The Importance of Mechanisms

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ABSTRACT

An inerting scenario has been used to study potential halon replacement agents, where agent, fuel, and air are premixed before ignition occurs. The results, including analyses of hydrogen fluoride (HF), are compared to tests utilizing Halon 1301 as an inerting agent. Since many of the potential replacement agents function primarily by a heat-absorbing mechanism, these agents are better suited to the inertion scenario than is Halon 1301, which functions primarily by a chemical mechanism. Data from experiments in a 20-liter chamber support this position.

Follow-up experiments with perfluoroethyl iodide (PFEI), an agent which should function by a chemical mechanism, gave surprising results. This agent proved more efficient than both the heat-absorbing agents and Halon 1301 in an inerting role. A possible mechanism to explain the unexpected ability of PFEI to act as a superior inerting agent involves relative bond strengths. The carbon to iodine bond in PFEI is approximately 9 kcal per mole weaker than the carbon to bromine bond of Halon 1301. Thus, the carbon to bromine bond of PFEI should break at a lower temperature than the carbon to bromine bond in Halon 1301, providing a lower temperature heat-absorbing mechanism.

Both chemical agents and heat-absorbing agents are usually assessed using the cup burner test. The fact that the agents function by different mechanisms must be taken into account if the heat-absorbing agents are used to replace Halon 1301 in fire protection installations. The heat-absorbing agents will not have as great a safety reserve factor as Halon 1301 has. This must be appreciated by those who are formulating specifications for the fire protection systems using new heat-absorbing agents.

Background

In the search for halon replacements, there is a temptation to take the attitude that all that is required is knowledge of the concentration of an agent (a clean, non-toxic, environmentally friendly agent) required to extinguish fire. A system can then be designed to dispense the agent at the minimum required concentration plus a safety factor. It is not necessary to know the mechanism by which the agent extinguishes fire. A knowledge of the required concentration is sufficient. Certainly, with the halons, systems were engineered successfully before detailed information on mechanisms was elucidated. Why should it be different with halon replacement agents?

This paper looks at the question of what influence fire suppression mechanisms should have on the design of fire-extinguishing systems.

The two main classes of mechanisms by which added agents suppress fires are chemical* and heat absorption. While many agents can function using a combination of the two mechanisms, in many scenarios one of the mechanisms predominates.

Inerting Experiments

A. 20-Liter Chamber

Experiments were conducted in a 20-liter stainless steel chamber using potential halon replacement agents in an inerting scenario. Fuel, air, and an agent were placed in the chamber at a total pressure of one atmosphere (101.3 kPa). Ignition was attempted using an exploding nichrome wire (40 J from a capacitance discharge device). The pressure spike associated with the ignition was recorded. The atmosphere in the chamber was analyzed for any hydrogen fluoride produced by the interaction of the inerting agent with the hydrocarbon flame. The results of these tests on two potential replacement agents and on Halon 1301 itself are given in Table 1. Note that a calculation was made of the percentage of agent molecules which produced hydrogen fluoride, assuming only one hydrogen fluoride forms from any agent molecule.

Perfluorobutane (PFB), which acts primarily by a physical (heat absorbing) mechanism, is less efficient than Halon 1301 at low agent concentrations. At low levels, neither agent can effectively inhibit the hydrocarbon flame, and the PFB, with more fluorines per molecule, produces more HF than does Halon 1301. However, at higher concentrations, less HF is produced by PFB than by the halon. This is explained by the difference in the interaction of these two agents with the flame produced by the ignition events. The PFB's main influence on the flame is to act as a heat sink. PFB is in the fuel-air mixture at the moment of ignition. It increases the heat capacity of the mixture and lowers the temperature of the flame. This inhibits the formation of HF. However, at PFB values close to the inerting concentration, the burn time is lengthened (up to 2.5 s). This tends to increase the HF concentration. The inerting concentration of PFB is reasonably close to the cup burner value of 5% (Ref 1).

