NOTES ON
A FEW VAPOR SUPPRESSION TECHNIQUES

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LOW EXPANSION FOAMS FOR FLAMMABLE LIQUIDS

Water-based foams have been used to extinguish pool and tank fires of flammable and combustible liquids for nearly half a century. Although many different types of fire fighting foams have been developed, they all extinguish fires in much the same manner. Foams cool the surface of the liquid fuel, block the passage of radiant heat from the flames to the surface of the fuel, act as a physical barrier between oxygen (in the air) and the liquid fuel, and reduce the rate of vaporization of the fuel. The last effect, vapor suppression, helps prevent the fuel from reigniting following extinguishment. Similarly, if the foam is applied before the fuel is initially ignited, it will help prevent ignition of the fuel.

The earliest mechanically produced (air-blown) fire fighting foams were developed by the U.S. military during World War II and were based on hydrolysis of certain naturally occurring proteins, such as animal horns and hooves. These protein-based foams were somewhat effective in suppressing the vaporization of water-immiscible flammable liquids. However, the "stiff" characteristic of protein foam prevented it from flowing easily over the fuel surface, and it needed to be applied gently or it would pick up hydrocarbons from the liquid pool. It also was not suitable for use on water-soluble liquids (e.g., polar liquids such as alcohols).

In the mid-1960s, a new type of foam was developed by adding small amounts of fluorochemical surfactants to protein foam. The resultant fluoroprotein foam was more stable and more fluid than regular protein foam. It was also olophobic, and thus more resistant to hydrocarbon contamination. This characteristic allowed the foam to be applied by less gentle methods and by subsurface injection.

During this same time period, aqueous film forming foam, AFFF, was being developed at the U.S. Naval Research Laboratory for use in fighting aircraft crash fires. AFFF concentrates were based on synthetic detergents (for creating the foam) and fluorochemical surfactants (to create the film). In comparison to fluoroprotein foams, AFFF contained a much higher concentration of fluorochemical surfactants. It was also more mobile than fluoroprotein foams, thus allowing it to quickly "knock down" an aircraft fuel fire so that rescue efforts could begin soon after reaching the crash site.

Although AFFF and fluoroprotein foams overcame some of the shortcomings of protein foams, they still could not be used on water-soluble liquids. When applied to polar liquids, the fuel tended to dissolve in the foam, and vice versa, thus destroying the foam layer. This deficiency was first rectified when alcohol-resistant AFFF agents were created by adding polymeric film forming compounds to AFFF. When applied to hydrocarbon liquids, these foams behave much like the normal AFFF, i.e., liquid foam solution draining from the foam creates an aqueous film between the fuel and the foam. When applied to polar liquids, the high molecular weight polysaccharides in the foam create a polymeric, water insoluble membrane between the

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fuel and the foam. This membrane protects the foam from the destructive effects of the polar liquid. Early versions of these alcohol-resistant foam concentrates typically needed to be proportioned at 6% concentration when used on polar liquids, but 3% concentration was sufficient for use on hydrocarbon liquids. At least two foam concentrate manufacturers now have alcohol-resistant AFFF agents on the market that can be used at 3% on hydrocarbons and polar liquids.

Prior to the development of alcohol-resistant AFFF agents, special foam agents had been formulated specifically for use on polar liquids. These foams (commonly called alcohol foams) typically incorporated metal stearates which precipitated from the foam to create a barrier between the water-soluble fuel and the aqueous foam. Some of these foams had to be proportioned at 10%, thus requiring a large supply of concentrate, and they were more expensive than typical fire fighting foams. Thus, with the advent of alcohol-resistant AFFF agents, alcohol foams became less desirable.

Another foam agent that has generated some interest is film-forming fluoroprotein, FFFP. This type of foam was developed by increasing the fluorochemical surfactant concentration of a fluoroprotein foam. The result is a foam that is based on protein, but has many of the same characteristics as AFFF.

Vapor suppressing capability of a fire fighting foam is affected by many factors. These factors include:

- the rate at which water drains from the foam into the liquid;
- the relative solubility of the foam in the liquid;
- the expansion ratio of the foam; and
- the initial thickness of the foam blanket.

