Dry Chemical Extinguishing Powders — A Review

04

by

T. P. SHARMA, B. B. LAL and JAGBIR SINGH

Central Building Research Institute, Roorkee (U.P.).

INTRODUCTION

Water and sand have been the most common extinguishants used for combating solid fuel fires. Water wets the surface, brings down the temperature and is more effective when its drop size is controlled with uniformity of spreading.

Therefore, quantity of water is not so important. Sand on the other hand cuts the supply of air from the material under fire so in this case quantity, as well as coverage both are important. Sand or clay is still used in the areas where water is not readily available or there are no means for its proper use. But both the extinguishants have their limitations; they cannot be used to extinguish liquid fuel fires because they are heavier than the common liquid fuels, that is why chemical extinguishing powders based on sodium bicarbonate etc. became popular in the early twenties. At that time dry chemical extinguishants were used manually either by throwing or sprinkling them on fire. About 64 years ago, a gas pressurised unit was developed in Germany which could expel the dry chemical at a higher velocity. The chemical used in this was sodium bicarbonate, containing 15 percent borax. Much interest was aroused after this and dry chemical powders are being widely used since 1945 with modifications/development both in dry powders and equipment used for their application. The important factors which are involved in modification of dry powder extinguishers/appliances are nozzle delivery, expellent gas, the size and number of containers and operations (manual control or remote control), while for dry chemical powder extinguishants the variables, which have been studied by different workers developing efficient powders are: (a) different chemicals—individual as well as their mixtures (b) particle size (c) flow and anti-caking properties and (d) compatibility of dry chemical powders with protein foam. This paper reviews the work done by different authors in this field for the above variables except compatibility with protein foam.

DIFFERENT CHEMICALS

In 1928, Thomas and Hochwalt[1] discovered the effectiveness of sodium and potassium carbonate solutions for extinguishing oil fires. They worked on a large number of water soluble salts by the application of salt solutions for extinguishing gasoline fire and thus determined the effective concentration of each solution.

However, most of the workers carried out studies to determine the effectiveness of dry powders dispersing in gas-air mixture either for reducing explosion hazards or for flame suppression. The first detailed study of this phenomenon was made by Jorissen[2] in 1933, who found that at a certain dust concentration, the mixture of methane and air was no longer explosive. In 1934

Dijksman[3] extended the work of Jorissen and observed that KCl, NaCl and NaHCO₃ were good extinguishants of methane-air explosions. Later, Jorissen using Dijksman's method and working near the lower flammability limits, found the effectiveness of alkali halides. Dufraisse[1] in 1938 investigated the effect of various dry chemicals on town gas, methane and carbon monoxide flames. He found that potassium bicarbonate was more effective than sodium bicarbonate. He showed that even oxidizing agents, such as potassium nitrate were capable of extinguishing flames. Further in 1953 Dufraisse[5] discovered that the most efficient extinguishing agent was potassium oxalate, whose efficiency could further be increased by adding materials like silica. He also showed that mixtures of potassium oxalate (30 per cent) and sodium bicarbonate (70 per cent) were more effective than the individual compounds. This was also confirmed by Laffitte and co-workers[6]. Dolan and Dempster[7] in 1955 tried about 47 compounds to see their quenching capability for methane-air ignitions. They concluded that with isolated exceptions, the alkali salts, particularly the alkali halides are the most effective group of compounds. The work of other researchers is shown in Table 1.
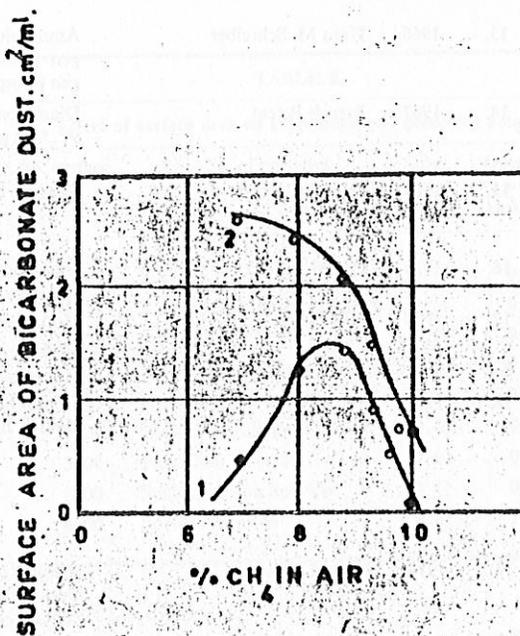
Fig. 1: The variation of suppression value (1) and quenching value (2) with percentage of methane.

