CONTROL OF UNCONFINED VAPOR CLOUDS BY FIRE DEPARTMENT WATER SPRAY HANDLINES

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INTRODUCTION

Fire departments are called more and more frequently to deal with incidents involving the release of hazardous materials. It is natural then that the tools and tactics used in fire fighting have come to be applied to hazardous material situations which are not yet involved in fire. One such situation is the release of a hazardous material with the subsequent formation of an unconfined vapor cloud or plume.

Hazardous material responders therefore often consider the use of water, particularly in the form of water spray or "fog" streams produced by handlines, as at least one element of a control strategy. This derives from several factors:

- traditional use of water by fire fighters to extinguish fires
- belief that water sprays may provide ventilation or disperse vapor clouds
- ready availability and relative ease of application of water sprays, and
- effectiveness of water sprays in controlling some of the hazards of these materials

Much research has been carried out on fixed water spray systems and sprinkler systems which has general application to the use of water on hazardous materials.* Additives such as foam, "light water," (TM) and "slick water" are available to enhance the performance of water in controlling vapor cloud formation. Much has recently been learned in both the laboratory and in the field about the uses and limitations of these chemicals. The many issues involved in the selection and safe use of these techniques and additives have been discussed in scattered technical presentations or in recondite learned journals. However, little of this vital information has been directed at those fire officers and haz mat team leaders who must daily cope with hazardous materials incidents.

Therefore, this brief article is written to serve two purposes:

- To gather together a bibliography of some of the major relevant technical articles, and,
- To discuss briefly the findings and issues involved in the use of water on hazardous materials.

This article will probably dissatisfy some at either end of the continuum of fire protection practitioners. For the technically trained, the fire protection engineer, the physical chemist, the researcher in combustion theory, it will offer an overly simplified view of their real world. For them we direct their attention to excellent reviews by Pikaar, Strehlow, or Gugan or research reports by McQuaid, Van Doorn and a host of others. To the fire fighters who believe that structural fire fighting tactics are adequate for any haz mat situation, a series of quotations from fire service leaders in haz mat are offered.

> In order to handle a hazardous materials incident a set of special skills is necessary. These skills are over and above that which is taught to fire fighters in structural fire fighting classes. As a result, those without the necessary knowledge and expertise have problems in deciding how to handle these incidents. Mistakes are made, which cause injury to emergency response personnel or the general public, additional property damage occurs, and there can be significant environmental damage.
>
> Warren Isman (1983)

> The few communities that do have contingency plans specifically addressing hazardous substances accidents have usually been influenced by the presence of a substantial risk (a large chemical manufacturing complex) or a past event. But for the most part, plans found in the field today are not realistically applicable to chemical events. This is not to say that the emergency forces found locally are inappropriate; the function of the firefighter, the sheriff, and the civil defense official is an absolutely vital part of the cleanup and mitigation effort. It is the application of these functions that can be at times a problem.
>
> Let us use the firefighter as an example. No group in this country is better trained and equipped to fight fires, but that is part of the problem. Training and planning mostly concern how to apply water to a fire, rearrange debris, isolate hot spots, remove and tend to injured, and protect personnel from smoke and fire. There are, however, a growing number of fires and potential explosions that need no application of water — where water, in fact, may well contribute to a major disaster. This involvement with chemicals is a whole new ball game.
>
> Al Smith (1981)

> Emergency response to hazardous materials incidents is unlike traditional firefighting in that response personnel must identify the specific chemical haz-

*See Exclusions cited on page 2.

ards facing them before approaching an accident or attempting a rescue mission.

Charles Wright, [In]
Office of Technology,
Assessment (1986)

An inappropriate response to an accident involving unfamiliar chemical products can endanger individuals, the surrounding community, and the environment. Local fire or police department personnel are usually the first to respond to a hazardous materials accident during transportation, and even in a plant, hence their training is of primary importance. Of the approximately 2 million people in the emergency response network, OTA estimates that a maximum of 25 percent have received adequate training to meet a hazardous materials emergency.

Office of Technology
Assessment (1986)

The Fire Services must learn to accept the fact that the training received and reinforced in fighting structural fires is, in most cases, *totally inadequate* to handle hazardous materials incidents safely. In many tragic instances, it has been dead wrong, [emphasis in original].

Frank Fire (1986)

The complexity of the subject chosen, control of hazardous materials by water, indicates that some subdivision of the data is required.

We have chosen four categories for discussion:

- Preventing vapor cloud formation
- Reducing vapor clouds
- Controlling vapor clouds
- Preventing or controlling vapor cloud ignition.

Although several topics could be discussed under more than one category, we have placed them in particular categories for ease of discussion, not to imply that other uses may not exist.

The reader is cautioned to carefully consider the entire document and urged to consult the references as available. In order to reduce the size of the article, we have usually stated a major point only once; therefore, skipping portions or using portions out of context may mislead the reader.

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EXCLUSIONS

- **Fixed Systems—Sprinkler or Water Spray**

Fixed systems used in control of hazardous materials in which water is the extinguishant, suppressant or other active agent are not covered by the discussion of this paper.

The National Fire Protection Association (NFPA) has developed a series of standards which may be studied for the particular limitations of each type of fixed system.

Sprinkler systems (NFPA 13), water spray fixed systems (NFPA 15) and explosion prevention systems (NFPA 69) possess many of the attributes of handlines but the need for brevity precludes their discussion.

Many of the studies cited however, are based on such systems since much information is available for fixed installations but not usually for handlines.

- **Explosion Suppression Systems**

Specialized explosion suppression systems engineered in accordance with the precepts of NFPA 69 can be effective in controlling and extinguishing incipient and developed explosions. Similarly, fixed tub systems have demonstrated adequate performance in test and field use for control of underground coal, methane or coal-methane explosions.

For information on these systems, the reader is directed to a few selected articles in the bibliography.

- **Fire Fighting**

While many of the principles outlined in this paper may apply to fire fighting (extinguishement) no attempt has been made to research or discuss this area. Readers may want to consult articles by Rasbash et al. (1954) (1960), by Haessler (1974) (1986), or by Drysdale (1986).

VAPOR CLOUD PRODUCTION

Fire fighters have traditionally not been concerned with the dispersion of products of combustion, "smoke," released into the atmosphere by free burning fires. Yet when hazardous materials are involved in a fire or a non-fire incident, airborne dispersion as "smoke," unburned vapor clouds or plumes, may pose the major threat to public safety — even more than the threat generated by the fire or release incident.