As might be expected, the "quality" of the foam starts to degrade nearly instantaneously once it is applied to the flammable liquid pool, and continues to degrade as time passes. Thus, the vapor suppressing capability of a foam blanket decreases as time (after application) increases. Therefore, in order to maintain some desired level of vapor suppressing capability, it is often necessary to reapply foam intermittently.

Figure 1 (taken from [Hiltz, 1987]) illustrates how the rate of water drainage from the foam and the initial thickness of the foam blanket affect the ability of the foam blanket to suppress vaporization of a benzene pool. The Type "A" foam used in these tests was the same type of foam as Type "B" and had the same expansion ratio as Type "B." However, Type "A" had a higher water drainage rate. As can be seen from the figure, a two-inch blanket of Type "A" was superior to a one-inch blanket of Type "A," but a one-inch blanket of Type "B" was superior to the two-inch blanket of Type "A."

All of the foams described above were originally developed as fire fighting foams. Although the ability of such foams to suppress vaporization (thus reduce the likelihood of reignition following extinguishment) is important, it is often secondary to the goal of rapid knockdown, control, and extinguishment. One of the newest foam agents was designed specifically to increase the vapor suppression capability of existing fire fighting foams [Hanauska, 1989]. This new agent and a fire fighting foam concentrate are added to water at the same time and in the same proportions to produce a foam solution that is 6% stabilizing agent, 6% foam concentrate, and 88% water. Within one to three minutes after passing through a foam-making nozzle, the foam gels due to a polymerization reaction caused by the stabilizing agent, and forms
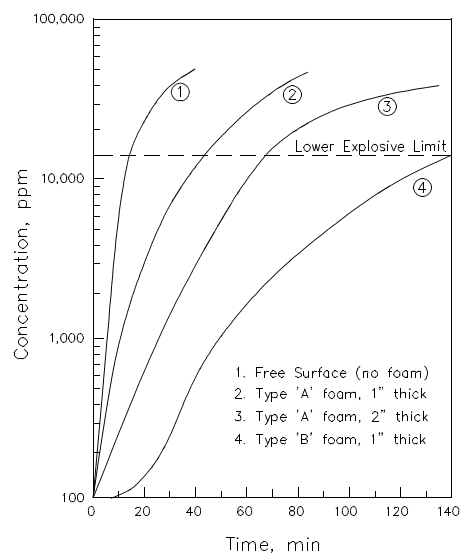

Figure 1
Vapor Control of Liquid Benzene
(From Hiltz, 1987)

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a non-mobile, tenacious blanket. The stabilized (gelled) foam retains water extremely well in comparison to other foams, making reapplication of the foam unnecessary in many situations. Of course, the foam will dry out due to evaporation and become less effective at vapor suppression as time passes.

Results of a few small-scale tests of this stabilized foam on acetone are shown in Figure 2. It illustrates how the weight of the foam blanket (per unit area of fuel surface) affects the rate of vaporization (flux). As the weight of the foam blanket increases, the vaporization rate of the acetone pool decreases. Whether or not a particular vaporization rate is sufficiently high to produce a flammable concentration of vapor immediately above the foam blanket depends on the wind speed and the size of the pool, as shown in Figure 3. The vaporization rate used in preparing Figure 3 is based on the results of the test that utilized a one-inch blanket of 3.5:1 stabilized foam (i.e., the 0.58 g/cm^2 (foam weight) test illustrated in Figure 2.
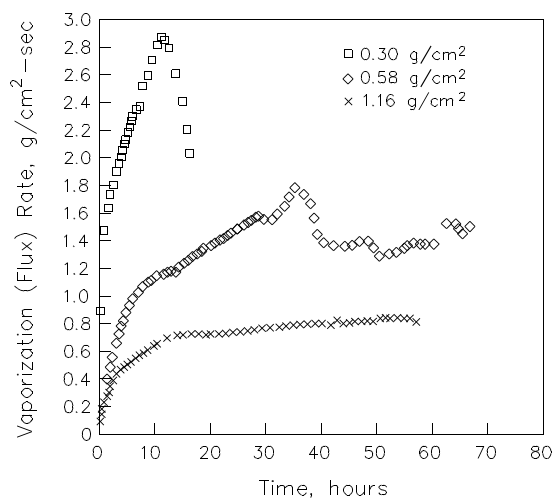