TABLE 1

Showing use of different Chemicals by different workers.

Sl. No.	Year	Research Worker	Basic chemicals used	Remarks
1	2	3	4	5
1.	1961	Karl Schwalb, Wolfgang Land Graf, Arthur B. Guise	Sodium and potassium bicarbonates particle size 0.01 — 1 mm. with 1/3 < 0.04 mm.	
2.	1961	Walter Brell	Sodium sulphate, Ammonium sulphate	
3.	1962	Karl Schwalb	40-80% mixture of NH$_4$Cl, Ammonium sulphate or phosphate and Urea : 20-60% Dicyanamide or their phosphate.	
4.	1963	Solway & Co.	Na & K bicarbonates	
5.	1963	Edward G. Crooke & Leslie Phoenix	Pot. sulphate and ammonium sulphate	
6.	1964	Voltrad Stepp	Monoammonium hydrogen phosphate, Ammonium sulphate, Barium sulphate	
7.	1966	Hans M. Schreiber	Ammonium phosphates or sulphate	
8.	1966	Zbigniew, J. Lobos	Ammonium phosphates	Suitable for Class 'A' fires
9.	1966	Denno Goldberg	Ammonium phosphate & Ammonium sulphate, Sodium bicarbonate 25% should be of 0.05 mm. size	
10.	1966	Arnold Gordy & Erich Ruehl	Sodium bicarbonate, Potassium bicarbonate and Ammonium sulphate	
11.	1966	Herman Dessart Salvay & Lie	Sodium bicarbonate, Potassium bicarbonate 10 μ particle size	
12.	1966	Patent (ICI Ltd.)	Molten Urea, Potassium, Sodium and Ammonium bicarbonates	The process occurred at 5 atm and 130° - 150°C. This solid product can also be used as coating material against fire on high temp.
13.	1966	Hans M. Schreiber	Ammonium sulphate, Di-ammonium hydrogen phosphate or Mono-ammonium hydrogen phosphate	Can be used against any kind of fire.
14.	1967	French Patent	Diammonium hydrogen phosphate (92.5—97.5%) particle size 10-20μ	The product was claimed to be superior to powders during humidity storage and flowing.
15.	1969	Erler & Gerber	Calcium lignin sulphonate	Good water repellent properties. It forms a crust thus preventing re-ignition.
16.	1970	Cottrel Arnold G.	Urea and Sodium Potassium bicarbonate sesquicarbonate and vapour	Called Monex.
17.	1970	Wilkingsen	Monex — Sodium bicarbonate; Monex — Ammonium phosphate; Monex — Ammonium sulphate	Suitable for flammable liquid; Suitable for Class 'A' fires.
18.	1971	Mark Walter	Ammonium phosphate & Ammonium sulphate 25-40% 20 μ , 55-85% 60 μ	After 12 min. of pre-burning period of wood the fire was completely extinguished without any residual glow spots, using an amount of extinguishing powder less by 1.2 Kg. than the agent of DIN formulation.
19.	1974	Hattori Yasuzo.	Sodium bicarbonate, burned alum, ammonium carbonate, Sodium & Calcium chloride, Sodium carbonate and Water glass	The powder should be applied through bursting device.
20.	1974	Cottrel Arnold G.	Potassium bicarbonate & Urea (size 0.1—100 μ)	

TABLE 1—Contd.

Showing use of different Chemicals by different workers.

