  $\mu\text{m}$ , the scheme would require repetition of the calculations approximately 2500 times. Such a large number of repetitions places severe constraints on the usefulness of this approach from a computational time aspect. Second, the result fails to address the changing concentration of water, solvent, and surfactants in successive layers of bubbles. Since each successive layer offers less resistance to transport, the method may provide underestimates of the flux of diffusions species.

Another approach which may prove useful is division of the foam layer into regimes. Such a scheme would be based on drainage from various heights or layers of the foam. This method might segregate the foam into four regimes: dry, semi-dry, semi-wet, and wet. The identification of regimes would be subjective and would rely on drainage calculations. This method would utilize the proposed calculational scheme and modify it to accommodate the changing concentrations through the foam matrix by estimating bulk regime concentrations based on drainage calculations. This approximation reduces computational efforts compared to a rigorous scheme but may introduce errors through the subjective



determination of foam regimes. Furthermore, this method ignores the resistance to transport offered by the air space inside a bubble which, although small, may prove significant across the entire foam depth.

The main limitation of the proposed calculational schemes is that the chemicals involved, especially the surface active agents, are obscure, and a complete list of physical constants is needed for the above calculations. For some foam concentrates, the identity of the surface-active agent is not definitely known. The uncertainty comes from the fact that the surfactants are the results of a complicated chemical synthesis which has not been completely characterized. Unfortunately, the foam concentrates which seem best suited for vapor suppression involve these surfactants.

Additional model limitations on a theoretical basis exist but are judged negligible. For example, to determine if the initial permeation of the lower bubble layer occurs in the liquid or vapor phase of the diffusing species is impossible. However, on the basis of the fact that vapor diffusion rates are typically higher than those of liquids and due to the high vapor pressure of many of the diffusing species examined, the probable case is gas permeation of the bubble wall. This is the mechanism selected for modeling. Another theoretical limitation exists in that the model views the diffusion of only a single component (chemical vapor) while ignoring the potential co-transport of water due to evaporation from the bubble wall and bulk phase transport. Although this situation is likely, the overall effects on transport are judged to be negligible.

The process of vapor suppression by foam is a complex interaction between the molecules that constitute the system. Many external factors, such as environmental conditions and water makeup, will affect the efficiency of the

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suppression vapor. These external factors are important in determining the quality of the foam which is related to vapor-suppression mechanisms. So that the problem can be reduced to a calculable one, idealized foam quality and environmental conditions will be assumed, and only the vapor-suppression mechanisms considered to be controlling will be modeled. These simplifications and assumptions may not be adequate to sufficiently model the vapor-suppression mechanisms and chemical interactions to predict vapor space concentrations.

### Chemical and Electronic Effects

An important consideration is chemical effects on gas solubility. In the preceding equations, in the estimation of the solubility of gas, the physical forces between solvent and solute were considered. These forces are not useful in accounting for the chemical effects that may be present. Chemical effects include hydrogen bonding, formation of acid-base complexes, and ionization of the chemical in the solvent. When the chemical effects are small, the physical theory offers a good approximation. Frequently, the chemical effects are dominant, and equations based on physical effects to predict thermodynamic parameters are not suitable because they do not account for the chemical effects.

Systematic studies of the effects of chemical force are rare, primarily because it is difficult to characterize chemical forces in a quantitative way. Brown and Brady (1952) were successful in quantifying the effects of an ionizing solvent on solubility, but specific measurements are required for the chemical effects present in the solution. It is important to consider that there are no sharp boundaries between physical and chemical effects. All molecules have forces acting between them, and it is these forces which determine the solubility regardless of their classification - chemical or physical.

Another important consideration is the influence that electronic effects exert on gas solubility. The proposed scheme considers the physical forces between solvent and solute to estimate solubility of the diffusing gas in the bubble layers. Regular solution theory is well adapted to non-polar solvents, but modifications need to be made to extend its applicability to polar solvents.

When the concentration of polar solvents in the bubble well is significant, regular solution theory may be severely limited in providing solubility estimates. Furthermore, when the diffusion species demonstrate significant polarity (amines, ketones, alcohols, etc.), the theory may prove limited. One method of incorporating such effects in the model relies upon Flory-Huggins expansion of lattice and regular solution theories to polymer solutions. The extension defines a dimensionless parameter, which is a measure of the solubility. In terms of regular solution theory, the parameter,  $\chi$ , is defined as:

$$\chi = \frac{v}{RT} (\delta_1 - \delta_2)^2 \quad (13)$$

where  $\delta$  are the solubility parameters which have been utilized in the proposed approach. This interface parameter may also be defined in terms of interchange energy as:

$$\chi = \frac{w}{kT} \quad (14)$$

where  $w$  is the interchange energy,  $k$  is Boltzmann's constant, and  $T$  is the absolute temperature. The interchange energy,  $w$ , may be related to the dipole moments, or polarizability of the molecules in the mixture. For some number of dissimilar molecules,  $z$ , interchange energy is expressed as a potential energy function:

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$$w = z(\Gamma_{12} - \frac{1}{2}(\Gamma_{11} + \Gamma_{22})) \quad (15)$$

The potential energy function,  $\Gamma_{ij}$ , may be determined for both permanent dipoles and induced dipoles. For permanent dipoles, the potential energy function is:

$$\Gamma_{Pij} = \frac{-2 \mu_i^2 \mu_j^2}{r^2 kT} \quad (16)$$

where  $\mu$  is dipole moment (debyes),  $r$  is the separation distance, and  $k$  is Boltzmann's constant. A value for  $r$  can be estimated as two times the longest chain present in the mixture.

The general debye formula for potential energy due to induction by permanent dipoles is:

$$\Gamma_{Iij} = \frac{(\alpha_i \mu_i + \alpha_j \mu_j)}{r^2} \quad (17)$$

where  $\alpha$  is the average polarizability.

The intermolecular forces between non-polar molecules may be determined on the basis of ionization potentials,  $I$ , as

$$\Gamma_{Nij} = \frac{-3\alpha_i \mu_j}{r^2} \frac{I_i I_j}{I_i + I_j} \quad (18)$$

Therefore the potential energy changes of solution due to electronic effects may be determined from utilizing the interchange energy.

The determination of interchange energy allows the proposed calculational scheme to be adapted to account for the detrimental effects of foam behavior observed when chemicals that exhibit high dipole moments are the diffusing species. Although the contribution of polar forces with dipole of 1 debye or less is small, this contribution becomes increasingly significant for dipoles of 1 debye or larger. It is anticipated that substitution on the basis of the dimensionless interchange parameter,  $\chi$ , will allow the Henry's law gas solubility relation to be adapted to fit these highly polar solvent/solute interactions. Thus, equating the dimensionless parameter on the basis of the regular solution theory and interchange energy:

$$\chi = \frac{\omega}{kt} = \frac{\omega}{RT} (\delta_1 - \delta_2)^2 \quad (19)$$

where  $\omega = (\Gamma_{12} - \frac{1}{2}(\Gamma_{11} + \Gamma_{22}))$  as previously defined. It is necessary to sum the potential energy contributions over  $z$  pairs of dissimilar molecules. To accomplish this, we must define the contributions and  $\Gamma_{ii}$  for interactions among same species. These interactions exist for dipoles and non-polar molecules separately. For dipole/dipole interactions of the same species:

$$\Gamma_{ii} = \frac{-2\mu_i^4}{r^4 kT} \quad (20)$$

and for non-polar interactions of the same species:

$$\Gamma_{jj} = \frac{-3 \alpha_j^2 I_j}{4r^6} \quad (21)$$

Application of the geometric mean formula allows determination of

$$\Gamma_{ij} = r(\Gamma_{ii} \Gamma_{jj}) \quad (22)$$

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We now sum the contributions due to dipole/dipole, dipole/non-dipole, and non-dipole/non-dipole interactions for both similar and dissimilar pairs. The bar of the potential energy function indicates the summed contribution of the various interactions.

