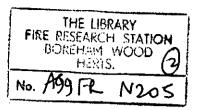
DEPARTMENT OF SCIENTIFIC AND INDUSTRIAL RESEARCH AND FIRE OFFICES' COLDITIES JOINT FIRE RESEARCH ORGANIZATION

VAPORIZING LIQUID EXTINGUISHING AGENTS

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SUMMARY

The use of vaporizing liquid extinguishing agents for fighting liquid fires is discussed with a critical review of the possibility of increased efficiency by the use of the newly-developed materials now available. An account is given of the application of one of these compounds, chlorobromomethane to aircraft crash fires. Substantial improvement in the fire-fighting efficiency of this material was obtained by application in the form of flat sprays.

INTRODUCTION

Vaporizing liquid extinguishing agents, such as carbon tetrachloride have been used for many years for the extinction of incipient fires involving combustible liquids and electrical apparatus. The ideal agent for these applications should combine a high extinction efficiency with low toxicity and cost, and should not give toxic or corrosive decomposition products when used on a fire.

Prior to 1939 the three agents in common use were carbon dioxide, carbon tetrachloride and methyl bromide. None of these compounds fulfilled all the requirements of the ideal agent. Carbon dioxide has a low toxicity and is cheap, but it has a very low efficiency and requires heavy, pressure-resisting containers. Methyl bromide has a high efficiency, but it is highly toxic and requires great care both in storage and use. Carbon tetrachloride, though less toxic than methyl bromide, has only a moderate efficiency and produces large quantities of texic compounds when used on a fire.

Because of the disadvantages of the established agents and the ever-increasing use of liquid fuels in both air and surface transport, there has been an active search for compounds both of greater fire-fighting efficiency and lower toxicity. A large number of compounds have been tested, particularly the halogenated paraffin hydrocarbons, including chlorobromomethane CH2CIBr, and a series of fluoro-brome-compounds such as trifluorobromomethane, CF3 Br. A comprehensive study of this last series of compounds was made on behalf of the U.S. Corps of Army Engineers (1), and the results of these investigations and other available information were surveyed prior to planning the work which is described in the report of the Committee of the Fire Research Board on Vaporising Liquid Extinguishing Agents (2).

ASSESSMENT OF NEW EXTINGUISHING AGENTS

In recent work at the Joint Fire Research Organization (3) attention has been mainly concentrated on the relative fire-extinction efficiency of the compound and the nature and amount of the decomposition products formed when the compound was used in a fire. It has not been everlooked that other factors, such as cost and availability, corrosion and various physical properties must influence the ultimate choice of the most suitable agent for practical application.

Extinction efficiency This was assessed in the laboratory by the effect of the agent on the flammability limits of n- hexane. When a small proportion of an extinguishing agent is added to mixtures of a combustible and air, the flammable range is narrowed, and with increasing additions

of extinguishing agent a point is reached at which the lower and upper limits of flammability coincide. This point therefore represents the minimum concentration of agent which will ensure that flame will not be propagated through the gas mixture whatever the relative proportions of combustible and air. This concentration has been termed the "peak value" (2), since it is at the highest point of the curve showing the effects of the agent on the flammability limits of the combustible. It can be used as a measure of extinction efficiency since the lower the "peak value", the more efficient the extinguishing agent. The laboratory tests are particularly useful for screening a number of possible agents but the ultimate choice must depend on practical trials, because of factors such as ease of handling, quantity of smoke formed etc. which are not assessed by the laboratory determination of peak values. Results of the laboratory tests for various agents are given in Table 1.

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Properties of vaporizing liquid extinguishing agents

		B.P.	Dens	sity	Peak value with n-hexane per cent by volume		
COMPOUND	°C	Liquid g/ml ⁻ 20 ^C C	Vapour g/l N.T.P.				
Carbon dioxide	CO ₂	-78.5+		1.98	28		
Methyl bromide	CHzEr	4•5	1.73 ^h	4.25	7•1		
Carbon tetrach- loride	CC14	76.8	1.60	6 . 84	9•7		
Chlorobromo- methane	CH ₂ ClBr	⁶⁸ /69	1.93	5.78	6•35		
Trifluorobromo- methane	CF3Br	-57.8	1,58	6.66	4 . 9		
Difluorodi- bromomethane	CF ₂ Br ₂	24.5	2.29	9.39	3 • 55		
Tetrafluorodi- bromoethane	C ₂ F ₄ Br ₂	47•5	2.18	10,62	3,22		
Ethyl bromide	C ₂ H ₅ Br	38	1.42	4.86	6.1		
Methyl icdide	CH3I	42.4	2.28	6.34	4.65		

⁺ sublimes

Toxicity The toxicity of the compounds has been investigated by experiments with small animals, particularly in U.S.A. (1). In the U.S.A. tests the vapour of the agent was pyrolised in a heated iron tube and the products passed into a chamber containing rats, mice or guinea pigs. The toxicity of the decomposition products was assessed from the effects on the animals.

