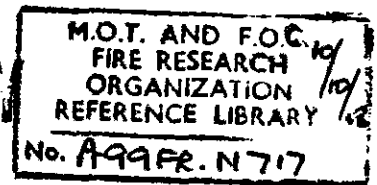


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SLURRIES OF SOLID CARBON DIOXIDE AS
EXTINGUISHING AGENTS

by

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SUMMARY

A preliminary assessment has been made on the effectiveness of slurries of solid carbon dioxide in liquid nitrogen and in vaporizing liquid extinguishing agents for extinguishing small flammable liquid fires. The slurry was applied by being tipped onto the surface. It has been found that the slurry is more effective than the solid or liquid phases used separately. The quantities of slurry needed to extinguish a kerosine fire was substantially smaller than other extinguishing agents commonly used at the present time, and was also comparable to the quantity predicted from theoretical considerations.

Key words: Carbon dioxide, solids, vaporising liquids, slurry, ~~extinguishing agents~~, fire, flammable liquids.

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INTRODUCTION

In a previous note¹ an estimate was made of the possible contribution of cooling the fuel to the extinction of liquid fires by vaporizing extinguishing agents. This estimate indicated that if the full cooling power of the agent was exerted in reducing the rate of burning of the fire, then the size of fire which could be extinguished by a given mass of agent could be multiplied by a factor of about three. In particular the possible contribution due to cooling power of solid carbon dioxide was substantially higher than either the inhibiting, inerting of the cooling power of any other common vaporizing agent. This suggested that slurries of solid carbon dioxide in a liquid vaporizing agent could in certain circumstances be effective extinguishing agents². The present note describes a preliminary experimental investigation carried out to assess the possibility of using slurries containing solid carbon dioxide as practical extinguishing agents.

EXPERIMENTAL

The experimental work may be divided into two parts:-

- a) Exploratory tests using liquid nitrogen and some halogenated hydrocarbons as the continuous phase for the slurry;
- b) A series of tests with a 50 per cent slurry of solid carbon dioxide in bromochlorodifluoromethane (BCF) to obtain a better definition of the quantitative effect of using slurry. These tests included observations on the physical behaviour of these slurries when applied to various surfaces.

Table 1 shows the methods of obtaining slurries and comments on the slurries obtained.

TABLE 1
Method of preparation and properties of
solid carbon dioxide slurries

Liquid forming continuous phase of slurry	Boiling point °C	Density	Method of making slurry	Properties of slurry
Liquid nitrogen	-196	0.8	Bubbling CO ₂ gas into liquid nitrogen	Powder settled downward. Could not obtain more than 15 per cent solid CO ₂
Dichlorodifluoromethane	-29	1.2	Solid carbon dioxide ground to a powder sieved through 1.5mm sieve and mixed with fluid	Powder settled downward slowly Held CO ₂ powder well even upto 75 per cent slurry
Trichlorofluoromethane	23	1.8		
Chlorobromomethane	67	1.9		
Bromochlorodifluoromethane	-4	1.8		Powder settled upward rapidly

Except in the case of liquid nitrogen all slurries were obtained by grinding solid carbon dioxide, sieving off particles greater than 1.5 mm, and mixing the ground material into the liquid agent. With liquid nitrogen an attempt was made to obtain the slurry directly in situ by bubbling the carbon dioxide gas into the liquid nitrogen, but although the particle size of the slurry was very fine it was not found possible to obtain a slurry with a solid content greater than 15 per cent in this way.

The test fires varied and in general were a few square feet in size, the fuel being either petrol or kerosine; a few tests were carried out on a 5m² fire. The method of application also varied, the one used mostly was direct tipping of the agent from a beaker into the fire. For purposes of comparison, tests with unslurried liquid nitrogen, chlorobromomethane and bromochlorodifluoromethane and also unslurried solid carbon dioxide were carried out on the same fires on which the corresponding slurry was used.