For dissimilar pairs:

$$\bar{\Gamma}_{ij} = \sum \sum (\Gamma_{Pij} + \Gamma_{Iij} + \Gamma_{Nij}) \quad (23)$$

$$\bar{\Gamma}_{ij} = \sum \sum \frac{-2\mu_i^2\mu_j^2}{3r^6kT} + \frac{\alpha_i\mu_j^2 + \alpha_j\mu_i^2}{r^6} - \frac{3\alpha_i\alpha_j I_j I_i}{2r^6(I_i + I_j)} \quad (24)$$

For similar pairs, the contributions are summed for dipole/dipole interactions and non-dipole/non-dipole interactions:

$$\bar{\Gamma}_{ii} = \sum \frac{-2\mu_i^4}{3r^6kT} - \frac{3\alpha_i I_i}{r^6} \quad (25)$$

Substituting the summed contributions, the interchange energy becomes:

$$\bar{\omega} = z(\bar{\Gamma}_{ij} - \bar{\Gamma}_{ii}) \quad (26)$$

and

$$\bar{x} = \frac{\bar{\omega}}{kT} \quad (27)$$

Therefore the expression can be adapted to fit polar solvent/solute interactions as:

$$\ln(H_{2,m}) = \sum x_j \ln(H_{2,j}) - \sum \sum \frac{\omega x_j (v_j + v_k)}{2 v_j \phi_j} x_i x_k \quad (28)$$

where the diffusing gas solute is designated by a subscript 2.

This method can be expanded to account for three body interaction parameters if needed. It would involve expanding the equations involving  $\Gamma_{ij}$  to include  $\Gamma_{ijk}$ . The expansion to include three-body interaction would be useful for describing more complex interaction.

This method allows a quantitative estimate of the effects of solvent/solute polarity in permeation rates. However, such estimates should be viewed as rough approximations due to additional interactions that occur among polar molecules. Such interactions as hydrogen bonding, pH shifts, or acid-base complex formations are not included in such calculations and, in fact, cannot be quantified due to limitations of solution theory at this time.

## CONCLUSIONS

On the basis of progress made during the last several months, the proposed calculational scheme is based on a single resistance offered by the foam. The calculational scheme will account for variances in the bubble wall composition over time. Figure 2 is a flow diagram of the iterative calculational scheme with references to equations of interest. The results from the model will be a theoretical percent reduction in vapor and reapplication time.

There are several limitations to the proposed calculational scheme. The equations used to determine the solubility of the gas in the bubble wall require information about the foam concentration which may not be available. Estimation techniques can be employed to obtain the needed physical properties, but they may not offer an accurate answer. The model used accounts for physical effects but does not account for chemical effects on solubility. In cases where chemical effects are dominant over physical effects, the proposed method may grossly underestimate the transport of vapor through the foam. No method exists for the quantitative chemical effects on solubility. A qualitative analysis could be accomplished but would require experimental data, which are not available.

The model also does not account for environmental effects on transport mechanisms or foam quality. The system analyzed is a theoretical ideal situation on a smooth water surface. The model does not account for changes in the temperature of the chemical pool. It is proposed that the heat transfer from the water is counterbalanced by the auto cooling by the pool to maintain the pool temperature at initial conditions.



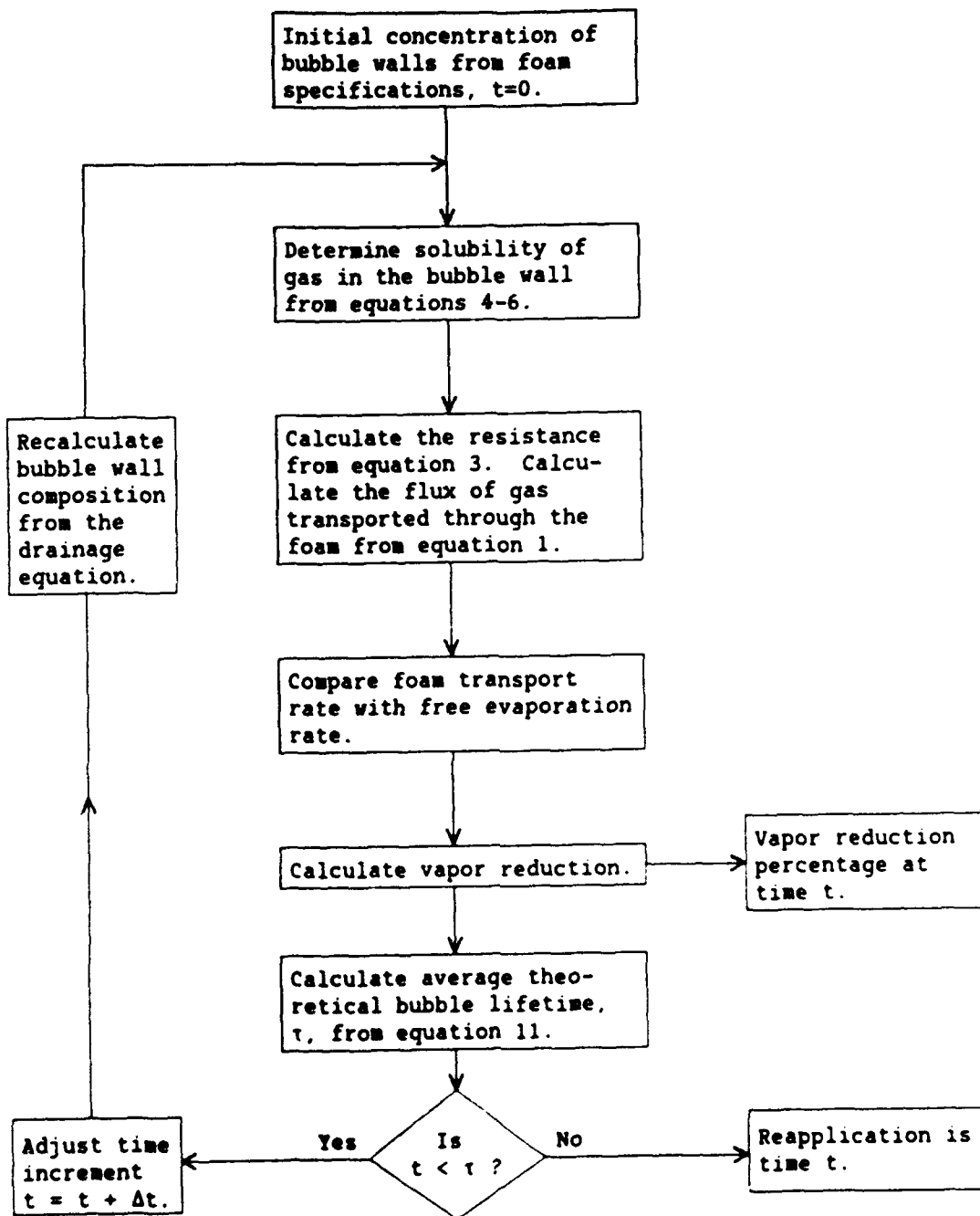


Figure 2: Flowchart for Time - Variant Computational Scheme

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Although the calculational scheme is based on sound thermodynamic relationships and mass-transfer principles, lack of quality data and experimental research hindered the development of the model to an operational stage. Several equations used in the calculational scheme for foam behavior were proposed based on theoretical considerations and have not been tested against field results.

## II. FOAM TESTS AT THE TRANSPORTATION TEST CENTER

Foam tests sponsored by National Foam at the Transportation Test Center were attended to gain a better understanding of foam application and behavior. Personnel who were conducting the tests had extensive backgrounds in development and application of foams. It was hoped that discussions with these personnel would be beneficial in gaining some insight into the mechanism of vapor suppression and variables which affect vapor suppression.

The tests of interest were for ethylene oxide and vinyl chloride monomer. Vinyl chloride monomer is one of the floating CHRIS chemicals and has a very high vapor pressure at ambient temperatures. Ethylene oxide is a CHRIS chemical but because of high water solubility, it is not classified as a floater. Vapor suppression was tested for both chemicals while only ethylene oxide will be tested for fire extinguishing qualities of foam.

The foam to be tested was National Foam's Universal Foam. This foam is an alcohol type foam (ATF). ATFs were developed for use on polar solvents which usually degrade other types of foam. ATFs have a polysaccharide additive which forms a polymeric gel at the foam/chemical interface, protecting the foam from the chemical. The polymeric gel is formed from water (draining from the foam), which has a high concentration of polysaccharides. At the foam/chemical interface, water is removed by chemicals with an affinity for water, leaving the polysaccharides. If the foam is applied to a chemical with little or no affinity for water, the foam behaves like an aqueous film forming foam.

