

FLAME EXTINGUISHMENT PROPERTIES OF DRY CHEMICALS: EXTINCTION WEIGHTS FOR SMALL DIFFUSION PAN FIRES AND ADDITIONAL EVIDENCE FOR FLAME EXTINGUISHMENT BY THERMAL MECHANISMS

by

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SUMMARY

An experimental study was made of the extinguishment of a small n-heptane diffusion flame (25.5 cm dia. pan) by a number of dry-chemical powders – KHCO_3 , $\text{NH}_4\text{H}_2\text{PO}_4$, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, $(\text{NH}_4)_2\text{SO}_4$, K_2CO_3 , $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$, Na_2CO_3 , K_2SO_4 , NaCl , $\text{Na}_2\text{C}_2\text{O}_4$, $\text{K}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$, and Monnex. The minimum weight of each required for flame extinction was determined as a function of particle size and sieve fraction. The sharp discontinuity previously observed¹ is shown to be a common phenomenon. The experimental procedure was such that complete flame penetration was achieved for all particle sizes of each substance. Therefore, all results are latent, or maximum possible, effectiveness values. Flame extinguishment effectiveness is defined as the reciprocal of the extinction quantity.

Substantial evidence, based on the new experimental data, is presented to support the propositions: (a) that particle sizes by sieve analysis below a limit size completely decompose and/or vaporize in the flame; and (b) that the observed optimum effectiveness at small particle sizes is reliably predicted by thermal mechanisms² with a flame heat balance and a predictable limit temperature.

BACKGROUND

Previous investigations¹⁻³ have presented evidence to support the following propositions:

- (a) Diffusion flames are principally extinguished by thermal or heat-extraction mechanisms at extinguishing concentrations that are quantitatively predicted by a simple heat balance^{2,3} and a predictable limit temperature which is defined by the properties of the flame and the extinguishant;
- (b) A dry chemical or gaseous agent extinguishes the flame when its concentration and associated endothermic sinks (heat capacity, dissociation, decomposition, and/or vaporization) remove the excess flame heat^{2,3} at the limit temperature;
- (c) The extinguishing effectiveness of a dry-chemical powder (the reciprocal of the minimum extinction weight or concentration) is indirectly but fully defined by particle size (and reactivity) – not surface area;
- (d) All particle sizes below a unique limit size for each dry chemical completely decompose and/or vaporize in the heptane-air flame, have the maximum cooling sinks, and the maximum flame extinguishing effectiveness;
- (e) Particle sizes above the limit size do not

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react in the flame, have only a small heat-capacity sink, and a small extinguishing effectiveness which decreases with increase in particle size.

The flame extinguishing properties of five common dry-chemical substances were extensively studied¹ using a small n-heptane diffusion flame (14.7 cm diameter pan) in a 422 liter chamber. Minimum extinction concentrations were generated for well-characterized powder samples, and these results established an experimental reference base. These concentrations were measured under total flooding conditions. Such concentrations, like those obtained with a cup burner, are known⁴ to be relatively independent of pan size and fuel burning rate. On the other hand, the latent extinction weight (per unit of fuel surface) has been shown⁵ to be proportional to burning rate when an extinguishant is applied at the base of a diffusion flame. Although extinction weight is a function of fuel burning rate, the extinguishing concentration of a substance as directly observed in the chamber system¹ or as predicted from the heat-balance equation^{2,3} is largely independent of burning rate and pan size.

The objectives of the small pan study reported here were (a) to generate in a short time reliable extinction weights as a function of particle size for as many different substances and particle-size fractions as possible; (b) to use these as a basis for scaling to real or large-pan effectiveness; (c) to establish, if possible, the relationship between extinction weight and extinction concentration; and (d) to test the proposition^{2,3} that the primary mode of flame extinguishment is by thermal mechanisms.