RESULTS

a) Exploratory tests. The slurries in liquid nitrogen were tested against a kerosine fire 0.5 m² after a preburn time of one minute. 1150 cc of the slurry were poured down a sloping channel so as to flow onto the kerosine fire; the time taken to pour the liquid was 83 seconds. Approximately one half of the

area of the fire was cleared of flame. A similar result was obtained when 1150 cc of liquid nitrogen were poured onto the fire in 80 seconds. An attempt to pour liquid nitrogen onto the fire more rapidly resulted in a surge of flame followed a few seconds later by a mild explosion. It was noted in the tests with the slurry that the solid carbon dioxide separated out in the channel and also coagulated into particles $\frac{1}{2}$ in to 1 inch diameter on the surface of the petrol. These were slow to evaporate. Of course, the temperature of this slurry was that of liquid nitrogen, i.e. -196°C , and therefore the solid carbon dioxide was cooled deeply below its sublimation point.

250 ml of the slurry in difluorodichloromethane was poured from a beaker on to a petrol fire 0.35 m^2 area after a preburn time of 30 seconds. The flames cleared from most of the fire area, but the fire was not quite extinguished. A similar result was obtained when the same quantity of slurry was ejected from an extinguisher body. 570 ml of slurry in chlorobromomethane ejected from an extinguisher extinguished the same petrol fire. Chlorobromomethane alone could not be used in a similar way in the extinguisher; 570 ml of this liquid poured on to the petrol fire within a period of 5 seconds almost, but not quite extinguished the fire. These tests suggested that the quantity required for extinction with slurry was about $1,500$ to $2,000\text{ g/m}^2$ (0.25 to 0.35 lb/ft^2), which is somewhat better than the quantity that might be expected to be needed if light water or dry powder were used as the extinguishing agent.

(b) Test series with (B.C.F.) slurry

Table 2 shows the results of the tests in which BCF solid CO_2 and BCF/ CO_2 slurry were applied to a fire in a tray 40 cm square. The agents containing liquid were applied by pouring from a beaker, the time of pouring being about 2 to 4 seconds. The solid carbon dioxide was applied from a small scoop the time of application being about 7 seconds. In the tests 37-43 of solid carbon dioxide on avgas and N.B.P. the operator used gloves and helmet for protection against the flames. This improved the performance of the extinguishing agent.

It was characteristic of all the extinctions that the flame was pushed sideways and upwards off the vessel. Photographs of the extinction with the kerosine fire are given in Fig 1-4. With petrol fires there was a greater tendency to reignite from a small pocket of flame remote from the vessel, even when the surface of the vessel had remained clear of flame for several seconds. A summary of experimental critical quantities required to extinguish fires in the different fuels is given in Table 3. For comparison estimated quantities of sodium bicarbonate dry powder and water in the form of light water foam needed to extinguish the fires have been included.

TABLE 2

The effect of BCF, BCF/CO₂ slurry and solid CO₂ on 1,600 cm² fire (1.8 ft²). Agent applied by pouring from beaker (BCF/CO₂) or sprinkling from scoop (solid CO₂)

(a) BCF alone on kerosine fire (AVTUR) preburn time 60 seconds (unless stated otherwise)

No.	Amount used	Remarks
1	250 ml	E. Fuel could not be reignited. Liquid temperature reduced to 55°C.
2	175	E. Fuel could not be reignited even after 5 minutes. Preburn 75 s.
3	130	E. Fuel could not be reignited. Liquid temperature 78°C.
4	100	E. Reignited with match. Liquid temperature 80°C.
5	50	E. Reignited with difficulty. Liquid temperature 93°C on surface, 80°C after mixing.
6,7	25 (Two tests) Limiting quantity 50 ml (90 g)	NE.

(b) BCF/CO₂ slurry on kerosine fire

8	175	E. Fuel could not be reignited. Liquid temperature 50°C.
9	130	E. Reignited with match. Liquid temperature 70°C.
10	100	E. Reignited with match. Liquid temperature 70°C.
11	50	E. 5 sec. Reignited with match. Liquid temperature 95°C on surface 80°C after mixing.
12	25	E. 3-4 sec.
13	25	NE. Slurry thick and not mobile.
14	25	E. (Carried out 30 seconds after test 7).
15	20	Fire almost extinguished. Carried out 30 sec after test 16.
16	15 Limiting quantity 25 ml (40 g)	NE.