In many fire incidents, the "smoke" plume is buoyed upward on the hot thermal column to disperse in the atmosphere. In many non-fire incidents no such convenient buoyant mechanism is available and the plume or cloud follows along the ground where it may contact a source of ignition (if it is flammable) giving rise to an unconfined vapor cloud explosion (Flixborough, 1974, 28 dead) or expose concentrations of people to toxic hazards (Bhopal, 1984, 2000 + dead).

Even some substances whose vapor densities are less than that of air, may, in some releases, form non-buoyant or "dense" vapor clouds.

Ammonia (vapor density of gas about 17/29 (0.59) that of air) may form dense vapor clouds depending upon how it is stored and the mode of container failure. Similarly methane stored as LNG or hydrogen fluoride or oxygen stored as liquid oxygen may not be as easily dispersed as simple chemistry may predict.

Therefore prevention or control of non-buoyant or dense vapor clouds is of prime importance in haz mat incidents.

I. CONTROLLING VAPOR CLOUD FORMATION

The first line of defense against exposure to vapor clouds is to prevent their formation. Useful tools and techniques are commonly available for controlling release of a hazardous material and for minimizing vaporization. Among the former are the plugs, valves, patches, clays, and tapes familiar to all haz mat responders. They are not discussed here but should always be used if feasible to keep the hazardous material contained.

Minimizing vaporization after a substance is released, or controlling the rate of release are usually accomplished with the traditional tools of the firefighter — water and sometimes water additives. These should be supplemented as appropriate by diking, damming (amount of vapor evolved is proportional to exposed area), neutralization, or other recognized techniques.

In each of the following uses of water spray, the importance of technical information about the specific hazardous material released is apparent.

CAUTION

SOME HAZARDOUS MATERIALS REACT SO DANGEROUSLY TO WATER THAT NONE OF THESE PROCEDURES ARE ALWAYS SAFE.

Cooling

Cooling a pool of spilled hazardous material by water ice has been investigated by Greer, et al. (1981, 1979) who found no significant cooling effect. Direct cooling of containers by water spray is an effective means of reducing the temperature of the contents and therefore retarding vaporization only when the relationships of exposed surface area of the container, the container volume, cooling water temperature and volume, vapor pressure of the material and specific and latent heats of evaporation are favorable. For example, spraying a nonexposed leaking propane tank car would probably not significantly reduce the leakage. The vapor pressure of propane at 100 °F is about 185 psia, reducing the temperature to 75 °F will still leave a vapor pressure of 130 psia. (The boiling point of propane is -44 °F.)

Water reactivity of the material may also limit the use of cooling. Under the conditions described above, for instance, the vapor pressure of chlorine could be reduced from 152 psia to 107 psia by applying water spray. However, the resultant acid formation and corrosion of tank or fittings may *increase* the size of the leak and increase leakage. This, of course, does *not* mean that we should not directly cool containers exposed to a fire or radiant heating. Cool containers that are significantly above normal temperatures (fire exposures) or when you have specific knowledge that cooling will be effective.

Heating

Water spray is discharged at the approximate temperature of the water supply. While we normally consider water as a cooling agent for fires whose kindling or ignition temperatures are in the hundreds of degrees F and whose flame temperatures may be in the thousands of degrees F, 70 °F may be quite warm in comparison to the temperatures that pools of some hazardous materials such as the cryogens might reach. For example, liquid oxygen is stored at temperatures below minus 300 °F or some 370 °F colder than our 70 °F water. If discharged on the ground by a leak, the liquid oxygen can only obtain heat to boil or evaporate from its surrounding air or the ground upon which it lies. Moisture in the surrounding ground is rapidly frozen partially insulating the pool of liquid oxygen and retarding its evaporation. Application of water spray can provide sufficient heat to increase the boiling of the liquid oxygen and create dense clouds of oxygen and frozen water spray. Tactical considerations will dictate whether or not this rapid vaporization is desirable.

Some non-cryogenic liquefied gases such as the low vapor pressure butane and chlorine may pool as will anhydrous ammonia which requires a comparatively high heat to vaporize (high latent heat of vaporization — 590 BTU/lb at its boiling point of 28 °F.). Even propane with its high vapor pressure and low latent heat of vaporization may pool in winter weather.

> 'The hydration of ammonia with water is exothermic. The contact of liquid ammonia with water will increase the evaporation rate as a result, whereas the natural evaporation of ammonia is endothermic, causing the remaining liquid to cool and spontaneously reduce the rate of evaporation further. First contact emergency response personnel, typically a local fire department, use water liberally to wash spilled materials away from the point of leakage. As with LPG, this can be hazardous. Emergency response personnel should attempt to avoid contact between water and liquid ammonia pools with the objective of reducing vapor generation rates."
>
> Desteese and Rhoads (1982)

Decisions to heat a pool of hazardous material must be based on a realistic appraisal of the ability to safely control the resultant vapor cloud.

