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THE USE OF LIQUID GASES TO EXTINGUISH FIRES

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SUMMARY

The theoretical basis for using liquid carbon dioxide and liquid nitrogen in place of water as a general extinguishing agent for fires has been examined. This examination indicates that there is unlikely to be a case for using liquid gases unless the fire is such that the use of water would result in a large part of the water not being vaporized. It is suggested that there may be scope for the use of liquid gases:-

- (a) Where the present use of water causes substantial water damage.
- (b) Where the extinguishing agent cannot be made to reach the source of fire directly.
- (c) Where a large flow of agent needs to be projected into a building from outside.
- (d) For certain large outdoor fires e.g. aircraft crash fires.

For the latter two applications liquid nitrogen is likely to be more effective than liquid carbon dioxide because of the inherent inability of the latter to remain a coherent liquid at atmospheric pressure. Operational problems likely to be encountered in bringing liquid gases into large-scale use at fires are outlined.

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Introduction

In recent years inert gases, particularly carbon dioxide and nitrogen, have become available as liquids in tonnage quantities and the possibility needs to be examined of the usefulness of these liquids as extinguishing agents. These agents have, of course, been used for many years on special types of fire purely as inert gases. However, owing to the increasing cheapness of the agents, a study is now timely of the potential of these agents in comparison with water, for general fighting of fires and particularly for fires in solid carbonaceous materials in buildings.

Thermodynamic aspects

As is the case with water ⁽¹⁾, liquid inert gases extinguish fires predominantly by cooling. The ability of the agents to remove heat from a fire is, therefore, of the highest importance. The relevant thermodynamic properties that govern this ability are listed in Table I. It should be noted that carbon dioxide does not exist as a liquid at atmospheric pressure; data are therefore given for both solid and liquid carbon dioxide. Although the form in which it is stored is a liquid, the form in which it is presented to a fire is either as a gas or as a mixture of solid particles and gas.

The cooling that brings about extinction is manifested in two quite different ways, cooling the fuel and cooling the flames. Cooling of the burning material itself causes a reduction in the flammable gases and vapours evolved so that eventually the amount evolved is not sufficient to burn; also the solid phase combustion processes such as smouldering and glowing of carbonaceous materials may be stopped when the heat removed from the solid exceeds the heat produced by the combustion process. For cellulosic substances burning with free access of air, it is sufficient to reduce the temperature of the solid to 250°C to extinguish the fire, therefore the cooling capacity that may be achieved by heating the extinguishing agent to this temperature is the maximum potential for cooling that may be exerted for this purpose. On the other hand, for a volatile flammable liquid, it is necessary for the liquid to be cooled to the fire point and this is often less than 0°C.

The cooling of the flame is usually thought of as a smothering process, since the presence of the inert liquid as a gas or vapour results in the reduction of the concentration of oxygen. However, oxygen does not need to be completely eliminated in order to extinguish flames nor does the agent, if it is very finely divided, need to be vaporised. It is, therefore, appropriate to regard the extinction of the flame also as a cooling process. A useful empirical concept that may be used here is that the agent, when mixed with either air or fuel vapour and whether in the form of fine particles or as a vapour, should reduce the adiabatic flame temperature to the temperature at the lower flammable limit, i.e. about 1300°C. For this reason, the whole of the heat removal capacity of the agent up to a temperature of 1300°C may be regarded as a useful cooling potential for extinguishing flame. However, if an agent is applied to a fire, in the form of a jet, the jet may not be vaporised until it hits a surface which could break the jet up and vaporise it. For this reason, the sensible and latent heat of the liquid itself may not contribute to the capacity of the liquid to remove the heat from the flame.

On the above basis Table II has been prepared, in which the potential for the removal of heat from fire as a useful contribution to an extinction process by liquid nitrogen, liquid carbon dioxide and water are compared.

