



Fire Extinguishing Agents

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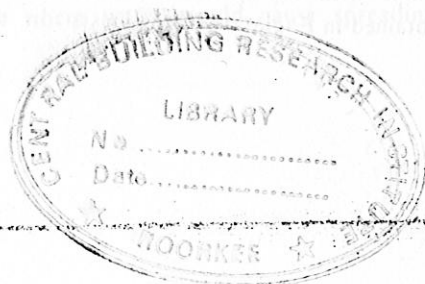
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A fire has been characterized chemically as 'an exothermic process of oxidation and combustion and physically as a rise in temperature of the ambient atmosphere and its pollution with fire gases'. As the definition of fire indicates, it is an exothermic process of oxidation and combustion, implying that when it occurs (either intentionally for some useful purpose or by any accident) it releases large amount of heat energy coupled with increase in volume of combustion products. This heat energy from the flames through radiation is responsible for heating and vaporization of fuel. In case of liquid fuels, the rate of vaporization at the liquid surface is determined by the nature of the

flames and, in turn, by the nature of the liquid fuel and the size of the pool. While in the case of wood piles, during the period of primary burning, volatiles are released at the upper level of the solid combustible material.

Thus fire, if starts, can be extinguished only by removing combustible material from the site or stopping air (oxygen) supply to fire (for materials not having inherent oxygen producing agents) or cooling the fuel or flame so that vaporization of fuel can be reduced and ultimately brought down below the maximum level at which fire does not occur. For cellulosic substances burning with ex-



ness of air it is sufficient to reduce the temperature of solid to 250°C to extinguish the fire, while in case of volatile flammable liquid, it is necessary for liquid to be cooled below fire point. Without going into details of physical and chemical mechanisms, it is worthwhile to mention that while the different extinguishing effects can be separated in principle, the action of a given extinguishing agent does not have to fall exclusively in the realm of one or another of the mechanism.

Extinguishing system which are in practical use, include :

- Water
- Carbon dioxide or inert gases
- Dry powder
- Volatile organic halides, and
- Foams

Water

Water is the primary extinguishing agent used by fire services. The fact that it is economically cheap liquid having a very high heat capacity which enables its cooling action to play a predominant part in the extinguishment of fires and is readily available in large quantities, makes it an almost ideal extinguishing agent. Water used for fire-fighting operation must be applied in a manner so that maximum quantity of water takes away heat from burning material and forms steam. Thus, the maximum rate of heat absorption, which may take place will depend on the exposed surface of water. It is a well known fact that fire-fighting efficiency of water can be improved by increasing the speed of water vaporization which can be obtained if water is used in atomised form or of very fine drop size. In practice it is required that water be discharged at a distance from and be brought to the surface of the burning object in sufficient quantities per unit time. However, very fine droplets cannot be easily focussed at an object from a distance to give proper coverage and they do not have sufficient energy to resist the upthrust of the combustion gases when entering the combustion zone. Radusch¹ found that 0.35 mm. drop size gives the maximum heat transfer, which is comparable with the optimum values of 0.4 to 0.6 mm. obtained in England during tests on the

extinguishment of liquid fires. The author also concluded that for a water flow of 100 liters/min. and with an initial drops velocity of 30 mm/sec., the absolute velocity of the drops at a distance of 8 mm. would be 4.2 mm/sec. which is presumed to be sufficiently high to allow the drops to reach the focal points of the fire against the upthrust of the combustion gases. The time of flight would be 0.45 sec. However gravity would make drops having 0.35 mm. dia, to fall a distance of 0.68 m. Rasbash and Stark² however found that extinguishment with water sprays should not be attempted where the fire diameters exceeds 10 ft. (3.04 m) and fire point exceeds 100°F (37.7°C) or when the fire point is less than 100°F (37.7°C) and the fire dia. exceeds 5 ft. (1.52 m). This emphasises the importance to develop atomizing nozzles which produce water drops of uniform size regardless of pipe pressure. Nash³ showed that there is a critical rate of water application necessary to achieve extinction which can be given by

$$R_c = \text{Constant } D^x$$

$$\Delta T^y$$

Where R_c = Critical rate of water application (litres: min.)

D = mass median droplet size (mm.)

ΔT = difference between water temperature and liquid fire point (°C)

x y are indices which are approximately equal to 1.

Nash also showed that if water application rate exceeds critical application rate, then extinction time of fire can be given by

$$t = 5.2 \times 10^5 \times D^{0.85} \cdot R^{-2.3} (\Delta T)^{-5.3}$$

where t = time of extinction in Sec.

D = mass median drop size in mm.

R = Rate of application l, m² Sec.

ΔT = difference between water temperature and fire points in °C.

Fig. 1 and Fig. 2 show the effect of mass median drop size on critical rate of application and time of extinction respectively,

However an undesirable characteristic of water is its high surface tension, which will not allow water to spread uniformly over a surface and

affects its wetting and penetration power. Much work has been done in the last twenty years to improve the effectiveness of plain water by addition of small amount of organic chemicals, known as surface active agents or wetting agents, by significantly reducing surface tension of plain water. Table 1 shows the effect of agents on surface tension.

