Fire Research Note

NO. 604

INHIBITION OF THE COMBUSTION OF LIQUID AND
   GASEOUS FUELS BY FINELY DIVIDED INORGANIC
   SALTS:
      - A LITERATURE REVIEW

      by

P. F. THORNE

FIRE

RESEARCH

STATION

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FUELS BY FINELY DIVIDED INORGANIC SALTS:
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SUMMARY

A detailed literature review of the inhibition of the combustion of
gaseous and liquid fuels by finely divided solids is presented.

On the basis of this review, some conclusions concerning effective dry
powder fire extinguishing agents are drawn.

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INHIBITION OF THE COMBUSTION OF LIQUID AND GASEOUS
FUELS BY FINELY DIVIDED INORGANIC SALTS:
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Introduction

The inhibition of combustion processes by organic and inorganic substances is widely known. Among the most common examples are inert gases and halogenated hydrocarbons. Both these classes of substances are used as fire extinguishing agents, among the best known examples are carbon dioxide (an inert gas) and chlorobromomethane (an halogenated hydrocarbon). The mechanism of inhibition is not the same for these two classes. Inert gases inhibit by the physical mechanism of cooling and dilution whereas the halogenated hydrocarbons, in general, interfere chemically with the combustion process.

The ability of inorganic salts, especially the salts of the alkali metals, to inhibit combustion was first mentioned by Dautriche[1] who observed the effect of sodium and potassium salts on "muzzle flash". Other common examples of the inhibiting power of inorganic salts include the fact that blast furnace gases burn regularly only when potassium salts held in suspension are removed[2], and the use of potassium salts to suppress 'after burning' in aircraft engines. The most common use of inorganic salts in this connection, especially in the form of a finely divided solid, is as fire extinguishing agents. Such use was first patented by Block[3] in the United States in 1928. Other finely divided solids, besides inorganic salts, such as certain organic salts (e.g. oxalates) and 'inert' solids (e.g. silica) are capable of extinguishing flame.

In general, as in the case of gaseous inhibitors, two different extinction mechanisms can be postulated and demonstrated. The one is a physical mechanism in which heat abstraction by the solid particles plays the major part and the other is a chemical mechanism in which interference with the combustion mechanism predominates.

This review covers the literature concerning the inhibition of the combustion of liquid and gaseous fuels by finely divided solids - inorganic salts, organic salts and 'inert' solids. The inhibition of combustion by inorganic salts in other physical forms e.g. aqueous solutions, salt and alkali metal vapour and surfaces coated with salts is also considered.

Friedman and Levy[4][5][6] and Skinner[7][8][9] have produced series of reviews covering many aspects of flame inhibition and extinction, including a consideration of finely divided solids, but generally not in any great detail. Hird[10] has reviewed the use of finely divided solids as flame extinguishers.

2. Inhibition of premixed flames

2.1. Premixed flames propagating in tubes

The majority of the experimental work has been performed with premixed flames propagating in tubes. The earliest interest was in the prevention of the ignition, especially by explosive charges, of inflammable fire-damp/air mixtures in coal mines, and most work has been concerned with the inhibition of methane/air flames.

Jorissen and co-workers[11] during their work on the inhibiting effect of different substances on combustion reactions were among the firs t to investigate the effect of finely divided solids on flame propagation in any detail. They attempted to ignite 10 per cent methane in air mixtures in tubes in which finely divided powders had been dispersed. They found that sodium chloride, potassium chloride, sodium bicarbonate, potassium bicarbonate, sodium fluoride, potassium antimonyl tartrate ("tartar emetic"), potassium pyrosulphate, barium nitrate and mercuric chloride were effective inhibitors.

Dufraisse et al[33][34] following experiments with gaseous diffusion flames (to be described later) found that inert substances such as talc were unable to attenuate coal gas/air flames propagating in tubes when the maximum quantity possible with the particular apparatus was dispersed, as a cloud, in the tube. On the other hand a mixture of 90 per cent potassium oxalate and 10 per cent silica and a mixture of 90 per cent potassium nitrate and 10 per cent silica were both very efficient inhibitors. Although it was one of the less efficient extinguishers of a coal gas diffusion flame, sodium silicofluoride was twice as efficient as the oxalate mixture in attenuating premixed flames.

Dijsksman[12] using a technique similar to that of Jorissen et al[11], was the first to demonstrate the importance of particle size. The weight required for extinction was proportional, within the range of sizes investigated, to the mean particle size. Thus the efficiency was inversely proportional to the particle size. Potassium chloride and sodium bicarbonate were found to be effective; barium sulphate, sodium silicafluoride and aluminium silicate were less effective and stone dust much less effective. The fuel/air ratio was also an important factor.

Jorissen, Snidjers and Vink[13] used a closed bomb technique in which dust was dispersed inside a $\frac{1}{2}$ litre spherical vessel by a jet of methane and spark ignition was attempted. The amount of powder, particle diameter being in the range $75\mu - 105\mu$, required to prevent ignition, in mg., was found. The results are summarized in Table 1.

Table 1

Powder dp : $75\mu- 105\mu$	Weight required to prevent ignition (mg.)
Lithium fluoride	<1
Lithium sulphate	40-42
Sodium fluoride	<1.5
Sodium chloride	<2
Sodium bromide	4-6
Sodium iodide	5-7
Potassium fluoride	1-2
" chloride	8-9
" bromide	8-9
" iodide	9-10
Calcium fluoride	2-3
Ground fluorspar	<1
Barium chloride	35-38
Barium nitrate	35-38
Barium sulphate	38-40
Barium oxide	23-25

Dolan and Dempster[14] propagated flames in vertical tubes, open at the top and closed at the bottom, firing end, upwards through methane/air mixtures into which a known quantity of powder had been uniformly dispersed. Ignition was by a spark. Using powders of mean particle size 5μ- 10μ they found that the important parameter was the surface area of the solid particles per unit volume of inflammable gas/dust mixture (cm^2/ml). They measured two dust concentrations as a function of fuel/air ratio:

1) 'Suppression Point' : at this condition flame is confined to a small kernel at the spark gap.