Halon 1301, however, acts as a chemical fire-extinguishing agent. It allows the flame to become established, then reacts with free radicals in the flame. Each bromine atom of the halon molecule can be responsible for removing many free radicals from the flame zone. This leads to extinguishment. Halon 1301 is not efficient in prevention of flame, only in extinguishing flame. This leads to an inerting concentration much higher than the cup burner value of 2.4% (Ref 1).

Perfluoroethyl iodide (PFEI) is a very interesting agent. While there are no data available on the mechanism by which it functions, it is assumed that it should be a good chemical agent. The iodine atom of PFEI should be able to remove many free radicals from the flame zone, just as bromine does. It is not expected to have a high heat capacity. Yet it is superior to PFB as an inerting agent. A possible explanation is that the relatively weak carbon-to-iodine bond of PFEI can be broken at a low temperature, providing a heat-absorbing mechanism which allows PFEI to act as a heat-absorbing agent.

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* Materials are said to be chemical fire-extinguishing agents if they react to remove active chemical species (free radicals) from the flame. The removal of active species must be catalytic, with a given agent molecule being capable of destroying several active free radicals. A one-to-one removal, one agent molecule removing one free radical, does not qualify the agent as a chemical agent.

Table 1. Hydrogen Fluoride Production From Agents in Butane-Air Mixtures

Butane (torr)	Agent (torr)	Agent (%)	HF (ppm)	Agent Molecules Yielding a HF (%)	ΔP (kPa)
	Halon 1301[a]	Halon 1301			
30	10	1.3	2,300	17.7	578
30	20	2.6	4,900 6,360 4,890	18.8 24.5 18.9	586 586 572
30	30	3.9	16,200 17,100 20,000	41.5 43.8 51.3	482 531 452
30	40	5.2	10,270	19.8	230
30	50	6.6	146	.2	3
	PFB[b]	PFB			
30	10	.3	2,400	18.8	582
30	20	2.6	7,820 10,270 11,250	30.1 39.5 43.3	499 593 593
30	30	3.9	8,310 10,270 15,120	21.0 20.3 38.7	529 538 537
30	50	6.6	6,360	9.2	62
30	60	7.9	235	0.3	0
	PFEI[c]	PFEI			
30	20	2.6	8,310	32.0	387
30	25	3.2	5,870	18.0	126
30	30	3.9	3,720	9.5	9
30	40	5.2	1,708	3.3	17
30	50	6.6	684	1.0	0

[a] Trifluoromethyl bromide

[b] Perfluorobutane

[c] Perfluoroethyliodide

$$CF_3CF_2I \rightarrow CF_3CF_2\cdot + I\cdot$$

C-I bond energy is 57 kcal/mole or less.

The temperature may be high enough to cause extensive breaking of this bond during the ignition process.

The heat-absorbing agents, such as PFB, are the agents of choice for flame prevention, while chemical agents, such as Halon 1301, are the agents of choice in fire extinguishment. PFEI may be an agent which can function in both roles.

B. Jacketed Fuel Cells

Experiments have been conducted at ARL using fuel cells surrounded by jackets of fire-extinguishing agents (Ref 2). A schematic of a jacketed fuel cell is given in Figure 1. When such a cell is struck by a weapon, both fuel and agent are released simultaneously, giving a pre-mixed fuel-air-agent mixture before ignition occurs. In firing tests of shaped charges against the jacketed fuel cells in an aluminum vehicle, strikingly different results were obtained when a heat-absorbing agent (water) was used in the jackets versus a chemical agent (bromochloromethane, BCM). More than twice the volume of water was required to prevent a sustained fire compared to the volume of BCM, which prevented sustained fires. When sufficient water was used, no fireball was observed and there was no evidence of high pressure inside the vehicle.

With BCM, there were large fireballs and evidence of high pressure inside the vehicle, even though there were no sustained fires. When the volume of BCM was more than doubled, there were still large fireballs and evidence of high pressure, with no sustained fires. The BCM gave surer protection from sustained fires than water gave, but the BCM could not prevent ignition and large fireballs. In contrast, when sufficient water was used, all indications are that the ignition process failed. Schematics of the contrasting situations of water versus BCM in jackets of a fuel cell are given in Figures 2 and 3. The energy-absorbing agent can prevent the formation of a fireball. One should have a knowledge of mechanisms when a selection of an agent is made for use in jacketed fuel cells.