Chemicals with a tendency to degrade foam include polar chemicals or chemicals with an ability to form hydrogen bonds with water. It is suspected that these chemicals degrade foam by interference with the steric equilibrium in the foam bubble matrix.

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The following sections offer a summary of the foam tests for ethylene oxide and vinyl chloride monomer and a summary of conclusions reached from discussions with National Foam personnel.

### Summary of Foam Tests

It was expected that since the ethylene oxide is soluble in water that it had the potential to destroy foam. To circumvent this problem, the concentration of the surfactant was increased to approximately 9%. The reasons for the increased concentration were: (1) an increase in foam stability; (2) a decrease water drainage; and (3) an increase in the amount of polysaccharide which would form a thicker polymeric film. The amount of polysaccharide present in the plateau borders would also increase and would serve to protect the bubble wall from loss of water from the hydrophobic chemicals.

The ethylene oxide was loaded into an insulated metal pan and the free evaporation rate determined. The pan was equipped with a load cell which could determine the amount of material which evaporated. The pan was refilled with ethylene oxide to an appropriate level. The ethylene oxide evaporates at a rate of about 1.5 lbs per minute. Approximately six inches of 9% universal foam was applied to the pan. No weight was lost for an hour. Before the foam application, downwind concentrations were recorded at 10% (8 feet from the pan). After an hour of no weight loss, the foam was carefully removed, and it was noticed that the polymeric film was frozen (approximately 1/4 inch thick) and leaking ethylene oxide (1 ppm).

The polymeric film was very effective in protecting the foam from the degrading nature of the chemical. With this protection, the foam was able to suppress vapors completely for an hour.

Next, a test was set up to ignite the chemical and to see if the Universal Foam could extinguish the fire. About 400 lbs of ethylene oxide were placed in a metal pan. The vapors were ignited with a flare. Foam was applied after about a minute or so of burning. A four-inch foam layer was applied and the fire was controlled. The foam had the same concentrate as the vapor suppression test (9%). The ethylene oxide continued to boil under the foam layer, mainly near the edges of the pan and with small flames burning the released ethylene oxide vapors. The pan was still hot from the burn, and the heat degraded the foam causing vapor releases around the edge. After about 7 1/2 minutes, a considerable flame started around one edge of the pan and another application of foam was required.

Since the ethylene oxide was hot, the frozen polymeric gel layer was never obtained. The ethylene oxide continued to boil under the foam, and the vapor rising through the foam caused it to overflow the pan. The foam which overflowed was saturated with ethylene oxide vapor and continued to burn slowly after falling to the ground. The ethylene oxide was allowed to burn slowly. The foam continued to expand and burn in a controlled fashion.

About twenty minutes after the second application, an attempt was made to totally extinguish the fire, but this was not accomplished. The shape of the pan along with the low drainage of the foam were probably the reasons for the inability of the foam to completely put out the fire. Nonetheless, the foam gave the opportunity for a controlled burn-off. This would be a safe and effective means for cleaning up spills of materials which burn clean.

In conclusion of the fire test, the foam provided an excellent means of controlling the fire and gave the opportunity to dispose of the material by a controlled burn back. One must keep in mind that the key to the success of the

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test was the quickness of the response. If, for instance, the fuel was allowed to burn for some extended time, heating both the fuel and surroundings, the fire most likely could not have been controlled.

A vapor suppression test was also conducted on vinyl chloride monomer. On the day the test was conducted, conditions were less than optimum with wind gusts up to 50 MPH. Although the conditions were not ideal, the test was conducted to gain experience in applying foam under difficult conditions.

It was decided to use a 9% Universal Foam concentration because of the high vaporization rates which could cause foam destruction. The pan was loaded with approximately 416 lbs of VCM. Initial vaporization was very high, approximately 5.0 lbs/min., but the pan began to autorefrigerate due to vaporization. After some thirty minutes, the rate of vaporization slowed considerably as the pan temperature dropped to  $-47^{\circ}\text{C}$ .

The foam was applied with great difficulty for approximately 35 seconds. The use of a backboard proved too difficult, and the foam was simply arched over the pan and the wind carried the foam to the pan. The foam froze upon contact with the VCM. About four inches of foam were applied, of which approximately two inches were frozen. The weight of the foam was around 100 lbs. The top two inches of unfrozen foam were quickly displaced from the pan. During the first 19 minutes 106 lbs of weight was lost, most of which was foam. After 28 minutes, the weight loss stabilized, and during the last five minutes, only 1 lb of weight loss was recorded.

An observer posed the question: "Could a water fog give the same frozen blanket?" Water was then added as a fog. The rate of vaporization quickly increased and the pan temperature rose quickly from  $-47^{\circ}\text{C}$  to  $-18^{\circ}\text{C}$  (which was

probably the boiling point at 4,600 ft. altitude). After some time, approximately five minutes), the temperature of the pan rose to 7°C. At this point, the mixture of water and VCM boiled rapidly.

Two reasons for the behavior follow. First, the foam, being mostly air, has very good insulating properties; since the foam drains slowly, no water is drained to the cold VCM during the first 45 seconds. This gave the foam the opportunity to freeze. Secondly, water has good thermoconductive properties and served as a heat source to the VCM.

In conclusion, the foam offered vapor suppression even though the conditions were not favorable. Vapor concentrations were reduced to 50 ppm just above the pan on the downwind side.

Additional foam tests for vapor suppression have been conducted, and a summary of the results is shown in Appendix C. These tests were developed to determine the feasibility of using foam as a vapor suppressant and not to collect precise data to be used in theoretical calculations. Therefore, the data are not suitable for the development of the foam based vapor suppressant model.

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**SUMMARY OF CONCLUSIONS REACHED FROM DISCUSSIONS WITH  
NATIONAL FOAM PERSONNEL**

Discussions with National Foam personnel were beneficial for gaining insight for foam application and mechanisms causing the suppression of vapors by foam. The conclusions are summarized below.

- o Foam used for vapor suppression should not be applied with non-air aspirating nozzles. Regular firefighting nozzles will produce a poor quality foam with non-uniform bubbles and non-homogenous surfactant concentrations. With non-uniform bubbles, the larger bubbles tend to cannibalize smaller bubbles and therefore degrade the foam.
- o Foam concentrate should always be proportioned and never added directly to the water tank.
- o Foam degradation is caused by losses of H<sub>2</sub>O from the bubble wall and shifts in pH, which disturb the equilibrium in the foam matrix.
- o Foam degradation due to a loss of water from the bubble wall can be avoided by the use of ATF/AFFF foams which protect the foam by a polymeric gel. The concentration of surfactant can be increased to as high as 12% for a chemical with high water solubility like ethylene oxide or for chemicals which shift the pH like triethylamine. This protects the foam from the chemical.
- o Chemicals with high heats of solution (in water) degrade foam. An example of this is foam application (NF Hazmat #2) to chlorosulfonic acid. The foam quickly collapsed.
- o Temperature and the mineral content of the water effect the quality of foam generated. Humidity and wind speed will effect the life of foam due to evaporation.
- o A statistical study conducted by Ed Norman to identify variables or groups of variables which can account for foam behavior reached no conclusion.
- o Primary alcohols are less degrading to foam than secondary and tertiary alcohols. An explanation for this phenomena has not been developed.



**RECOMMENDATIONS**

Recommendations for further work on the development of a foam based vapor suppression model focus on compiling experimental data. The areas which require experimental data include foam drainage behavior, vapor suppression by foam, and a characterization of compatibility between foam and floating CHRIS chemicals. To obtain this data, an experimental method would have to be developed. The data could then be used to correlate parameters such as mass-transfer coefficients and drainage rates which could ultimately lead to estimating the efficiency of the vapor suppression.

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### III. CHEMICAL COMPATIBILITY BETWEEN SPILLED CHEMICALS AND RESPONSE EQUIPMENT

An important consideration for response efforts is the compatibility between spilled chemicals and response equipment. Present technology can produce strong, durable materials which are used in the construction of containment and removal devices. These polymeric materials are susceptible to deterioration from contact with chemicals in which the polymeric material is soluble. The effects from contact with solvents can be total destruction of the material, swelling from absorption of chemicals, or stiffening and buckling due to loss of plasticizers. Since the floating CHRIS chemicals exhibit a broad range of chemical characteristics, it is likely that some chemicals will cause adverse effects to polymeric materials.