2) 'Quenching Point' : at this condition flame just propagates the full length of the tube.

Of the two, the 'Suppression Point' was the more definite condition.

Within the range of particle sizes investigated, it was found that the surface area of the powder per unit volume of mixture was essentially constant at each condition. For sodium bicarbonate and a 9.8 per cent mixture of methane in air, the concentrations required were those shown in Table 2.

<div align="center">Table 2</div>

Average Particle diameter (μ)	Specific surface (cm^2/gm)	Concentration at suppression		Concentration at quenching	
		gm/1	cm^2/ml	gm/1	cm^2/ml
2.4	11,500	0.066	0.760	0.046	0.530
5.9	4,600	0.160	0.740	0.112	0.520
8.5	3,200	0.231	0.740	0.158	0.510

The surface area concentrations at the suppression point with 9.8 per cent methane in air mixtures, for various substances, are given in Table 3.

<div align="center">Table 3</div>

Substance	Specific surface (cm^2/gm)	Suppression point (cm^2/ml)	Quenching point (cm^2/ml)
Aluminium chloride	1400	0.10	–
Ammonium bicarbonate	1200	0.27	–
Sodium sulphate	1200	0.50	–
Sodium sulphate – exsicated	6200	0.54	–
Potassium acetate-trihydrate	7600	0.87	–
Potassium carbonate	8000	0.91	–
Cuprous oxide	4000	0.92	–
Cobaltous chloride (hexahydrate)	2200	0.99	–
Barium hydroxide (octahydrate)	6400	2.48	–
Copper acetate	13200	2.66	–
Ammonium chloride	4200	–	0.80
Sodium carbonate	5500	–	0.98
Sodium sulphate (decahydrate)	3500	–	1.00
Barium chloride	6300	–	2.19
Sodium bicarbonate	11500 – 3200	0.76	0.52
Sodium chloride	6500 – 2300	1.84	0.57
Potassium fluoride	800	0.25	0.08
Potassium iodide	900	0.50	0.04
Sodium aluminium fluoride	2200	0.61	0.40
Potassium chloride	5700	0.64	0.40
Sodium silica-fluoride	8000	0.68	0.47

It can be seen that for suppression, potassium compounds are more effective than the corresponding sodium compounds, halides are better than carbonates and amongst the halides the order of increasing effectiveness is chloride, iodide, fluoride. Broadly speaking, Dolan and Dempster found that salts melting or decomposing below $200^{o}C$ were the most effective, exceptions being the alkali metal salts and cuprous oxide. Substances decomposing above $200^{o}C$ were generally ineffective. The only hydrated salts to be effective were cobaltous chloride and barium hydroxide. Cobaltous chloride loses its water of crystallisation below $100^{o}C$ and may also sublime. The following substances were ineffective:

Chalk	Magnesium sulphate decahydrate
Magnesium carbonate	Ammonium nitrate
Cupric carbonate	Litharge
Lead acetate	Sodium thio-sulphate
Barium sulphate	Zinc sulphate
Cupric oxide	Hydrated zinc sulphite
Silica	Talc
Alum	

Dolan and Dempster assume a minimum flame temperature for sustained propagation of $1330^{o}C$ and by assuming thermal equilibrium between powder particles and gas calculated, by a graphical method, equilibrium temperatures for a number of substances which are given in Table 4.

Table 4

Substance	Concentration at suppression (cm^2/ml)	Equilibrium temperature (^{o}C)
Ferric oxide	15.0	1230
Potassium fluoride	0.25	1500
Potassium iodide	0.50	1500
Potassium chloride	0.64	1650
Sodium chloride	1.84	1400
Sodium aluminium-fluoride	0.61	1600

Thus only ferric oxide cooled the gases below the minimum required for propagation. Two distinct mechanisms of extinction were proposed.

(1) A physical mechanism in which flame is extinguished by heat abstraction by the powder particles.

(2) A chemical mechanism in which complete or partial vaporisation of the particles occurs, followed by interference of the combustion process by the salt vapour.

Dolan[15] subsequently showed that quenching occurred, for any given substance, at the same linear flame velocity, i.e. flame temperature, thus indicating a thermal mechanism. On the other hand the concentration at suppression is at all times size dependent and not weight dependent even for very small particles for which the assumption of thermal equilibrium can be justified; this would indicate a mechanism dependent on surface area rather than heat capacity. The energy input of the ignition source was also important.

Laffitte and co-workers have investigated the effect of finely-divided solids on both deflagrations[16][18] and detonations[17][18][19][20]. In this work, weighed quantities of powder were dispersed by the shock wave travelling ahead of the deflagrating combustion wave. Within the range 25μ - 100μ extinguishing efficiency increased as particle size decreased except for potassium and sodium oxalates, alumina and silica, for which efficiencies were but little dependent on particle size. The oxalates were, at 100μ diameter, more efficient than other salts at 25μ diameter. (See Table 5).

Table 5

Substance	Quantity required to extinguish 9 per cent CH_4/air flame (mg.)			
	d = 100μ	75μ	50μ	25μ
Potassium chloride	80	41	20.5	10
Sodium chloride	160	62	32	9.5
Potassium sulphate	48	41	18	4.0
Sodium sulphate (decahydrate)	51	45	21	4.5
Potassium chlorate	57	42	19	4.5
Sodium chlorate	115	57	21	4.8
Potassium chromate	85	67	51	5.7
Sodium chromate	105	65	31	6.2
Potassium bitartrate	50	17	12	6.0
Sodium bitartrate	25	20.5	17	6.5
Potassium oxalate	2.5	2.5	2	0.8
Sodium oxalate	3.5	3.5	3	1.4
Ferric oxide	130	130	46	30
Aluminium oxide	38	37	37	37
Silica	46	46	45	44

Differences between substances are minimised at 25μ. In the work on detonations the powder was dispersed mechanically into the path of the detonation wave. Detonations could be attenuated completely or degraded into deflagrations. For methane/air detonations and powders of mean diameter within the range 5μ - 20μ, sodium bitartrate appeared to be the least effective substances whilst silica was one of the best, on the basis of the total surface area required. However, comparisons are

difficult as no indication was given of the densities of the dispersions. The mechanism of the extinction of detonations appeared to be basically that of the dissociation of the combustion wave from the pressure wave and the subsequent quenching of the combustion wave.