EXPERIMENTAL METHOD

A simple experimental system was designed to generate fast and reliable weight measures of latent extinguishing effectiveness. Small powder samples were to be used which could be classified as to particle size with ATM Sonic or U.S.A. Standard Testing Sieves. Initially, the flame extinguishing characteristics of round pans measuring 20, 25.5, and 30.5 cm diameter with n-heptane fuel were studied. The 25.5 cm

pan with a 1.6 cm lip was chosen for the study since latent effectiveness levels were achieved with this pan for almost all substances and all particle sizes at safe, and readily attainable, powder discharge pressures of 40 to 50 psi.

A dispenser, fixed nozzle, and controlled air supply were used to dispense the powder sample onto the pan. The nozzle was aimed downward at a 30 degree angle toward the center of the pan. The distance between the pan and nozzle (normally 79 cm) was adjusted for a few samples to match powder spread with pan size. The pan was positioned on a round aluminum plate (38 cm diameter x 0.6 cm) which could be removed and quickly cooled between experiments. This 38 cm plate was in turn positioned at the center of a 90 cm square supporting plate. A curved back-stop (90 cm wide, 10 cm high, and 1.5 meter radius) was positioned 53 cm from the center of the fuel pan and directly opposite the nozzle. The dispenser was identical to that used and described for the chamber study¹.

The selected nozzle had eight 0.27 cm diameter holes equally spaced radially on an average diameter of 1.1 cm and drilled at a 15 degree divergent angle with the centerline. Extinction weights for samples covering the experimental range of density and particle size were determined to be independent of nozzle size by a series of comparison tests with nozzle openings of 0.24, 0.27, and 0.32 cm.

The actual measurement of the effectiveness of an extinguishant powder was rapid and simple. The fuel pan and the 38 cm plate were cooled to room temperature. A measured volume of fuel (285 cc) was added to the pan and ignited. A weighed sample of the powder (after prepressurization, generally 50 psi, and vibration) was dispensed onto the pan and flame. This was repeated with varying sample weight to determine the minimum weight required for flame extinguishment. A small fraction of the powder was generally deposited at the front and sides of the pan. This was collected, weighed, and subtracted from the total. Samples were carefully protected from moisture at all times. Handling and loading operations were performed in a dry box. Screen classifications were performed in sealed

sieve systems. Results for all substances were found to be independent of the air or nitrogen used for discharging; air was generally used.

Radiometer readings were used to determine the time of powder introduction. The apparent burning rate of n-heptane in the 25.5 cm pan was found with a radiometer to vary significantly over the two-minute burn period during which heptane entirely covered the pan. Extinction weights for several powders were initially observed at two different radiometer readings – one at initial fuel boil and the other at moderate to heavy boil. Comparable results at the two apparent burning rates were consistent, but extinction weights for the higher rate at heavy boil were 1.75 times those at initial boil. Further analysis of radiometer readings over the full burn period showed that readings (and presumably burning rates) remained reasonably constant for the 20-30 seconds at the point of first boil. In the relatively draft-free enclosure, the radiometer reading at first boil was surprisingly duplicatable. Hence, it was convenient to use the point of first boil with an occasional radiometer reading as the criterion for powder introduction. Since seasonal changes could have influenced the measurements, periodic checks were made with KHCO_3 (0-20 μm) or some other “standard” substance to make certain that the first-boil criterion continued to be valid.

PHYSICAL AND CHEMICAL MEASUREMENTS ON POWDERS

Twelve of the test substances in 100 to 200 pound lots were ground by the Amerex Corporation, Trussville, Alabama. The powders were coated for protection against moisture, and small amounts of mica and silica were added to improve and standardize fluidizing properties.

Particle-size fractions required for test or for the formulation of modified mixtures were prepared by sieve classification with a Ro-Tap or an ATM Sonic Sifter. Several sieve passes were generally required to remove fines from larger particle-size fractions. No effort was made to measure specific surface area since this property was shown in previous work¹ to be unimportant. The analyzed chemical purity for small particle-size fractions (less than 30 μm) of eight different powders was

97 to 99%. Three other powders were 95 to 96%. Sodium chloride had the lowest purity, (93%) but did contain KCl which has almost the same flame extinguishing effectiveness. Most of the impurities were, of course, silica and mica added to improve fluidity. No adjustment to the data was believed to be required, and none was made.