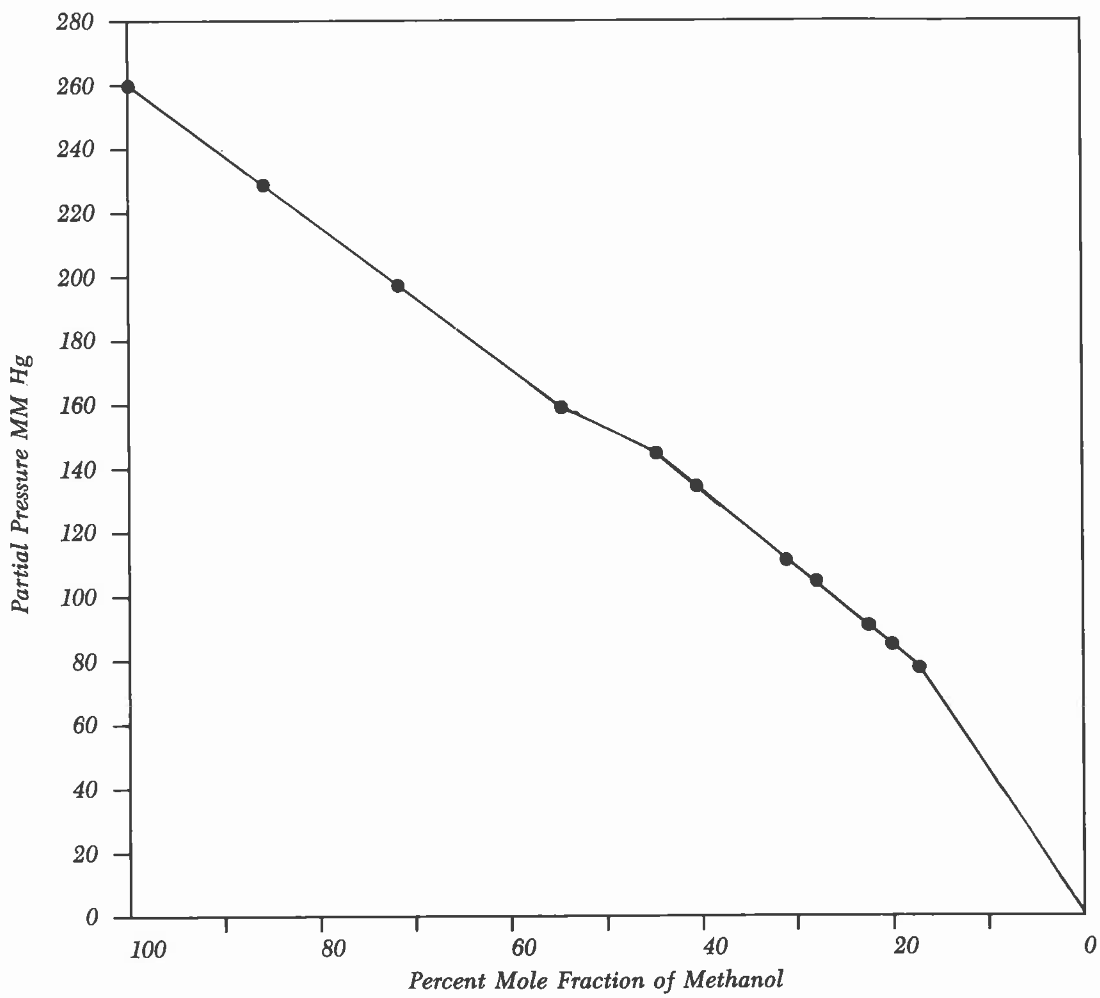
Dilution

Water miscible solvents such as acetone, methanol or ethanol can be diluted by application of water to form non-flammable mixtures. Large quantities of water are required in relationship to the size of the spill or tank since dilution to ratios of 4 to 5:1 (water to alcohol) may be required to prevent ignition.

As the concentration of water increases, the partial pressure of the solvent and hence its ability to vaporize decreases. Eventually not enough vapor can be evolved to burn and the fire goes out or cannot be ignited.

This is illustrated in the following graph which shows the vapor pressure (or the ability

Partial Pressure of Methanol in Water



to vaporize) decreasing as the concentration of methanol decreases with the addition of water.

Reducing vapor pressure by dilution will not decrease vaporization in every case. If the water adds significantly to the temperature of the material, vaporization may increase.

Knowledge of the thermodynamic properties of both water and the hazardous material are required to use dilution safely for other than simple solvents such as methanol (Thorne, 1977/78).

Covering

Not all hazardous liquids are lighter than water. Carbon disulfide for instance, has a density or specific gravity of 1.26 (about 25 percent heavier than water) and is insoluble in water. Vaporization of carbon disulfide has been controlled by gently applying a layer of water to float on the surface of the tank or spill. (Cases 309 and 558 in MCA, 'Case Histories of Accidents in the Chemical Industry.")

Low velocity water spray from an applicator may be required to minimize mixing.

Emulsification

Water discharged on the surface of some viscous liquid materials may form an emulsion which can froth into a foam-like blanket. This may serve to seal the surface of the hazardous material and retard evaporation. This method of vaporization control is seldom used and then usually only in a fixed system with specially designed coarse water spray nozzles. Caution must be exercised since in liquids of appreciable depth, frothing may cause the material to overflow the container, spreading contamination.

Attempts to use handlines, especially with straight streams or narrow spray patterns may cause violent frothing and slop-over if the temperature of the liquid is above the boiling point of water (212°F) and the material is sufficiently viscous. (API, 1980)

Special emulsifying agents may be applied by handlines using mechanical foam equipment. The effectiveness of this technique has not been adequately demonstrated.

Phase Separation

Gasohol, a mixture of gasoline and one of the light alcohols (usually ethanol) has the foam-destroying properties associated with the alcohols or other polar solvents.

Applications of non-alcohol resistant foams on gasohol will not form stable foam blankets and therefore it is difficult to retard vaporization. Alcohols which are equally miscible in both water and gasoline are subject to phase separation if the water tolerance of the fuel is exceeded. (Phase separation means that the gasoline will separate from the alcohol and float to the top of the container and the alcohol and water will sink to the bottom.) The concentration of water required to exceed the water tolerance is about 2 percent by volume for common gasohol mixtures. DiMaio (1980 (a), 1980 (b)) has proposed the application of water to a gasohol tank or spill to separate and isolate the alcohol leaving the upper (exposed) gasoline layer suitable for the application of non-alcohol foams. While this has not been tested to our knowledge, Noll (1986) advises, '...the use of the phase separation technique is not recognized as a viable tactic when dealing with large quantities of alcohol containing fuels."

Plant operating personnel may be aware of the water tolerance of other separable materials and could advise trying a phase separation.

Water Additives

The properties of water which make it an attractive agent for control may sometimes be enhanced by the use of water additives.

The most commonly used water additives are the various "foam" liquids which are designed to lower the specific gravity of water, to lower its surface tension, or to change other physical properties.

The first may be done through traditional mechanical foams, either at high or low expansion ratios, the second through use of newer aqueous film forming foams which may be applied with or without mechanical expansion, and the third by addition of other special chemical additives.

Other additive functions may include:

1. "Wet" water to decrease surface tension;
2. 'Slick" water to modify flow characteristics;
3. "Thickened" water to increase viscosity;
4. "Dry" water to form a powder covering on the liquid surface; and
5. Emulsifiers or dispersants.

None of these other additives have found widespread use in controlling vaporization of hazardous materials.

The literature of foam application to hazardous materials is quite large and inappropriate to discuss in this paper. However, mention should be made of work by DiMaio et. al. (1984) and by Cousin and Briggs (1986) which indicate the low effectiveness of nonaspirated (unfoamed) AFFF and the possibility that it may enhance ignition of a flammable liquid.

We have included some selected references in the bibliography.

II. REDUCING VAPOR CLOUDS

Direct attack on a vapor cloud using waterspray may remove vapor from the atmosphere by combining the hazardous material with the water.