Figures 4, 5, and 6 show the contrasting situations of the ignition of a fuel-air mixture, the ignition of a fuel-air plus heat-absorbing agent mixture, and ignition of a fuel-air plus chemical agent mixture.

The Cup Burner Test

It has been reported (Ref 3) that when Halon 1301 is used in the cup burner test, the overall fire suppression mechanism is 80% chemical and 20% heat absorption. The bromine atom of the agent is responsible for 55% of the suppression (catalytically), and the CF_3 radical is responsible for 25% of the suppression (noncatalytically). Yet these numbers on suppression can be changed by simply altering the experiments. In the cup burner experiment, the agent and air are premixed. They react with the fuel in a diffusion flame. The effectiveness of the bromine atom in removing free radicals, as shown by

$$\begin{aligned}
CF_3\,Br + H\cdot &\rightarrow CF_3\cdot + HBr\\
HBr + H\cdot &\rightarrow H_2 + Br\cdot\\
Br\cdot + Br\cdot + M &\rightarrow Br_2 + M^*\\
Br_2 + H\cdot &\rightarrow HBr + Br\cdot
\end{aligned}$$

is limited by the time the bromine is in the flame zone. The bromine can be expelled from the flame zone, due to the forced convections of the system, before it has used its full catalytic activity to remove active free radicals. Thus, HBr is a reaction product. This is shown in Figure 7. While bromine has been responsible for removing free radicals from the flame, its full potential is not exploited in the diffusion flame of the cup burner apparatus. There is a chemical reserve that has not been used. This is due to the fact that the conditions of the experiment do not allow enough residence time for the bromine to use its full power of fire suppression by the catalytic removal of free radicals from the flame.

The value of the minimum concentration of Halon 1301 (or any other chemical fire suppression agent) required to extinguish fire, from the cup burner test, is a conservative value. Given a different scenario, the bromine might be more fully exploited and a lower minimum concentration could be found.

In contrast, a heat-absorbing agent, used in the cup burner apparatus, should come up to the flame temperature, as shown in Figure 8. Since all a heat-absorbing agent does is experience a temperature rise (to flame temperature), it has done the maximum that it can do. There is no reserve to exploit in another scenario. The cup burner value of minimum concentration of agent required to extinguish is not a conservative value.

Fire-Extinguishing Systems

Many total flooding fire-extinguishing systems have been designed successfully using Halon 1301, a chemical agent. A reliable system can be engineered by using the appropriate cup burner data and adding a safety margin, say 20%. However, in a scenario different from the cup burner situation, the safety factor associated with Halon 1301 may be significantly larger than the 20%. In situations where the fire-extinguishing system does not function perfectly, the large reserve inherent in the Halon 1301 may still allow successful extinguishment of the fire.

Taking the lessons learned with Halon 1301 and applying them to agents which function by a different mechanism (heat absorbing) may lead to situations in which a partial malfunction of an extinguishing system can cause loss of fire suppression ability. It is possible that the safety margin added to cup burner minimum concentration of a heat-absorbing agent should be larger than the safety margin added to a chemical agent.

Conclusion

A knowledge of mechanisms is desirable when a solution is required for a fire suppression problem. Then, a proper safety margin, consistent with the type of agent to be used, can be determined.

A program to determine the proper safety margin required for different agents has been initiated at ARL.

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3. R. S. Sheinson, Halon Alternatives Extinguishment Pathways. *Proceedings of the Halon Alternatives Technical Working Conference*, pp. 71–82, Albuquerque, NM, 30 April–1 May 1991.