Particle-size fractions, particle densities, and chemical analyses were determined for all the Amerex-prepared powders, for all commercial powders (as received), and for a number of particle-size modifications. Particle-size fractions of all powders are presented in Table 1. Fractions for ranges below 20 μm were determined with the SediGraph 5000 Particle Size Analyzer by the Micromeritics Instrument Corp., Norcross, Georgia. Fractions for larger sizes were based both on sonic sieve tests and on the sedigraph results to 100 μm . Particle densities were also measured at Micromeritics, and chemical analyses were performed by Galbraith Laboratories Incorporated, Knoxville, Tennessee.

CONCEPT OF LATENT EXTINGUISHING EFFECTIVENESS

The latent effectiveness of a powder is defined as the limiting or maximum possible flame extinguishing effectiveness. This condition is achieved when all particle sizes, large and small, are made to penetrate the updraft of the flame without physical loss prior to their actions on the flame. All sizes, then, play their respective parts in the extinguishment of the flame. The plume velocities with the 25.5 cm pan were low; and, at discharge pressures of 50 psi, all powders including those with the very finest particle sizes, could be introduced without physical loss. This is based on two types of observations – the stability of the latent value with increasing discharge pressure and the reliability of mixture relationships (Equations 1 and 2) in correlating latent effectiveness for all particle sizes. The extinguishing effectiveness as reported for each sample of powder is, therefore, a latent value. The actual effectiveness of a powder can be reduced significantly with high velocity flames⁵ where the smaller more effective particles can be preferentially lost to the updraft and where the proportion of large to small particles⁵ becomes important.

Table 1.
PARTICLE-SIZE FRACTIONS^b FOR DRY CHEMICALS

(a = KHCO_3 , b = NaHCO_3 , c = NaCl , d = MonnexTM, e = $\text{NH}_4\text{H}_2\text{PO}_4$, f = $\text{K}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$,
g = $\text{Na}_2\text{C}_2\text{O}_4$, h = $(\text{NH}_4)_2\text{SO}_4$, i = K_2SO_4 , j = K_2CO_3 , k = $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$, l = Na_2CO_3 , m = $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$)

SAMPLE NUMBER	Weight Fraction Below Given Particle Size														
	1A	22A	25A	30A	32A	33A	34A	35A	36A	36B	37A	38A	39A	40A	42A
BASE CHEMICAL	(a)	(e)	(d)	(a)	(e)	(f)	(g)	(h)	(i)	(j)	(i)	(c)	(k)	(l)	(m)
100µm	0.96	0.92	0.73	0.99	0.92	0.40	0.99	0.96	0.98	0.91	0.98	0.97	0.61	0.97	0.92
80 µm	0.92	0.83	0.62	0.98	0.86	0.29	0.98	0.90	0.96	0.80	0.96	0.94	0.51	0.95	0.89
70µm	0.89	0.77	0.55	0.96	0.81	0.24	0.97	0.84	0.93	0.73	0.94	0.92	0.45	0.94	0.84
60µm	0.86	0.71	0.48	0.92	0.74	0.19	0.97	0.78	0.89	0.61	0.92	0.89	0.40	0.93	0.78
50µm	0.80	0.63	0.40	0.88	0.66	0.18	0.96	0.69	0.85	0.47	0.90	0.84	0.35	0.92	0.71
40 µm	0.70	0.54	0.32	0.81	0.56	0.15	0.95	0.56	0.74	0.34	0.88	0.74	0.30	0.89	0.64
30µm	0.57	0.41	0.23	0.66	0.44	0.12	0.91	0.40	0.59	0.23	0.82	0.60	0.25	0.86	0.54
25µm	0.50	0.34	0.18	0.57	0.37	0.11	0.85	0.32	0.52	0.19	0.77	0.51	0.23	0.83	0.48
20µm	0.43	0.28	0.12	0.47	0.30	0.10	0.73	0.23	0.42	0.15	0.69	0.42	0.20	0.78	0.42
15µm	--	0.20	0.06	0.36	0.23	0.09	0.52	0.17	0.32	0.11	0.55	0.33	0.16	0.70	0.35
10µm	--	0.13	0.00	0.26	0.17	0.08	0.22	0.10	0.22	0.08	0.35	0.22	0.09	0.45	0.28
5µm	--	0.06	--	0.12	0.08	0.06	0.01	0.04	0.12	0.06	0.15	0.09	0.01	0.15	0.19