Commonly used polymers for response equipment include poly vinyl chloride, chlorinated poly ethylene, urethane, and hypalon. For harsh environments which degrade most polymers, manufacturers have developed chemical resistant materials made up of a combination of polymers.

Response personnel would benefit from an analysis of the effect of contact between polymeric materials and floating CHRIS chemicals. The literature was searched for information on chemical resistance of commonly used polymers. The information found was general. Several sources (Perry, Encyclopedia of Polymers) gave ratings for broad classifications of polymers for selected functional groups. An example is polyurethane's chemical resistance (excellent, good, fair, or poor) to hydrocarbons, both aliphatic or aromatic, oils, fuels, salt water, etc. Since both polymer materials and chemicals within each classification will exhibit a broad range of characteristics, this information would offer only a very general guideline for use.

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A quantitative method is needed to predict the compatibility between a specific polymeric material and a given CHRIS chemical. Such a method exists and involves using solubility parameters.

The idea of a solubility parameter originates from theoretical methods used to predict vapor-liquid equilibrium and is defined as

$$\delta = (\Delta\mu^V/v)^{1/2}$$

where  $\Delta\mu^V$  is energy of complete vaporization and  $v$  is liquid molar volume. The solubility parameter is a function of temperature and pressure, although the difference between the solubility parameters of two chemicals is nearly independent of temperature. The solubility parameter can be thought of as a measure of intermolecular attraction of a chemical. By comparing solubility parameters of different chemicals, information can be gained as to the similarity of the chemicals. Similar chemicals will have solubility parameters of approximately equal values.

For polymeric solutions, a dimensionless parameter  $\chi$  is defined in terms of solubility parameters.

$$\chi = \frac{v_1 (\delta_1 - \delta_2)^2}{RT}$$

where  $\delta_1$  - the liquid molar volume of the solvent

R - the ideal gas law constant

T - temperature

$\delta$  - the solubility parameter.

The subscripts for the solubility parameter refer to the solvent and solute.

$\chi$  for a thermal solution is zero and for mixtures of components which are

chemically similar  $\chi$  is small. Predictions of good solvents for polymers can be made by considering the following criterion.

$$\delta_1 \approx \delta_2$$

It is usually sufficient that the difference between solubility parameters be less than 1.0 for a polymer to be soluble.

In some cases, polymers may be soluble in chemicals with differences in solubility parameters of greater than 1.0. This is due to some interaction between dissimilar molecules which enhance solubility. This interaction is commonly strong hydrogen bonding. Because of this interaction, solubility parameters of solutes are published in ranges for poor, moderate, and strong hydrogen bonding chemicals. Solubility parameters for solvents are usually accompanied with a classification of its ability to form hydrogen bonds.

Comparison of solubility parameters of polymeric materials with floating CHRIS chemicals would provide a qualitative basis for polymer solubility. One advantage of using this method to predict chemical resistance is that definitive data is not needed for the mixture, thus making it possible to determine the interaction between polymeric materials and spilled CHRIS chemicals.

The literature provides an extensive list of experimentally determined solubility parameters for both polymeric materials and solvents. Table 1 provides some of these parameters (Barton, 1983 and Brandrup and Immergut, 1966).

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TABLE 1. SOLUBILITY PARAMETERS FOR SOME SELECTED SOLVENTS AND POLYMERS\*

<u>Solvents</u>	
	$\delta$ (cal/cc) <sup>1/2</sup>
2-ethyl hexanol	9.5
methyl isobutyl carbinol	10.0
2-ethyl butanol	10.5
n-pentanol	10.9
n-butanol	11.4
n-propanol	11.9
ethanol	12.7
methanol	14.5
<u>Polymers</u>	
polyethylene	8.1
polypropylene	9.4
polyurethane	10.0
poly vinyl chloride	10.8

\* Data from: J. Brandrup and E. H. Immergut, Polymer Handbook, John Wiley & Sons, New York, 1966.

For materials or chemicals with no published solubility parameters, a method exists to predict its solubility parameter (Small, 1953). The method uses molar-attraction constants for different functional groups which constitute the molecule. Table 2 provides molar-attraction constants,  $G$ , for chemical groups. The solubility parameter is related to the molar-attraction constants by the following equation:

$$\delta = \sqrt{\Sigma G/M}$$

where  $\Sigma G$  is the sum for all the atoms and groupings of the molecule,  $d$  is density, and  $M$  is molecular weight. The method is useful for estimating solubility parameters with an accuracy to the first decimal place, which is adequate for practical purposes. The method should not be used for alcohols, amines, carboxylic acids or other strong hydrogen bonded compounds unless such functional groups constitute only a small part of the molecule. A most valuable application of Small's method lies in estimating the solubility of polymers in solvents.

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TABLE 2. MOLAR-ATTRACTION CONSTANTS AT 25°C

Group	G	Group	G
-CH <sub>3</sub>	214	CO ketones	275
-CH <sub>2</sub> - single-bonded	133	COO esters	310
-CH<	28	CN	410
>C<	-93	Cl (mean)	260
CH <sub>2</sub> =	190	Cl single	270
-CH= double-bonded	111	Cl twinned as in -CCl <sub>2</sub>	260
<C=	19	Cl triple as in -CCl <sub>3</sub>	250
CH=C-	285	Br single	340
-C=C-	222	I single	425
Phenyl	735	CF <sub>2</sub> n-fluorocarbons only	150
Phenylene (o,m,p)	658	CF <sub>3</sub>	274
Naphthyl	1146	S sulfides	225
Ring, 5-membered	105-115	SH thiols	315
Ring, 6-membered	95-105	ONO <sub>2</sub> nitrates	440
Conjugation	20 - 30	NO <sub>2</sub> (aliphatic nitro-compounds)	440
H (variable)	80-100	PO <sub>4</sub> (organic phosphates)	500
O ethers	70	Si (in silicones)*	-38

\* estimated by H. Burrell (6).



Another method for determining solubility parameters was developed by Hanson (1969). This method would be useful for polar solvents or chemicals with an ability to form hydrogen bonds. The method is referred to as the three-dimensional solubility parameters model. The Handbook of Solubility Parameters and Other Cohesion Parameters (Barton, 1983) provides a list of these experimentally based parameters for a variety of organic solvents.

By making use of the aforementioned method, it is possible to construct a matrix of the interactions of various polymers with some floating CHRIS chemicals. All of the floating CHRIS chemicals cannot be considered because of the limitations of the method. The composition of polymeric materials which may come in contact with spilled floating chemicals would have to be described in detail. Each type of molecule in the material will have to be considered separately as a possible solute. Information on the material may be difficult to find and limit the use of the method. The best source of information on chemical compatibility between chemicals and response equipment is the manufacturer.

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**APPENDIX A  
CALCULATIONAL SCHEME FOR LAG TIME**

- ASSUMPTIONS:** 1) Vaporization remains constant.  
2) Early vapor transport is suppressed by countercurrent washing of vapor by the draining foam.

The calculation is for the suppression of benzene vapor by the application of 20 inches of high expansion (500:1) emulsiflame. Data are taken from MSA's report (Gross and Hiltz, 1982).

A two-parameter drainage equation was fitted to the drainage data supplied by the MSA report. The equation used is:

$$R = a (bt + 1)^{-1.667} \quad (\text{A-1})$$

where the constants were found to be  $a = 15.696$  and  $b = 0.35$ .

The units for R are cubic centimeters per minute. The units needed for a velocity component are centimeters per minute. From the expansion ratio, the area available for flow is:

$$A_{\text{flow}} = A_{\text{Total}} / \text{Expansion Ratio} \quad (\text{A-2})$$

The following equation, given by Matsak (1963), was used to estimate the vaporization rate:

$$S = (5.38 + 4.1 V) P M^{\frac{1}{2}} \quad (\text{A-3})$$

where S = the vaporization rate, g/cm<sup>2</sup>-hr

V = the wind speed, m/sec

M = the molecular weight

P = the vapor pressure, mm Hg

With the use of the density of benzene vapor, the vapor rate can be converted into units of centimeters per minute, which is a vapor velocity component.

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A slip velocity is a measure of the magnitude and direction of the bulk fluid (vapor or gas). The slip velocity is defined as follows:

$$U_s = U_g + U_l \quad (A-4)$$

where  $U_s$  is the slip velocity,  $U_g$  is the velocity component of vapor, and  $U_l$  is the velocity component of liquid. The sign conversion is negative for down and positive for up. When the sign of the slip velocity changes, the vapor begins to migrate through the foam.