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In the work by the Joint Fire Research Organization no attempt has been made to asses toxicity directly, but the nature and amounts of the various compounds have been determined by chemical analysis. From these results the toxicity can be assessed from the known toxic properties of the individual compounds.

Some tests (3) were carried out of the decomposition products formed in a 500 cu. ft. room where the agent had been prejected onto a petrol fire. Measurements were also made of the atmosphere in the cockpit of a burning aircraft when the fire was attacked with chlorobromomethane (2). With all the compounds tested, the major toxic constituents of the decomposition products were hydrogen halides, and the concentrations were above those usually regarded as safe, even for short exposures. is often stated that appreciable quantities of phosgene and similar compounds are produced when this type of agent is used on a fire. experiments at the Joint Fire Research Organization the concentrations of such gases were very low, and in comparison with the concentrations of hydrogen halides obtained in the same tests, would have a negligible effect. There was no relation between the extinction efficiency of a compound and the amount of halogen acids produced. The amounts were greater with chlorides than with bromides and least with fluorides. thus, greater quantities of hydrogen halides were produced by carbon tetrachloride than by trifluorobromomethane, although both contain four halogen atoms, but trifluorobromomethane produced more than methyl bromide which contains one halogen atom. Under practical conditions the quantities produced would be influenced by the extinction efficiency since less of the more efficient compounds would be needed to achieve extinction and this would reduce the quantities of decomposition products. assessment of the hazard is difficult because of the lack of information on the effects of brief exposures to heavy concentrations of the toxic gases.

PRACTICAL APPLICATION OF NEW AGENTS

In spite of the extensive investigations carried out in this country and abroad, no single compound has been found which meets entirely the requirements of high efficiency with low toxicity (both of the compound itself and its decomposition products) nevertheless considerable improvements in fire-fighting efficiency can be effected by the introduction of the newer agents, particularly for special risks.

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The most effective agents are the fluoro-bromo compounds, and as they tend to have low texicities. Considerable attention in U.S.... (4) has been devoted to the study of the application of some of these compounds, trifluorobromethene, diffluorodibromomethene and tetrafluorodibromomethene to aircraft protective systems and portable extinguishers. Data for some relevant physical proporties of these agents and their effect on metals and plastics have also been published (5).

With the co-operation of the Army Fire Service, the Joint Fire Research Organization was able to carry out some tests on petrol fires with trifluorobromomethane, in comparison with carbon dioxide, methyl bromide and carbon tetrachloride. The results are given in Table 2, and clearly indicate the great potentialities of this compound; it is not however, yet manufactured in this country on a commercial scale.

Ethyl bromide has also been suggested (4); its extinguishing efficiency is rather higher than that of methyl bromide and it is much less toxic, but it is flammable under certain conditions. Methyl iodide was also suggested as a highly effective extinguishing agent, unfortunately it is highly toxic(6).

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	Applian	Results					
		Average rate of discharge		Time for extinction	Quantity of agent used		
Compound	Туре	Weight g/sec	Volume of vapour e/sec	seconds	Weight grammes	Volume of vapour litres	Notes
Carbon dioxide	Compressed gas applied through a horn.	37•9	19• 3	Did not extinguish	1705	862	The fire was controlled very quickly but there was insufficient agent available for complete extinction. The atmosphere after the test was telerable.
Carbon tetrachloride	Liquid pressurized with CO2. Deliver ed as a broken stream.	31•5	4•6	n -	1320	193	The intensity of the fire was reduced, but there was a considerable amount of smoke. The atmosphere after the test was very acrid.
Methyl bromide CH ₃ Br	Liquid pressurized with nitrogen. Delivered as vapour through a plain nozzle	29•0	7-0	13	377	89	Burning petrol vapour floated above the layer of vaporized agent. The atmosphere was acrid but there was less smoke than with carbon tetrachloride.
Trifluorobromomethane CF3Br	Compressed gas applied through a CO2 extinguisher type horn.	24	3 • 6	7 1 2	180		Burning petrol vapour floated above the layer of trifluoro-bromomethane, as with methyl bromide. The atmosphere was slightly acrid and there was a little smoke.