Rosser, Inami and Wise[21] measured the velocities of stoichiometric methane/air flames propagating upwards in tubes, 6 cm I.D. through uniform suspensions of various powders with mean particle diameters in the range $3\mu - 11\mu$.

With a given powder, the flame speed decreased linearly with increase in powder concentration until a flame speed of 15 cm/sec was reached; thereafter any increase in powder concentration resulted in little or no further decrease in flame speed. From the results of Rosser et al[21] Table 6 has been compiled, which shows the concentrations of powder required to reduce the flame speed to 15 cm/sec.

<p align="center">Table 6</p>

Substance	Particle diameter (μ)	Specific surface (cm^2/gm)	Weight concentration mg/ml	Surface concentration cm^2/ml
Sodium carbonate {	4.9	4940	0.010	0.049
	2.2	10800	0.0058	0.062
Sodium bicarbonate {	3.5	7760	0.028	0.195
	2.3	11900	0.0115	0.136
Potassium bicarbonate	2.2	12400	0.006	0.075
Sodium chloride	6.0	4500	0.013	0.057
Cuprous chloride	5.7	3000	0.017	0.051
Potassium sulphate	4.3	5200	0.010	0.052

Potassium bicarbonate is about twice as effective as sodium bicarbonate. The differences between different sizes of the same powders may be due to agglomeration especially with the very fine powders; thus the impression that the cuprous chloride is more efficient than potassium bicarbonate may be false.

Sodium bromide and sodium fluoride were found to be good inhibitors although poor dispersibility prevented precise results from being obtained. Calcium hydroxide, calcium carbonate and calcium fluoride were not good. The authors present a theoretical analysis of the temperature history of a particle on passing through a flame front and show that for those powders which were found to be effective inhibitors, a significant amount of evaporation occurs.

Their hypothesis is that the evaporated material then decomposes or reacts to liberate metal atoms which then inhibit the combustion process. In support of this proposition, experiments are described in which a small amount of methyl chloride, not in itself enough to reduce the flame speed significantly in the absence of powders, was added to the methane/air mixture. Under these conditions, the effectiveness of sodium carbonate was approximately halved.

The carbonate was thought to decompose after evaporation producing sodium atoms, the concentration of which was reduced by reaction with chlorine produced by the decomposition of the methyl chloride to form sodium chloride which was, in itself, relatively inactive. In the case of sodium chloride, sodium atoms were thought to be produced by the following reaction.

$$NaCl + H \quad Na + HCl$$

The reaction would not be complete and sodium chloride would be present together with sodium atoms and a little hydroxide, the sodium atoms themselves being the only active inhibiting species. Thus the effectiveness of a substance would depend not only upon the volatility but also upon the availability of the metal atoms produced after evaporation had occurred. It was thought that the ability to inhibit combustion was not limited only to alkali metal atoms in view of the similar results obtained with sodium chloride and cuprous chloride, the volatilities of which are similar. A suggested mechanism for sodium was as follows.

$$OH + Na \overset{M}{} NaOH \qquad M = a \text{ third body}$$

$$H + NaOH \quad Na + H_2O$$
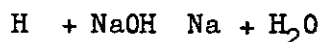
Chemical inhibition could only reduce the concentration of reactive radicals in the flame zone to that in the post-flame gases. Any further reduction could only occur in the presence of a gross reduction in temperature. Therefore heat losses, both to powder particles and to any containing walls must administer a "coup de grace". This view is consistent with the fact that the efficiencies of the powders are greatly reduced below a flame speed of 15 cm/sec.

2.2. **Premixed flames stabilized on burners**

Levy and Friedman[22][23] have studied the effect of aluminium chloride vapour on premixed methane/air flames at 200°C. Burning velocity decreased with increase in inhibitor concentration but flattened out at high concentrations. Stoichiometric and rich flames were affected more than lean flames. It is known that the inhibiting effect of halogenated methanes increases with increase in the number of halogen atoms and on the assumption that the inhibiting effectiveness of chlorine is essentially independant of the nature of the chlorine carrier, it would be expected that aluminium chloride (Al_2Cl_6) would be half as effective again as carbon tetrachloride (CCl_4) on a molar basis. Levy and Friedman found that this was approximately so and concluded that in the case of aluminium chloride, the mechanism of extinction was similar to that of carbon tetrachloride, i.e. a mechanism involving chlorine atoms.

These authors later[24][25] added the vapours of alkali metals and alkali metal salts to premixed and diffusion flames. With premixed flames, burning velocity was reduced by the addition of alkali metal salt vapour. The species thought responsible for the removal of chain carriers, in the case of potassium, was potassium hydroxide which would be readily produced early in the flame. The following reactions were suggested.

$$KOH + H \quad HOH + K$$
$$KOH + OH \quad HOH + KO$$

Elemental potassium was found not to inhibit diffusion flames (under the particular experimental conditions) and this was attributed to the slow rate of conversion to potassium hydroxide via the reactions possible in a diffusion flame.