The following is an example of the results of the suppression of benzene vapors:

<u>time (minutes)</u>	<u><math>U_g</math> (cm/min)</u>	<u><math>U_l</math> (cm/min)</u>	<u><math>U_s</math> (cm/min)</u>
1	2.14	9.518	-7.378
5	2.14	2.906	-0.766
6	2.14	2.381	-0.241
7	2.14	1.992	+0.8609

This shows that vapor begins to migrate through the foam 7 minutes after application. Results from the MSA report show a lag time of 10 minutes.

**APPENDIX B  
CALCULATIONAL SCHEME FOR MASS TRANSPORT THROUGH FOAM**

The flux of chemical through the foam can be determined by a common equation used in mass-transfer operations:

$$N = k_x a (x_b - x_i) \quad (B-1)$$

where  $N$  = permeation rate, g-moles/unit volume

$k_x$  = mass transfer coefficient, g-moles/unit volume-unit time

$x$  = mole fraction of permeating component in the bulk phase and at the gas-liquid interface

$a$  = interfacial area available for mass transfer

The mass-transfer coefficient can be determined from an equation derived by Cheng and Lemlich (1985):

$$P = \frac{H_{2,m} D_{r3,2}}{3 D (1-D')} \quad (B-2)$$

where  $H_{2,m}$  = Henry's constant

$D_{r3,2}$  = the sauter mean-bubble diameter

$D$  = the diffusivity

$D'$  = the foam fraction that is liquid

To obtain the proper units for Eq. B-1,  $P$  must be multiplied by the ratio of the interfacial area/molecular weight.

The concentration at the gas-liquid interface is set equal to zero to obtain the maximum permeation rate. The concentration in the bulk phase can be calculated by a method outlined by O'Connell and Prausnitz (1964) for gas solubility in mixed solvents.

The solubility of the diffusing chemical into the bubble wall can be determined by:

$$f_1 = \phi_1 Y_1 P = H_{1,\text{solvent}} x_1 \quad (B-3)$$

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where  $f$  = fugacity

$\phi$  = gas-phase fugacity coefficient

$H_{i,\text{solvent}}$  = Henry's constant

$x_i$  = liquid-phase mole fraction of component

$y_i$  = gas-phase mole fraction of component

At low pressures (below 5 atm), the gas-phase fugacity coefficient is equal to unity.

For the calculation of the solubility of the component in the solvent,  $x_i$ , a value for Henry's constant is needed. The following expression can be used to calculate Henry's constant for a mixed solvent:

$$\ln(H_{2,m}) = \sum x_i \ln(H_{2,i}) - \sum \sum a_{ij} x_i y_j \quad (\text{B-4})$$

With a value for Henry's constant, the solubility of the gas in the mixed solvent can be determined. From considerations of the foam makeup, the concentration of the solubilized component can be determined and ultimately the rate of permeation from Eq. B-1. The constant  $a_{ij}$  can be calculated from the following derived equation to account for polar solvents:

$$a_{ij} = \frac{(v_i + v_j) x_i \omega/kT}{2 v_j \phi^2} \quad (\text{B-5})$$

where

$$\phi_i = \frac{x_i v_i}{x_i v_i} \quad (\text{B-6})$$

$v_i$  is the liquid molar volume, and  $\omega$  is the interchange energy, which will be discussed later. The liquid molar volume can be estimated by a method given in The Properties of Gases and Liquid (Reid et al., 1977). This method utilizes empirical parameters based on the structure of the molecule.

A value for the interfacial area can be estimated from various experimentally determined bubble radii published together with theoretical equations developed by Lemlich (1982) which define the distribution of bubble radii.

Equations from Lemlich are of the following form:

$$\phi(R,0) = \frac{\pi}{2} r \exp\left(-\pi \frac{R^2}{4}\right) \quad (B-7)$$

where  $\phi(R,0)$  is a dimensionless number-frequency distribution function of bubble radii and  $r$  is the bubble radius,  $r$  divided by the initial arithmetic number-mean radius,  $r_{1,0}(0)$ .

If the distribution of bubble size is known, a value for the surface area can be determined which can be used to calculate an interfacial area,  $a$ , defined by:

$$a = \text{surface area/volume} \quad (B-8)$$

A Sauter mean-bubble diameter can then be calculated from the following expression:

$$D_p = \frac{6\Upsilon}{a} \quad (B-9)$$

where  $\Upsilon$  is the volume fraction of the dispersed phase.

A theoretical bubble lifetime can be calculated by the following equation developed by de Vries:

$$\tau = \frac{P_a r^2 P}{2\Upsilon R T} \quad (B-10)$$

where  $P_a$  = the pressure  
 $r$  = the mean-bubble radius  
 $\Upsilon$  = the surface tension  
 $T$  = the absolute temperature

This equation predicts the lifetime of the bubbles in the foam on the basis of the diffusion of gas between bubbles.

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The preceding equations will be used to calculate the solubility of gas in the bubble wall. For variations over time in the concentration of the bubble walls, the above equations will be used in conjunction with fitted drainage equations. The variations in composition during an increment of time can be accounted for by the drainage equations. The new value for the permeation through the bubble wall and theoretical bubble lifetime can then be calculated.



**APPENDIX C  
MATRIX OF HAZARDOUS VAPOR SUPPRESSION TESTS\***

Chemical	ATF	AFFF	Fluoroprotein	Protein	Surfactant		Special Foams
					Low	High	
Acetone	R	U	U	U	U	U	NT
Ammonia	S	S	S	S	S	R	NT
Benzene	R	U	S	S	U	S	NT
Butanol	R	U	U	U	U	U	NT
N-Butyle Acetate	R	R	R	R	R	NT	NT
Bromine	U	U	U	U	U	R	R <sup>2,3</sup>
Carbon Disulfide	NT	NT	NT	U	NT	NT	R <sup>2,3</sup>
Cholorosulfonic Acid	NT	NT	NT	NT	NT	NT	U <sup>2</sup>
Cyclohexane	R	S	R	R	S	S	NT
Ethane	S	U	S	S	S	R	NT
Ethylamine	R	U	U	U	U	U	R <sup>1,3</sup>
Ethyl Benzene	R	R	R	R	R	S	NT
Ethylene	S	U	S	S	S	R	NT
Ethylene Diamine	R	U	U	U	U	U	R <sup>1,3</sup>
Ethylene Oxide	R	U	U	U	U	U	NT
Ethyl Ether	R	U	U	U	U	U	NT
Gasoline	R	S	R	R	R	R	NT
Heptane	R	S	R	R	R	R	NT
Hexane	R	S	S	S	S	S	NT
Hydrochloric Acid	NT	NT	NT	NT	NT	NT	R <sup>2,3</sup>
Hydrogen Chloride	NT	NT	NT	NT	NT	NT	R <sup>2,3</sup>
Hydrazine	R	U	U	U	U	U	R <sup>1,3</sup>
Kerosene	R	S	R	R	R	R	NT

\* Data extracted from The Handbook for Using Foams to Control Vapors from Hazardous Spills (Evans and Carrol, 1986) and qualitative considerations developed under this work.

APPENDIX C con'd.  
MATRIX OF FOAM VAPOR SUPPRESSION TESTS\*

Chemical	ATF	AFFF	Fluoroprotein	Protein	Surfactant		Special Foams
					Low	High	
Kerosene	R	S	R	R	R	R	NT
Liquefied Natural Gas	U	U	U	U	U	R	NT
Methanol	R	U	U	U	U	U	NT
Methyl Acrylate	R	U	U	U	U	U	NT
Methylamine	R	U	U	U	U	U	R <sup>1,3</sup>
Methyl Butyl Ketone	R	U	U	U	U	U	NT
Methyl Ethyl Ketone	R	U	U	U	U	U	NT
Methyl Mercaptan	R	NT	NT	NT	NT	NT	NT
Naptha	R	S	R	R	R	R	NT
Nitric Acid	NT	NT	NT	NT	NT	NT	R <sup>2,3</sup>
Octane	R	S	S	S	S	S	NT
Octanol	R	S	S	S	S	S	NT
Paint Thinner	R	S	R	R	S	S	NT
Silicon Tetrachloride	U	U	U	U	U	R	NT
Sulfur Trioxide	U	U	U	U	U	R	R <sup>2,3</sup>
Titanium Tetrachloride	NT	NT	NT	NT	NT	NT	R <sup>2,3</sup>
Toluene	R	S	R	R	S	S	NT
Vinyl Acetate	R	S	R	U	U	U	NT
Vinyl Chloride	R	NT	NT	NT	NT	NT	NT

1 - Hazmat #1  
2 - Hazmat #2  
3 - Type V

Key for Symbols  
R - Recommended  
S - Satisfactory  
U - Unsatisfactory  
NT- Not Tested

\*Data extracted from The Handbook for Using Foams to Control Vapors from Hazardous Spills (Evans and Carrol, 1986) and qualitative considerations developed under this work.