Footnote:
b Particle-size fractions for 1A, 4A, 5A, 7A, 9A, 10A, 12A, and 13B were reported in Reference 1.
TM Monnex is a trade name of $\text{K}_2\text{N}_2\text{H}_3\text{O}_3$.

MATHEMATICAL RELATIONSHIPS

The experimentally observed limiting size, S_L , for a substance, discussed earlier, is the size at which there is a precipitous change in the flame extinguishing effectiveness. The effectiveness of a powder as defined for this study and as used in the mixture relationships is the reciprocal of the extinction weight or concentration. All powders of a given substance with particle sizes below the limit size exhibit the same maximum effectiveness; powders with particle sizes above the limit exhibit particle-size dependence but significantly reduced effectiveness. Extinction concentrations and latent extinction weights have been found in this, and a concurrent study⁵, to rigorously obey certain mixture relationships. If X_r is taken as the weight fraction of each substance with all particles below its limit size, Equation 1 may be used to correlate and predict the effectiveness of a powder containing one or more different substances. The same relationship is equally valid where Q is the minimum latent extinction weight or the minimum extinction concentration.

$$1/Q = [\sum(X_r / Q_{XT}) + \sum(X_{nr} / Q_{nr})]_i \quad (1)$$

where

X_r is the weight fraction of substance i in the sample which is below the limiting size of i ;

Q_{XT} is the observed optimum latent extinction quantity of i ;

X_{nr} is any weight fraction of substance i in the sample where all particles are above the limiting size of i ;

Q_{nr} is the observed latent extinction quantity corresponding to X_{nr} ;

Q is the extinction concentration or the latent extinction weight of the composite powder; and

Subscript i refers consecutively to the different substances.

Another form of Equation 1 has been used in correlating data. If X_r is again taken as the weight fraction of particles below the limiting diameter, $(1-X_r)$ becomes the fraction above, and it follows for a single substance that

$$Q = Q_{XT} / [X_r + (1-X_r) (Q_{XT} / Q'_{nr})] \quad (2)$$

where

Q'_{nr} is the observed extinction quantity for that fraction of a powder corresponding to $(1-X_r)$ with all particles above the limiting size.

RESULTS

Blowoff Phenomenon

An aerodynamic carrier phenomenon was identified and characterized in the companion paper⁵ where larger dry-chemical particles, with higher momentum, entrain and drag smaller more effective particles into the flame. The effectiveness of a carrier in transporting smaller particles (weight of small particles per unit weight of powder) was experimentally shown⁵ to be inversely proportional to the square of the average particle size.

Another phenomenon, blowoff, which we believe is closely related to the aerodynamic carrier effect, was identified and characterized in this study. With the 25.5 cm pan it was possible with many substances and with classified fractions (at discharge pressures below 80 psi) to sweep off and extinguish the flame at apparent effectiveness levels independent of the type of carrier. The common curve and blowoff effectiveness levels for several different substances are presented in Figure 1. It was necessary to characterize the phenomenon in order to measure and differentiate true effectiveness from an apparent value due to blowoff.

Several characteristics of the blowoff state and its relationship to the real effectiveness state were important in separating real from blowoff quantities. These characteristics were the following:

- Apparent effectiveness levels at blowoff were independent of the type of substance and were not consistent in mixture-law calculations.
- Classified powder fractions with all particle sizes below 38 μm always extinguished the flame without blowoff at discharge pressures to 80 psi.
- Classified powder fractions, i.e., 38-63 μm and 63-106 μm , for most substances were highly susceptible to blowoff at all pressures at or above 50 psi.
- Particle-size mixtures formed from classified powder fractions with optimum aerodynamic ratios of small-to-large particles as

defined in the concurrent study⁵ were resistant to blowoff at pressures up to 80 psi.