Sl. No.	Year	Research Worker	Basic chemicals used	Remarks
1	2	3	4	5
21.	1976	Kretzschmar, Axel Richel Heinz	Alkali metal salts & Urea	
22.	1977	Nakayama Isoc., Tanaka Chiharu	Alkali metal bicarbonate, Basic phosphates & Alkali metal halide. 72 litres solution prepared by dissolving 600 gms. Alkali bicarbonate 425 gms. Diammonium hydrogen phosphate.	Applied in liquid form by reacting with H_3PO_4 (1.3 lit. of aq. 85% H_4PO_4)
23.	1977	Kennington Rowland, Wolf House Andrew	Bicarbonate & Urea (in molar ratio 1 : 0.5 to 2)	Reaction in a fluidised bed furnace at 100° — 170°C in presence of water vapour.
24.	1978	Moro Kaoru	Potassium bicarbonate	
25.	1978	Balintion, Ionel Proca Teodor, Amuliv	Potassium bicarbonate & Urea	$KHCO_3$ & Urea were ground with 40% K_2O & Na_2SiF_6 as catalyst at 50°C for a certain period in which it attains other physical properties.
26.	1978	Demzen, Zoltan Ponubszky, Ivan Szekely, Gyorzy Czotter, Otterkar	Alkali carbonate & Alkaline earth carbonates	

TABLE 2

Effect of particle size in quantity of dry chemical

Substance	Quantity required to extinguish a CH_4/air flame in (mg)			
	100 μ	75 μ	50 μ	25 μ
KCl	80	41	20.5	10
NaCl	160	62	32	9.5
K_2SO_4	48	41	18	4.0
$Na_2SO_4.10H_2O$	51	45	21	4.5
$KClO_3$	57	42	19	4.5
$NaClO_3$	115	57	21	4.8
K_2CrO_4	85	67	51	5.7
Na_2CrO_4	105	65	31	6.2
$K_2C_2O_4$	2.5	2.5	2	0.8
$Na_2C_2O_4$	3.5	3.5	3	1.4
Fe_2O_3	130	130	46	30
Al_2O_3	38	37	37	37
SiO_2	46	46	45	44

TABLE 3

Effect of surface area on suppression and quenching point.

Sp. surface cm²/g	Avg. dia. of particles (μ)	Supp. point cm²/ml	Quenching point cm²/ml
11500	2.4 ⎫ Sodium bicarbonate	0.76	0.53
4600	5.9 ⎬ Sodium bicarbonate	0.74	0.52
3200	8.5 ⎭	0.74	0.51
800	Potassium fluoride	0.08	0.25
900	Potassium iodide	0.04	0.50
2200	Sodium aluminium fluoride	0.40	0.61
5700	Potassium chloride	0.40	0.64
8000	Sodium silicon fluoride	0.47	0.68
6500	Sodium chloride	0.57	1.84

PARTICLE SIZE

The most important parameter of any powder besides its chemical composition is fineness, which is defined by its specific surface (cm²/g). Not only is the

119

particle size/fineness of the powder important but the way in which these are distributed is also very important because this decides its flow and settling behaviour.

In 1934, Dijksman[3] was able to establish an approximately linear relationship between specific surface and extinguishing efficiency of a dry powder. Laffitte and
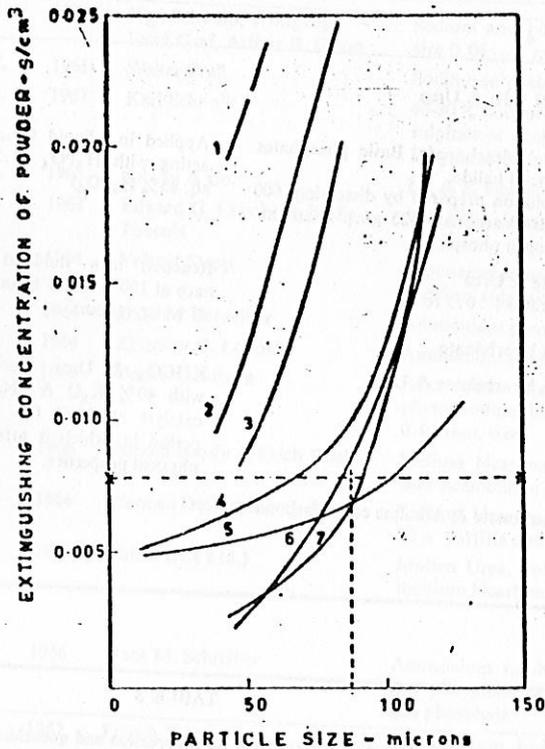
Fig. 2 : Effect of particle size on the extinguishing concentration of various powders.