It will be seen, except for the extinction of a fire in a volatile liquid, the potential for a given mass of agent for removing heat from fires is much less for liquid nitrogen and liquid carbon dioxide than it is for water. Therefore, if water is used at a fire under conditions in which it vaporises completely, water is substantially more efficient than both the other agents. However, it will be seen that the major part of the cooling capacity of all three agents, lies in the ability of the vapours that are evolved to cool the flames. In many fire situations the major drawback in the use of water is the difficulty of vaporising it because of its high boiling point and high latent heat of vaporisation. If the water runs off unvaporised, then the whole potential of removal of heat from the flames by the vapour remains unused. It may be estimated from Tables I and II that, in fire situations where more than about three-quarters of the water applied would be expected to run off unvaporised, water would be less effective per ton delivered to the fire than liquid carbon dioxide and liquid nitrogen. This does not take into account any effect of water damage caused by the unvaporised water.

Transfer rate aspects

In the process of extinguishing a fire by cooling there are at least three different heat and mass transfer processes that are of some importance, as follows:-

- 1) Cooling of hot and burning solids by the agent prior to vaporisation.
- 2) Complementary to 1) but not identical, the production of vaporised agent at hot surfaces.
- 3) The cooling of hot surfaces by the vaporised agent.

In comparing the efficiencies of the different agents it is instructive to compare the maximum rates at which the above process may take place. In the first two of the above processes, the factor which controls the maximum rate at which heat is transferred is the thermal resistance of the solid material itself. The maximum rate of cooling of this hot solid takes place when the outside surface is held at the temperature of the agent impinging upon it, and the maximum rate of vaporisation when the surface temperature is at the temperature of vaporisation. In the third process, the controlling thermal resistance is in the vapour phase rather than in the solid, and it is necessary to take into account differences in the thermal properties of the vapour. In Table III, the maximum rates of the above process are compared on a relative basis with the appropriate maximum rate for water being unity in each case. In all three processes it will be seen that the maximum rates of cooling and vaporisation that are possible with liquid carbon dioxide (solid carbon dioxide at atmospheric pressure) and nitrogen are greater than the maximum rate for water. This difference is particularly marked in the far greater rate that the condensed inert gases may be vaporised by hot solids. This difference is important since, as indicated above, the vapours produced can have a marked cooling effect on the flame; the difference would become even more marked as the temperature of the hot solids are reduced to below 1000°C . Thus, water would run off solid surfaces at a temperature less than 100°C in the neighbourhood of a fire and the cooling potential of the water almost entirely wasted. On the other hand, these surfaces would still allow a vaporisation rate of solid carbon dioxide and liquid nitrogen at a rate equal to about one-fifth of the rate that would occur if the surface were at 1000°C .

In addition to the above heat transfer processes associated with solids, there are also processes which occur in the flame. In general, vaporisation will only occur if drops are fine but in order to be sure of getting the liquid agent to the seat of a fire it is generally necessary to provide a forceful jet which reaches the burning material. For a given set of conditions, however, liquid nitrogen and solid carbon dioxide would vaporise about ten times more readily in flames than water. The vapours, once formed in a fire zone, will cool the flame at the rate with which they can mix, either with the fuel vapour or the air feeding the flame. Here one may take the rate of the cooling process of the vapours as substantially proportional to the cooling potential of the vapour i.e. to be approximately twice as high for water vapour as it is for gaseous nitrogen or carbon dioxide.

Broadly, one may summarize this section by the statement that in a given fire situation it is possible for the heat associated with the fire to vaporise carbon dioxide and nitrogen from the condensed phase at least ten times the rate at which it is possible to vaporise water; and that the flaming combustion that could be subdued by this higher rate of vaporisation is at least five times greater. If the liquid agent cannot be made to reach a very hot zone at the heart of the fire, then the above differences would be substantially greater.