E. Extinction over the whole surface area of the vessel.
NE. Fire not extinguished over whole surface area of vessel.

TABLE 2 (cont'd)

(c) Solid CO₂ alone on kerosine fire

No.	Amount used	Remarks
17	80 g (particle size < 1.5 mm)	NE. 40 g added after one minute preburn, slight clearance. Followed in 10 seconds by further 40 g. Clearance over 4/5 area but no extinction.
18	95 g (particle size < 1.5 mm)	E. Applied within 7 seconds. Extinction at 10 seconds. An agglomeration of particles continued to evaporate after extinction.
19	70 g (particle size < 1.5 mm)	NE. Applied within 7 seconds. 4/5 clearance no extinction.
20	100 g (particle size > 1.5 mm) Limiting quantity 90g	NE. Applied within 7 seconds. 9/10 clearance within 10 seconds but no extinction.

(d) BCF alone on petrol (narrow boiling point 62/68°C) fire preburn time 30 seconds

21	100 ml	NE.
22	150	NE.
23	250	E. Fire driven from tray in 4-5 seconds, but remained alight at edge - spread back in 5 seconds.
	Limiting quantity 250 ml (450 g)	

(e) BCF/CO₂ slurry on petrol fire

24	100 ml	E. Extinguished except for small flame at a distance about 1 m from vessel. Flashed back in 5 seconds.
25	100	E. Result as for test 24.
26,27	150 (two tests)	E. Extinguished 3 to 4 seconds. Surface temperature 23 to 24°C. Temperature after mixing 18°C. Could be reignited by a match.
28	250	E. Extinguished in 4-5 seconds. Temperature reduced to 12-13°C. Reignition difficult.
29,30	500 (two tests)	E. Extinguished temperature reduced to about -10°C. Could not be reignited even with large torch.
	Limiting quantity 100 ml (160 g)	

TABLE 2 (cont'd)

(f) BCF/CO₂ slurry on AVTAG fire. 60 seconds preburn

No.	Amount used	Remarks
31	150 ml	E. In 3.5 seconds
32	100	E. In 3.0 "
33	50	E. In 4.5 "
34	25	NE. Tray surface almost clear of flame.
35	35	NE. Tray surface clear of flame except for two small edge flames and some flame hovering outside tray.
	Limiting quantity 50 ml (.80 g)	

(g) CO₂ powder (<1.5 mm particle size) on AVGAS fire. Preburn 30 seconds. Particles sprinklered evenly on surface from scoop

36	200 g	NE. But tray almost clear of flame.
37*	300	E. 10 seconds
38*	220	E. 12 "
39*	200	E. 12 "
40*	200	E. 10 " but reignition from small pocket of flame outside tray
41*	180	NE. Fire just not extinguished
42*	150	NE. Fire not extinguished.
	Limiting quantity 200 g	

(h) CO₂ powder (<1.5 mm particle size) on NBP fire

42*	250 g	E. Fire out in 10 sec. 10 g lump of agglomerated CO ₂ left in tray after extinction.
43*	200	E. Fire just out in 12 seconds.

*Helmet and gloves worn, because of extra time (about 4 seconds) needed to apply agent over surface.

(k) BCF/CO₂ slurry on AVGAS. 30 seconds preburn

44	125 ml	E. Extinction in 5 seconds
45,46	100	E. Extinction in 5 seconds on tray, but reignition from small pocket outside.
47	85	NE.
48	75	NE.
	Limiting quantity 100 ml (160 g)	

TABLE 3
Experimental critical quantities 1600 cm² fire,
Quantity of agent needed (grams)

	Awtur (kerosine)	Aetag	Avgas (petrol)	Petrol (NBP)
Liquid BCF	90	-	-	450
BCF/CO ₂ slurry	40	80	160	160
Solid CO ₂ alone	100	-	200	200
Sodium bicarbonate Dry powder ()	Approximately		250	
Light water foam ()	Approximately		500	

Table 3 shows that for both the petrol fire and the kerosine fire rather less than half the amount of slurry was needed to extinguish the fire than with BCF alone. However, both agents were very much more effective on the kerosine fire than on the petrol fire. With the BCF/CO₂ slurry on the kerosine fire substantially less agent was used than would be expected if foam or dry powder were used, but the improvement for the petrol fire was not so marked.