1. Potassium Sulphate
2. Potassium Chloride
3. Sodium Borate
4. Sodium Bicaronate
5. Potassium Bicarbonate
6. Mono Ammonium Phosphate
7. Di Ammonium Phosphate

co-workers[6] tried different dry chemical powders of 25µ, 60µ, 75µ, and 100µ in deflagration combustion studies. They found that efficiency of these powders increased as particle size was reduced except for sodium and potassium oxalates mixed with alumina and silica. The oxalates even of 100µ particle size were more efficient than other salts of 25µ particle size.

Dolan and Dempster[7] in 1955 also found similar relationship between surface area and effectiveness of chemical powders in extinguishing fires. In fact it was the first attempt to report the importance of surface area rather than weight of the extinguishing media for suppression and quenching points. Table 3 gives the data for different compounds while Fig. 1 illustrates for sodium bicarbonate only.
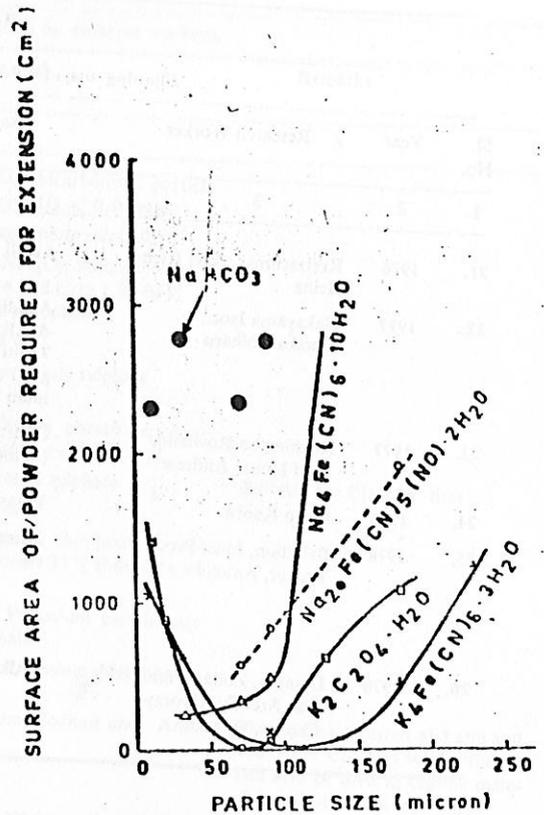
Fig. 3 : Variation with particle size in the surface area of powder required to extinguish town's gas diffusion flame.

P. F. Thorne[15] in 1968 developed an apparatus to determine and compare the extinguishing concentration of chemical powders in relation to their particle size using propane gas-air diffusion flames in his experiments. The flow rate for extinction of different powders was plotted against the gas flow rate; it gave a straight line,

TABLE 4

Effect of particle size on the surface area of different chemicals

Particle size	Surface area of original solid required for extinction cm²/g			
	NaHCO₃	K₂C₂O₄. 2H₂O	K₄Fe(CN)₆. 3H₂O	Na₄Fe(CN)₆. 10H₂O
231	—	—	1260	—
181	—	1102	447	—
128	—	621	554	> 3000
90	2762	48	125	495
70	2367	41	46	350
31	2762	—	626	272
23	—	—	563	—
19	—	900	—	—
12	2310	1430	—	—
9	—	—	1078	—

TABLE 5

Flowing and anticaking agents used by different workers.