Table 1 : Effect of Surface Active Agents on Surface Tension of water

Agent	Conc ^a in H ₂ O	Surface tension Dynes cm.
Water at 250°C	100	71.97
B	0.05	32.0
	0.1	32.3
	0.3	32.5
C	0.1	31.4
	0.3	28.7
	1.0	28.4
E	0.05	34.9
	0.1	32.4
F	0.05	27.8
	0.1	27.8

Some laboratory tests were conducted by Los Angeles Fire Services⁴ to compare surface penetration and internal wetting ability of various liquids when applied to a standard mattress. In this test, a fixed volume of solution is applied at a uniform rate to a standard insulated mattress. The application is repeated at intervals of 90 sec. for six applications. The weight of the run-off water (gross weight at any time minus gross weight at starting) is measured prior to each application. The absorption of solution is run-off weight for plain water minus run-off weight for conc^a of the solution at the same time. Results of the experiments are shown in Fig. 3.

Modern technology is trying to help fire-fighting personnel with some notable contributions. Beside 'wet water', 'slippery water' is one of these, resulting from mixing the organic chemicals such as polyethylene oxide with water thus reducing the energy required for pumping.

When water is pumped through a hose, the pressure loss occurs. The small percentage of this loss due to overcoming true friction, the attraction between the molecules of water and between the water & walls surface of hose. The remaining portion, which is major one is lost due to turbulence of the water, flowing through the hose line. The long polyethylene molecule, which is made up of many thousands of small molecular units strung together in an immensely long skeleton like chain, reduces the wildly random fluid motion caused due to turbulence and thus reduces the loss of energy in these unproductive motions. Purington⁵ measured the friction loss studies using 0.0127 m fire hose. In his experiments, he injected the polyethylene oxide into the water which was fed into 0.0127 m dia. rubber booster hose of 30.48 m length. The pressure transducers, the signals from which were fed to a strip recorder, were connected to both ends of hose. Thus the friction loss in the test section was recorded by a strip chart recorder. Purington found that injection of polyethylene oxide in the water stream reduced the friction by an average of 44%. The results are shown in Fig. 4.

Carbon dioxide or inert gases

There are two basic reasons for using built-in fire extinguishing system—(i) the size of fire and rate of development likely are such that staff on the spot with portable extinguishers are inadequate and the fire brigades attendance time is too long for the particular risk and (ii) the nature of the risk is such that a specific, clearly defined method of extinguishing is required rather than a general fire extinguishing approach.

The most common built-in system is a sprinkler or water-deluge system but for three types of risk it is preferable to use inert gas extinguishing agent such as carbon dioxide, nitrogen etc. These are;

- (a) where water could cause unacceptable damage (electronic or other delicate equipment).
- (b) where water would cause spreading of

the fire (process tanks of flammable liquids etc.)

- (c) where water is unable to penetrate to the seat of the fire (jute, high piled stock, expanded plastics etc.).

The cooling of the flame by inert system is usually thought of a smothering process, since the presence of inert extinguishing material results in the reduction of the concentration of oxygen. However carbon dioxide or inerting system when used as extinguishing medium not only have the smothering effect but also have cooling phenomenon which also plays very important role depending upon the mode of application, application rate and place of application. 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.

- (1) Cooling of hot and burning solids by the agent prior to vaporisation.

- (2) Complementary to (1) but not identical, the production of vaporized agent at hot surfaces, and
- (3) The cooling of the hot surfaces by the vaporized agents.

Thus in the cooling process, which is associated with the extinction of fires, liquid CO₂ and N₂ have a substantially lower capacity to remove heat than water. However, these liquids are vaporized more easily than water and a substantial part of the extinguishing capacity of all these agents lies in the vapour form. Therefore it may be beneficial to use liquid N₂ and CO₂ for fires where the use of water results in most of the water running off unvaporised. These type of fire may broadly be classified as those where burning surfaces cannot be directly reached by the jet. Cooling capacities of these for solids, liquids and for flames are given in the following table :

Table 2 : Thermodynamic properties of liquid agents

Agents	Pressure in atm	Boiling or sublimation point °C	Latent heat of vaporization Cal/gm	Heat content of vapour or gas Cals/gm.			
				Boiling or sublimation point °C H ₁	0-100 °C -H ₂	0-250 °C H ₃	0-1300 °C H ₄
Water	1	100	540	—	44.5	113.5	691.3
CO ₂ Liquid	21	-10	67	12.6	20.8	50.2	363.7
CO ₂ Solid	1	-78	137	15.5	-do-	-do-	-do-
N ₂	1	-196	48	49	24.8	62.4	354

Table 3 : Cooling capacities of liquid agents

Agent	Conditions	Capacity for cooling (burning cellulosic solids)	Cap. for Cooling (Burn. lqd. fire point)	Capacity for cooling flames	
				Gas alone	Gas/condensed phase
Water	15°C, 1 atm	694	None	847	1472
CO ₂	0°C, 21 atm	136	80	376	443
N ₂	-196°C, 1 atm	156	97	403	451

Thus Carbon dioxide and inert gas system have following advantages :

- (1). Cheapness
- (2). Ease and speed of refilling
- (3). Absence of contributory damage.
- (4). Shear volumetric flow rate which is safeguard against difficult conditions at time of fire.