A comparison of tests 3 and 9 in Table 2 indicates that although the slurry could cool the liquid more effectively than the BCF alone, it was not quite as effective in preventing reignition. This suggested that the solid carbon dioxide vaporized preferentially to the BCF. This would be expected from the lower temperature of volatilization of the carbon dioxide.

In tests when the fire was not extinguished, particularly on the petrol fire it was noted that the surface bubbled vigorously after the failure to extinguish and the fire burned with the production of black smoke. This suggested that B.C.F. was being vaporized from the fuel:

after
Also the residual fuel/tests 29 and 30 contained a substantial amount of BCF, even after standing for 24 hours.

Tests on spread of slurry on surfaces

Four samples of BCF/CO₂ slurry were applied to a layer of fuel in a vessel 30 cm square under ambient (non burning) conditions. The results are shown in Table 4. On Avtag and Avtur the agent spread evenly across the surface and the evaporation was not violent. With NBP and Avgas the agent spread patchily and the evaporation was violent and of much shorter duration.

TABLE 4
Spread and evaporation tests of BCF/CO₂ slurry on a series of fuels

Fuel	Evaporation time(sec)	Observations
NBP (62/68°C)	2.2	}slurry spread unevenly }over whole tray surface }leaving patches of }uncovered fuel
AVGAS	2.4	
AVTAG	5.7	}slurry spread evenly }over whole tray }surface
AVTUR	16.0	

With solid carbon dioxide, a 5 g sample of the powder spread to about 10 to 20 cm and evaporated in 1.2 to 1.5 seconds on the petrol and 2.5 to 3.5 seconds on the kerosine. A 5 g sample of the coarser particles 5 mm diameter evaporated in 12 seconds on the petrol and 15 seconds on the kerosine.

When the slurry was poured on concrete there was little spread and aggregates of the slurry tended to evaporate in isolated small patches about 1 to 2 cm diameter. The slurry poured on water froze it almost instantly. If applied to one spot quite a large lump of ice formed which appeared to enclose the slurry and restrict further evaporation.

Large scale tests

A few tests were carried out with a 5 m² Avtur fire burning in a square tray. Attempts were made to extinguish the fire by merely throwing the BCF/CO₂ slurry directly on to the fire from a Dewar flask. The depth of fuel used was 1 cm and the preburn time one minute.

1300 g of slurry - the scaled up quantity for the critical rate for the small scale fire - had little effect when thrown on to the 5 m² fire. However when followed after 5 seconds by a further 1300 g a clearance of flame from three quarters of the fire area was obtained.

2500 g of slurry thrown on to the fire resulted in a mild explosion followed by a clearance of flame from 50 per cent of the fire area. When followed by a further 2500 g of slurry 95 per cent of the fire area was cleared of the flame.

DISCUSSION

In qualitative terms the possible contribution which solid carbon dioxide could make by cooling to the extinction of a liquid fire has been appreciated for some time. An extensive series of small-scale tests³ were carried out by Burgoyne, Katan and Richardson in 1949 on the extinction of small liquid fires by dry ice. These indicated that direct cooling of the liquid made a useful contribution for fires in liquids with flash points above ambient temperature but not for more volatile liquids e.g. petrol. On the other hand for less volatile liquids the stirring resulting from the vaporizing process was important. It was assumed that for the more volatile liquids the low flash point prevented the liquid from being cooled to the fire point and therefore cooling was not an effective mechanism.

On the basis of the theoretical analysis¹ referred to previously, it may be shown that as long as vaporization takes place evenly near the surface, then the contribution of cooling to the extinction of fire may be substantial even if the liquid is not cooled to the fire point. The present tests confirm this, in many of the extinctions with both petrol and kerosine the fuel was not cooled to the fire point and flash back or reignition took place very easily following the transient period during which extinction took place. This was particularly the case when the amount of slurry or BCF used was small.