APPENDIX D

FOAM VAPOR-SUPPRESSION METHODS FOR CHRIS CHEMICALS  
THAT FLOAT ON WATER

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**FOAM VAPOR-SUPPRESSION METHODS FOR CHRIS CHEMICALS  
THAT FLOAT ON WATER**

**Introduction**

The United States Coast Guard, by virtue of federal legislation, provides the predesignated federal On-Scene-Coordinator (OSC) for response to hazardous chemical releases occurring in the coastal zones, Great Lakes waters, and intercoastal waterways. The responsibility includes minimization of the hazardous impacts to the population and cleanup of a variety of hazardous chemicals that vary greatly with their behavior on water and with hazards associated with their release. The United States Coast Guard has identified over 1,100 hazardous Chemical Hazard Response Information System (CHRIS) chemicals that are transported on coastal and intercoastal waterways.

A handbook covering response methods for 313 floating CHRIS chemicals was developed for the OSC (Szluha et al., 1985). The handbook outlines the sequence of events that follow the release of materials.

A major concern associated with the release of a hazardous chemical is the production of flammable and/or toxic vapors that, when dispersed by winds, could adversely affect a large area. An efficient technique is needed to reduce the impact of these hazards. Recent research on methods for vapor mitigation has concluded that the most feasible technique to accomplish vapor suppression is the application of an aqueous foam (Moran et al., 1971; Friel, 1973; Greer, 1976; and others). This paper attempts to establish guidelines for the application of the wide variety of foams available on the market.

**Vapor Suppression**

During the early 1970's, foams were identified as a means of suppressing vapors from hazardous chemicals. Foams are produced by using vendor-supplied

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foam concentrates and foam generating equipment. By mixing foam concentrates with water in the proper proportions and entraining air, foam can be produced. The foam produced is an agglomeration of air bubbles with an interstitial mixture of water and foam concentrates. Foam applied to a volatile chemical reduces the amount of vaporization by reducing diffusion and by insulating the chemical against radiant and convective heat transfer; this results in a lower vapor concentration of hazardous chemical.

### Foam Types

Foam concentrates have the ability to produce foam because they contain surface-active agents. These surface-active agents lower the surface tension of the solution and thus enable the solution to foam. Foam types can be categorized by their compositions: (1) regular protein foams; (2) fluoroprotein foams; (3) surfactant foams; (4) aqueous film-forming foams (AFFF); (5) alcohol-type or polar solvent-type foam (ATF); and (6) special foams.

Most of these foams were developed for firefighting and have poor vapor-suppression qualities. ATFs and special foams have been engineered for better vapor-suppression characteristics.

The ATFs were developed to combat hydrocarbon and polar solvent fuel fires. These foam concentrates consist of an AFFF, a regular protein, a fluorocarbon surfactant, or a fluoroprotein base with a metal stearate and polysaccharide additive. The metal stearate is added as a foam stabilizer. The polysaccharide additive coalesces into a polymeric gel at the chemical/foam interface when applied to a chemical with an affinity for water. This tends to protect the foam from the destructive action of the chemical.

For chemicals with strong affinities for water, the proportioning concentration of the foam concentrate can be increased to protect the foam. Foam manufacturers' specifications contain a list of proportioning concentrations for classes of chemicals. The polymeric gel also suppresses vapors. In limited tests, ATFs have shown good results for the suppression of hazardous vapors. ATFs are useful for controlling vapors produced from a wide range of flammable and toxic liquids. ATFs can be used in low- and medium-expansion ratios (foam volume/liquid volume) and do not tolerate large shifts in pH.

Special foams have been developed for specific applications. Hazmat #1 and Hazmat #2<sup>®</sup> have been marketed for use on alkali and acid spills, respectively. Type V<sup>®</sup> can tolerate a pH between 2 and 10 and is marketed for vapor control of spills of water reactive, volatile chemicals. The Type V foam can be applied as low-, medium-, or high-expansion ratios.

Table 1 shows a foam application matrix for some selected floating CHRIS chemicals.

#### **Variables Affecting Foam Vapor-Suppression Efficiency**

The variables affecting foam vapor-suppression efficiency are foam quality, physical properties of the spilled chemical, foam behavior, compatibility between the foam and chemical, and environmental conditions. Foam quality refers to the distribution of bubble sizes and the mixing of the foam concentrate with water. Foams with a broad distribution of bubble sizes do not suppress vapor as well as foams with uniform small bubble sizes. Good quality foam is also distinguished by a homogeneous mixture of foam concentrate and water. Good foam quality can be achieved by using air aspirate nozzles or foam generating equipment.

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TABLE 1. FOAM EVALUATION FOR SOME SELECTED FLOATING CHRIS CHEMICALS

Group Chemical	Protein Foam	Fluoroprotein Foam	Surfactant Foam		Aqueous Film Forming Foam	Alcohol Type Foam
			Low	High		
<b>ALCOHOLS:</b> Methanol Octanol	NT SQ	NT SQ	NT SQ	NT SQ	NT SQ	RT RQ
<b>ALDEHYDES AND KETONES:</b> iso-Butylaldehyde Methyl Butyl Ketone	NQ NT	SQ NT	NQ NT	NQ NT	NQ NT	RQ RQ
<b>AMINES:</b> Di-n-Propylamine Triethylamine	NQ NT	SQ ST	NQ NT	NQ U	NQ NT	RQ RT
<b>ETHERS:</b> Ethyl Ether N-Butyl Acetate Methyl Acrylate	NT ST NT	NT ST NT	NT ST U	NQ U U	NT ST NT	RT RT RT
<b>HYDROCARBONS: (ALIPHATIC)</b> Ethane Hexane Octane	SQ SQ ST	SQ SQ ST	SQ SQ ST	RQ SQ U	NQ SQ ST	SQ RQ RT
<b>HYDROCARBONS: (AROMATIC AND ALICYCLIC)</b> Benzene Cyclohexane Ethyl benzene Toluene	ST RT RT RT	ST RT RT RT	ST ST RT ST	SQ SQ ST ST	ST ST RT ST	RT RT RT RT
<b>HYDROCARBONS: (INDUSTRIAL)</b> Gasoline Kerosene Naptha	RT RT RT	RT RT RT	RT RT RT	RT RT RT	ST ST ST	RT RT RT
<b>LIQUEFIED ORGANIC GASES:</b> Ethylene Oxide Vinyl Chloride Monomer	NT NQ	NT NQ	NT NQ	NT NQ	NT NQ	RT RT

RT - Recommended based on testing  
 RQ - Recommended based on qualitative considerations  
 ST - Satisfactory based on testing  
 NT - Not recommended based on testing  
 U - Limited data or no data; capabilities uncertain  
 NQ - Not recommended based on qualitative considerations



The physical properties of the spilled chemical will also affect the efficiency of the vapor suppression. The two most important physical properties are the vapor pressure and the solubility of the chemical in water. The higher the vapor pressure, the higher the amount of material vaporizing. Water solubility can be used to measure the permeability of the chemical through the foam. As a rule of thumb, higher water solubility relates to increased permeation through the foam.

Behavior of the foam is also important to vapor-suppression efficiency. The characteristics of importance are the drainage rate and expansion ratio. The drainage rate of foam is the rate at which excess water drains from the foam. This is quantified as quarter-drainage time which is the time needed for 25 percent of the liquid volume to drain from the foam. Longer quarter-drainage times are usually reflective of more efficient vapor-suppression foams. High-expansion foams are generally more efficient at suppressing vapor than lower expansion foams. Expansion ratio is related to drainage rates. For a given foam, increasing the expansion ratio will increase quarter-drainage times and thus improve vapor suppression efficiency.