One available mechanism is through solution of the hazardous material in the water. A second is physically binding the material to the water particle which then rains out. Chemical reactions may also take place which change the hazardous material. In some instances, these water reactions may result in a less harmful or easier to handle substance. In other instances, a more severe problem could be created.

The only widespread use of vapor reduction by fire departments has been in controlling anhydrous ammonia releases through sorption. Other uses are not common.

Sorption

Some gases dissolve readily in water and from relatively harmless compounds. Ammonia, for example, is soluble in water to about 43 percent by weight (Braker and Mossman, 1971) allowing ammonia vapors to be easily dissolved by water spray. This results in the formation of a solution of ammonium hydroxide.

Greiner (1984) has demonstrated the effectiveness of this technique in more than 300 demonstrations throughout North America. Studies by Eggleston, Herrera and Pish (1975) with vinyl chloride (solubility 0.11 percent by weight), and with ethylene (solubility 0.01 percent by weight) indicated that sorption of these gases by water spray was insignificant. Chlorine is more soluble in water than either vinyl chloride or ethylene (7.3 percent by weight), but the production of hypochlorous and hydrochloric acid solutions which are highly corrosive limits the usefulness of waterspray (Kelly 1977).

Where both high solubility in water and relatively harmless reactions and reaction products will occur, waterspray sorption may be tried. However, Whiting and Shaffer (1978) feel that air entrainment which "dilutes" the water may be a limiting factor in widespread use of sorption.

Scrubbing

Reduction or removal of aerosols (dusts and mists) may sometime be accomplished by scrubbing the plume with water spray. This technique has been shown to be effective for the removal of coal dust (Tomb, et al. — 1972 Nagy, et al. 1974) and for industrial dust control (McCoy et al. 1983, Jayaraman et al. 1981).

Effectiveness of water-spray protection for mists of heat transfer agent (HTA) was established by Vincent, et al. (1976 (a)). They pointed out 3 cautions in the design of such systems:

1. "Vapor-air or gas mixtures such as methane, ethylene, ether, etc. are not scrubbed by water fog; and this system should not be depended upon to protect against these hazards,"
2. "Water fog is believed to be generally applicable to mist and dust type explosions..." but they only tested against one HTA; and,
3. "The space immediately surrounding a large HTA vapor leak will have vapors and mist in combustible concentrations even with water fog nozzles operating. An ignition source very near a large leak can start a fire which the water fog will not extinguish."

Scrubbing with handlines has not been adequately investigated for its use to be recommended.

III. CONTROLLING VAPOR CLOUDS

Vapor clouds may drift with the winds following local terrain and structures, or they may initially be propelled with some force such as occurs when a compressed gas is released from its container. In either case, vapor clouds are subject to control or dissipation by the impact of water sprays or of air entrained by water sprays. In a given situation, it may be difficult to determine which factor of air entrainment, mixing, dilution or a combination of these factors are operating.

As will be noted later, uses of water spray for maximum air entrainment tend to minimize the effect of water spray impact and vice versa.

The factor of selection seems to be based on the driving force behind the vapor cloud. If strong, such as a compressed gas release, then impact of water spray (the barrier effect) may be more effective. For a drifting cloud, ventilation or dilution may be the method of choice depending upon cloud size. Ventilation or dilution of massive clouds is impractical due to quantities of water required.

Ventilation

Water sprays may contain large quantities of air which can be used for dilution or redirection of vapor clouds. Eggleston, et al. (1976) point out the high degree of variability of air flow produced by water spray and the fact that air velocities developed are quite low. They recorded flows from downward directed nozzles of 87-226 cfm/gpm depending upon nozzle type and height above the ground. Other studies cited in Eggleston, et al. (1976) which were evaluated by Factory Mutual found entrainment at rates as high as 1,080 cfm/gpm in tiered water-spray systems. Teele (1981) gives values of 6,500 cfm for an 1½-inch spray nozzle and 8,700 cfm for a 2½-inch. Using average flows of 100 gpm and 250 gpm, respectively this gives an entrainment rate of 35-65 cfm/gpm. Haessler (1986) writing in the 16th Edition of the Fire Protection Handbook gives a value of about 30 cfm/gpm for handlines while Rosenham (1986) in the same volume, gives a value nearly 6 times higher or 170 cfm/gpm. Neither article cites a source.

Fitzgerald (1958) using a 2½-inch fog nozzle achieved flows of 50,000 to 96,000 cfm in a tunnel (ducted flow) at nozzle pressures of 100 psi and 70,000 to 131,000 cfm at nozzle pressure of 150 psi. Nozzle type or waterflow were not given but based on common water-spray nozzles, we could estimate entrainment rates at 100 psi of 200 to 384 cfm/gpm (ducted). Note the increase in entrainment with increased nozzle pressures.

Whiting and Shaffer (1978) using a 250 gpm nozzle and a 750 gpm deluge set estimated entrainment rates of 338 cfm/gpm. They estimated that the experimental oil smoke was diluted by a factor of greater than 10. They pointed out that, 'large spills of very toxic and highly volatile chemicals would be difficult to dilute below the toxicity limit, however, the flammability limits are about three to four orders of magnitude higher which indicates that even large spills of flammable chemicals would be ameliorated using this system."

Heskestad, et al. (1976) found that for a given nozzle size, spray angle and distance from the nozzle, entrainment flows tended to be proportional to the water flows. Spray angle was found to be critical with a 90 degree pattern entraining 5 times as much air for a given water flow than did a nearly 30 degree pattern. Of course, using a wide pattern reduces the effective horizontal reach of a 1½-inch handline about 30 percent (from about 54 feet to 38 feet) thereby requiring a much closer approach to a vapor cloud.

Therefore, we could expect the most effective ventilation (air entrainment) from a high flow, high pressure, wide angled pattern. Safety considerations of maneuverability and reach limit these parameters to common handline values (for 1½-inch 100 to 150 gpm at 100 psig at <90°). Assuming an entrainment rate of 50 cfm/gpm then a "standard" 1½ handline could be expected to entrain about 5,000 cfm.

In comparison with usual fire department smoke ejectors, a 1½-inch handline approximates the air flow of a 16 inch diameter ejector and a 2½-inch approximates a 20 to 24 inch diameter ejector. (Super Vacuum Manufacturing Co., undated)

To relate this entrainment to a cloud of vapor, assume a hemispherical cloud 100 feet in diameter. It has a volume of 260,000 cubic feet. To reduce this vapor cloud to a concentration of one percent will require 26,000,000 cubic feet of air. Moving 5,000 cfm it will take nearly 87 hours for this dilution assuming perfect mixing, no cloud drift, or dispersion.