Halogenated Hydrocarbons

Besides the liquid extinguishing agents, there are other well established extinguishing agents, which are formed by replacement of hydrogen atom or atoms from hydrocarbon by halogen atom or atoms. The halogen atom may be same as in case of carbon tetra chloride (CCl_4), which has become obsolete due to its high toxicity or of different nature as bromochloro methane (halon 1011), bromochloro difluoro methane (B.C.F. halon 1211) Bromo trifluoro methane (CF_3Br) etc. These agents extinguish the fire mainly by inhibition but cooling also plays important role though to a lesser extent. A detailed and classic review on some fundamental knowledge of flame inhibition has been reported by Raymond Fredman and Levy⁶. Wise, Rosser and their co-worker⁷ concluded that (1) for halogenated hydrocarbon compounds, compounds, containing iodine and bromine were equally effective but both being more effective than chlorine containing compounds (2) for Bromine - containing compounds the flame inhibiting effectiveness was proportional to the number of bromine atoms per molecule (3) inhibition by these agents was not accompanied by any reduction in flame temperature. The boiling points of halogenated extinguishing agents are shown below:

Agents	Boiling Point °C
CH_3Br	356
CH_2ClBr	68
CF_2ClBr	4.0
CF_2Br_2	22.8
CF_3Br	-57.9

Limiting oxygen Index method seems to be a practical means of determining the relative efficiency of volatile fire extinguishing agent.

$$\text{LOI} = \frac{0.21 (\text{Volumetric flow of air})}{\text{Volume flow of air} + \text{volume flow of agent}}$$

Where LOI is limiting oxygen Index and volume flow are expressed in cc/sec. Petrello and Sellers⁸ varied the air flow rates for 0.617 cc/sec. flowrate of propane and found Limiting Oxygen Index for inhibited propane flame. The results are shown in Fig. 5.

The main advantages of these system are their high rate of vaporization, damage of the material on which they are applied and their utility for electrical fires. The recent development is self heat actuated bromochloro difluoro methane extinguisher.

Dry powder extinguishant

Sand has been the most common extinguishing medium for combating solid fuel fires and is still used in areas where either water is unavailable or proper means of fire-fighting are not available. Since sand has limitation as its efficiency is low and it cannot be used for liquid fuel fires, hence dry chemical extinguishing powder based on sodium bicarbonate became popular in early twenties. Different research workers have developed different dry chemical powders⁹, majority of them is based on sodium/potassium bicarbonates. It can be concluded very well that flame extinguishing dry powders have one or more of the following characteristics :

- They are generally salts of alkali metals or of ammonia.
- The effectiveness of the metal cation increases with molecular weight. Thus potassium salts are more effective than sodium salts.
- The most effective anions are of two types; (a) the halides and (b) the bicarbonates.
- The chemical bonding is ionic.
- They are salts having a low melting point or decomposition temperature.
- They decompose readily in flames producing new surfaces.

Besides other properties of dry chemical powder such as its specific gravity, corrosiveness, conductivity etc., its particle size, caking and foam compatibility properties are very important. The efficiency of a dry chemical powder increases with increase in its surface area. However there is an optimum and practical limit below which decomposition of the powder occurs before it reaches flame front and above which little decomposition occurs within the residence time of particles in a flame. Proportion of different particle size fractions is also very important to improve its flow and anticaking properties. Besides particle size, certain substances decompose in flames to give solid product resulting in large surface area. Birchall¹⁰ tried bicarbonates of sodium and potassium, potassium oxalates and potassium ferrocyanide. There was apparently no change in case of sodium and potassium, bicarbonates particles passing through the flame, but in case of potassium oxalates and ferrocyanides, he found that average particle size of efflux was one micron (1μ) resulting sixty fold increase in surface area. The results are shown in fig. 6. On the basis of this finding, Harpur¹¹ developed a new chemical dry powder, which is a reaction product of alkali bicarbonate and urea named as 'Monex' which behaves in flames in a similar manner as potassium oxalate. The efflux from the flame in case of 'Monex' were of 0.01 to 0.1 micron particle size.