Compatibility between the foam and spilled chemical is probably the most important consideration in foam efficiency. Some chemicals have the ability to collapse foam. These chemicals usually have an affinity for water or an ability to cause pH shifts. ATF foams have proven successful for vapor suppression for a limited number of chemicals that are known to collapse foam.

Environmental conditions affect vapor suppression in several ways. Wind-induced waves vibrate the foam and thus increase the rate of foam collapse. Temperature, humidity, and intensity of sunlight affect the amount of water lost

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from the foam due to evaporation. Loss of water causes foams to be susceptible to collapse. Rain or hail can adversely affect vapor suppression by destroying the foam.

### Guidelines on Foam Use

The efficiency of foam vapor suppression is dependent on the spilled chemical involved and is hard to predict accurately without prior testing. The interaction between the foam and chemical will determine the efficiency of the vapor suppression. Response personnel can estimate the degree of vapor suppression by characterizing the spilled chemical with some key physical properties. Chemicals that are polar (dielectric constant  $> 2.5$ ) and water soluble have a strong potential to degrade or quickly saturate the foam. Both degraded and saturated foams provide little protection from the associated hazards of the spill. ATFs with a polysaccharide additive offer protection from polar or water soluble chemicals. The proportioning concentration of the ATF concentrates can be increased for chemicals with a strong affinity for water.

Applying foam to cryogenic materials or low boiling point materials may not be an effective method for controlling vapors. Water drainage from the foam acts as a heat source increasing vaporization. The rapid vaporization of the chemical can cause chimneys in the foam or foam collapse. In situations where control of vapors from cryogens or low boiling point materials is crucial, some vapor control may be accomplished by using a slow-draining, high-expansion foam. The initial drainage from the foam will increase vaporization but then drop off as the drainage slows. After the initial increase in vapor production, tests have shown some vapor reduction by using a slow-draining, high-expansion foam (Gross et al., 1982).

To ensure the most efficient suppression of vapor, response personnel must apply foam properly. After mixing the selected foam concentrate with water, the foam should be generated with air aspirating nozzles or foam generating units to obtain good quality. Foam should be applied indirectly to the spilled chemical surface to avoid mixing of the foam and chemical. With the use of a backboard, foam can be gently applied to the chemical. This can also be accomplished by "rolling" the foam onto the chemical surface by aiming at the ground or a ramp in front of the spill. Response personnel may be required to construct some makeshift ramp or backboard for foam application. Foam generated the first 15 to 30 seconds should not be used because it is poorly mixed, and therefore its ability to suppress vapors is reduced (Norman and DiMaio, 1986).

The contained spill should be completely covered for suppression of vapor. If the spill becomes partly uncovered due to wind or wave action (or aging), the foam must be reapplied to avoid exposing the spill to the atmosphere and thus increasing the hazards to response personnel. High-expansion foams are more susceptible to displacement because the foam layer for high-expansion foams is thicker than that for low- or medium-expansion foams. A 9-mph wind can displace a high-expansion foam layer of 4 inches. A 5-mph wind can displace a 6-inch foam layer (Robinson, 1979).

Foams lose their ability to suppress vapors due to aging or environmental effects. Response personnel can judge effectiveness of the foam by observing or monitoring vapor concentrations. If the foam has lost its effectiveness, another layer of foam must be applied to ensure the safety of response personnel. Foam can become saturated with vapors from the chemical and thus create the potential for ignition. A reapplication of foam on top of the saturated

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foam would provide a barrier for protection against ignition as well as suppress vapors issuing from the saturated foam.

Foam manufacturers' results for vapor-suppression efficiency are based on a small bench scale apparatus or a beaker test. Owing to experimental setup, these results are probably indicative of land-based spills. Response personnel should be aware of test conditions leading to manufacturers' results for vapor suppression when considering foam applications to spills on water surfaces.

### Mechanisms of Vapor Suppression

Data for vapor-suppression efficiency and duration for the 313 floating CHRIS chemicals would be beneficial to response personnel; however, obtaining such data would be both time consuming and costly. The mechanisms of vapor suppression by foam have been identified from a thermodynamic analysis of foam/chemical interface. Presently, a computerized mathematical model based on the identified vapor-suppression mechanisms is being constructed. A major obstacle to overcome for proper verification of the mathematical model is reliable test data for foam vapor suppression. Proposed research by the United States Coast Guard and the Environmental Protection Agency should supply the needed data for verification in the near future.

To understand the mechanisms of vapor suppression, one must begin with the structure of the foam. Foam applied to the surface of a vaporizing chemical offers a medium less favorable for diffusion than air. The foam forms a barrier with a high resistance to both convective and molecular diffusion as well as an ability to absorb vapors. Collectively, this results in a reduction in the concentration of the diffusing component in the vapor space above the foam. An important variable related to the efficiency of vapor suppression is the water

solubility of the vaporizing chemical. It is proposed, on the basis of similar situations of diffusion of gas into bubbles, that the controlling step in the suppression of vapor is the diffusion of the gas through the bubble wall. For convenience, chemicals will be divided into two categories - soluble and insoluble in water.

The characteristics of insoluble chemicals will be discussed first. In early foam life, the primary barrier to gas permeation is the foam lamellae (bubble wall), which are predominately water. The ability of gas to permeate is proportional to the product of its solubility and diffusivity in the lamellae (Cheng and Lemlich, 1986; Li, 1971). Foam concentrates are generally mixed with between 2 and 10 percent water to produce foam. The concentrates are typically made up of around 40 percent organic solvents and around 40 percent surface-active agents. The organic solvents are usually glycol ethers, such as butyl ethoxy ethanol. The surface-active agents include sodium laryl sulfonates, proteins, or synthetic fluorinated hydrocarbons. Foam concentrates also contain a variety of additives for foam stability, foam protection, and optical determination of foam concentration. As the foam drains (drainage is proposed to be mostly water), the concentration of the surface-active agents and solvents increases. This results in a mixture that is more favorable for permeation. The greatest resistance to diffusion is offered at the chemical/foam interface because the foam there is the last to drain to the more desirable concentration for diffusion. Therefore a semipermeable barrier is produced. The persistence of this barrier is proportional to the drainage rate of the foam (Gross, 1982).

The foam barrier for chemicals that are soluble in water is much the same as that stated above. The only two differences are that the chemical is more

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permeable through the lamellae during early foam life and the physical characteristics of soluble chemicals may affect the stabilizing forces in the foam.

The mechanism of vapor transport through the foam bubble matrix is one of slow permeation through the bubble walls. Vapor suppression immediately after the application of foam is probably aided by a washing effect from the draining foam. This effect is short lived, especially for low- and medium-expansion foams, which drain quickly. After the washing effect ceases, the resistance to diffusion is from the bubble wall. Little resistance to diffusion is offered by internal gas of the bubbles; therefore the proposed limiting step for vapor suppression by foam is the diffusion of gas through the bubble wall (MAXIMA, 1987).

### Mass Transport Effects

Since the proposed controlling step for the transport of vapor through the foam is the diffusion of gas through the bubble wall, mathematical expressions are needed to describe the solubility of gas in the bubble wall. The concentrations of the bubble wall change during drainage to a composition more favorable for diffusion. The thickness of the bubble walls and their geometry also change during drainage. In early foam life, bubbles are spherical and the bubble walls are relatively thick. As the foam drains, the bubble walls become thin and the shape of the bubbles changes from spherical to polyhedral. Together, the lowering in the concentration of water and the thinning of the bubble walls create a system that is favorable for mass transfer of the chemical through the foam.

The proposed mathematical treatment of the mechanism incorporates a method outlined by Prausnitz (1969). The system is characterized as gas solubility in

mixed solvents. Henry's law states that the concentration of the solubilizing chemical in the liquid phase is proportional to that of the gas phase.

$$f_i = \phi_i Y_i P = H_{i, \text{solvent}} x_i \quad (1)$$

where  $f_i$  - fugacity  
 $x_i$  - liquid-phase mole fraction  
 $Y_i$  - gas  
 $H_{i, \text{solvent}}$  - Henry's constant

The gas-phase fugacity coefficient,  $\phi$ , at low pressures is equal to unity.