CHLOROBROMOMETHANE

Chlorobromomethane is less efficient and rather more toxic than some of the fluorobromo-compounds but it is already available in commercial quantities in this country, and is less expensive than the compounds containing fluorine. It is much less toxic than methyl bromide, and compared with carbon tetrachloride it has a much higher extinguishing efficiency and a much lower toxic hazard when used on fires. It has therefore been suggested (2) that serious consideration should be given to the general substitution of chlorobromomethane for carbon tetrachloride and methyl bromide.

The rest of this paper will deal mainly with work of the Joint Fire Research Organization on the development of chlorobromomethane as an extinguishing agent for petrol fires, with special reference to its application to aircraft crash fires.

Early in 1954 some tests were made for the Air Ministry Fire Service with chlorobromomethane on petrol fires involving aircraft (2). During these experiments it appeared that the efficiency of the method of application of the chlorobromomethane could be improved, with a resultant economy in the use of the agent, so that it was decided to use chlorobromomethane as an auxiliary to foam in the airfield heavy crash tender. The Ministry of Supply asked the Joint Fire Research Organization to carry out work to determine the best method of application of the agent.

The programme of experiments was divided into three parts: firstly, preliminary experiments with small fires to compare methods of application, secondly experiments with fires up to 4 ft. diameter to examine the effects of factors such as drop size, rates of application and spray pattern. Finally, large scale trials, on fires up to 10 ft. sq. and on fires involving aircraft were carried out to test the performance of the best type of applicator developed as a result of the small-scale tests under conditions simulating those expected in practice.

The preliminary trials to determine the best method of application were made with plain jets, cone sprays and flat sprays (produced by a jet impinging on a flat metal plate). The efficiency of extinction was measured by the relative time taken to extinguish a 11 in. diameter petrol fire with carbon tetrachloride as the agent. Flat sprays were superior to cone sprays, and both sprays were superior to a plain jet. The speed of extinction increased as the delivery rate was increased, and the effect was most marked with the flat sprays.

The preliminary trials were followed by experiments on 24 in. and 48 in. fires. Carbon tetrachloride or chlorobromomethane was applied as a flat spray at rates ranging from 0.3 gal/min. to 1.6 gal/min. The rates were varied by changing the nozzle pressure or the diameter of the nozzle or by using two nozzles.

The rates of delivery with the apparatus available were insufficient to achieve extinction of the 48 in. fire with carbon tetrachloride, although extinctions were obtained with chlorobromomethane. The results with flat spray using chlorobromomethane on a 4 ft. diameter petrol fire are shown in Figure 2.

At rates of delivery below 0.7 gal/min. the time for extinction decreased rapidly as the delivery rate was raised, so that the total amount of agent used was decreased. At rates above 0.7 gal/min. the effect of further increase in the delivery rate was less marked and the time for extinction appeared to approach a minimum (5-10 secs.) which was probably related to the time required for the operator to traverse the fire. It was apparent also that there was a minimum rate of delivery below which extinction would be very slow if not impossible.

The patterns of the sprays were measured and for similar rates of delivery, the nozzles with wider spread gave the more rapid extinctions. In order to produce a wide spreading spray with the minimum rate of delivery of the agent, experimental applicators were made using systems of batswing gas burners. These gave a very thin flat spray with a wider distribution of agent for a given rate of delivery than the sprays tested earlier.

With the experimental sprays the 48 in. diameter fire was extinguished in 8 seconds with about $\frac{1}{4}$ pint of chlorobromomethane (0.01 gal/sq.ft./min.) provided that the lateral spread was sufficient to cover the fire. Curves showing the relationship between lateral spread and speed of extinction are given in Figure 3.

The experiments also showed that the nextle pressure should be kept as low as possible since at higher nextle pressures more air is entrained with the spray, thus reducing the preportion of agent in the mixture. In addition, of course, a higher rate of entrained air may actually increase the rate of burning and therefore the time for extinction. It did not appear that variations in drop size produced any significant effect on the speed of extinction within the range studied (0.1 - 1 m.m. diameter).