However the main advantage of dry powder is its capability of reducing radiation intensity virtually in no time but unfortunately this advantage is coupled with drawback which is its cooling-incapability. These two opposite properties exist together require another extinguishing medium which should be used in conjunction with dry chemical powder in case of big fires such as aircraft fire or petro-chemical industrial fires etc. Since it has to be used in conjunction with foam, dry chemical powder thus used for reducing radiation intensity must be compatible with mechanical foam which is to be used for cooling the flammable material below ignition temperature besides blanketing effect. Harpur also claimed that 'Monex' possesses a high degree of compatibility with protein foams,

Foam Systems

The extinction of a flammable liquid fire with foam is a blanketing mechanism in which the foam layer, spreading on the flammable liquid progressively, shields its surface from the flames radiation thereby reducing the rate of evaporation from the surface and thus starving the flame zone of the flammable vapours necessary for combustion. Since flame zone does not get minimum flow rate of vapours, it collapses and causes extinction of fire. Laurent in 1904 first used chemical foam to extinguish naphtha fire. Wagner in 1927 developed a mechanical foam by the mechanical agitation of a foam producing liquid, water and air. Then came the use of protein based foam liquids or compounds which can be derived from the most varied sources such as blood, skin, bones, hoof, horn, feathers, crushed grain and residues of vegetable oils which contain vegetable protein and a variety of other substances. Protein foam compounds produce a highly stable foam whose stability can be further increased by the addition of salts of heavy metals. Some fluoro-chemical agents when added to protein based liquid increases its fluidity, stability and efficiency beyond the level attainable by normal protein liquids. However in recent years, there has been a significant increase in the production of surfactant which are used in the form of solutions and foam concentrate for different branches of industry. Surface active foam compounds and solutions are of particular importance for fire-fighting, since small amount of these when added to water not only increases its efficiency (app. two times) but also reduces extinction time in addition to minimizing the damage to property caused by excessive application of water. The properties normally used to describe a foam are (a) expansion (b) critical shear stress and its drainage characteristics. The value of these properties are dependent upon the foam liquid used, its concentration in solution and the type of foam-making equipment employed. However drainage characteristics of foams are affected by the flammable liquid to be extinguished.

The most recent development in this field is development of light water which is a new Synthe-

tic, foam forming concentrate for flammable liquid fire extinguishment. When it is used in suitable foam making equipment of the mechanical or air foam type, it generates a white, non-toxic, vapour action which is unique in itself.

Los Angeles city fire services¹² carried out comparative evaluation of protein foam and light-water. The results obtained by them and analysed by Hy-Cal Engineering are shown in a tabular form:

nations participated. These companies between themselves marketed different kind of foam compounds. As reported by a Soviet author¹³ out of these 24 foam compounds products, 3° percent were protein based foam compounds, 20 percent were based on surface active agents (synthetic), 21 percent were fluoroprotein foams and 12 percent were fluorosynthetic. Thus 60 percent were protein based and 40 percent were synthetic type of foam compounds. However despite the good stable characteristics of protein foam compounds,

Table 4 : Comparative Evaluation of Protein Foam and Light Water

Test No.	Max. intensity BTU/ft ² /hr	Fire area sq. ft	Distance from feet	Type	Fuel Volume gallon	Extn. Agent	Time to ext. Sec.
2A	225	1000	70	JP ₄	300	Light water	29.65
2B	190	1000	70	JP ₄	300	Protein	52.41
3A	135	1000	70	..	300	Protein	31.20
3B	98	1000	70	..	300	Light water	11.58
4A	120	2730	100	..	900	-do-	35.00
4B	130	2730	100	..	900	Protein	77.33
5A	215	2730	99	..	1000	Protein	46.79
5B	100	2730	99	..	1000	Light water	12.83

The effectiveness of both the extinguishing media for suppressing the flame intensities are shown in Fig. 7. There was marked difference between the performance of light water and protein foam for different application rates. Fig. 8 shows the effect of application rate of both the extinguishment media on extinguishment rate.

Fuel containing a proportion of water miscible flammable liquid are, of course, very damaging to foam. Thus an admixture of 20 percent of wood alcohol to straight petrol can increase the critical rate of application of normal protein foam by a factor of 3 to 8 depending upon the application whether it is gentle or forceful. However fluoroprotein and fluorochemical foams are less susceptible to this effect than protein foam.

An International Exhibition was held in U.S. S.R. "Fire Fighting Technique 75" where number of industrial companies from industrially developed

their low efficiency leads to high rates of consumption.

Discussion and Conclusion

All extinguishing media as discussed above are not suitable for all types of fires. Depending on the nature of combustible material, the use of a particular dual extinguishing medium media can be recommended. However the extinguishing efficiency of a known extinguishing medium can be increased sufficiently by using the medium with suitable appliances keeping in mind that its main purpose is either to extract maximum heat from fire or combustible material or to stop air supply to combustion zone or to blanket the fuel surface so that fuel vapour may not contribute in keeping combustion zone alive; thus water, if used as available in nature with ordinary nozzle will extinguish the fire, but if the same is used with wetting agent, its superiority can be