Dunderdale and Durie[26] have investigated the nature of deposits formed on a stainless steel probe placed in a stoichiometric propane/air flame to which sodium had been added in various forms, e.g. metal vapour, sodium chloride, sulphate, carbonate and oxalate.   It was found that sodium sulphate produced deposits of sulphate, sulphite and carbonate; the sulphate being concentrated towards the edge of the flame.   In lean mixtures, the amounts of carbonate decreased whilst sulphite was found only in fuel rich mixtures. Sodium chloride produced deposits of chloride only.   Sodium oxalate produced carbonate deposits and traces of hydroxide.   Elemental sodium vapour produced carbonate and a probe coating of hydroxide was converted to carbonate air a flame containing no additive.   It was thought that the alkali metal hydroxide was produced early in the flame which, in the absence of any other anion-forming entity was rapidly converted to carbonate.   When other anion forming entities are present then other salts are formed in the order

$$SO_4^{--}, \quad Cl^-, \quad SO_3^{--}, \quad CO_3^{--}, \quad OH^-$$
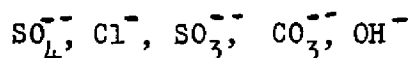
Dewitte et al[27] have studied the effect of particles of mean diameter in the range 20μ to 100μ on methane/oxygen/nitrogen and propylene/oxygen/nitrogen flames stabilised on an inverted burner (introducing the powder with the fuel/air mixture).   They measured the effect of mass concentration on flame temperature and burning velocity.   The mass concentration required to extinguish a flame decreased with increasing flow rate until at flow rates approaching "blow off", the amounts of powder required were very small.   The powder concentration at zero flow rate was obtained by extrapolation and taken as the standard measurement.

Two types of substance was investigated, thermal inhibitors which reduced the flame temperature, and 'chemical' inhibitors which increased the flame front thickness.   In the case of alumina, mean particle diameter 20μ, the flame temperature at extinction was found to be the lower limit temperature.   It was believed that none of the powders evaporated or decomposed in any way on passing through the flame as no change could be detected upon microscopic examination, and no decomposition products could be detected in post-flame gases.   The proposed mechanism for 'thermal' inhibitors, which incidentally were noticed to be compounds of a covalent nature, was that of cooling only, the relative efficiencies of the various powders being reflected in the relative heat capacities of the substances.   The mechanism for 'chemical' inhibitors was one of destruction of active radicals at the surfaces of the particles only. Differences between substances were reflected by the ease with which a free electron can be made available to a colliding radical, for adsorption.   This would be more readily provided by a substance having a polar bond.   Differences between the alkali halides reflected the energy necessary to bring an electron from the crystal lattice to the particle surface.

The reaction scheme suggested is

$$R + M \rightarrow RM$$
$$RM + R' \rightarrow RR' + M$$
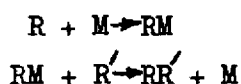
Where R R' are free radicals and M is a third body such as the particle surface.

Relative efficiencies ($\mathcal{E}R$) were calculated, these being the reciprocal of the weight required to reduce the burning by a given amount, and are expressed on a basis of $\mathcal{E}_R = 1$ for potassum sulphate in Table 7.

Table 7

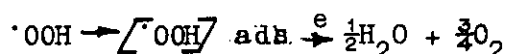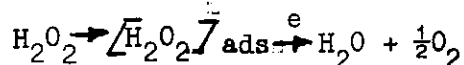| Substance	$\mathcal{E}_R$
Lead oxide	3.1
Potassium chromate	2.7
Sodium sulphite	1.7
Potassium carbonate	1.4
Barium nitrate	1.3
Aluminium chloride	1.2
Potassium sulphate	1.0
Cupric chloride	0.8
Potassium iodide	0.7
Potassium nitrate	0.6
Potassium bromide	0.5
Potassium chloride	0.4
Sodium carbonate	0.4
Sodium nitrate	0.3
Sodium chloride	0.2
Ammonium chloride	0.2

The authors calculated that the interparticle distances were of the same order as the quenching distance (0.3 mm) and the whole process of heterogeneous inhibition was considered to be that of quenching at solid surfaces. However, certain effects of heat capacity and of the chemical nature of the surface were noticed which have not been a general feature of quenching distance measurements using techniques such as the 'flash back' method involving a parallel plate burner. This will be discussed in the following section.

2.3. Effect of surface coatings on quenching distances, spontaneous ignition and flammability limits

Potter[28] in his comprehensive review of flame quenching by solid walls has discussed the effects of wall coatings on quenching distances. Quenching surfaces of nickel, platinum, bright gold, roughened gold, potassium chloride, water glass, clean pyrex and pyrex coated with various salts showed no detectable differences when quenching distances were measured using the "flashback" technique. However, workers measuring low pressure flammability limits have observed that tubes when evacuated at very low pressures for long periods quench flames at higher pressures than the normal limiting pressure.

Once a flame has passed through the tube, the normal limit is observed. Smith[29] has shown that the efficiencies of various surfaces for recombination of hydrogen atoms depends on the degree of dryness of the surface, very dry surfaces being the most active. Thus it seems likely that the surfaces in the "flashback" experiments were poisoned by adsorbed water, being exposed to the combustion products from the flame which is stabilised by the quenching surfaces. The effect of surface coatings on slow combustion and explosion limits in closed vessels has been reviewed and discussed by Minkoff and Tipper[30]. In general three classes of surface can be distinguished.

(i) Acidic surfaces which are capable of donating protons. This class includes surfaces treated with hydrofluoric acid and titanium dioxide. Hydrogen peroxide is preserved on these surfaces and the $\cdot OOH$ radical is either preserved or converted to H_2O_2.

(ii) Surfaces which are strong donators of electrons e.g. silver and gold. Both H_2O_2 and $\cdot OOH$ radicals are destroyed on these surfaces by reactions involving adsorption on the surface.

$$H_2O_2 \rightarrow \overline{/H_2O_2/} \text{ ads} \xrightarrow{e} H_2O + \tfrac{1}{2}O_2$$

$$\cdot OOH \rightarrow \overline{/\cdot OOH/} \text{ ads} \xrightarrow{e} \tfrac{1}{2}H_2O + \tfrac{3}{4}O_2$$

(iii) Surfaces which are intermediate between classes (i) and (ii). This class includes metal oxides and salts. H_2O_2 and $\cdot OOH$ are destroyed by reactions similar to those in Class (ii).

The effectiveness of a surface as an inhibitor thus depends in part on its ability to retain an adsorbed chain propagating species for a sufficient time for a termination reaction to occur.

Jorissen and Lebink[31] investigated the effect of surface coatings on the combustion of mixtures of methane and oxygen by measuring the minimum temperature at which detectable reaction occurred when such mixtures were passed through heated tubes coated on the inside. The minimum temperatures increased in the following order for the alkali metals.