From available information on the burning rates of kerosine and petrol fires⁴ it may be estimated that the rate of burning of the 1,600 cm² kerosine and petrol fires are respectively 2.3 and 3.2 grammes per second. On this basis, and assuming an extinction time of 5 seconds for the slurries and BCF and 10 seconds for the solid carbon dioxide the amounts of application of agent to the fires that would have been expected to extinguish them, have been estimated and have been compared with the amount actually used in Table 5.

TABLE 5

Comparison of theoretical and experimental amounts of extinguishing agents

Agent	Kerosine		Petrol (NBP)	
	Experimental	theoretical	experimental	theoretical
BCF	90	20	450	30
BCF/CO ₂ slurry	40	13	160	20
Solid CO ₂ alone	100	18	200	25

In all cases the estimated quantity is substantially less than the experimental quantity. The difference was least for BCF/CO₂ slurry on the kerosine fire. Moreover if in this particular instance of the longer evaporation time of 16 seconds indicated in Table 4 is used instead of the extinction time of 5 seconds to estimate the theoretical quantity then the difference between the experimental and theoretical quantity would disappear. In other instances however, the use of the data in Table 4 instead of the extinction time does not improve agreement. The observations on the way the agent evaporated when applied to the surface of the different fuels give some insight into these discrepancies. When the slurry was applied to kerosine the agent spread rapidly and evenly to the whole surface and then continued to evaporate uniformly for a sufficiently long time to ensure the extinction of all flames that were pushed off the fire. When the slurry was applied to petrol, the slurry tended to evaporate violently over a short period. This led to an unevenness in evaporation, a stirring effect within the liquid and an entrainment of fuel from bursting bubbles into the flame. As a result of this in the fire tests more fuel was fed into the flames and the transient clearance was not sufficiently long to prevent a flash-back. The solid carbon dioxide did not spread as well as the slurry on kerosine and tended to evaporate too quickly. The lack of agreement between the theoretical and experimental results indicate that there is ample room for improvement in the performance of the agents and the observations on the way the agents evaporate suggest a number of ways in which this improved performance may be obtained. Application of the agent as a coarse spray should allow more uniform application of agents and should reduce the violence of the evaporation. A change in the particle size of the slurry and the nature of the continuous phase could also reduce the violence of the evaporation of the slurry on the petrol fire.

Possibly coating the solid carbon dioxide with a surface active agent may help disperse the solid carbon dioxide particles over the surface of the liquid. Indeed the tests suggest it may be possible to tailor a slurry to suit a given fuel under a given fire condition.

The rate of burning per unit area of the 5 m² fire would have been about twice as great as the rate of burning of the 0.16 m² fire. On this basis the theoretical quantity of slurry needed would have been twice as much. 2500g when thrown on the fire in two lots cleared flame from three quarters of the fire area and as one lot from one half of the area. This suggests that a less crude method of application may well have brought about extinction of the fire with 2500g of the slurry, which is the expected quantity needed after making allowance for the greater burning rate of the fire.

It is clear from the results that when the nature of the extinguishing agent and its application are such that the cooling effect in reducing the burning rate can be efficiently exerted, then a highly effective agent may be obtained. Thus, the amount of BCF/slurry required to extinguish a kerosine fire was far less than the amount which would be expected if light water or sodium bicarbonate dry powder were employed. Knock-down is very fast indeed and was of the order of seconds. Moreover, although the amount of agent used is insufficient to cool the fuel to the fire point when the minimum amount of agent is used and the fuel can be easily reignited, the continued application of the agent does cool and inhibit the flammable liquid making it very difficult to reignite. The 50 per cent BCF/CO₂ slurry is very effective on kerosine and Avtag. This agent may, therefore, have application to aircraft crash fires which in general are large spill fires in these fuels, and larger scale tests are therefore recommended. Moreover although the tests on the 5 m² fire indicate that a certain degree of sophistication in the agent is required to obtain the best results they also suggest that useful results could be obtained by very crude methods of application. It may be possible therefore to dump the agent from a helicopter on to a fire or even propel the agent in to the centre of a fire by using a homing rocket; in the latter use of course the agent would need to be in a weak container which could be made to burst harmlessly. However it would be difficult to use slurries containing solid carbon dioxide in common extinguishers because of the necessity of keeping the agent at low temperatures.