noticed very easily by observing rapid reduction of fire intensity which will allow the fireman to move in more quickly. The wetting agent can be mixed either in reservoir or in extinguisher but a method may be used by which wetting agent can be directly induced to the nozzle from where water is being applied. Similarly droptime of water should be so adjusted so that maximum quantity of water is evaporated. In case of chemical dry powders, the powders which are being developed or already developed are primarily based on the decomposition of the powder particles in a flame which not only have the smothering effect but also appreciably cut back supply of radiation from flame to fuel. Thus the efficiency of powder will depend on the density of cloud formation which not only depends upon the dry powder but also on the extinguisher nozzle and carbon dioxide expulsion rate. Besides these, it is very important for a dry powder to be foam compatible also with which it is to be used to control big petrochemical or aircraft fires. Chemical foams have been obsolete in developed countries and mechanical foams are being used to a greater extent to combat flammable liquid fires. However fluoro-carbon surfactants (light water) is finding more applicability in large fires than protein foams. But it is fire services personnel or fire-fighters who have to use their discretion in fighting a fire for selecting which extinguishing medium will be best suited for them and how they can attack the particular fire keeping in mind that fire will not spread to the surroundings. Hence the feed-back from the fire-fighters will be a great help to a scientist or to a design engineer for the effective development of fire extinguishing medium and appliances.

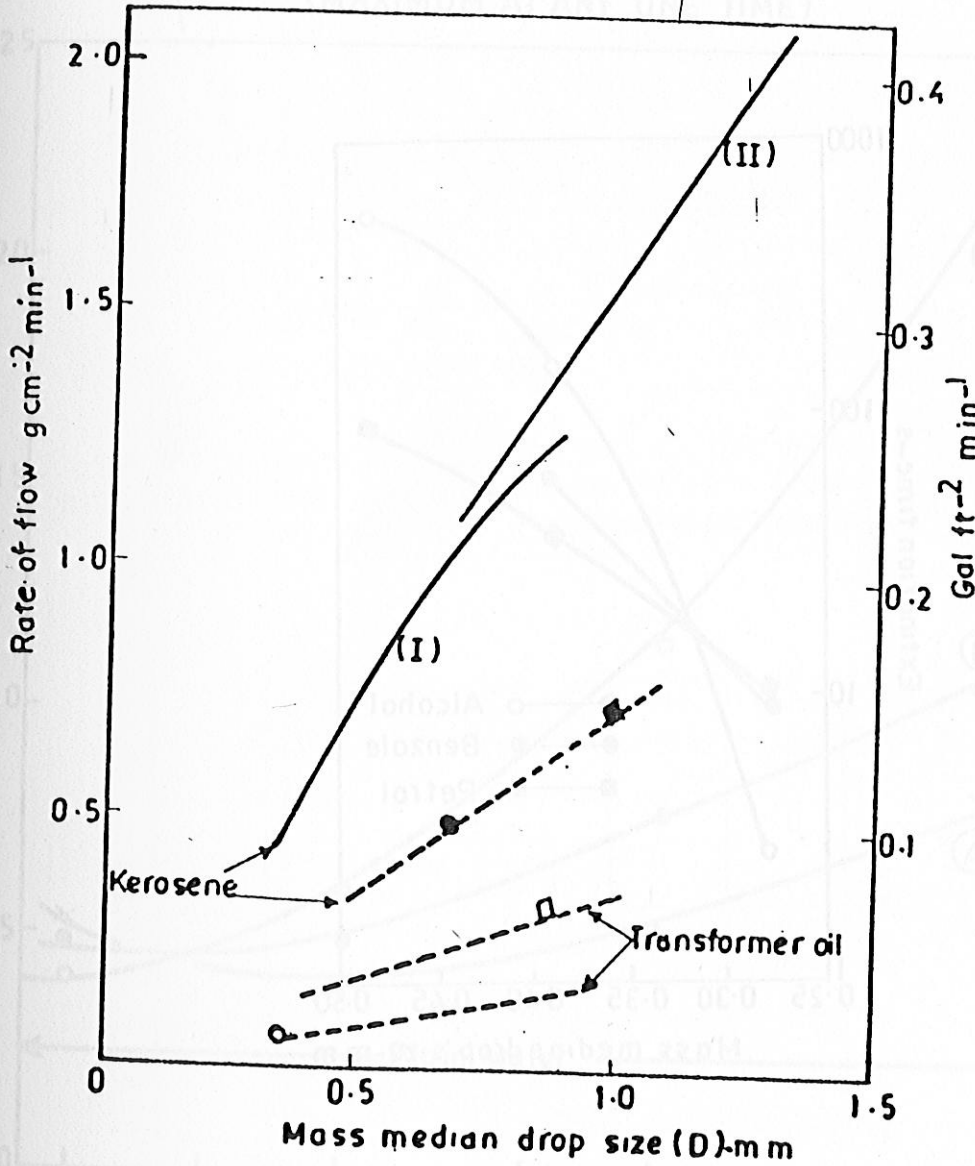
ACKNOWLEDGEMENT

The authors are grateful to Dr G.N. Badami, Head, Fire Research for his guidance and to Prof. Dinesh Mohan, Director, Central Building Research Institute, Roorkee for according his kind permission for publication of this paper.