Li   Na   K   Rb

and for the halides in the order

F   Cl   Br   I

3. Inhibition of Diffusion Flames

3.1. Gaseous diffusion flames

Calcium oxide coated with bismuth will luminesce when placed in a hydrogen diffusion flame, due to the impact of free hydrogen atoms. Stephens et al[32] added alkali halide vapour to an hydrogen diffusion flame and noted that the luminescence mentioned above was quenched, indicating a significant reduction in the concentration of hydrogen atoms in the flame. The vapours of sodium chloride, potassium chloride, thallous chloride and metallic lead were effective in this way. Other substances, e.g. SO_2, CH_4, CO_2, C_6H_6 were capable of quenching the luminescence and also the D-lines of sodium in a hydrogen diffusion flame containing sodium. Thus it was concluded that

atomic sodium was produced in a hydrogen diffusion flame by a mechanism involving atomic hydrogen:

$$i.e. \quad H + NaX \rightarrow Na + HX$$

similarly for potassium.

The above reaction is sufficiently rapid to effect a significant reduction in the concentration of hydrogen atoms in the flame.

In the screening tests of Dufraisse et al[33][34], already mentioned, over 250 different substances were tested by injecting weighed quantities of powder into a coal gas diffusion flame. A limited number of powders were also tested on hydrogen, methane and carbon monoxide flames. It was found that sodium and potassium chlorates intensified the combustion of hydrogen and coal gas due possibly to the release of oxygen on decomposition. In general the order of ease of extinction of the flames was carbon monoxide, methane, coal gas, hydrogen. Potassium bicarbonate was better than sodium bicarbonate and nitrates were found to be better than bicarbonates. Potassium oxalate was found to be the most efficient extinguisher of coal gas flames, especially when mixed with 10 per cent silica. This performance could be improved by mixing with potassium bicarbonate, the optimum mixture being 30 per cent oxalate, 70 per cent bicarbonate. In general the order of effectiveness was: oxalates > carbonates > bicarbonates > chloride > iodide. No mention was made of the particle sizes involved and the authors themselves point out that differences in the ease of dispersion could mask any differences due to chemical composition.

Friedrich[35] has also carried out extensive screening tests on hydrogen, coal gas, carbon monoxide and carbon disulphide diffusion flames. Carbon monoxide was the easiest flame to extinguish and hydrogen the most difficult, but carbon disulphide flames could not be extinguished. Over 70 powders were tested, with a mean particle diameter of 44μ.

Hydrogen flames could be extinguished only by oxalates which were the best extinguishants for the other flames. In general efficiency increased with basicity from ammonium salts through to caesium salts, and from fluorides to iodides. The best individual substances were the hydrated oxalates of potassium, rubidium and caesium. The amount of decomposition of powders passing through the flame was usually less than 1 per cent except for the oxalates in hydrogen flames when this figure was 2-3 per cent. Ammonium iodide decomposed readily in coal gas but not in carbon monoxide flames. The oxalates decomposed rapidly at low temperatures (approximately 500°C) producing the carbonate, together with soot. It was suggested that this carbonate would be in a very finely divided and active state. Oxalic acid itself was found to be ineffective, thus only the inorganic residue is effective and the organic radical does not contribute towards extinction.

Friedrich found evidence that peroxides were destroyed by the powders and pointed out that peroxide solutions are destroyed by alkali metal compounds, the amount of decomposition increasing from lithium to caesium, this being the same order as for flame extinguishing efficiency.

The electrical conductivity of the flames increased markedly in the presence of powders, the amount of increase reflecting, broadly, the efficiency of the powder. Friedman and Levy[24][25] found that elemental sodium and potassium vapour had no inhibitive effect on diffusion flames within the range of concentrations studied. As previously mentioned,

these authors attribute the inhibitive effectiveness of alkali metal compounds to the hydroxide which is formed as an intermediate. The ineffectiveness of metal vapour on diffusion flames was attributed to the slow rate of conversion of the metal to the hydroxide via the reactions possible in a diffusion flame. Skinner[8] reports a similar negative result with sodium vapour in a hydrogen diffusion flame.

Pieters[36] dispersed powders into a stream of air feeding a butane diffusion flame and found that potassium oxalate, sodium oxalate, potassium nitrate and potassium dichromate were effective extinguishants.

Using a similar technique, Dessart and Melarme[37] compared sodium and potassium bicarbonates of various mean particle diameters and "mobilities". The basis on which "mobility" was assessed was not stated. They expressed "efficiency" as the number of extinctions of a butane diffusion flame possible with 10 gms of powder - see table 8.

<div align="center">Table 8</div>

Powder	Main constituent	Mean diameter (μ)	"Efficiency"	"Mobility"
A	$NaHCO_3$	5	16	Good
Proprietary powder	"	10	10	Good
B	"	10	9	Medium
C	$KHCO_3$	10	25	Good
D	$NaHCO_3$	20	5	Good
E	"	20	4	Poor

3.2. Liquid Fuel Fires

Hird[38][39] showed that the efficiency of finely divided sodium bicarbonate as a fire extinguishant depends largely upon the specific surface.   Powders were applied to a 3 ft x 3 ft patrol fire in a flat spray.   The critical rate of application (R_c lb/sec) below which it was not possible to extinguish the fire in any length of time was determined.   By plotting the total weight of powder applied to the fire against rate of application an optimum rate resulting in a minimum quantity of powder was found.   The results are summarised in table 9.

<div align="center">Table 9</div>

Powder	Specific surface	Critical rate (lb/sec)	Optimum rate (lb/sec)	Total quantity at optimum rate (lb)
A	3930	0.17	0.3	1.0
B	1320	0.20	0.4-0.6	2.5
C	1230	0.27	c. 0.9	3.5

When the rate of surface application (cm^2/sec) was plotted versus extinction time, then the results for all three powders could be represented by a single curve. The critical rate of application was 2 ± 1 cm^2/sec.