The Henry's constant for the mixture can be calculated from the following equation derived by Prausnitz and O'Connell (1964):

$$\ln(H_{2,m}) = \sum x_i \ln(H_{2,j}) - \sum \sum a_{ij} x_i Y_k \quad (2)$$

The constant  $a_{ij}$  can be calculated from the following derived equation to account for polar solvents:

$$a_{ij} = \frac{(v_i + v_j) x_i \omega/kT}{2 v_j \phi^2} \quad (3)$$

where

$$\phi_i = \frac{x_i v_i}{\sum x_i v_i} \quad (4)$$

$v_i$  - liquid molar volume  
 $k$  - Boltzman's constant  
 $\omega$  - interchange energy

The liquid molar volume can be estimated by a method given in The Properties of Gases and Liquid (Reed et al., 1977). This method utilizes empirical parameters based on the structure of the molecule.

After the solubility of the chemical into the bubble wall is determined, the diffusion of chemical through the foam can be calculated by the equation commonly used for mass transfer operations:

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$$N = k_x a(x_b - x_i) \quad (5)$$

where N - number of moles of chemical absorbed by unit volume per unit time  
k<sub>x</sub> - mass transfer coefficient  
a - interfacial area  
x - concentration of the diffusing chemical in the bulk solution and at the interface

The mass transfer coefficient can be calculated from a equation derived by Cheng and Lemlich (1986):

$$P = \frac{H_{2,m} D_{r3,2}}{3 D(1-D')} \quad (6)$$

D<sub>r3,2</sub> - sauter mean bubble radius  
D - diffusivity  
D' - volume of foam that is liquid

This equation is based on the diffusion of gas between bubbles. The result from Eq. 6 is in units of centimeters per second.

The preceding calculational scheme reduces the problem to a single overall resistance due to the application of foam. This resistance is based on the proposed rate-controlling step of the diffusion of vapor through the bubble lamellae. For variances over time, the calculational scheme will take advantage of the fitted drainage equation to account for the drained water from the foam. If the volume drained is known, a new expansion ratio of the foam can be calculated from Eq. 6. The interfacial concentration in Eq. 5, which is initially assumed to be zero, can be increased over the foam life to account for the saturation of the foam by the diffusing gas.

An attempt to account for the foam lifetime (reapplication time) can be made by using results from de Vries (1957). de Vries combined the classical law of Laplace and Young with a form of Fick's law of diffusion to yield the following equation:



$$\tau = \frac{P_a r^2}{2 R T J} \quad (7)$$

where  $P_a$  - surrounding pressure  
 $r$  - the bubble radius  
 $\gamma$  - the surface tension  
 $J$  -  $1/P$   
 $T$  - absolute temperature  
 $R$  - gas constant

Eq. 7 estimates the lifetime of a small spherical bubble on the basis of diffusion of gas between bubbles. As the vapor from the chemical spill saturates the foam, Eq. 7 can be recalculated to yield the estimated bubble lifetime. Also, from the drainage equation, the concentrations of solvent, surface-active agents, and water will change over time. The solubility of the diffusing gas in this mixture can be adjusted by Eqs. 1 and 2 to account for the changing composition of the lamellae.

#### Conclusions

The proposed calculational scheme is based on a single resistance offered by the foam. The calculational scheme can account for variances in the bubble wall composition over time. The results from the model will be a theoretical percent reduction in vapor and reapplication time. Figure 1 shows a flow diagram of the proposed calculational scheme.

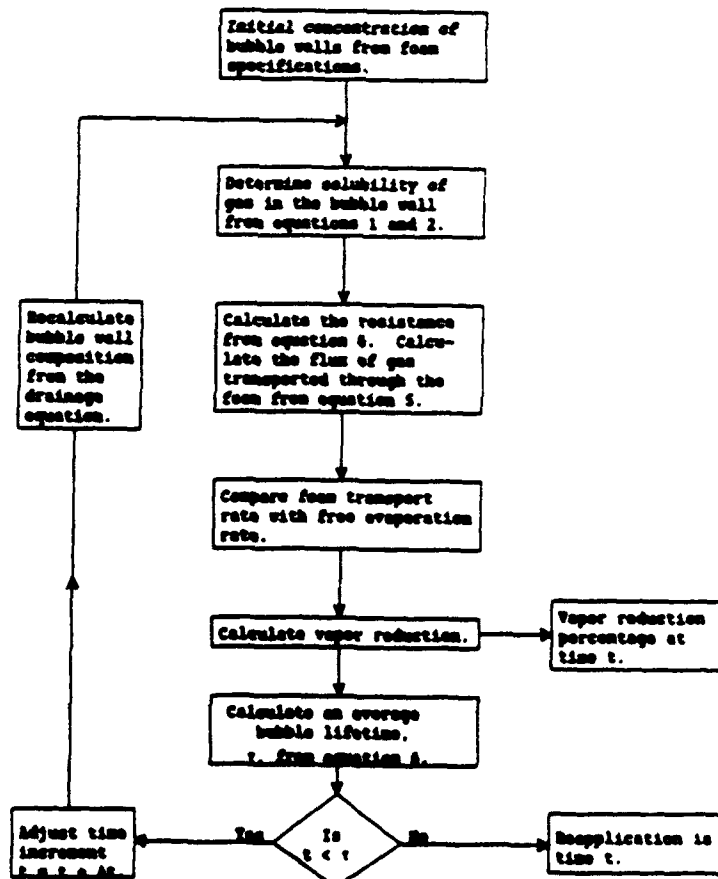
There are several limitations to the proposed calculational scheme. The equations used to determine the solubility of the gas in the bubble wall require information about the foam concentration which may not be available. Estimation techniques can be employed to obtain the needed physical properties, but they may not offer an accurate answer. The model proposed accounts for physical effects but does not account for chemical effects on solubility. In cases where chemical effects are dominant over physical effects, the proposed method may grossly underestimate the transport of vapor through the foam. Presently, no

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method exists for a quantitative analysis of chemical effects on solubility. A qualitative analysis could be accomplished but would require experimental data, which are not available.

The model also does not account for environmental effects on transport mechanisms or foam quality. The system analyzed is a theoretical ideal situation on a smooth water surface. Also, the model does not account for changes in the temperature of the chemical pool. It is proposed that the heat transfer from the water is counterbalanced by the auto cooling by the pool to maintain the pool temperature at initial conditions.

The calculational scheme is based on sound thermodynamic relationships and mass transfer principles. The response personnel must use their judgment, based on the environmental conditions, to determine what degree the theoretical results hold true.



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**APPENDIX E  
NOMENCLATURE**

a	Constant in Eq. 1 or interfacial area, area/volume
$a_{ij}$	Binary interaction parameter
b	Constant in Eq. 1
$B_t$	Thickness of diffusion space
D	Diffusivity, area/time
$D_{r3, 2}$	Sauter mean-bubble diameter
$D'$	Liquid foam fraction
$G_x$	Liquid mass velocity, $g/m^2$ -sec
$G_y$	Gas mass velocity, $g/m^2$ -sec
$H_{2, m}$	Henry's constant
I	Ionization potential
k	Boltzmann's constant
$k_x$	Liquid mass-transfer coefficient
M	Molecular weight
N	Mass flux, moles/volume-time
P	Vapor pressure, mm Hg or permeability, cm/sec
$P_a$	Atmospheric pressure, $g/cm^2$ -sec
R	Drainage rate or gas constant
r	Bubble radius or separation distance, Eq. 16
S	Vaporization rate, $g/cm^2$ hr
T	Absolute temperature, °K
$U_s$	Slip Velocity
$U_g$	Velocity component of vapor
$U_l$	Velocity component of liquid
v	Wind speed, cm/sec

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APPENDIX E  
NOMENCLATURE con'd.

$V_l$	Liquid velocity component, m/sec
$V_g$	Gas velocity component, m/sec
$x$	Liquid mole fraction
$y$	Gas mole fraction

Greek Letters

$\alpha$	Average polarizability
$\delta$	Solubility parameter
$\phi$	Volume fraction defined by Eq. 7
$\phi$	Fugacity coefficient
$\Gamma$	Potential energy function
$\gamma$	Surface tension, g/sec <sup>2</sup>
$\mu$	Dipole moment, debyes
$v$	Liquid molar volume
$\rho$	Molar density
$\tau$	Bubble lifetime
$\chi$	Dimensionless parameter defined by Eqs. 13 and 14
$\varphi$	Volumetric fraction of the dispersed phase
$\omega$	Interchange energy

Other Symbols

$f$	Fugacity
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