Figure 2
Effect of Foam Weight Per Unit Area on the
Vaporization Rate of an Acetone Pool
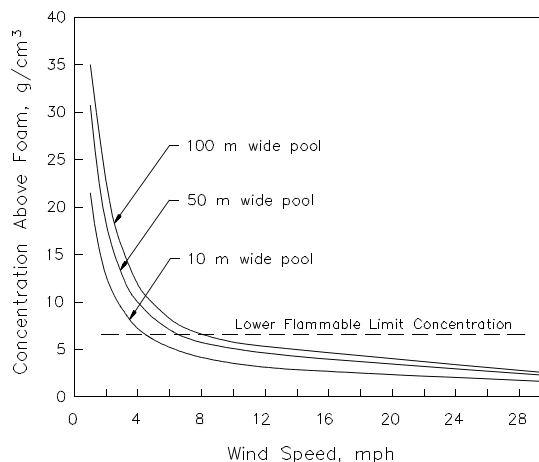**(from Hanauska, 1991)**

Figure 3
Calculated Effect of Wind Speed and Pool
Width on the Concentration of Acetone
Above a One-Inch Layer of Foam
(from Hanauska, 1991)

Although many vapor suppression tests have been conducted with several types of foam on a variety of flammable liquids, there is still no universally accepted test methodology. This makes it difficult to compare the results of two experimental studies that used different foams on the same fuel. In addition, much of the available test data comes from the manufacturers of foam agents and from laboratory-scale tests. Independent data from large-scale field tests are rare.

The available test data do point out some of the limitations of low expansion foams as vapor suppressants. For example, the data indicate that the rate at which vapor released by the liquid pool permeates the foam blanket increases as the vapor pressure of the liquid increases and the size of the vapor molecules decreases. Thus, the liquids that would produce the largest flammable clouds if released (i.e., the more volatile liquids) are the very ones for which the foams are least effective.

Another limitation of foam as a vapor cloud mitigation technique is the time required to respond to the liquid spill, get the foam-making equipment operating, and cover the entire liquid pool with foam. For most spills of flammable liquids, the flammable vapor cloud will have already reached its maximum size before the foam blanket can be applied. Although foam application may reduce the size of the flammable cloud, one of the most dangerous periods of the accident will have already passed without harm. Of course, the danger is still

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not over and the foam blanket may provide significant protection against ignition during spill cleanup and removal efforts when personnel must work in close proximity to the flammable pool.

Perhaps the ultimate difficulty in assessing the efficacy of low expansion foams as vapor suppressants on flammable liquids is the inability to determine how they performed in actual emergency situations. If foam is applied to an accidental release of flammable liquid and the spill is cleaned up without a fire occurring, who is to say whether the foam had any effect. Perhaps the spill would not have ignited even if foam had not been applied.

In summary, low expansion foams can suppress the rate of vaporization of a variety of flammable liquids and may be effective when used for post-release mitigation of flammable liquid spills. However, users of these foams should be aware of their limitations and not expect perfection.

HIGH EXPANSION FOAMS FOR FLAMMABLE LIQUEFIED GASES

Although low expansion foams may be effective in suppressing the rate of vaporization from spills of ambient temperature flammable liquids, they are not effective on spills of liquefied gases, and may even be counterproductive. If a liquid pool accumulates as a result of a liquefied gas release, the temperature of the pool will be less than or equal to the boiling point of the liquid. Application of low expansion foam to this type of cold liquid pool generally increases the rate of vaporization because the water in the foam provides additional heat to the liquid. The resultant freezing of the foam causes it to collapse and sink, thus allowing the next "layer" of foam to contact the cold liquid and provide more heat for vaporization.

The search for a type of foam that would be effective on liquefied gas pools eventually led to high expansion foams, i.e., foams with expansion ratios greater than 250:1. These foams are based on synthetic detergents and were originally developed as a method for fighting fires in buildings with large, undivided areas, such as aircraft hangers or paper warehouses. Foam-makers located near the ceiling of such a building could quickly fill the entire enclosure with foam.