Large scale tests The conclusions reached in these experiments were tested on a practical scale in cooperation with the Air Ministry Fire Scrvice and Ministry of Supply and trials were made on 10 ft. square petrol fires, and on fires involving aircraft. The experimental flat spray was compared with the cone spray nozzles used in the previous trials (2). The results of these trials are given in Table 3.

The 10 ft. square fire of petrol floating on water was extinguished in 11 seconds with 0.62 gallons of agent when the wind speed was 6-8 m.p.h., and in 20 seconds with 1.44 gallons with a 9-16 m.p.h. wind. The cone spray extinguished the fires in 38 and 39 seconds with 3.8 and 3.9 gallons of agent. The similarity in the extinction time with this spray, despite the different wind conditions, was probably due to the fact that the extinctions were mainly effected by diluting the petrol with agent until it was almost non-flammable. This view is supported by the observation that after extinction the petrol was difficult to re-ignite.

In order to observe the effect of the type of ground two tests were made with 10 ft. square areas containing an uneven bed of damp sand, on which 15 gallons of petrol were distributed. The fires were less intense than those from the petrol floating on water and extinction was easier. The experimental applicator extinguished the fire in 8 seconds with 0.6 gallons of agent and the cone spray in 14 seconds with 1.4 gallons. The smaller effect of the type of jet observed in this test is probably due to the fact that the time of extinction was of the same order as that required to traverse the fire.

Two trials were made with the aircraft, in winds of 9 and 12 m.p.h. The aircraft, a Spitfire without engine or wheels, was collapsed on the tarmac, and three steel trays each 7 ft. x $3\frac{1}{2}$ ft. were arranged under the forward bulkhead to give a fire area 7 ft. x 11 ft. These contained a total of 15 gallons of petrol, and additional petrol, at about 3 g.p.m. was allowed to run down the bulkhead into the centre tray during the fire. The aircraft was pointed into the wind. In these trials the fire was considered to have been extinguished when it would have been safe for rescue crews to approach the cockpit, although small fires of hydraulic liquid and hose connections persisted behind the engine bulkhead after the main fires had been extinguished. The attacks on the fires were started with one nozzle and the second brought into operation later when it became evident that one nozzle alone could not extinguish the fire.

The first fire was attacked with cone sprays and extinguished in 55 seconds with 9.5 gallons of chlorobromomethane. The residual fire was extinguished with water, but not until the fuselage had been damaged.

TABLE 3

Comparison of flat sprays and cone sprays.

Summary of results of large-scale trials with chlorobromomethane

Fire		Applicator						Extinction	
	Wind	Туре	Delivery rate		Spray pattern		Time	Volume of agent	
	speed m.p.h.	of nozzle	gal/ft ² /min	Total gal/min	Lateral spread ft.	Forward throw ft.	sec.	used galls	
Open fires 10 ft. square 25 gallons of petrol on water 22 secs preburn 15 gallons of petrol on damp sand. 45 seconds preburn.	6-8 (Flat spray	0- 028	3•41	16	8	9•5	0•57	
		Cone spray	0•109	6	8	10-12	39•5	3-95	
	16 (Flat spray	0+034.	4•13	16	8	20	1 • 44	
		Cone spray	0•109	6	8	10-12	38		
	16 {	Flat spray	0•034	4•13	16	8	8•5	0•60	
		Cone spray	0•109	.6	8	10–12	14•0	1•40	
Aircraft Fires Steel trays 11 ft. x 7 ft. containing 15 gallons of petrol and 3 g.p.m. running during the test. 60 seconds proburn. (9 ·	Two cone sprays. Second spray started 15 seconds after first	0•109 per nozzle	6 per nozzle	8 - per nozzle	10-12 per nozzle	55	9•5	
	12	Two flat sprays. Sccond spray started 22 seconds after first This fire was more intense than in previous test	0•034 por nozzle	4•13 per nozzle	16 per'nozzle	8 per nozzle	4.7	4 - 95	

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The water used for extinction flooded the tarmac, so that petrol used for the second test floated on this and the second fire was more intense and extensive than the first. It was however extinguished in 47 seconds with 5 gallons of agent using the flat spray.

The trials demonstrated that the flat spray as produced by the experimental nozzle was more efficient than the cone spray, whether the fire was from a flat surface as in the 10 ft. square fire, or whether there were obstructions as with the aircraft.