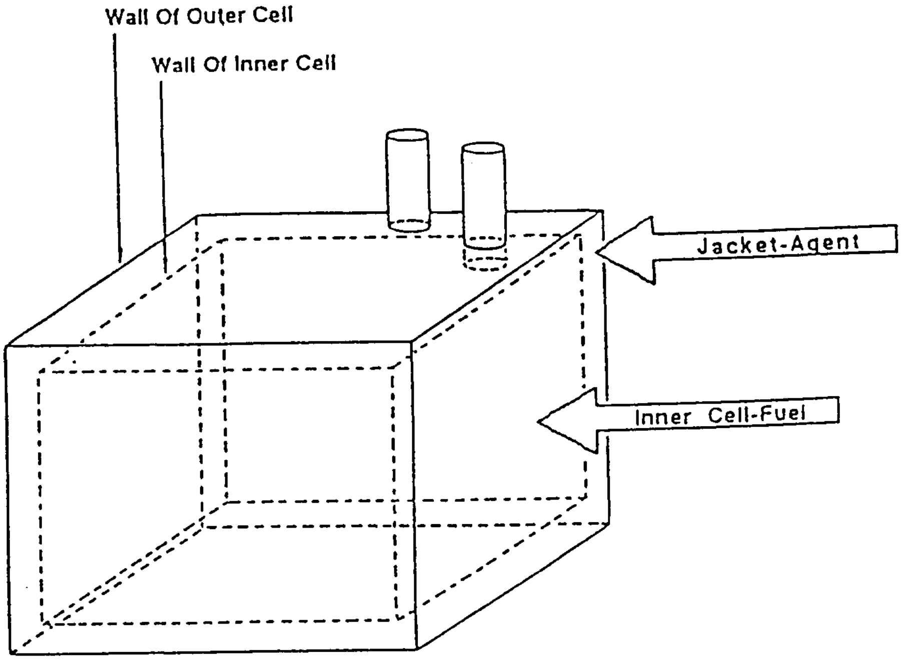
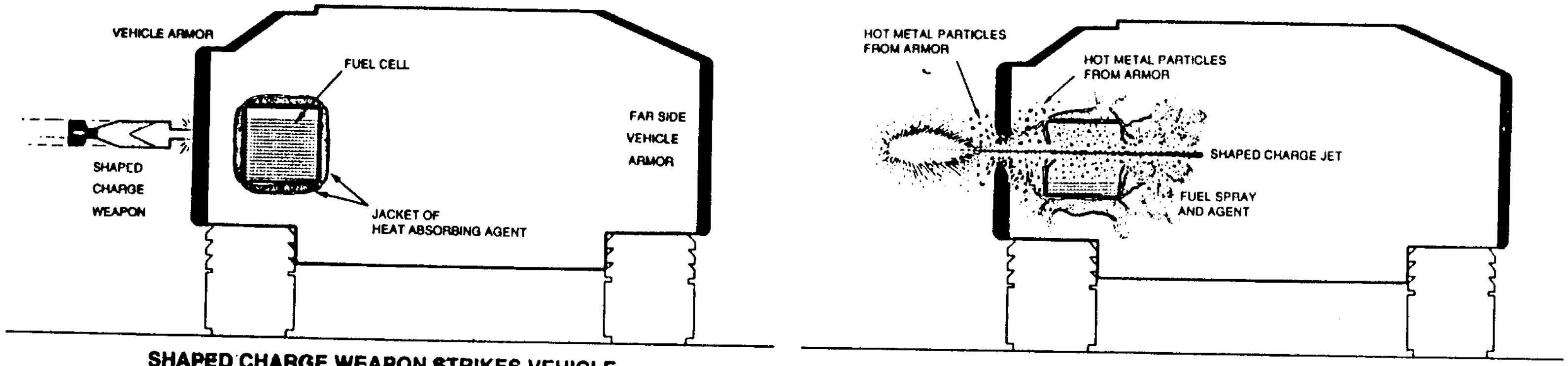
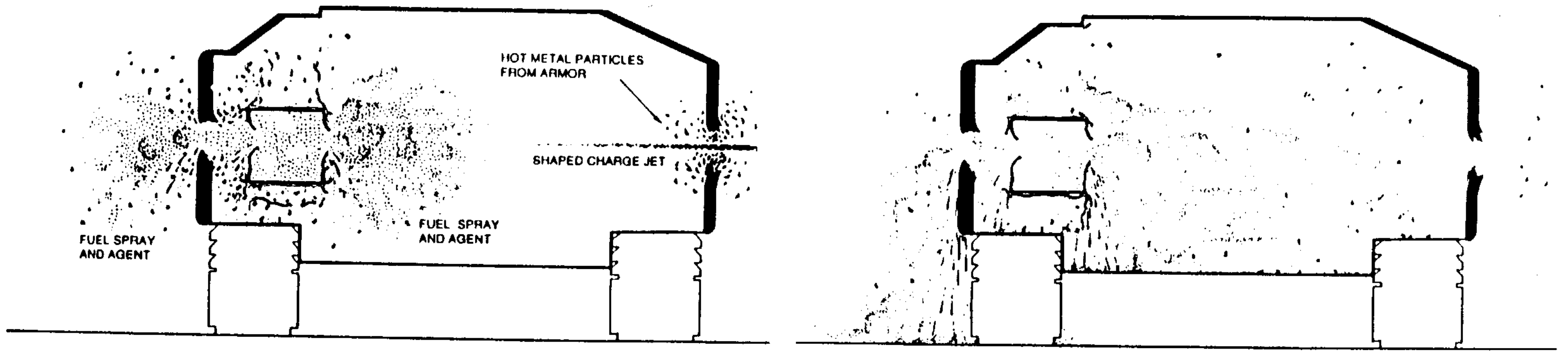