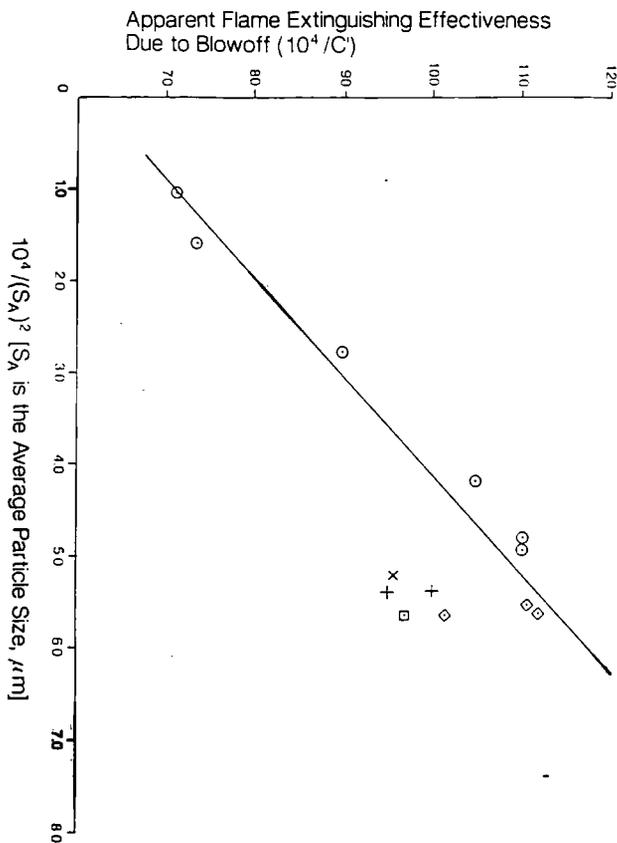


Figure 1. Apparent flame extinguishing effectiveness ($1/C'$) of powders at blowoff conditions versus the reciprocal of the square of the average particle size. C' is the apparent minimum concentration at flame extinction. Blowoff observations were made for various particle-size fractions of Na_2CO_3 , K_2CO_3 , $(\text{NH}_4)_2\text{SO}_4$, NaCl , and K_2SO_4 .

The characteristics of blowoff as described above strongly suggest that this is an aerodynamic effect. This is further confirmed by the common blowoff effectiveness levels (see Figure 1) observed for different substances, by their dependence on the average particle size of the carrier, and by other similarities with the aerodynamic carrier phenomenon reported for solid particles⁵.

Remeasurement of the Limiting Size S_L with the 25.5 cm Pan and the Relationship Between Extinction Concentration and Weight

The limit size, S_L , is the largest particle size which completely reacts in the flame. Extinction concentrations and limit sizes for KHCO_3 , $\text{NH}_4\text{H}_2\text{PO}_4$,

and Monnex were previously measured with the chamber system¹ and the 14.7 cm pan. For these three substances, many of the same commercial powders, particle-size fractions, and mixtures were remeasured with the 25.5 cm pan. The objectives were to determine limiting particle diameters with the larger pan fire and to compare these with those observed in the chamber study¹.

The results of this study for the three substances are presented in Figures 2-4. The data points on each figure represent experimental observations with commercial powders and classified distributions covering particle-size regimes above and below the limit. However, one or two careful observations were made for each substance at particle sizes below the limiting size, S_L , in order to determine the minimum extinction weight, W_{XT} . These are included on the figures.