Conclusions

- (1) A slurry of solid carbon dioxide in bromochlorodifluoromethane was about ~~two-thirds~~ ^{two to three times} as effective in extinguishing petrol and kerosine fires as the liquid agent alone or solid carbon dioxide alone. In all cases the agent was applied by being poured onto the surface of a fire from a beaker or a scoop.
- (2) Comparatively small quantities of the slurry were needed to extinguish a kerosine fire (25 grams per ft²).
- (3) The quantity of slurry used for the kerosine fire was comparable to the amount which might be estimated from a theoretical approach. However, the amount used for the petrol fire was much greater than that estimated theoretically.
- (4) There is scope for improving efficiency of the slurries varying their properties improving the method of application to the fire
- (5) It appears possible to obtain effective slurries with solid carbon dioxide and a range of halogenated hydrocarbons and vaporizing liquid agents, including a mixture designed to have the same density as solid carbon dioxide, which may be useful for certain practical risks e.g. aircraft crash fires fighting where a very rapid control with a small quantity of agent appears feasible.
- (6) Slurries of solid carbon dioxide in liquid nitrogen do not appear to be very effective because of the deposition of the solid carbon dioxide and the preferential vaporization of the liquid nitrogen.

References

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FIG. 1. 0.16 M² KEROSENE FIRE BEFORE
APPLICATION OF BCF/CO₂ SLURRY.
PREBURN 60 SECONDS