Sl. No.	Author	Flowing Agents	Anti-caking & water repellent agents
1.	Karl Schwalb, Wolfgang Landgrof, Arthur B Gouise	Al_2O_3, SiO_2 Attopulgus clay bentonite, Fuller's earth Hallaysite, $MgCO_3$, $CaCO_3$.	Salts of fatty acids (6 to 10 Carbon atoms amount 0.2 — 2%)
2.	Walter Brell	Copper sulphate, Silver nitrate, Manganese sulphate and potassium oxalate.	Metal stearates
3.	Karl Schwalb	Calcium carbonate and Magnesium carbonate	
4.	Solway & Co.	Talc, Hydroxy apatite, Slinar	Metal stearates
5.	Voltrad Stepp	SiO_2	Silicon oil (0.05%)
6.	Voltrad Stepp	SiO_2 (fine)	Dialkylpolysiloxane
7.	Zbigniew J. Lobos	Magnesite — 15% SiO_2 — 0.4%	Me_2SiCl_2 Dimethyl ethoxysilane 0.6%
8.	Patent	SiO_2, Alkali carbonate & Mica	Dialkyl polysiloxane & Alkylarylpolysiloxane
9.	Hans M. Schreiber	Cresol formaldehyde resin and Asbestos powder used as filler	Mg stearate
10.	Zbigniew J. Lobos	SiO_2 (0.3%) Size 45 microns	Org. acids, Glycerine (polymerizing agents) Dimethyl diethylsilane
11.	Arnold Gordy & Herman	$MgCO_3$, ketone aldehyde resin, $CaCO_3$	Metal stearate
12.	Dessart Salvay & Lie	Talc (size 1 μ) Silica fine 1.05 μ	Silicon oil (0.5—2%)
13.	Patent	Cresol-formaldehyde resin dye	Mg stearate
14.	Patent	SiO_2	Silicon oil
15.	Mark, Walter, Doerfer, Arthur	Flowing agents	Sulphur & Silicon oil
16.	Birchall, James, Phillips, D. Arthur	Graphite, SiO_2	Polysiloxane
17.	Clements, Henry G.	Perlite	
18.	Cottrell, Arnold, G. Paton, John M.	Sand	$Hg(SCN)_2$. Methyl ethyl Cellulose Hydrophobic agent
19.	Moro Kaoru	Kaolin, SiO_2	Hydrophobic agent
20.	Balintion Ionel, Proca Teodor, Amuliv	Graphite, (Na_2SiF_6) activated	Ca stearate
21.	Demzen, Zoltan; Ponubszky, Ivan; Szekely, Gyorzy; Czotter, Otterkar	Inorganic oxide or ceramic mass	Zn stearate or Ca, Mg stearate

the slope of which was described as extinguishing concentration of powder. He studied different dry chemicals of particle sizes of 45-58 microns; 75-90 microns; 105-135 microns. It was observed (Fig. 2) that the efficiency of chemical powders increased as the particle size decreased. Sodium and potassium bicarbonates were found more efficient than sodium borate, potassium sulphate, potassium chloride, mono and diammonium phosphates over the major particle size range. In the coarser particle size range potassium bicarbonate is more effective than other chemicals while for particle size below 70μ ammonium phosphates were found more efficient than potassium bicarbonate.

J. D. Birchall[13] used another apparatus to determine the effectiveness of dry chemical powders for flame extinction and also suggested a number of mechanisms of flame inhibition. He injected various powders into town gas-air flame. It was noticed that there was an optimum size, below which decomposition occurred before the flame front was reached and above which little decomposition occurred within the residence time of particles. In a flame. He also tried different chemicals to see the effect on surface area of powders required for extinction. The results are shown in Fig. 3 and Table 4.
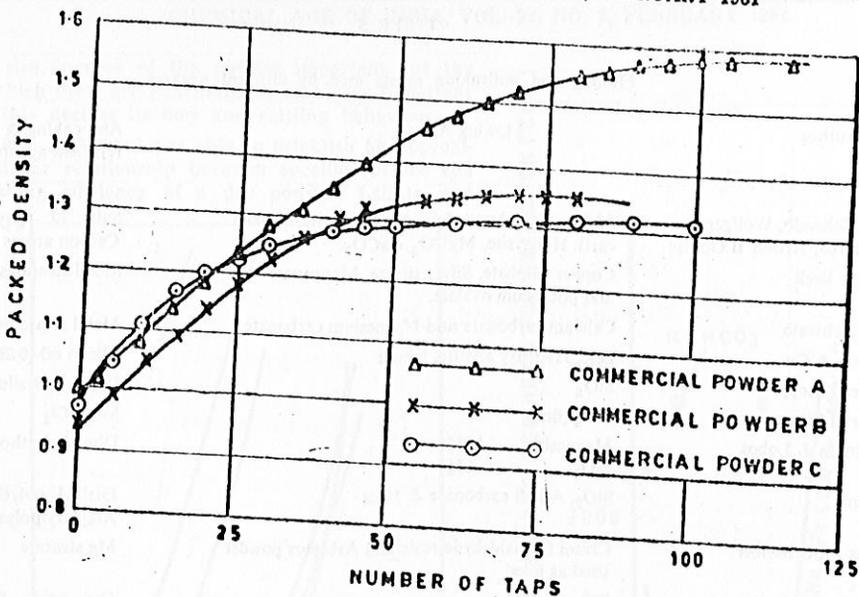
121