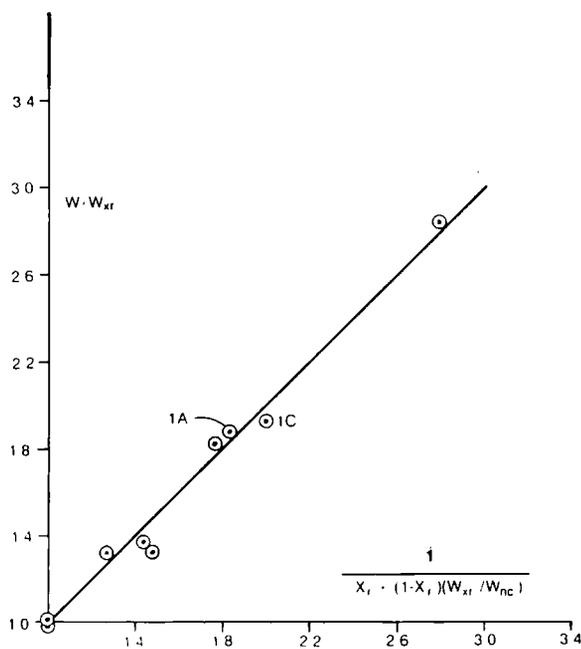


Figure 2. Correlation of experimental data for KHCO_3 based on limiting particle-size concept and Equation 2: S_L , 20 μm ; 1A and 1C are commercial powders, as received; unidentified points are for mixtures prepared from classified particle fractions. All variables are identified with Equation 2. W , W_{XT} , and W_{NC} are experimental quantities; X_f is from particle-size fractions (Table 1 or Reference 1).

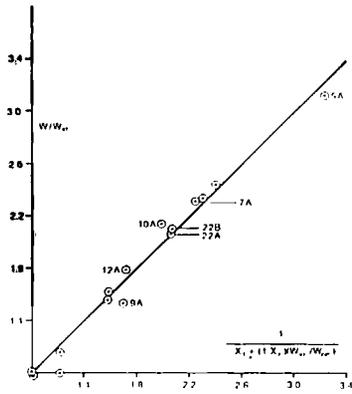


Figure 3. Correlation of experimental data for $\text{NH}_4\text{H}_2\text{PO}_4$ based on limiting particle-size concept and Equation 2: S_L , 29 μm ; 5A, 7A, 9A, 10A, 12A, 22A, and 22B are commercial powders, as received; unidentified points are for mixtures prepared from classified particle fractions. All variables are identified with Equation 2. W , W_{XT} , W_{nr} are experimental quantities; X_r is from particle size fractions (Table 1 or Figure 1).

The correlation presented on each figure was based on Equation 2 and required for each datum point or powder sample, a selected value of S_L ; an observed value of W_{XT} ; an observed value of the extinction weight, W_{nr} , for the particle fraction above S_L ; and a particle-size fraction curve (Table 1) which sets the value of X_r corresponding to S_L . Particle-size fractions not in Table 1 are in Reference 1. The final and selected value of S_L for each substance was that which gave the highest degree of correlation of all data. Values of W_{XT} and W_{nr} for this procedure were obtained from experimental data (Figures 5-7).

The limiting diameters as defined by the correlations and the 25.5 cm pan data are presented in Table 2 and are compared to the limits generated with the 14.7 cm pan¹. All the new limits are slightly lower than those obtained previously but the differences are probably within experimental error. The extinction weights observed with the

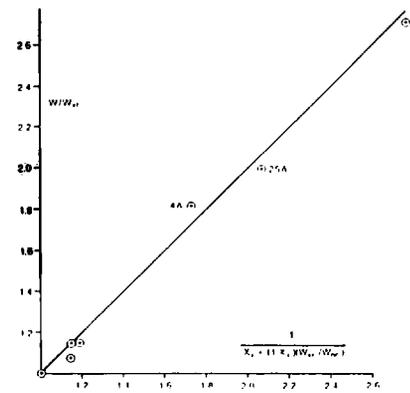


Figure 4. Correlation of experimental data for Monnex based on limiting particle-size concept and Equation 2: S_L , 51 μm ; 4A and 25A are commercial powders, as received; unidentified points are for mixtures prepared from classified particle fractions. All variables are identified with Equation 1. W , W_{XT} , and W_{nr} are experimental quantities; X_r is from particle-size fractions (Table 1 or Figure 1).