Medium-scale field tests conducted with high expansion foams in the early 1970s demonstrated that foams with expansion ratios from 350:1 to 1,000:1 were effective in reducing gas concentrations downwind of liquefied natural gas pools [AGA, 1974]. Other tests indicated that high expansion foam was also effective at mitigating vapors from ethylene pools (see Figure 4 [Hiltz, 1987]), but was counterproductive when applied to propane pools [Welker and Cavin, 1982].

When applied to a pool of cold, liquefied gas, some of the high expansion foam gives up its heat to the pool. This causes an increase in vaporization rate and creates a layer of frozen foam. Even though the foam will collapse somewhat as it freezes, it retains sufficient air to remain buoyant; thus, the foam floats on top of the liquid. The frozen foam layer acts as insulation and protects the foam above it from the cold liquid. As vapor from the liquid moves through this unfrozen foam, it gains heat from the foam. If heated sufficiently, vapors from liquefied natural gas (primarily methane), ethane, ethylene, and ammonia will become buoyant with respect to the ambient air. These vapors will then tend to disperse upward, thereby decreasing the downwind concentrations. The vapors from
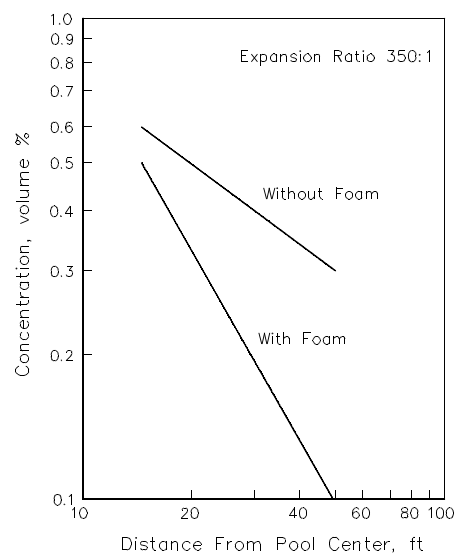

Figure 4
Gas Concentrations Downwind of an
Ethylene Spill, With and Without
High Expansion Foam
[Hiltz, 1987]

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cold pools of heavier liquefied gases, such as propane and butane, are much denser than air when they are cold, and remain more dense than air even when heated to the same temperature as the ambient air. As a result, high expansion foam is not effective at mitigating vapors from liquefied gases with molecular weights greater than about 29 (the average molecular weight of air).

The preceding paragraph follows the most commonly expressed view of how and why high expansion foam is effective at mitigating vapors produced from certain light hydrocarbon spills. However, a simple heat balance calculation will readily show that the amount of heat available in the foam blanket is not sufficient to heat all of the vapor to the temperature necessary to make it buoyant with respect to ambient air. Therefore, some other mechanism must also be at work. One possible explanation is "channeling" of the vapors through cracks in the frozen foam layer. This effect has been observed during foam tests on chlorine [Thomerson, 1991] and LNG. By restricting the flow of vapor to certain flow paths or channels, the upward velocity of the vapor as it leaves the liquid pool is markedly increased. The increased velocity increases the rate of dilution with air near the pool, and increases the tendency to disperse upward rather than downwind. Since tests with propane indicate that downwind vapor concentrations increase when high expansion foam is applied, the effect of channeling is obviously not sufficient to overcome the combined effect of increased vaporization rate and high vapor density.

As is the case with any vapor mitigation technique, high expansion foam has its limitations and disadvantages. The equipment required for producing large quantities of high expansion foam is quite expensive and, thus far, it has proven to be effective on only a few liquefied gases. The low density of the foam limits the distance that the foam can be projected from the foam-maker. (It's a little like trying to throw soap suds.) The foam moves over the liquid pool only when the height of foam near the foam-maker is sufficient to overcome the foam's natural angle of respose, thus causing the pile to slide forward and reduce the angle at the leading edge of the foam. Field tests have demonstrated that it would be very difficult to completely cover the surface of any pool that is more than 50 meters wide [Lev, 1981].

The low density of the foam makes it very susceptible to the wind. Winds in excess of just a few miles per hour can prevent the movement of high expansion foam, and may even blow the foam off the pool. This effect increases as the expansion ratio increases. Also, like low expansion foams, some period of time will be required to establish the initial foam blanket, and the high expansion foam will need to be reapplied periodically to maintain the desired foam depth and degree of vapor mitigation.