Fig.: 4 Variation of packed density wit tamping.

Results show that high efficiencies of alkali metal salts are due to their ready decomposition in a flame with the generation of submicron particles. W. W. Harpur[17] in 1970 also claimed decrepitation of monex in a similar manner to potassium oxalate in a flame.

CAKING AND FLOW PROPERTIES

The next important properties of a chemical powder which determine its effectiveness against fire are free flowing and easy dispersability. These should not only be tested just after its manufacture but also after its storage for certain periods. It has been established by different workers that high efficiency of different chemical powders is achieved by reducing their sizes, but reduction of sizes increases caking of powder and it becomes increasingly difficult for particles to penetrate through the flame. The powder should also be free from the formation of lumps or cakes due to the absorption of moisture by dry powder. In an extinguisher, the practical way. of assessing storage performance of a dry powder is to discharge the powder and to measure both the rate of expulsion and the weight of the residue remaining in the body of the extinguisher. However, according to R. M. Forward[18] a continuous value over the whole period of discharge as a measure of the characteristics of the dry powder is more important. Fig. 4 shows some typical results obtained for commercial powders. Under similar conditions powder A is more easily dispersed than powder B. It has been suggested that the caking tendency of dry powder extinguishants is best determined by making a standard pallet of known volume and packing density, placing it in an atmosphere of 92 per cent and 0 per cent relative humidity for six hours and 24 hours respectively and then determining the force necessary to crush the pellet. The crushing force for an ideal pellet has been arbitarily fixed at 400 gm/cm². Powders requiring higher crushing strength

are considered unsatisfactory. For both treated and untreated powders the crushing strength is found to be the same. Addition of a small percentage of stearate or other similar long chain fatty acids gives a marked increase in the bulk density. Addition of 0.1 per cent stearate exerts considerable effect on the proofing of sodium bicarbonate powder. Different workers have used different flowing, anti-caking and water repellent agents as shown in Table 5.

Wesson[13] studied the effect of particle size on the flow characteristics of dry chemicals. He showed that a coarse powder (say 50 per cent through 325 mesh) causes excessive surging in hose line application giving relatively low rate and requires more total gas quantities, resulting in a relatively inefficient unit clearent capacity. A fine powder say, 90 per cent through a 325 mesh gives similar results but not to the same degree as coarse powder.

DISCUSSION AND CONCLUSION

Although dry chemical powders are being used for the last 50 years, experiments carried out formerly by different workers were aimed at ascertaining the effect of these on suppression of gas-air or dust-air ignitions and explosion besides extinguishing fires. These effects were studied by either dispersing them in the finely divided state with combustible gases or dust-air mixture or applying them directly on fires. From this work is not possible to conclude that a particular chemical is best suitable for extinguishment of any particular type of fire. However, it can well be concluded that flame extinguishing dry powders have one or more of the following characteristics :—

(1) They are generally salts of alkali metals or of ammonia.

122

(2) The effectiveness of the metal cation increases with molecular weight. Thus potassium salts are more effective than sodium salts.

(3) The most effective anions are of two types; (a) the halides, (b) the bicarbonates which after decomposition give carbonate.

(4) The chemical bonding is ionic.

(5) They are salts having a low melting point or decomposition temperature.

(6) They decompose readily in flames producing new surfaces.