Figure 1. Schematic of a jacketed fuel cell.



SHAPED CHARGE WEAPON STRIKES VEHICLE

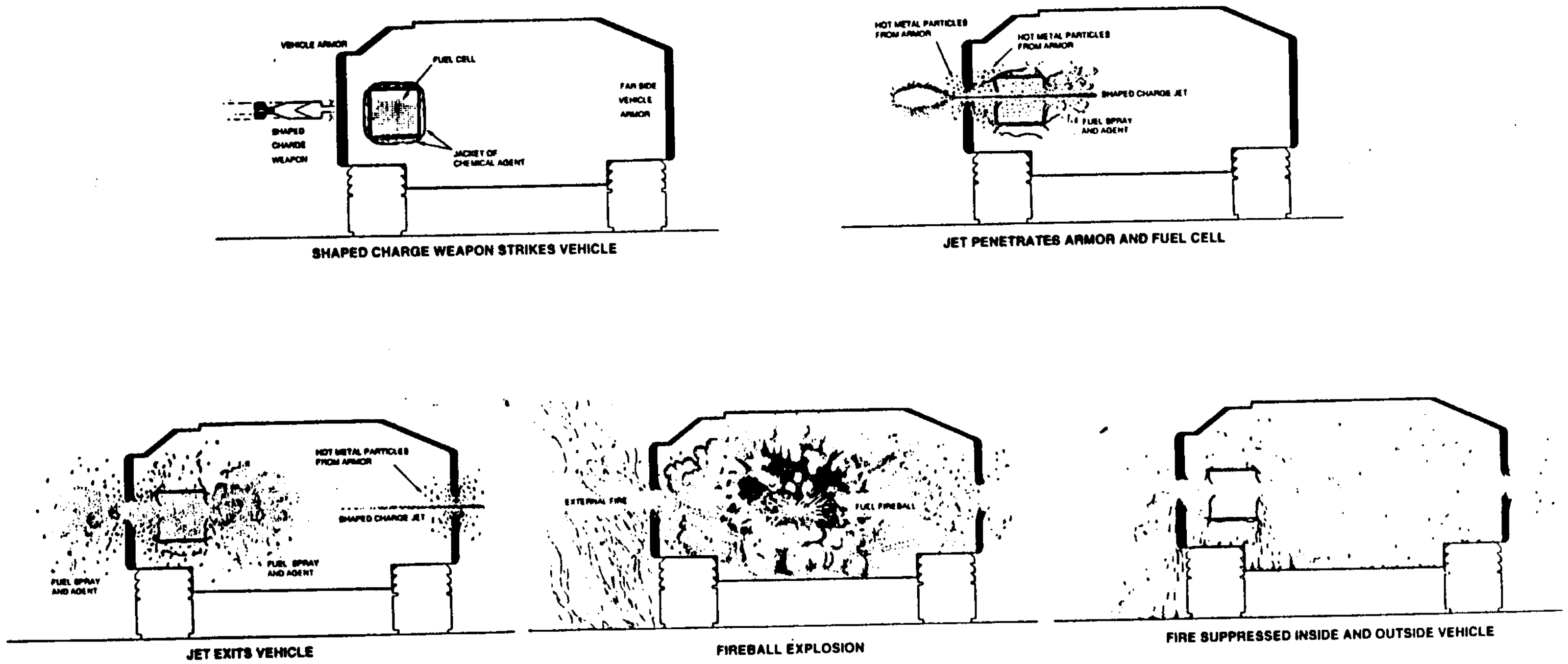
JET PENETRATES ARMOR AND FUEL CELL



JET EXITS VEHICLE

FIRE SUPPRESSED INSIDE AND OUTSIDE VEHICLE

Figure 2. Process by which a heat-absorbing agent in a jacketed fuel cell suppresses both the mist fireball explosion and a sustained fire.



SHAPED CHARGE WEAPON STRIKES VEHICLE

JET PENETRATES ARMOR AND FUEL CELL