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FIG-1-EFFECT OF MASS MEDIAN DROP SIZE ON CRITICAL RATE OF APPLICATION FOR KEROSENE AND TRANSFORMER OIL.



1. 30cm Ø KEROSENE FIRE SPRAY APPLIED DOWNWARDS
2. 11cm Ø KEROSENE FIRE SPRAY APPLIED DOWNWARDS

FIG:-2.EFFECT OF MASS MEDIAN DROP SIZE ON EXTINCTION TIME OF VOLATILE LIQUIDS

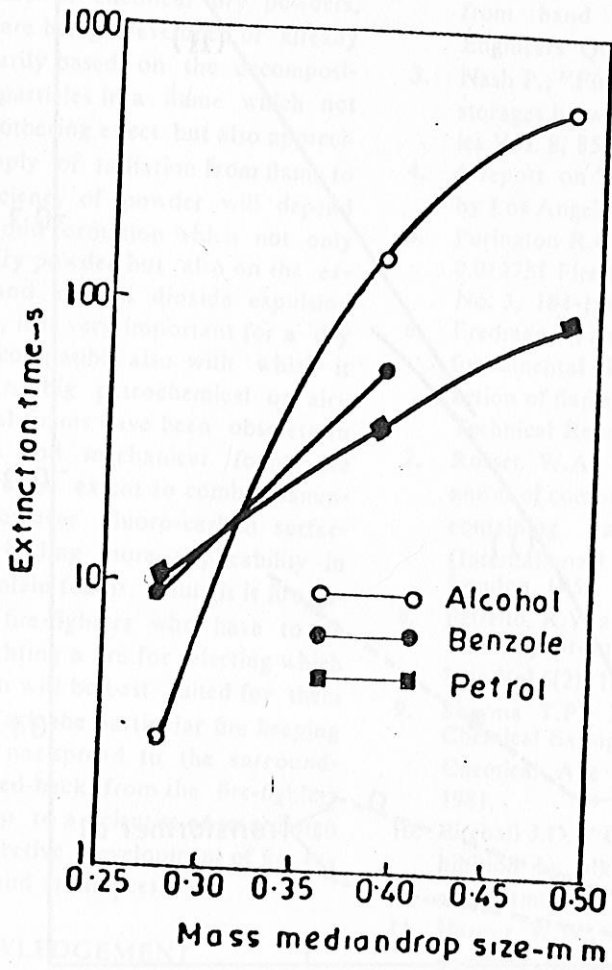
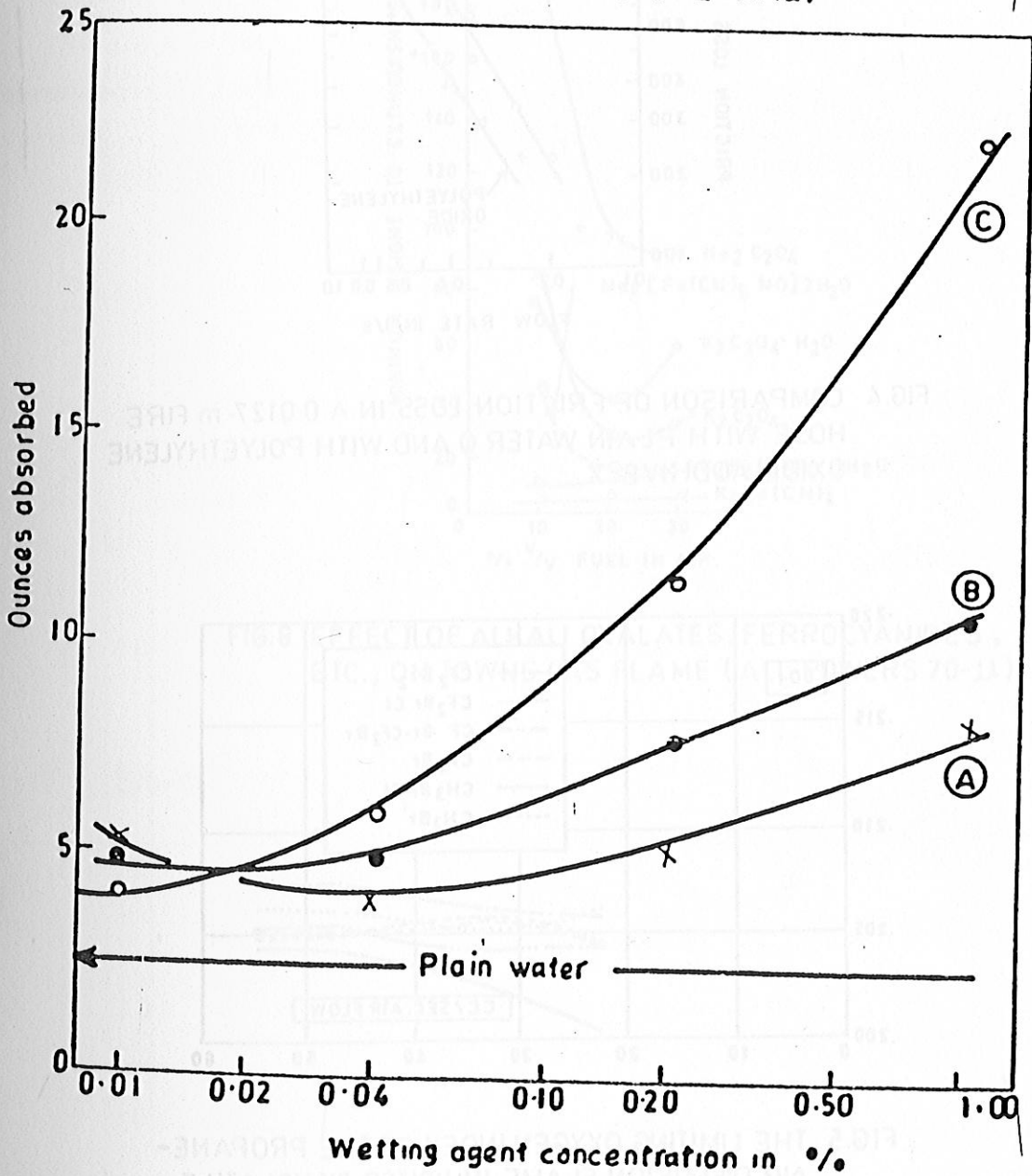