McCamy, Shoub and Lee[40] after conducting screening tests on 4 ft x 4 ft gasoline fires using a number of powdered materials concluded that the two most likely mechanisms of extinction were chain breaking and the shielding of the liquid fuel surface from radiation from the flames. Following the latter idea, they measured the attenuation of thermal radiation by a cloud of dry powder. The radiation from a hydrocarbon diffusion flame was simulated by a hot wire at $1200°$K with a spectral distribution around 2.4μ. The powder cloud consisted of a free falling column of 40μ diameter powder, 4 cms in diameter, the powder flow rate being 0.012 gm/sec cm^2. This cloud attenuated 20 per cent of the infra-red radiation and it was estimated that in a practical fire fighting situation this figure would be of the order of 90 per cent. Experiments were then conducted into n-heptane fires in pans 10 cm diameter with transparent bottoms. The intensity of radiation from the flame transmitted through the transparent bottom was compared with the intensity from the flame as measured from a point above the fire. When the fire was extinguished by a cloud of dry powder, about half the radiation was attenuated, the cloud thickness being about 6 inches. It was estimated that when the powder cloud concentration was below about 10^{-4} gm/cc, the fire was never extinguished.

Neill[41] compared sodium and potassium bicarbonate powders on 3 ft x 3 ft gasoline fires. He found that the minimum rate of application for extinction for sodium bicarbonate was twice that for potassium bicarbonate and that the total amount of sodium bicarbonate required at that rate of application was twice that of potassium bicarbonate. The minimum rates were 4 gm/ft^2. sec. and 2 gm/ft^2 sec. respectively. Tests on larger fires also reflected these results. For very short extinction times, i.e. high rates of application, the performances of the two powders were almost identical.

Pieters[36] carried out both small and large scale fire tests on 13.5 cm diameter benzene fires and 2 metres x 3 metres petrol fires, using three samples of sodium bicarbonate of different particle sizes. These were, below 100μ, below 75μ and below 50μ. He showed that the efficiency increased with decrease in particle size but found that moisture uptake and caking increased with the smaller sized powders. Sodium bicarbonate recovered from the fire was found to be only slightly decomposed. Pieters results do not indicate what the minimum rates of application were.

Friedrich[35] also conducted tests on 60 cm diameter petrol fires using sodium bicarbonate and found that about 3 per cent of the bicarbonate was decomposed on passing through the fire. He also found that dispersibility was an important factor and that there was an optimum distance of 10-12 ft from which to fight the fire, with his particular apparatus, giving the minimum extinguishing time. No detailed results are presented.

Lee and Robertson[42] have performed a series of experiments on a number of different size n-heptane fires; $1\frac{1}{8}$ in diameter, 6 in diameter and $22\frac{3}{4}$ in diameter. The powders used were potassium iodide, potassium and sodium bicarbonates, potassium oxalate of mean particle diameters in the range 6-12μ and glass beads. The powders were applied to the smallest fire by gravity from above the fire by means of a shaker device and propelled into the larger fires from a horizontal nozzle by a blast of compressed air.

For the $1\frac{1}{8}$ in fire, plots of the rate of surface application versus mean particle size showed a minimum at about 18μ, except potassium oxalate which showed little dependence on particle size. It was thought that the largest particles fell too quickly through the flame for them to have any effect and the smaller particles could not penetrate the rising plume of hot post flame gases. The minimum rates of surface application found are given in table 10.

Table 10

Substance	Minimum rate of surface application to $1\frac{1}{8}$ in. dia fire (cm^2/sec)
Sodium bicarbonate	65
Commercial) "dry chemical")	58
Potassium bicarbonate	30
Potassium iodide	15
Potassium oxalate	15

Mixtures of potassium oxalate (mean particle diameter 8μ) and glass beads (mean diameter 22μ) were applied to the $1\frac{1}{8}$ in fire. The mass rates of application necessary for extinction were found to agree with those values calculated on the assumption that the glass beads acted as an inert 'carrier' for the smaller oxalate particles. Thus a mixture containing equal amounts of each constituent required twice the application rate of the oxalate alone. It was suggested that the high momentum of particles such as glass beads might provide a suitable means of introducing small particles of effective materials into a fire.

For the larger fires, plots of rate of surface application versus extinction time were similar to those obtained by Hird[39] the minimum rates found are given in table 11.

Table 11

Substance	Minimum rate of application (cm^2/sec)	
	6" fire	22$\frac{3}{4}$" fire
Potassium oxalate	0.46×10^3	5.5×10^3
Potassium bicarbonate	0.77×10^3	10.0×10^3
Potassium iodide	0.84×10^3	10.0×10^3
Sodium bicarbonate	2.00×10^3	25.0×10^3
Glass beads	3.62×10^3	–

For all the fires, by plotting the minimum application rate (cm^2/sec) versus fire diameter and liquid burning rate (ml. fuel/sec) versus fire diameter; both on a log-log basis, it was found that the minimum rate of application ran broadly in parallel with the liquid burning rate. The results of Neill[41] could be included in the correlation but the J.F.R.O. results[39] showed a higher rate of application than would be expected from the correlation due possibly to the rather large free board of $2\frac{1}{2}$" which would need additional cooling to below the flashpoint of the fuel. The graphical correlations shown by Lee and Robertson can be represented by the following equations:

For Sodium bicarbonate $\quad\quad\quad\quad$ $Rc = 66.1\ D^{1.9}$

$\quad\quad$ Potassium bicarbonate diodide $\quad$ $Rc = 27.5\ D^{1.9}$

$\quad\quad$ Potassium oxalate $\quad\quad\quad\quad$ $Rc = 15.1\ D^{1.9}$

Where Rc = minimum, critical, rate of application for extinction (cm^2/sec)

$\quad\quad$ D = fire diameter (inches)

The results for the $1\frac{1}{8}$ in fire with potassium iodide seems to be anomolous in that they indicate that potassium iodide is more effective on this small fire. The method of application in this case was by gravity from above and the increased effectiveness under these conditions is probably due to the high density of potassium iodide enabling the particles to penetrate more easily into the fire. This effect was also noticed with the other powders, the larger (22μ) particles being more effective than the smaller $(6-12\mu)$ particles.