In summary, high expansion foams can be useful in mitigating the vapor dispersion downwind of pools created by releases of liquefied hydrocarbon gases with molecular weights less than 29. However, the size of pool that can be covered is limited (even under calm conditions), and wind may adversely affect the performance of the foam even on small spills.

DRY POWDERS FOR WATER-REACTIVE CHEMICALS

Releases of water-reactive chemicals, such as sulfur trioxide, oleum, anhydrous hydrofluoric acid, and chlorine, present special problems during spill control and cleanup efforts. If water is applied to a liquid pool of one of these chemicals, the vaporization rate increases as the liquid temperature increases due to the heat of reaction. This behavior also decreases the effectiveness of most water-based foams, although some foams are at least moderately successful in suppressing the vaporization from such spills.

One potentially attractive method for mitigating the hazards created by spills of water-reactive chemicals is to apply certain chemicals (in the form of dry powder) to the spills. The dry powder reacts with the spilled chemical and produces nonhazardous reaction products. Ideally, the reaction should not be too vigorous or the vaporization rate may increase dramatically as the heat of reaction raises the temperature of the liquid

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pool. In the past few years, small-scale field tests of dry powder agents on water-reactive chemical pools have produced mixed results. Attempts to neutralize liquid chorine with anhydrous caustic resulted in a greatly increased rate of vaporization due to the speed and energy of the reaction [Thomerson, 1991]. Soda ash was then tried, but it did not react with the chlorine. Subsequently, a small amount of water was added to get the reaction started. The vaporization rate increased slightly as a result of the reaction.

A proprietary dry powder has been tested on 55-gallon spills of sulfur trioxide, oleum, and chlorosulfonic acid [Engman, 1991]. In these tests, the dry powder was discharged from equipment based on typical dry chemical fire extinguishers. Along with the dry powder, a fine water spray was applied intermittently in order to complete the reaction between the dry powder and the acid. Application of the dry powder and water spray effectively neutralized most of the acid, but caused a temporary increase in acid dowwind of the pool. After this spike, the airborne acid concentration returned to the level observed for a free-evaporating pool, as illustrated in Figure 5.
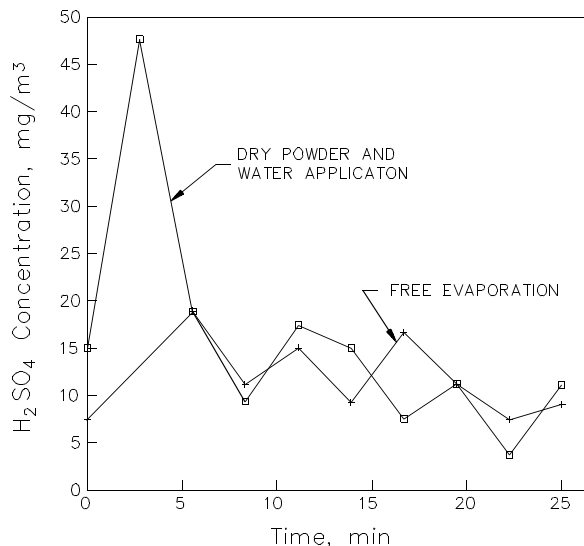

Figure 5
H_2SO_4 Concentrations (Measured as Acid Mist)
100 Meters Downwind of an Oleum Spill,
With and Without the Application
of Dry Powder and Water
(from Engman, 1991)

Although this technique increases the size of the toxic vapor cloud, at least temporarily, it can greatly reduce the length of time the hazard exists. If a fuming acid spill is not neutralized, it may create a hazardous area that persists for several hours. By using dry powder to neutralize the acid, the hazardous area will be larger, but may only persist for a few minutes. In addition, cleanup and disposal of the acid spill is much simpler once it has been neutralized by reacting with the dry powder.

In summary, dry powders may be used to neutralize spills of some water-reactive liquids, but response personnel must be aware of the increase in vaporization rate that will occur as the neutralization reaction proceeds. When using dry powders to mitigate spills of water-reactive liquids, the advantage of controlling the hazard quickly is partially offset by a temporary increase in the area exposed to the hazard.

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