FIG- 3.
MODIFIED ASTM D 583 63
CONCENTRATION VS. TOTAL MIXTURE ABSORBED
(MAXIMUM AT ANY ONE TIME)



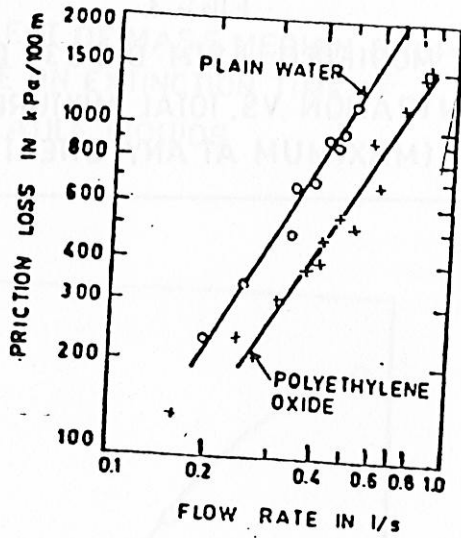


FIG.4 COMPARISON OF FRICTION LOSS IN A 0.0127-m FIRE HOSE WITH PLAIN WATER O AND WITH POLYETHYLENE OXIDE ADDITIVE X

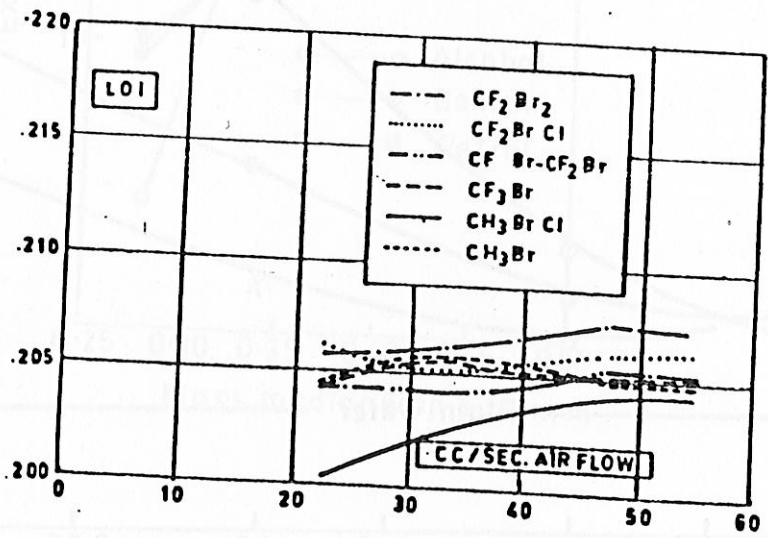


FIG.5 THE LIMITING OXYGEN INDEX OF THE PROPANE-AIR DIFFUSION FLAME INHIBITED BY VOLATILE HALOGENATED AGENTS.