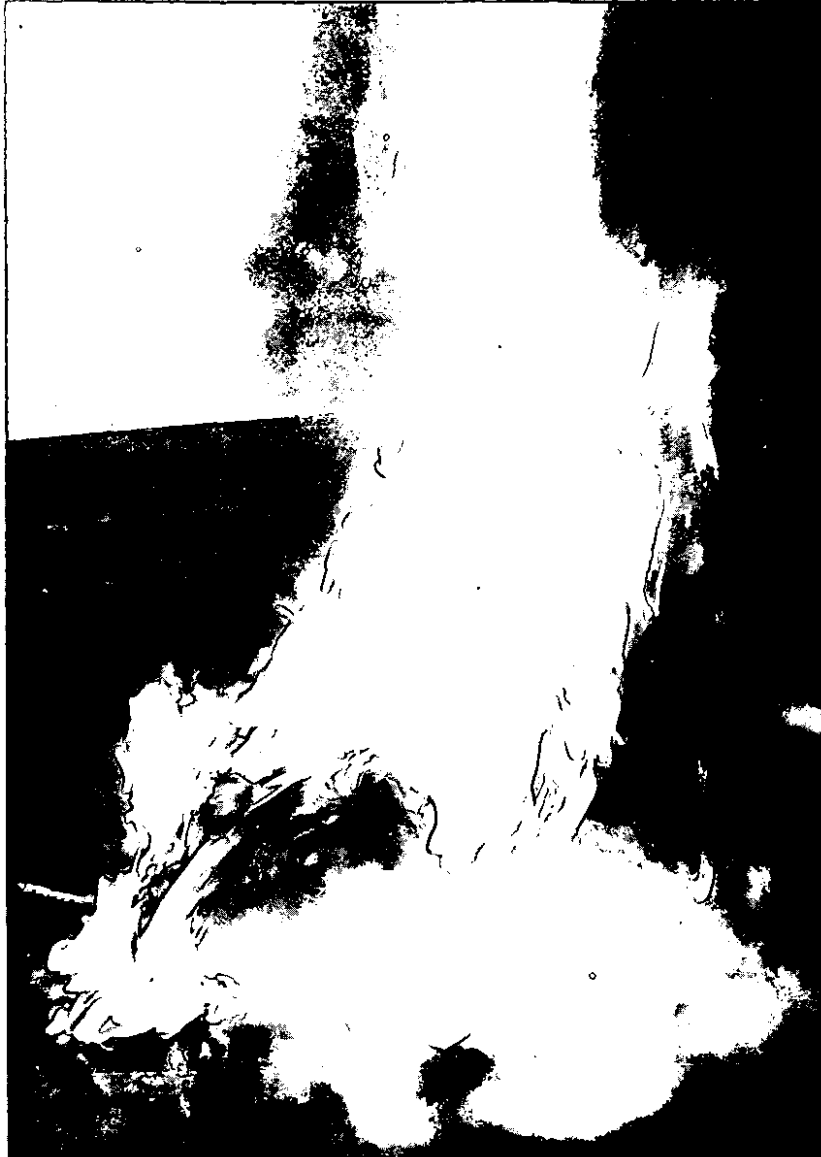


FIG. 2. 1 SECOND AFTER APPLICATION
OF 50 CM² (80 GMS) BCF/CO₂ SLURRY

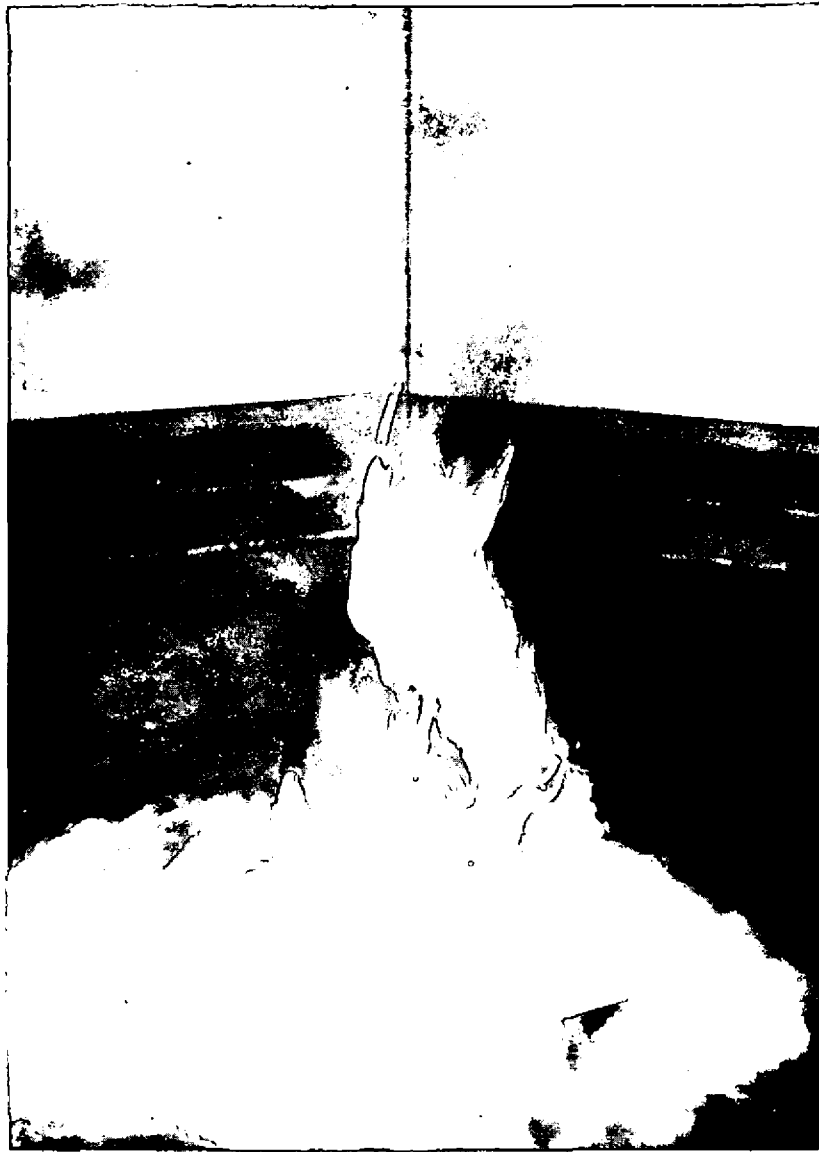


FIG. 3. 3 SECONDS AFTER APPLICATION OF SLURRY



**FIG. 4. 4.5 SECONDS AFTER APPLICATION OF SLURRY.
FIRE COMPLETELY EXTINGUISHED IN SECONDS**