Watts (1976) using a downward pointing nozzle that entrained 24,000 cfm of air found that a vapor cloud of 50 percent ethylene fed by a 600 cfm ethylene source could be reduced to the lower flammable limit (LFL) (3.1 percent by volume in air) in less than 11 seconds.

Beresford (1981) describes the use of a combination of two 200-500 gpm flat fan sprays and two 300-1500 gpm (1000-3500 gpm, total) wide angle monitors to raise and disperse gas leakages from pipelines and storage containers. "Two monitors set to operate on a wide-angled spray are placed approximately 30 feet apart and arranged so that the water will discharge in the form of an inverted vee 40 to 50 feet above ground level. The water spray feathers at this point and the resultant droplets fall to the ground like heavy rain. Two flat-fan sprays are set up at right angles to the monitors and they discharge a fan shaped vertical curtain of water some 40 feet wide and 40 feet high. The overall effect is to surround the leaking gas with an upward moving screen of water to create the desired chimney effect. To ensure that the gas is not passing through the sides of the chimney, one or more gas testers patrol the periphery testing continuously. If a breakthrough of gas is detected, an extra flat fan spray is quickly placed in position to seal off the gap. If correctly set upon initially, there has been no necessity to augment the initial layout.

The reason for this combination of spray methods is that the flat fan sprays have been found to effectively stop the lateral spread of gas and the monitors to provide the massive air movement essential for dilution and dispersion."

Included in this study are the following case histories and his evaluation of the method.

"• Propylene discharging from a 2-inch diameter drain line at 400-psig and at atmospheric temperature at a rate of approximately 100-tons per hour which could not be isolated for several hours.

• Methane at 60-PSIG and at atmospheric pressure leaked at a rate of 50-tons per hour for thirty minutes from a fracture at a bend in a 6-inch diameter pipeline.
• Ethylene gas at 500-PSIG leaked from the flanged joint of a 14-inch diameter pipe for some fifty minutes, impinging on steelwork at high velocity.
• Ethylene gas leaking from pipelines and spheres at varying temperatures and pressures has been successfully contained and safely dispersed on a number of occasions.
• The vapors from leakages of Ethylene Oxide, LPG, Gasoline, Naphtha, Benzene and Hydrocarbon Solvents have also been safely contained using the methods described.

Such methods are not capable of dealing with catastrophic failure of equipment, the result of which should be carefully considered at the design stage and steps taken for secondary containment where considered necessary. However, these procedures are suitable for serious gas leaks which could escalate into a major incident if not quickly controlled.

The drawback of this method of containment is the time taken to set up the equipment currently available. Study of gas leakage incidents where explosions have taken place has shown that ignition of the gas/air mixture has often taken place in between three and five minutes of the leak commencing. This leaves little time for equipment to be set up so automatic detection and protection would appear to be the only feasible solution to this kind of problem."

Barrier

One traditional use of water spray which seems to be well supported by research is forming a water curtain or barrier to *vapor*, (not *flame*), travel with multiple handlines. This is illustrated in Figure 3-4.8(a) of the NFPA "Manual on Aircraft Rescue and Fire Fighting Techniques for Fire Departments Using Structural Fire Apparatus and Equipment" (NFPA-1975). Air entrainment by water sprays depends upon transfer of momentum from the water drops to molecules of air thus causing the air to move (Smith and Van Doorn 1981). Similarly, momentum transfer to vapor or gas molecules or to aerosols also occurs causing this movement. Advantage can be taken of this imparted momentum to control the travel of a vapor cloud or to redirect it away from sources of ignition or other areas of danger. Smith and van Doorn, (1981) report that the effectiveness of a water spray in inducing velocity to air (or vapor) is droplet size dependent:

> "Momentum transfer between the rain of droplets and the ambient air induces large scale movement: fine droplets lose their momentum rapidly and so tend to move large volumes relatively slowly. Coarse droplets penetrate much further and although entraining less air, the induced velocities are generally higher."

Momentum of the water spray varies with the spray pattern. We see this in the increase in nozzle reaction as the spray cone is narrowed into a straight stream from a wide pattern spray. Likewise, we know that a straight stream or narrow spray pattern has better reach against the wind than does a wide pattern spray (it is better able to overcome the momentum of the air; i.e., wind). Increased nozzle pressure also increases the momentum available to transfer to the vapor of air.

Escaping hazardous materials may have a high momentum caused by tank pressures, temperature, static pressure, wind or a combination of any or all of these factors. If we want to oppose the vapor travel, we must supply momentum in another direction which will stop or redirect this flow.

As a general rule, control of materials escaping under pressure will require higher nozzle pressure, narrower spray patterns and coarser spray droplets than would be required for control of a vapor cloud.

Numerous other studies of ventilation and barrier production are contained in the bibliography.

IV. PREVENTING OR CONTROLLING VAPOR CLOUD IGNITION

Much research has been conducted on the effects of water spray on the energy required to initiate a fire in a flammable vapor cloud, the effectiveness of water as an inerting material for flammable vapor clouds, the quenching of a flame by water spray, and the attenuation of infrared radiation by water curtains.

Each of these issues will be discussed in turn but a few cautions should be observed in any use of water spray on an unignited flammable atmosphere.

• "WATER IS CAPABLE, UNDER SOME CIRCUMSTANCES, OF PROMOTING EXPLOSIONS OF HYDROCARBON-AIR MIXTURES RATHER THAN INHIBITING THEM" (Mullins and Penner 1959).
• "WATER SPRAYS MAY INCREASE THE RATE OF FLAME TRAVEL" (Eggleston, Herrera, and Pish 1975).

The practical consequences of these two factors is still in debate. However, Pikaar (1985) cautions:

"WHATEVER THE TRUE CONCLUSION, CAUTION REQUIRES THAT WHERE SUCH MEASURES [WATER SPRAYS] TO PROMOTE FLAMMABLE CLOUD DISPERSION ARE APPLIED, THE SYSTEM SHOULD BE ABLE TO DILUTE THE RELEASE TO BELOW THE LFL [LOWER FLAMMABLE LIMIT]."