MECHANISM OF EXTINCTION

During the tests on 24 in. fires it was observed that chlorobromomethane extinguished the fire in approximately one-third the time taken by carbon tetrachloride, although from consideration of peak values the superiority was about 1½. The results for both agents are given in Figure 3. The greater superiority under practical conditions is probably due to the particularly marked effect of small concentrations of this agent on rich fuel-air mixtures, and this suggests that for greatest efficiency the agent should be applied in a thin flat spray to the base of the flame where the fuel-air mixture is richest in fuel.

SUMMARY AND CONCLUSIONS

From the discussion on new extinguishing agents it is apparent that while all the newer agents tested had certain technical and economic disadvantages, considerable advance in fire-fighting technique could be achieved by their use in certain risks. In particular, the use of chlorobromomethane would enable considerable advantage to be achieved by comparison with the agents used at present in this country.

The main part of this paper therefore deals with the application of chlorobromomethane to petrol fires with special reference to aircraft crash fires. For rapid extinction of such fires it is essential to use a method of application giving a lateral spread of the agent rather wider than the fire, and this can be done with greatest economy in the use of the agent by using flat sprays rather than the conventional type of come spray normally used in fire-fighting. With such experimental flat-spray apparatus it was found possible to extinguish an aircraft fire with a rate of application of 0.034 gal./sq. ft./min. Other experiments showed that under most favourable conditions the minimum rate of application for petrol fires might be reduced to 0.010 gal./sq. ft./min., though obviously in practice a rather higher rate would be used.

In the course of this work, it was found that the relative superiority of chlorobromomethane to carbon tetrachloride was much greater than could be accounted for by the difference in the respective peak values. It is suggested that this is due to the very marked effect of small quantities of chlorobromomethane on petrol-air mixtures near the upper limit of flammability.

The decomposition products from some of the large-scale fires were analysed, the chief toxic products are hydrochloric and hydrobromic acids, with much less significant amounts of phosgene and carbonive bromide, the texic hazards involved in the use of this agent while much lower than those of carbon tetrachloride are not negligible, and must be carefully assessed in any proposed application.

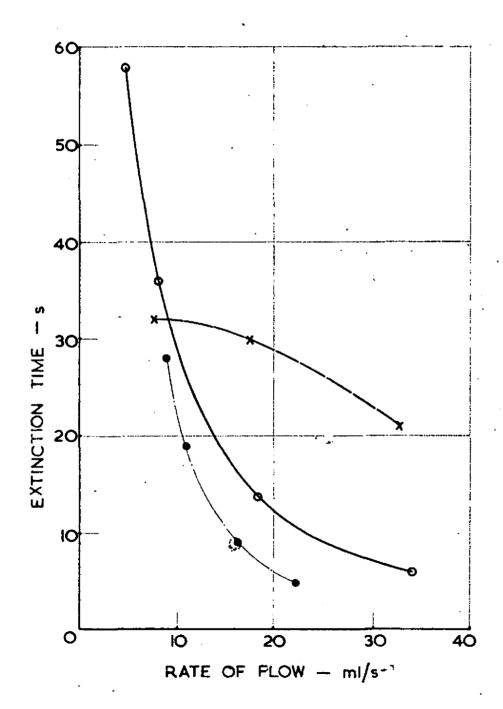
While, as has been shown, the use of chlorobromomethane in apparatus specially designed has made possible a considerable advance in fire-fighting technique, it should be emphasised that in special risks certain of the fluoro-bromo-compounds show promise of even further advance in spite of their greater cost. The success achieved with chlorobromomethane should therefore stimulate rather than retard further work on the development of the fluoro bromo compounds.