By expressing the results in the form of the ratio of the minimum critical application rate (Rc) to the liquid fuel burning rate (Rb) it is seen that this ratio tends to decrease with increasing fire diameter, although the amount of variation is not great. Results for sodium bicarbonate are shown in table 12.

Table 12

Fire Diameter	Rc (cm^2/sec)	Rb (cm^3/sec)	Rc/Rb (cm^{-1})
1.18"	68	0.0028	8.7×10^3
"	90	"	11.3×10^3
6.0"	2,100	0.23	9.1×10^3
22.8"	25,500	6.00	4.2×10^3
40.6" (JFRO)	200,000	32.00	6.2×10^3
" (Neill)	63,000	32.00	2.0×10^3

From the results on the smallest fires, it was concluded that the ability for a given powder cloud to penetrate a flame and its residence time in that flame would be important factors in extinguishing larger fires and suggested that secondary factors such as the velocity of the expellent gas, the powder concentration in the cloud formed and particle size distribution should be controlled and investigated.

Brief mention will be made of some experiments in which fires were extinguished by aqueous solutions of various salts.

Thomas and Hochwalt[43] tested a large number of water soluble salts expressing the efficiency as the reciprocal of the lowest effective normality capable of extinguishing the flame under the test conditions. Only the salts of the alkali metals were capable of extinction, the order of effectiveness increasing with atomic weight. Salts containing oxygen were more effective than the corresponding salts containing no oxygen. Thus potassium perchlorate was five times as effective as potassium chloride. Oxidising agents were only effective when combined with an alkali metal, thus perchloric acid itself was ineffective.

Similar experiments were performed by Rakuzin[44] and Friedrich[45] who found that high enthalpy fuels required more solution than low enthalpy fuels. Friedrich also found that potassium carbonate resulted in the greatest improvement and sodium bicarbonate the least with potassium bicarbonate and sodium carbonate intermediate.

Abrams[46] applied aqueous solutions to potassium and sodium bicarbonate, as sprays, to premixed hydrogen/air and methane/air flames. He found that lean flames required more solution for extinction than rich flames.

4. Discussion

Salts of the metals in Group I (especially group 1A) of the periodic classification are the most efficient flame inhibitions. Group 1A metals are the alkali metals Lithium, Sodium, Potassium, Rubidium, Caesium. Each of these metals has one electron in its outer shell and eight electrons in the penultimate shell. For a given anion, the effectiveness of the metal cation increases with molecular weight. The first ionisation potential decreases with increasing molecular weight for the metals.

viz.

Metal	First Ionisation Potential (eV)
Lithium	5.39
Sodium	5.14
Potassium	4.34
Rubidium	4.18
Caesium	3.89

The group 1B metals (Copper Silver Gold) have one electron in the outermost shell, but 18 electrons in the penultimate shell. Although, in general the properties of the IB metals are completely different from these of the IA metals, they all exhibit combustion inhibiting properties. Cuprous, but not in general cupric, salts inhibit flaming combustion and gold and silver surfaces, when free of adsorbed impurities, inhibit slow combustion by mechanisms previously mentioned. The free univalent cuprous ion is unstable and readily decomposes forming the curpic ion and releasing an electron $Cu^+ \rightarrow Cu^{++} + e$.

Some other metals have been found to exhibit inhibiting properties e.g. Chromium and Thallium.

Chromium is an exception in its group (VIA) in having one electron in the outer shell, the other members having 2. Thallium has three electrons in the outer shell, but the number of electrons in the outer (lowest energy) orbit in that shell is one. Other elements with similar structures are Boron and Aluminium.

Thus it seems that a characteristic of an effective cation is that the metal has one electron in the outer shell. It is interesting to note, that the ammonium ion has the same electronic structure as the sodium ion. Its shell is, however, expanded by the inclusion of four protons so that is radius ($1.43\overset{o}{A}$) approximates more closely to that of the potassium ion ($1.33\overset{o}{A}$) than to that of the sodium ion ($0.98\overset{o}{A}$). Thus ammonium salts are more like Potassium salts than sodium salts.

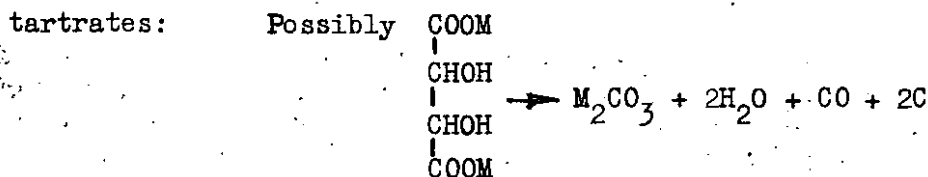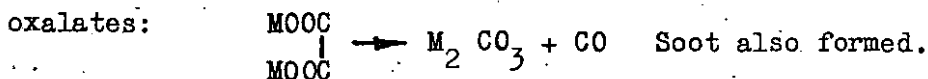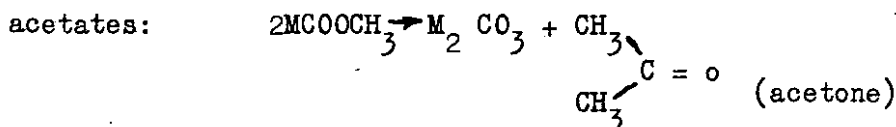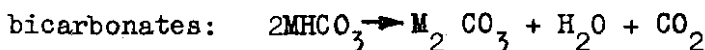The most effective anions are, in general, one of two types.

a)   The halides

b)   Anions which decompose thermally to give the carbonate.

Halogens are known to be inhibitious of combustion, per se. But when combined with a metal to form a halide, this inhibiting property does not seem to make itself felt. Rather, the contribution of the halogen seems to be related to the nature of the bond between it and the metal. Fluorine is the most electro-negative of the halogens and forms, with a given cation, the most ionic bond of the family. Electro-negativity decreases, therefore, from fluorine though to iodine and this is, in general the order of decreasing efficiency. The efficiency of halogens themselves as inhibitors increases from iodine through to fluorine. In general, polar or ionic salts were effective extinguishers whilst salts with covalent bonds were not.