Experimental studies

Controlled experimental studies on liquid agents are comparatively rare, particularly studies in which there is a comparison between different agents. A series of tests was carried out some years ago on the extinction of fires after flashover in a furnished room 50 m³ (1750 ft³) volume using water sprays and jets at flow rates of between 23 - 110 l (5 and 25 gallons) per minute (2). In these tests there was practically no run off of water and this shows that for this type of fire, water can be used very efficiently. The quantity of water used to control the fire was of the order 30 l (7 gallons) and to extinguish, 77 l (17 gallons). There was not clear evidence to show whether the extinction was by cooling the burning solids or extinguishing the flame by steam. However, Table II indicates that if these experiments were to be repeated using either liquid carbon dioxide or nitrogen, one would expect that substantially greater quantities of the agent would be needed to extinguish the fire whichever mechanism operated. The difference would be a factor of about 5 if the mechanism was cooling the solid and 2 if the mechanism was smothering (cooling) the flame. In these experiments conditions were inherently favourable to water in two respects: firstly, the flow rates used were such as to allow the nozzle to be easily manipulated by the operator; secondly, there were large areas of burning surface present most of which could be impinged upon directly by the jets or spray. That these circumstances need not necessarily hold even for small fires was shown recently in a comparative study on the extinction of a crib fire using liquid nitrogen and water (3). A 3 ft cube crib composed of sticks 1 in square was extinguished using approximately one-quarter of the amount of liquid nitrogen than water. When the liquid nitrogen was used the agent completely vaporised and small flames in the interior of the crib were rapidly extinguished. When water was used the bulk of the water ran off without vaporising and great difficulty was found in extinguishing lingering flamelets. These tests also showed that a liquid nitrogen jet could extinguish a petrol fire in an open vessel, but at high flow rates the violence of the vaporisation of the liquid gas could eject burning fuel from the vessel.

Scope for operational use of liquid gases

It is clear that for fires in rooms in dwellings which have passed the flash-over stage, that if water can be injected directly into the room its efficiency as an extinguishing agent cannot be improved upon either by liquid nitrogen or carbon dioxide. However, if the fires have not passed the flash-over state, or if access to the seat of the fire is difficult because of smoke, then the fraction of water that runs away may begin to become a substantial fraction of the amount of water used. If more than three-quarters of the water runs away a case begins to build up for the use of liquid gases. Probably in the first instance, the main argument in this case is not the improved intrinsic efficiency of the liquid inert gas extinguishing agent, since water is of the order of 1000 times cheaper than these agents, but the reduction in water damage that would ensue if these agents are used. There is little firm information on the extent to which water damage occurs at fires but generally fire and water damage are comparable. The data available from recent studies⁽⁴⁾ on water usage indicates that although for most fires the amount of water used by brigades is of the same order as the amount that would be theoretically expected, for some large fires about 100 times this quantity is used. The replacement of water with a liquid gas costing 2/6d. per gallon can begin to be worth while if a substantial portion of the total damage can be eliminated.

When water at a high rate is projected onto the upper floors of a building from the outside, then, as a rule, a large fraction of the water runs away unused. The reason for this is probably that the manoeuvrability of the jet is low and the flow rate is probably too high to vaporise at the limited area of hot surface on which the jet impinges. Under these conditions, it might be worth while using high rates of liquid inert gas predominantly for reasons of improving fire fighting efficiency. It would be useful to carry out comparative tests to check this point.

An important limiting factor here is the limited extent to which jets of liquid gas can maintain their coherence when projected from a nozzle. Carbon dioxide suffers particularly in this respect since although it might be ejected from a reservoir as a liquid it is transformed under atmospheric conditions almost immediately to a suspension of a fine solid in a gas. The movement thereafter follows the general pattern of a high velocity gas jet with consequent rapid dilution of the jet by air entrainment. Indeed after travelling 10 - 20 ft there might be so much dilution that the resulting mixture would be incapable of extinguishing flame. Substantial dilution due to air entrainment might also be expected wherever a jet of liquid carbon dioxide is injected into a building through a large opening. The effect of air entrainment may be reduced by increasing the diameter of the gaseous jet and decreasing its velocity before it leaves the nozzle e.g. by use of a horn.

Another type of fire where the direct use of a liquid gas might bring about an improvement in fire fighting efficiency is for a fire in extensive premises which have become smoke-logged. The agents can be injected at accessible points and the vapours produced allowed to waft through the building to reach the seat of the fire. The feature restricting the use of these agents for such fires is the limited capacity of those parts of the premises near the point of injection to vaporise the liquid gas since when these parts are reduced to a low temperature they will cease to vaporise the liquid rapidly. Once a pool of liquid nitrogen or a heap of carbon dioxide snow is built up on the floor, then continued vaporisation would be slow. The use of liquid inert gases for this type of fire has been described in greater detail elsewhere⁽⁵⁾. The use of liquid carbon dioxide in protective installations⁽⁶⁾ to flood a whole compartment with inert gas is, of course, well established.