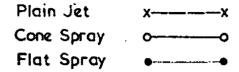
ACKNOWL DGEMENTS

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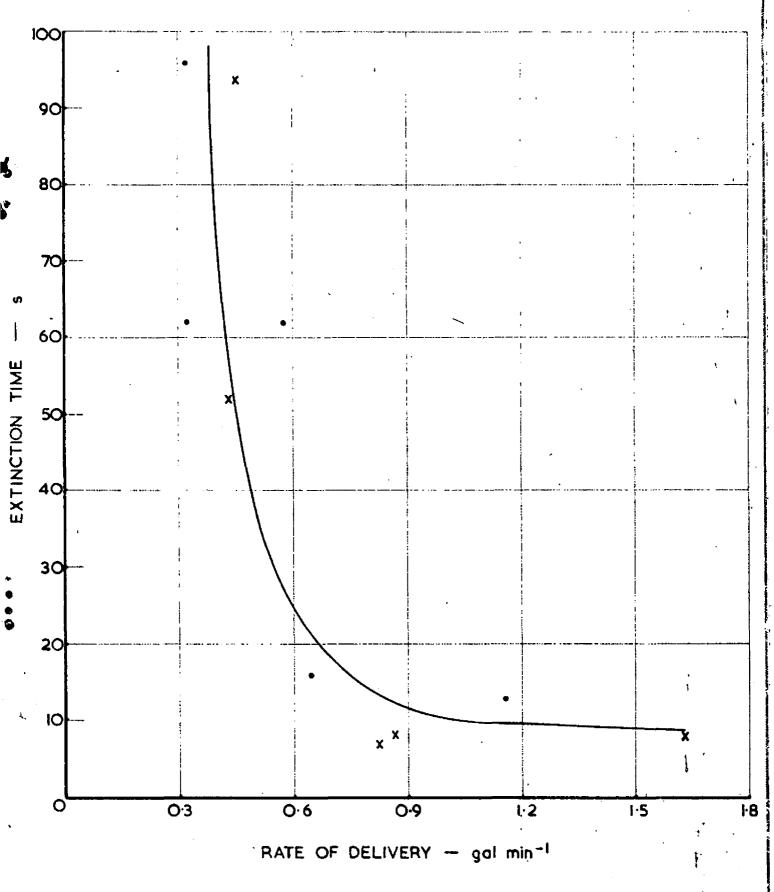




Il in. Petrol fire attacked with Carbon tetrachloride.

FIG.I. COMPARISON OF PLAIN JETS, CONE SPRAYS AND FLAT SPRAYS.

RELATIONSHIP BETWEEN RATE OF FLOW AND EXTINCTION TIME.

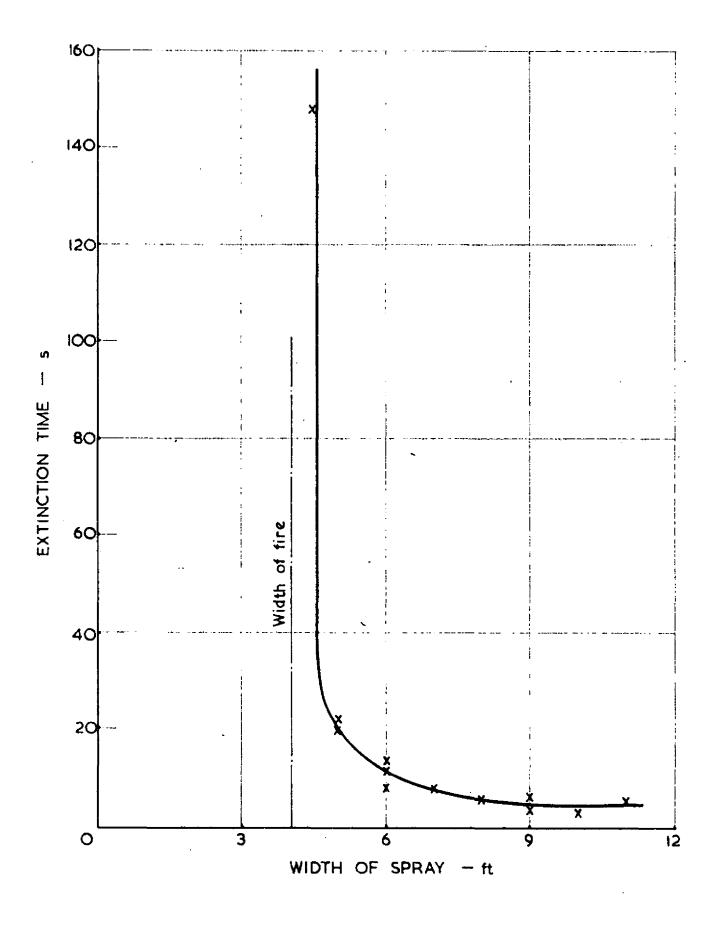


x — at 60 lb/in, nozzle pressure.

- at 30 lb/in. nozzle pressure.

Flat sprays on 4ft. diameter petrol fire.

FIG. 2. EFFECT OF RATE OF DELIVERY OF CHLOROBROMOMETHANE ON EXTINCTION TIME.



Chlorobromomethane used with experimental flat spray on 4ft. petrol fire.

FIG. 3. EFFECT OF WIDTH OF SPRAY ON EXTINCTION TIME.