JET EXITS VEHICLE

FIREBALL EXPLOSION

FIRE SUPPRESSED INSIDE AND OUTSIDE VEHICLE

Figure 3. Process by which a chemical agent in a jacketed fuel cell allows the mist fireball explosion to occur but prevents a sustained fire.

Figure 4. Ignition of a fuel-air mixture.

Figure 5. Ignition of a fuel-air mixture containing a heat-absorbing agent.

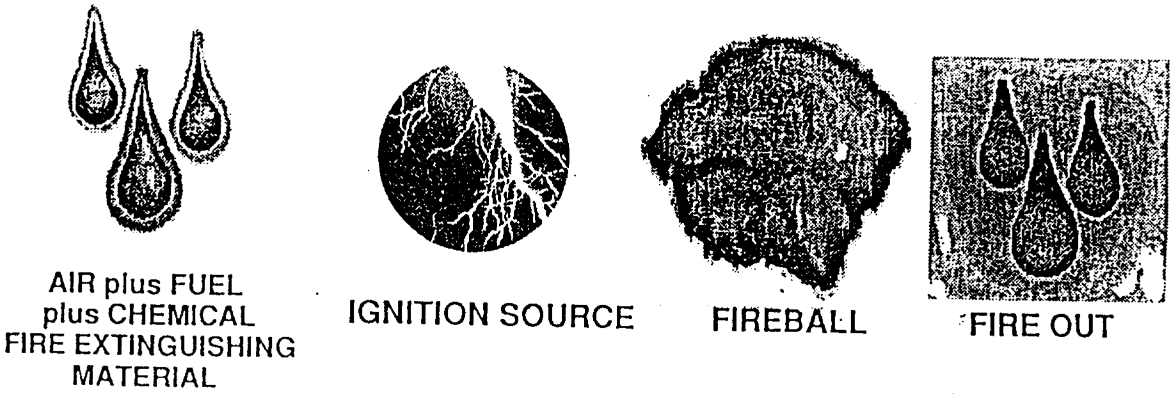


Figure 6. Ignition of a fuel-air mixture containing a chemical agent.