Anions which readily decompose on heating to form carbonate are very efficient. These are bicarbonates, acetates, oxalates, tartrates. By the same argument, formates should be efficient. The reactions for the complex anions tartrates and oxalates are complex, but the general scheme is as shown below.

M represents alkali metal cation.

bicarbonates: $2MHCO_3 \rightarrow M_2CO_3 + H_2O + CO_2$

acetates: $2MCOOCH_3 \rightarrow M_2CO_3 + CH_3$

$$CH_3 \diagup C = O \quad CH_3 \quad (acetone)$$

oxalates:
$$\begin{array}{c} MOOC \\ | \\ MOOC \end{array} \rightarrow M_2CO_3 + CO \quad \text{Soot also formed.}$$

tartrates: Possibly
$$\begin{array}{c} COOM \\ | \\ CHOH \\ | \\ CHOH \\ | \\ COOM \end{array} \rightarrow M_2CO_3 + 2H_2O + CO + 2C$$

formates
$$2MHCO_2 \rightarrow \begin{array}{c} MOOC \\ | \\ MOOC \end{array} + H_2 \quad \text{then as for oxalate}$$

In practical situations the amount of decomposition has been found to be less than about 4 per cent by weight. This would, of course, occur at the surface of the particles producing a layer of freshly formed and very reactive carbonate. For a 20μ diameter particle decomposing, without vapourisation, to this extent than the surface layer would be 0.14μ thick.

Other anions have been found to be effective including nitrates, sulphates, thiosulphates, sulphites. Water of crystallisation has also been found to be beneficial. In general substances which undergo some endothermic processes (e.g. melting, decomposition, vaporisation, loss of water) at low temperatures, are effective.

Several extinguishing mechanisms have been proposed from time to time. These are:-

1) Throttling or Blanketing. The supply of fuels to the flame is reduced or stopped.

2) Smothering. The supply of air to the flame is reduced or stopped.

These two mechanisms are relevant only to actual fires. The following mechanisms would apply to all flames.

3) Dilution by either (a) the powder or

                     (b) gases liberated on decomposition of the powder.

or both.

4) Blowing-out. The physical removal of the flame as a result of aerodynamic disturbance of the flame zone.

5) Cooling.   a) Heat abstraction from the flame

                b) Cooling of the fuel, in the case of a flammable liquid, to below the fire point.

6) Radiation shielding. In the case of burning liquids, the powder cloud dispersed between the liquid surface and the flame zone attenuates the radiative heat transfer to the liquid surfaces thus reducing the rate of fuel evaporation.

7) Preferential oxidation of the extinguishing material.

8) Chemical inhibition - a) Heterogeneous inhibition

                          b) Homogeneous inhibition following complete or partial evaporation of the particles.

Powders of similar particle sizes and dispersibility would be expected to contribute equally to mechanisms (1) (2) (3a) (4) and (6).

Mechanism (3b) is not plausible as a major mechanism. It is known that 5 lbs of sodium bicarbonate will extinguish the same fire as 10 lbs of carbon dioxide. Even if all the bicarbonate decomposes this gives rise to only 2$\frac{1}{2}$ lbs of carbon dioxide, for anhydrous bicarbonate. But dry powder decomposes only to the extent of a few per cent by weight so that the amount of CO_2 liberated would be small.

Mechanism (5) is dependant upon the thermal properties of the powder e.g. specific heat, thermal conductivity, melting and boiling points and latent heat. Dolan and Dempster found that the most effective salts melted or decomposed below 200°C but were able, for the less efficient powders, to correlate thermal properties with efficiency.

Mechanism (8(a)) has already been discussed and is probably the formation of new, chemically reactive surface which then acts as an efficient destroyer of chain propagating radicals.

Possible mechanisms being

$$R + M \rightarrow RM \qquad\qquad M = \text{third body (new surface)}$$

$$RM + R' \rightarrow RR' + M$$

$$RM \rightarrow M + \text{stable products}$$
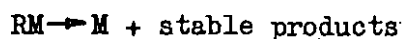
R has to be adsorbed on the surface for sufficient time for collision and reaction with R' to occur.

Mechanism (8b) requires at least partial vapourisation of the particles and would apply for small particles ($< 10\mu$) with long residence times in the flame zone. [Mechanism (8a) is more applicable to large particles ($> 50\mu$)] It is thought that the hydroxide is formed early in the flame probably via
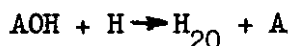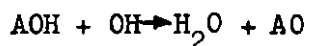
$$AX + H \rightarrow A + HX \qquad\qquad A = \text{metal cation}$$

$$OH + A \xrightarrow{M} AOH \qquad\qquad X = \text{anion}$$

then,
$$AOH + H \rightarrow H_{20} + A \qquad\qquad M = \text{third body}$$

$$AOH + OH \rightarrow H_2O + AO$$

Thus it appears that there are two main types of extinction mechanism:

(1) Physical mechanisms involving heat abstraction and also in the case of liquid fuel fires, radiation shielding and aerodynamic disturbance of the flame zone.

(2) Chemical mechanisms involving the destruction of chain propagating radicals either heterogeneously on the particle surfaces or homogeneously following partial vapourisation of the particles.

In a practical fire fighting situation, the actual extinction mechanism may well be a combination of those outlined above. However, it would appear that the relative importance of different contributory mechanisms depends on the rate of powder application. Chemical effects seem to be most pronounced at rates near the critical minimum and are minimised and possibly obscured, at higher rates of application.

Thus powders which are efficient flame extinguishing agents have the following properties and characteristics.

- 19 -

1) The cation is an alkali metal or metal with similar outer electron shell structure.

2) The anion is one which will readily decompose on heating producing carbonate,

or 3) one which produces an ionic bond with the cation,

or 4) results in a compound having low melting point or decomposition temperature.

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