Thus Dolan and Dempster[7] found that generally alkali halides are the most effective group of extinguishing agents for methane-air ignitions. The potassium salts are, in general, more effective than the sodium salts, the fluoride more effective than iodide which in turn is more effective than chloride and finally the halides are more effective than bicarbonates. However, according to Willbourn and Hinshelwood, iodides are more effective than fluorides, bromides, chlorides or sulphates. Hydrated salts have been proved ineffective except cobalt chloride hexahydrate and barium hydroxide octahydrate. J. D. Birchall also found (using diffusion flame experiments) that hydrated salts are less effective than corresponding anhydrous salts. However, Friedrich found contradictory results. He observed that hydrated materials were less reduced in size compared to anhydrous material and a proportion of it passed through flame un changed. It was interesting to find synergistic reaction of two compounds where the mixture of the two is found to be more effective than the individual compounds.

Further the efficiency of a dry chemical powder increases with the size reduction. 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 caking properties. The effect of particle size is so important that below 70μ both mono and diammonium phosphates are found to be better than potassium bicarbonate. The importance of surface area has also been accepted by all workers, specially in cases where decomposition of particle takes place. The behaviour of such different powders can generally be described by the reaction:—

Solid A $\rightarrow$ Solid B + Gas
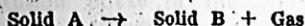
For both sodium and potassium bicarbonate little change in particle size is observed after passage through the flame although the normal translucent crystal becomes opaque and their surfaces are converted to normal carbonate. However in the case of oxalates, ferrocyanides and sodium nitroprusside the efflux from the flame is finely particulate smoke, where many particles are less than 1μ in diameter. In case of monex (which is a reaction product of alkali bicarbonate and urea) the efflux from the flame is of 0.01μ to 0.1μ particle size.

The results of different workers are not comparable as some have used premixed flames while others have used diffusion flames, the latter representing generally the actual fire conditions. Except one or two cases where air is either steaming through combustible material or if air/oxygen is inherent in combustible material represent premixed flames. Further, the apparatuses used for finding effectiveness of dry powders are also different. In some cases the flame points upwards while in others it is in a downward direction. The comparison of the efficiencies of different chemicals which have been found by these apparatuses have not been correlated with actual fire tests. However the earlier studies are very useful as the powders which have been developed recently and which are being developed are primarily based on decomposition of the powders particle in a flame to give very minute particles.

ACKNOWLEDGEMENT

REFERENCES

1. Thomas, C. A., and Hochwalt, C. A., *Ind. Eng. Chem.* 20 675 (1928).

2. Jerissen. W. P. et. al., *Rev. Tran. Chem* 52 493 (1933).

3. Dijksman, A. J., *Chemical Weekblat*, 12, 1 718 (1934).

4. Dufraisse, C., Le Bras and German, M., *Compt. Rend.* 207, 1221 (1938).

5. Dufraisse, C., and German, M., *Compt. Rend.* 236 164-167 (1953).

6. Barchet, R., Celbourgo, R. and Laffette, P., *Compt. Rend.* 242 2152 (1956).

7. Dolan, J. E. and Dempster, P. B. *J. Appl. Chem.* 5 510-517 (1955).

8. Karl Schwalb, Wolfang Landgraf and Arthur B. Guise, Ger., Patent 1098368 Jan. 26, 1961.

9. Walter Brell Fr. Patent 1223656, June 10, 1960.

10. Volrad Stepp Ger., Patent 1161114, Jan. 9, 1964.

11. Hans M. Schreiber, Belgian Patent 659312, May 28, 1965.

12. Erler Verner G., Gerber Siegfried, U.S. Patent 3464921, September 2, 1962.

13. Mark Walter, Doerfer Arthur, Ger. Patent 1160736, Jan. 2, 1964.

14. Demzen, Zoltan; Ponubszky, Ivan; Szekly, Gyorzy; Czotter, Otterkar, Hung. Teljes, 13, 371, 28 June 1977.

15. Thorne, P. F., Fire, October 1968.

16. Birchall, J. D.; *Combustion and Flame*, 14, 86-96 (1970).

17. W. W. Harpur, *Fire International 3* (29) 5762 (1970).

18. Forward, R. M., F. R. Note No. 487 and 488.

19. Wesson, H. R., *Fire Technology* 8, 173 (1972).