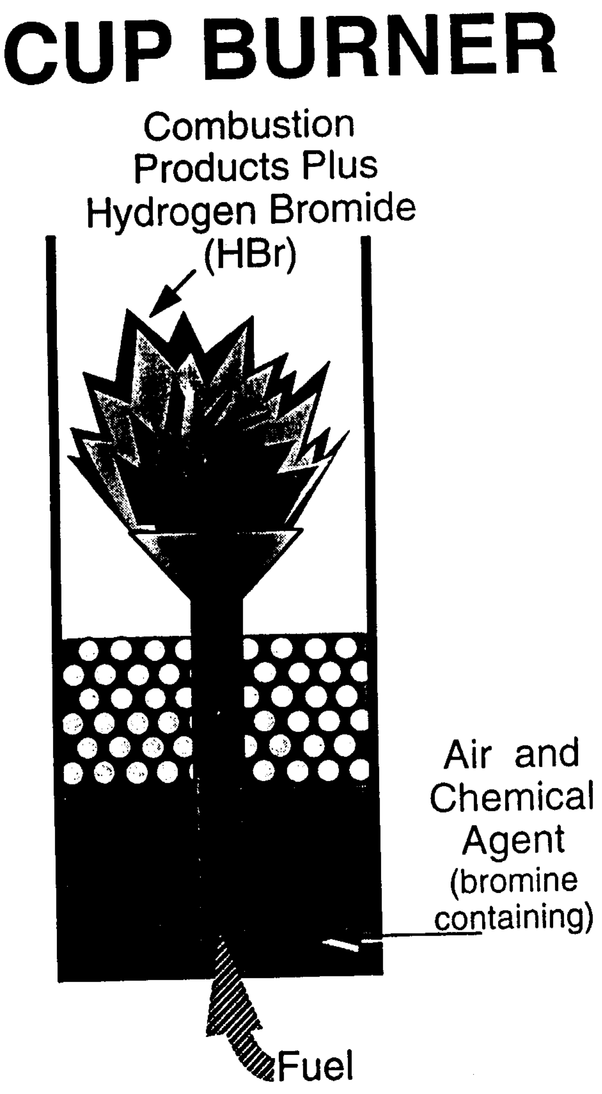


Figure 7. Cup burner apparatus with a chemical agent added to air.

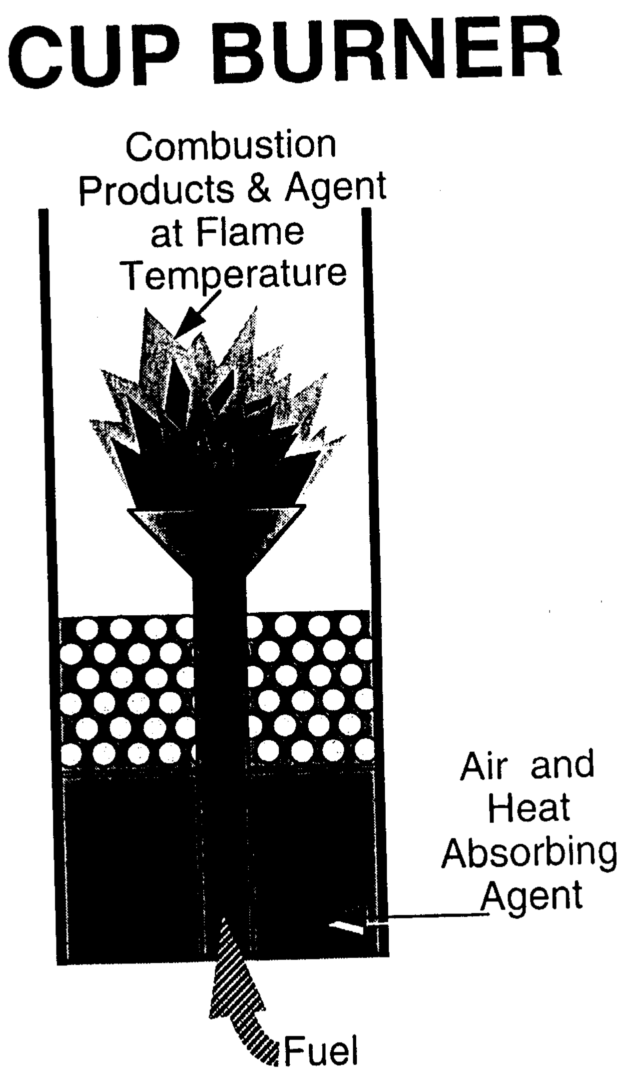


Figure 8. Cup burner apparatus with a heat-absorbing agent added to air.