Ignition Suppression

Eggleston (Eggleston, Herrera, and Pish 1975) in an investigation of the use of water spray found that ignition of a flammable mixture was possible even when an unusually high water rate of 1.8 gpm/feet^2 was used. (Design density of sprinkler systems range from less than 0.1 to 0.6 gpm/feet^2, (Bryan 1976). Those of water spray systems for prevention of flammable gas cloud formation range upwards from 0.6 gpm/feet^2 (NFPA, 1985). The 1.8 gpm feet^2 is equivalent of the discharge of a 100 gpm 1½-inch 60° pattern handline about 7½-feet from a fire.)

They concluded, that, "Any ignition source which could exist within a typical [water] spray would also serve to ignite a flammable vapor mixture. The protection afforded by the water spray would serve only to make the existence of an ignition source less probable." (Eggleston, Herrera, and Pish 1975)

Rothchild and Guzdar (1976) studied the use of passive systems for ignition prevention and suppression at cutter heads in mining equipment. They found that water spray systems could reduce the frequency or probability of ignitions through two mechanisms:

- Directly, acting as a coolant
- Indirectly, as an aid to ventilation

Agbede, et al. (1982) were able to effectively control ignitions by applying water sprays to the back side of mining cutters to cool the hot rock pathway. They found that spray orientation, water pressure, flow, and spray nozzle pattern and characteristics were important.

Tests by Watts (1976) using the explosive PETN as a source of ignition of ethylene-air or hydrogen-air mixtures found that the amount of PETN required to detonate these mixtures was increased some 3 or 4 times when water spray was applied. The water spray did not stop a detonation or deflagration after ignition, it only raised the energy required for ignition.

Water spray is able to reduce the probability of ignition of a flammable vapor cloud but seemingly only if it can quickly cool the ignition source. As pointed out by Eggleston, et al. (1975) if the ignition source could survive the water spray then ignition of the vapor cloud was possible.

CAUTION: IF OPEN FLAMING OR SPARKING OF THE IGNITION SOURCE CONTINUES DURING APPLICATION OF WATER SPRAY, IGNITION OF A FLAMMABLE ATMOSPHERE SHOULD BE ANTICIPATED.

Inerting

Water as an inert diluent has been used for many years in steam smothering systems in process plants and aboard ship. (One may remember the attempt at Texas City to smother with steam the ammonium nitrate fire in the ship's hold) (Greiner 1972).

Rothchild and Guzdar (1976) found in the mining study, that, "... some atmospheres, such as methane and air that would otherwise be explosive can be made inert by the addition of water."

Based on theory, 18 percent of water (liquid) by weight is required to inert a methane-air atmosphere. 'Fine fogs with water droplet size around 1 micron [1/25,000 inch] can inert the atmosphere as predicted, but the combination of fine drops and high water content is difficult to achieve in practice," (Rothchild and Guzdar 1976).

Spray systems may produce an average droplet size of around 100 microns which is far too large. Therefore even at 18 percent concentration, spray systems are completely ineffective at inerting the atmosphere. Hodnett (1981) states that the optimum size of droplets in a spray for fire fighting is in the range of 300 to 1,000 micons. (The NBFU (1955) gives a figure of 350 microns.)

Note that these droplet sizes are 300-350 to 1,000 times the size effective for inerting at the 18 percent concentration. If water vapor is used instead of fine spray, the concentration required jumps to approximately 26 to 27 percent water by weight to inert a methane-air atmosphere. Liquid water is more effective than water vapor as a coolant because of the high latent heat of water (970 BTU/lb.) compared to its specific heat (1 BTU/lb.). Even with fine mists, the total moisture content that can be produced is generally less than 3 percent by weight or only ⅒ that required.

The problem in developing water spray inerting nozzles may be the air entrainment. Rothchild and Guzdar (1976) found that fine sprays tend to educt a large quantity of air "... thus diluting the moisture concentration with air. This dilution effect is particularly severe when large quantities of fine sprays are used to achieve high moisture concentration limiting the maximum concentration achievable to a low value." As we noted previously, fine sprays entrain more air than coarse sprays. Therefore, if inerting spray nozzles are designed for handline use, they may have to be of a radical design which minimizes air entrainment. Inerting with current handline nozzles is impractical.

Quenching

Quenching, as used in this context, is analogous to the prevention of flame travel or propagation by fine mesh or narrow spaces, the principle behind flame arrestors and electrical equipment for hazardous locations.

In general, water sprays outside the laboratory have not been successful in quenching flame propagation through a flammable vapor cloud. Watts (1975) and Eggleston et al. (1975) have experimented with large scale confined vapor clouds. They both concluded that the water spray curtain would not act as a flame arrestor. In fact, Eggleston et al. (1975) and others have reported that flame propagation as measured by flame speed and luminosity were enhanced by the water spray.

Studies at the U. S. Bureau of Mines by Liebman, et al. (1978) and by Sapko, et al. (1977). and as reported by Stafford (1981) (see also Smith and Van Doorn (1981)) indicate that practical quenching systems for mining equipment seemed feasible but that they required more water than for inerting systems. It should be noted that the volume to be protected by these systems was quite limited, about $0.45m^3$, and flows of 9 gpm were required with a 56 micron SWM (surface weight mean) droplet. Sapko, et al. (1977) also felt that this water requirement could be reduced if the droplet diameter were also reduced. Water volume requirements were increased if particle size were increased. Raising the droplet to 100 microns (SWM) diameter almost doubled the water requirement. Gugan (1979) has calculated that a water spray system to protect an area of some 200 m square would require flows of about 1,125,000 gpm even with very fine droplet size. With the droplet size found useful for fire fighting handlines (350 to 1,000 microns), the water requirements are extremely large.

Therefore, quenching with currently available handline nozzles is not practical even on a very modest scale.

Infrared Radiation Attenuation

Water curtain protection of exposures has been used for many years in an attempt to prevent ignition through radiant heating.

Little research has been conducted on the effectiveness of such systems, but one paper by Heselden and Hinkley (1965) found transmission of radiation from a standard radiant panel ranged from 8 to 95 percent. Factors of importance in their calculations were droplet size, spray density, and the length of travel through the water spray. Using flows of 3 gal/ft/min they felt that at least a 50 percent attenuation could be achieved at pressures within normal for handlines with nozzles giving coarse droplet size spray comparable to sprinklers. Higher pressures gave finer-sized spray and greater attenuation.

Reischl (1979) conducted experiments using a liquid propane burner and a steel reflector and applied water spray streams from two commercially available 1½-inch nozzles and one booster nozzle. The streams were directed toward the burner/reflector to simulate normal protective shielding by handlines.