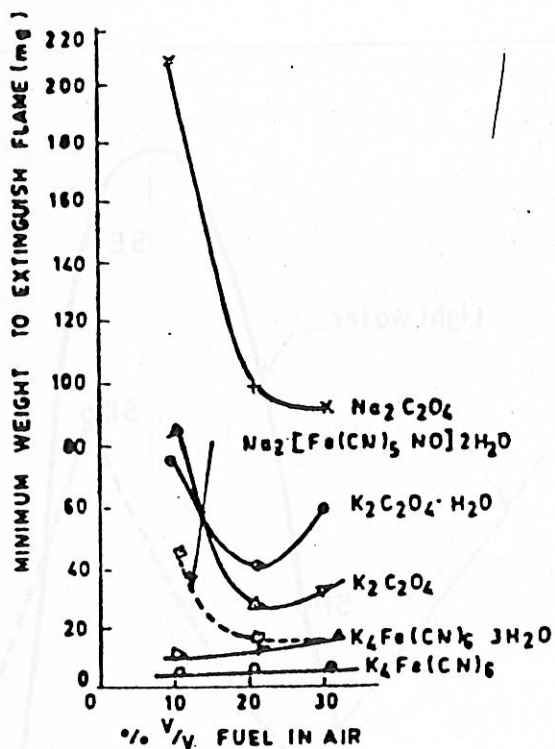


FIG.6 EFFECT OF ALKALI OXALATES, FERROCYANIDES, ETC., ON TOWNS GAS FLAME (ALL POWERS 70- μ)

FIG-7· FLAME INTENSITY VS. TIME - TEST NO.2

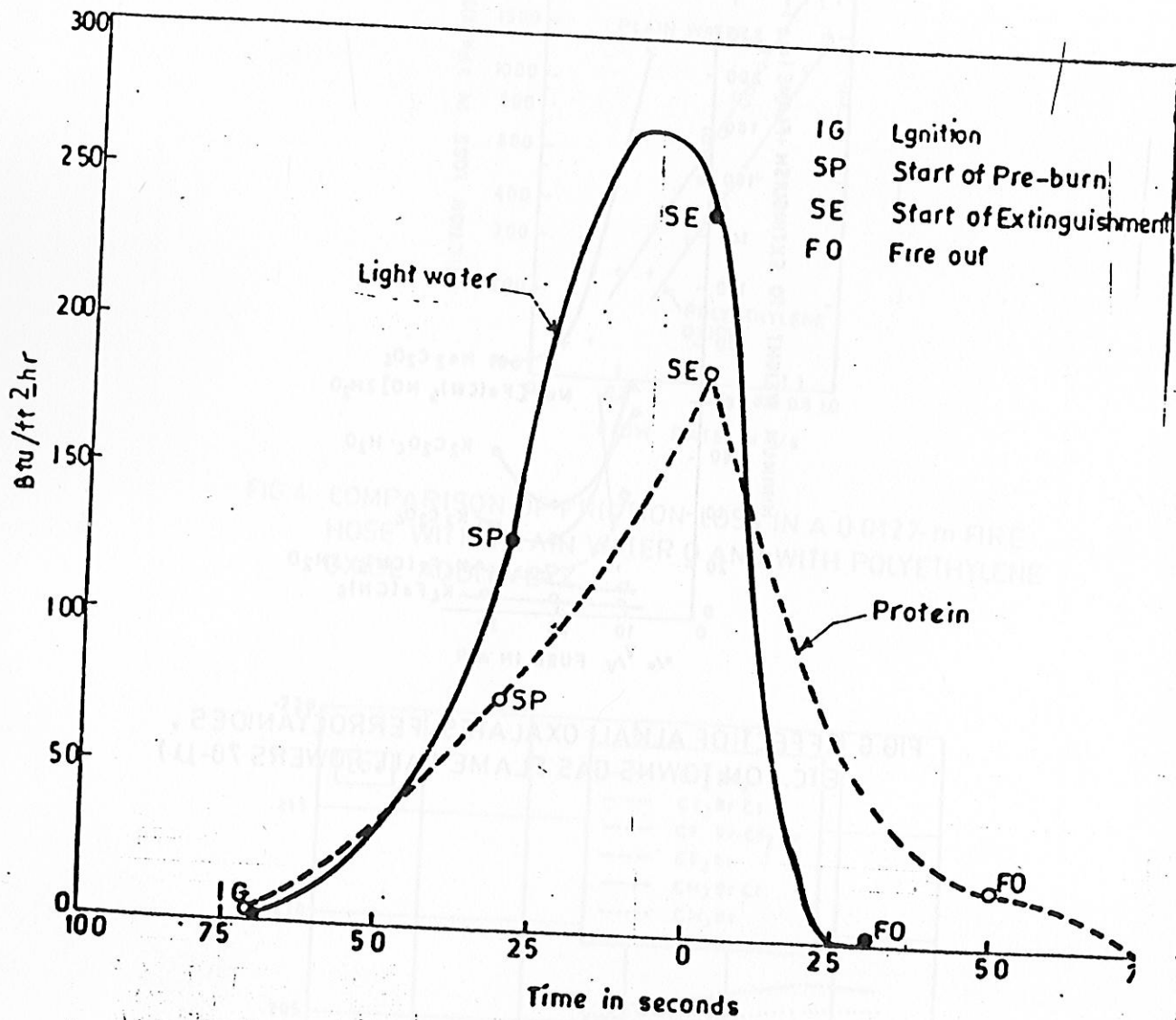


FIG-6-EXTINGUISHMENT RATE VS. APPLICATION RATE OF FOAM