Another possible use for liquid nitrogen, although not to the same extent for liquid carbon dioxide is for fighting large fires on the ground in the open. An example is the aircraft crash fire. In this type of fire the material burning is mainly a large spillage of liquid fuel which in most cases will have a fire point above -20°C and in all cases above -40°C . If liquid nitrogen is dumped on the fire it should flow over this fuel and would soon reduce its temperature to the fire point. The heat that must be removed from a liquid fuel at its boiling point to reduce the temperature to the fire point is approximately 100 cal/g of fuel. This is far less than the heat of combustion of the fuel (10,000 cal/g) or the heat removal from the flame required to extinguish the flame (4,500 cal/g). However, to extinguish a fire by cooling to the fire point the liquid nitrogen would also need to absorb the heat radiated from the flame on to the fuel surface. The nitrogen gas formed in this process may be sufficient to snuff out the flames. In a recent experiment it was found that approximately 5 lb of liquid nitrogen extinguished fire in four pounds of gasoline merely by being poured into it. (3) After the experiment the fuel was very difficult to ignite, indicating that it had been cooled to the fire point. This suggests that the quantity of liquid nitrogen required for the above purpose is approximately the same as the amount of fuel that is burning. There may possibly be also some virtue in dumping liquid nitrogen in a similar way on timber yard fires and forest fires, although in these cases one would rely more upon the nitrogen gas emanating from the dumped liquid snuffing out flames in the burning fuel.

It is unlikely that liquid carbon dioxide can be dumped in the above way because of the property it has of changing into a mixture of gas and fine solid when the pressure is reduced to atmospheric. The fine powder in this gas will either be evaporated in the flames, or carried away by the upward motion of the flames or build-up to a heap in the neighbourhood of the point where the agent is dumped.

Practical considerations

Water can be made available to fire in unlimited quantities but, as far as the foreseeable future is concerned, liquid inert gases can only be made available at a rate equal to the rate at which they can be taken to the fire in tankers. These, at present, hold up to 15 tons of agent. There is probably no upper limit to the rate at which the agents can actually be delivered from a tank to a fire although with carbon dioxide, care would need to be taken not to lower the pressure too much in the tank or the delivery lines as the agent would then solidify, and with nitrogen there would be difficulty in conveying the liquid through long lengths of hose line. The upper limit of flow rate that can be handled by a man would be less than that for water because a heavier hose would be required in order to insulate the liquid agent. Therefore high flow rate nozzles will tend to be held as monitors. However, if liquid nitrogen is dumped on to an outdoor fire difficulties of the above kind should not arise, since as the application of the agent to the ground the pressure head in the storage tank can be used and the delivery duct can merely lie on the ground. Alternatively, the liquid nitrogen might be allowed to fall from a helicopter. Care would need to be taken to avoid freezing accidents, particularly when high flow rates of gas are used. For example, when several tons of liquid gas are dumped on the ground the latter might become frozen and difficulty may be found in walking across the ground. Finally, where the gases escape from a fire area there may be a danger to the public because of the asphyxiation hazard. This is likely to be of some importance for carbon dioxide but of only marginal importance for nitrogen. Indeed, if liquid nitrogen is used to cool a volatile fuel to below the fire point and if there is an associated life hazard it may be possible to incorporate a certain amount of liquid oxygen with the liquid nitrogen to prevent the gases evolved giving rise to an asphyxiation hazard.

Conclusions

In the cooling processes associated with the extinction of fires, liquid carbon dioxide and nitrogen have a substantially lower capacity to remove heat than water. However, these liquids are very much more easily vaporized than water and a substantial part of the extinguishing capacity of all three agents lies in the vapour. Therefore, it may be beneficial to use liquid nitrogen and carbon dioxide for fires where at present the use of water results in most of the water running off unvaporized. Such fires would broadly include all those where most of the burning surfaces cannot be reached directly by the jet. They may also include large outdoor fires, particularly those involving large spillages of flammable liquid. In the use of liquefied gases their higher cost might be offset by a reduction in water and steam damage. Certain operational factors are very important. Liquid gases, although they could be made available in large quantities, such quantities would not be virtually unlimited, as is the case with water. There are also development problems outstanding in the actual handling of liquid gases in quantity at fires.