Pattern and flow were the major determinants of attenuation. The booster line flowing 25 gpm provided far less protection at any pattern than did the 85-95 gpm 1½-inch lines.

Patterns of 90° were somewhat more protective than those of 60°. Thirty degree patterns from the booster line were about half as effective as the booster line 90° pattern. Reischl calculated that the 90°, 1½-inch pattern could about double the time a fire fighter could safely stay exposed to a 'hot" (radiant) fire.

Direct application of water spray to the exposed surface is more effective in preventing ignition than attempts at shielding the infrared radiation (Hodnett, 1986 (a)). Shielding of nozzlemen seems to be the only practical use of handline infrared attenuation.

Conclusions

In concluding this brief overview of some of the major questions involving use of water spray for control of vapor clouds, we will summarize each of the four areas considered.

- **Preventing Vapor Cloud Formation**
Work by Greer et al. (1980, 1981 (a) (b)) which was sponsored by the USCG and later the USEPA led to the conclusion that the only feasible control technique for the prevention or control of vapor or cloud formation using water was when it was enhanced by a foam liquid and applied as a foam over the exposed surface. Foam application is well established for flammable liquid control. Special HAZ MAT foams have been investigated and control or reduction of vaporization documented.
- **Reducing Vapor Clouds**
(Gross and Hiltz (1985). Covering with a layer of water has been used on a small scale in controlling a carbon disulfide spill and was credited with limiting the extent of a subsequent fire. (MCA) Emulsification has been used with some success but mainly in fixed systems (Hodnett, 1986 (a)).

Again, Greer (1980, 1981 (a) (b)) found that vapor scrubbing or vapor phase reaction were impractical or ineffective as general tools for reduction of vapor clouds.

Anhydrous ammonia sorption by handlines as demonstrated by Greiner (1984) seems to be one exception to Greer's evaluation.

- **Controlling Vapor Clouds**

Several studies have indicated the effectiveness of ventilation or barrier effects (air movement) in controlling vapor clouds. Yet Greer (1980, 1981 (a) (b)) found them to be either impractical or ineffective. Perhaps the question is not *are* they effective but *how* effective and what limits should be placed on the size of cloud you attempt to control. McQuaid and Roberts (1982) indicate that fixed water spray ventilator systems may be effective at material discharge rates of up to 10 kg/s. Watts (1976) found a control limit for ethylene at 600 cfm using a single downward spray entraining about 24,000 cfm. Calculations based on fixed sprays indicate water spray handlines may only be 20 to 25 percent as effective as the spray used by Watts. Beresford (1982) has suggested upward spray chimneys using standard fire department deluge sets or monitors and at flows (1,000 to 3,500 gkp) and pressures compatible with modern fire pumps.

- **Preventing or Controlling Ignition of Vapor Clouds**

Water spray handlines are ineffective in preventing or controlling ignition unless they are capable of extinguishing the ignition source.

Water spray can be effective in reducing radiant heat exposures of fire fighters and thus provide some protection against radiant (flash) burns. Direct application of water spray to the exposed surface is even more effective.

General Rules for Using Water Spray Handlines in Controlling Vapor Clouds

- *Preplan* your response
- *Evacuate* as necessary before cloud arrival
- *Control* all sources of ignition
- *Never enter* a flammable vapor cloud
- *Never enter* a toxic vapor cloud without adequate personal protective equipment
- *Ventilate* as required to render the cloud non-toxic or non-flammable
- *Provide* a dependable backup water supply and reserve lines for rescue.

Can water spray *increase* the hazard of a flammable vapor cloud?

Water Reactions with Enriched Gas or Vapor Mixtures

Billett (in Mullins and Penner, 1959) and others have shown that the presence of water vapor in confined vapor-rich spaces (concentrations about twice stoichiometric) can give rise to very rapid flame travel, with the normally slow moving luminous flame becoming quite rapid and nonluminous denoting more complete combustion. Temperatures are too low to attribute this phenomena to simple chemical dissociation of the water and subsequent hydrogen burning. From the literature it is not clear what effect, if any, could be attributed to the turbulence or increased mixing of the fuel-air mixture caused by the introduction of the water.

Similar effects have also been noted by Eggleston, et al. (1975), and by Watts (1979) in field tests of fixed water spray dispersion systems using nearly stoichiometric mixtures.

Flame speeds of some 130 feet/sec. have been measured with water spray in contrast to an average 30-40 feet/sec. without waterspray. (Pikaar, 1985). Tests indicate that at the lower flame speeds, pressure rise at the edge of vapor clouds is insignificant (Pikaar, 1985).

McQuaid and Roberts (1982) state that computer models indicate flame speeds on the order of 165 feet/s can produce noticeable blast effects. Pikaar (1985) and McQuaid and Roberts have (1982) calculated that flame speeds from 500 to 1000 feet/s can create devastating pressure waves.

The question is, can water spray accelerate flame speeds into ranges which produce significant pressure effects from deflagration and/or can water spray enhance the transition from deflagration to detonation?

We do not know the answer to this question, but both Gugan (1978) and Pikaar (1985) after extensive review of the literature caution on the use of water spray.

As Pikaar (1985) warns,

"Attention has been drawn to turbulence in all stages of cloud development and combustion. Turbulence promotes dilution in the release and dispersion phases while in the combustion phase it enhances flame speeds. However, comparison of flame speeds in large bag tests with those measured in field trials shows that normal atmosperic turbulence has no great effect on cloud combustion. The situation may be different if special measures are taken to excite turbulence in a cloud with the aim of promoting its dilution, for instance, the installation of water sprays. Previous experiments to answer this question suggest that water sprays created higher flame speeds though opinions as regards the interpretation of results differed. Whatever the true conclusion, caution requires that where such measures to promote flammable cloud dispersion are applied, the system should be able to dilute the release to below the LFL."

NIOSH ALERT

JULY 1985

APPENDIX II

Request for Assistance in Preventing Hazards in the Use of Water Spray (Fog) Streams to Prevent or Control Ignition of Flammable Atmospheres

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
PUBLIC HEALTH SERVICE
CENTERS FOR DISEASE CONTROL
NATIONAL INSTITUTE FOR OCCUPATIONAL SAFETY AND HEALTH

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REQUEST FOR ASSISTANCE IN PREVENTING

HAZARDS IN THE USE OF WATER SPRAY (FOG) STREAMS

TO PREVENT OR CONTROL IGNITION OF FLAMMABLE ATMOSPHERES

WARNING!

FIRE DEPARTMENTS AND TEAMS RESPONDING TO INCIDENTS INVOLVING FLAMMABLE GAS OR VAPOR MIXTURES ARE CAUTIONED THAT THE USE OF WATER SPRAY (FOG) STREAMS TO PREVENT IGNITION OR CONTROL FLAME PROPAGATION MAY BE EXTREMELY DANGEROUS:

- SIGNIFICANT FIRES OR EXPLOSIONS CAN OCCUR DESPITE THE USE OF WATER SPRAY. UNDER CERTAIN CONDITIONS, THE USE OF WATER SPRAY MAY IN FACT INCREASE THE SEVERITY OF SUCH FIRES AND EXPLOSIONS.

- IT IS UNLIKELY THAT HANDLINES USING STANDARD FIRE DEPARTMENT WATER SPRAY (FOG) NOZZLES UNDER FIELD CONDITIONS CAN PREVENT IGNITION.

- IT IS UNLIKELY THAT HANDHELD HOSE STREAMS CAN PRODUCE A WATER SPRAY WITH SUFFICIENTLY SMALL DROPLET SIZE AND UNIFORMLY HIGH WATER CONCENTRATIONS TO RENDER INERT A FLAMMABLE ATMOSPHERE.

- THE USE OF WATER SPRAY CANNOT BE RELIED UPON TO QUENCH A FIRE IN A FLAMMABLE ATMOSPHERE.

INTRODUCTION

In response to requests for assistance by Federal, state, and local health agencies who have jurisdiction, the National Institute for Occupational Safety and Health (NIOSH) conducts selected investigations of occupational fatalities. Recently NIOSH was called to investigate an incident which occurred as a hazardous materials (HAZMAT) team responded to a "man down" emergency in a storage tank recently emptied of toluene. In the attempt to gain immediate access to the tank to rescue the victim, members of the team began to saw an opening in the side of the tank while blanketing the area being cut with water fog, both inside and outside the tank. An explosion occurred which instantly killed one HAZMAT team member and injured 15 others.

July 1985

BACKGROUND

Water, in the form of "water spray" or "fog patterns," is frequently used by fire departments and other response teams to prevent or control fire when dealing with flammable materials. The use of water sprays in this way derives from several factors:

- traditional use of water by firefighters to extinguish fires,
- belief that water sprays may provide critical ventilation,
- ready availability and relative ease of application of water sprays, and
- effectiveness of water sprays in controlling some of the hazards of flammable materials.

In investigating the circumstances of the incident summarized above, investigators from NIOSH also reviewed various reported uses of water sprays to control hazardous materials.* This review identified at least 20 different suggested uses of water in the control of hazardous materials. In at least some of the situations described, the use of water fog actually posed a significant additional risk to the safety of firefighters or other personnel. One example is the attempt to prevent, control, or diminish a gas-air or vapor-air explosion using water spray or fog delivered by handlines.

Accordingly, this alert, directed to fire departments and HAZMAT teams specifically, warns that certain uses of water may be hazardous. These dangerous uses of water should be avoided.

REPORTED USES OF WATER SPRAYS

Studies by numerous laboratories have identified four prime mechanisms through which water spray could influence the ignition and propagation of a fire or explosion in a flammable atmosphere. Water spray has been used to:

- ventilate or otherwise reduce the concentration of the fuel to a level below that which is flammable,
- raise the required ignition energy beyond that available,
- render the flammable atmosphere inert, or
- quench or prevent the propagation of an incipient or developed flame front.

*The National Institute for Occupational Safety and Health (NIOSH) intends to publish a more detailed report on water spray at a later date.

The water spray requirements for each of these control mechanisms differ, as do their methods of application. Experience with use of water sprays for these purposes, including potential hazards, is briefly summarized below.

1. Concentration Reduction

Various techniques involving use of water spray have proven successful in laboratory and field trials and in some actual incidents. For example, air entrained in water spray has been shown to dilute, ventilate, or move flammable vapors or gases. In addition, water droplets in spray may absorb soluble vapors or gases under certain conditions.

However, in some experimental cases the water spray did not reduce the concentration of flammable vapors below the threshold of flammability, and ignition occurred. In those instances, the flame traveled through the water spray resulting in a more severe fire or explosion than would have occurred without the water spray.

2. Raising Required Ignition Energy

The results of several laboratory studies indicate that water sprays directed on "hot spots" caused by frictional cutting can significantly reduce the likelihood of ignition. By using a fine water spray directed on the hot path of a mining bit cutting into rock, researchers have prevented ignition of a flammable methane-air mixture. The water density of the covering spray, the size of droplets, and the work surface being cooled were critical factors in the success of this control measure.

Other studies using an explosive as the source of ignition of flammable ethylene-air or hydrogen-air mixtures showed that the strength of the charge necessary to obtain an explosion was considerably increased with the use of a water spray. In both situations, however, higher levels of ignition energy still caused ignitions, i.e., the water spray was not sufficiently effective to prevent ignition.

3. Rendering a Flammable Atmosphere Inert

Water as steam can render a flammable atmosphere inert. For example, when the concentration of water in the atmosphere was about 26% by volume, a highly flammable methane-air mixture was rendered inert. This concentration of water in the atmosphere is approximately 10 times that which the atmosphere can normally contain at room temperatures. This approach is normally impractical for field use because it requires production of a droplet size 30-100 times finer than that produced by standard fire department water spray (fog) equipment.

4. Quenching Flame Propagation

Quenching, or cooling a flame below the temperature required to propagate it in a flammable atmosphere, can be achieved only if the water droplets can be made small enough so that the distance between them is below a critical dimension. To produce a sufficiently fine mist in a fixed spray system usually requires a pressure in excess of 1,000 psig. Further, some systems even require the use of a high explosive to break up and disperse the water droplets.

Fire departments and other teams responding to incidents involving flammable gas or vapor mixtures are urged to approach the control of flammable atmospheres with extreme caution. The use of a water spray (fog) does not eliminate the need for other recognized control methods to dilute the flammable atmosphere and to prevent ignition due to sparks, arcs, or open flames.

REQUEST FOR ASSISTANCE

NIOSH requests that the technical information and warning contained in this ALERT be disseminated to personnel of fire departments, HAZMAT teams personnel, fire training academies, and other emergency response organizations.

Should further information be desired, please contact the Division of Safety Research, 944 Chestnut Ridge Road, Morgantown, West Virginia 26505-2888, Telephone (304) 291-4809.

We greatly appreciate your assistance.

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