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Table I

Thermodynamic properties of liquid agents that
control extinguishing efficiency

Agent	Pressure at m	Boiling or sublimation point.	Latent heat of vaporisation (sublimation) cal/g (B.Th.U./lb)	Heat content of vapour or gas. cal/g (B.Th.U./lb)			
				Boiling or sublimation point to 0°C ΔH_1	0 - 100°C ΔH_2	0 - 250°C ΔH_3	0 - 1300°C ΔH_4
Water	1	100°C (212°F)	540* (970)	- -	44.5 (80)	113.5 (204)	691.3 (1243.0)
Carbon dioxide (liquid)	21	-18°C (0°F)	67 (120)	12.6 (22.7)	20.8 (37.4)	56.2 (102)	363.7 (654)
Carbon dioxide (solid)	1	-78°C (-109°F)	137 (246)	15.5 (28)			
Nitrogen	1	-196 (-321°F)	48 (86.4)	49 (88)	24.8 (44.7)	62.4 (112.0)	354 (638)

*In addition water if normally at 15°C can absorb 85 cal/g (153 B.Th.U./lb) on being heated to 100°C.

Table II

Cooling capacity of liquid inert gases
for extinction processes
expressed as cal/g of agent

Agent	Conditions	Capacity for cooling burning cellulosic solids	Capacity for cooling burning liquid (fire point 0°C)	Capacity for cooling flames	
				In gas phase alone	Total gas phase and condensed phase
Water	15°C 1 atm	694	None	847	1472
Carbon dioxide	0°C 21 atm	136	80	376	443
Nitrogen	-196°C 1 atm	156	97	403	451

Table III

Relative transfer rates for condensed inert gases
assumed temperature of solid surface = 1000°C

Agent	Rate of cooling of solid by condensed agent a	Rate of vaporisation of condensed agent b	Rate of cooling of solid by vaporised agent c
Water (liquid)	1	1	1
Carbon dioxide	1.15*	11	1.9
Nitrogen (liquid)	1.3	12	1.3

*Calculated for the solid that may be obtained from the release of unit quantity of liquid at 0°C.

- a Calculated on the basis that heat transfer is proportional to ΔT , difference between solid temperature and the vaporising temperature of agent.
- b Calculated on the basis that vaporisation rate is proportional to the quotient - $\frac{\Delta T}{L}$ - L being heat of vaporisation.
- c Calculated on the basis that heat transfer follows relationship for natural turbulent convection (i.e. $Nu \propto (Pr Gr)^{1/3}$) see e.g. Ref. 7.

CHAPTER 12

THE HISTORY OF THE UNITED STATES

Year	Event
1776	Declaration of Independence
1787	Constitution signed
1791	Bill of Rights adopted
1800	Washington moves to D.C.
1820	Missouri Compromise
1861	Civil War begins
1865	Emancipation Proclamation
1877	Compromise of 1877
1890	Wounded Knee Massacre
1901	Spanish-American War
1914	World War I begins
1918	19th Amendment
1929	Stock Market Crash
1933	Prohibition ends
1941	Pearl Harbor
1945	World War II ends
1954	Brown v. Board of Education
1963	John F. Kennedy assassinated
1968	Richard Nixon elected
1973	Watergate scandal
1979	Iranian Revolution
1981	Reagan elected
1989	Berlin Wall falls
1991	Soviet Union collapses
1993	Clinton elected
1994	NATO expansion
1997	Clinton impeached
1998	Clinton re-elected
1999	Clinton impeached again
2001	Bush elected
2002	Iraq War begins
2003	War in Afghanistan
2008	Obama elected
2009	Financial Crisis
2011	Arab Spring
2012	Obama re-elected
2013	Syrian Civil War
2014	Ukraine Crisis
2016	Trump elected
2017	Trump's policies
2020	COVID-19 Pandemic
2021	January 6th
2022	Russia invades Ukraine
2023	U.S. withdraws from Afghanistan

THE HISTORY OF THE UNITED STATES

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