25.5 cm pan were found to conform to the mixture relationships (Equation 1 and 2) and to be completely independent of discharge pressures.

In order to study the relationship between latent extinction weights (25.5 cm pan) and minimum extinction concentrations (chamber system¹), extinction quantities for many of the same powders and particle-size fractions were measured in both systems. The experimental results for this comparison are shown in Table 3. Latent extinction weights from the 25.5 cm pan are consistent with and proportional to the more generally applicable extinction concentrations. Therefore, the minimum extinction concentration for any dry-chemical powder can be obtained directly (see Equation 3) from the latent extinction weight observed in the 25.5 cm pan. This interconversion capability is also important, because the minimum extinction concentration is the quantity derived theoretically from the heat-balance equation^{2,3}.

Table 2.

COMPARISON OF LIMITING DIAMETERS AS OBSERVED WITH 14.7 cm AND 25.5 cm N-HEPTANE PAN FIRES

Substance	Limiting Diameter, S_L , μm	
	25.5 cm Pan	14.7 cm Pan
KHCO_3	20	22
Monnex	51	52
$\text{NH}_4\text{H}_2\text{PO}_4$	29	33

$$C_{(\text{mg/liter})} = 0.72 \times W_{(\text{L,g/sq m})} \quad (3)$$

where

$W_{(\text{L,g/sq m})}$ is the minimum latent weight of the substance which is required to extinguish the 25.5 cm n-heptane pan fire, g/m²; and

$C_{(\text{mg/liter})}$ is the extinction concentration of the substance based on the volume and the average temperature in the chamber¹ at the time of flame extinction.

Latent Flame Extinguishing Effectiveness of Nine New Substances

Experimental data illustrating the discontinuity in effectiveness for seven additional substances are presented on Figure 5. It was demonstrated

experimentally for $\text{K}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$ in this study and for several salts in the previous study¹, that the maximum latent extinguishing effectiveness ($1/C_{\text{XT}}$ or $1/W_{\text{XT}}$) is independent of particle size for all samples of a given substance in the particle-size region below the discontinuity. However, as particle size and distribution are increased above the limit size, S_L , effectiveness drops dramatically to a value which is only a fraction of that for the small particle-size region. At still larger particle sizes, the observed effectiveness continues to decrease almost linearly, but moderately, with increase in particle size.

The results reported on Figure 5 are limited to those for powders with particle-size fractions restricted to either the regime above or below

Table 3.

EXPERIMENTAL DATA: GENERATION OF CONVERSION FACTOR FROM EXTINCTION WEIGHT (25.5 cm PAN SYSTEM) TO EXTINCTION CONCENTRATION (CHAMBER SYSTEM¹)

Substance ⁿ Particle- Sizes μm	Pressure psi	Extinction Conc. mg/l from Chamber System	Extinction Wt. g/m ² from 25.5 cm Pan System	Conversion Factor W_L , g/m ² to C, mg/liter
22B (0-38)	50	59.3	82.5	0.72
22A (0-20)	50	59.4	82.5	0.72
38A (0-20)	70	49.6	69.9	0.71
40A (0-20)	70	40.9	59.9	0.68
37A (0-20)	70	30.6	42.4	0.72
33A (0-38)	70	32.9	47.1	0.70
33A (0-38)	70	32.8	48.3	0.71
30A (0-20)	60	34.6	46.6	0.74
13C (0-38)	60	46.7	63.6	0.73
40A (0-20)	70	40.9	59.3	0.69
22A (38-63)	50	337	470	0.72
9A (38-63)	50	337	470	0.72
0.5[1C(38-63)] -0.5[1C(0-38)]	50	76.4	107	0.72
0.5[1C(38-63)] -0.5[1C(0-38)]	70	76.4	108	0.71
3A (As Rec'd)	60	112	149	0.75
3A (As Rec'd)	50	112	147	0.76
2A (As Rec'd)	70	112	165	0.68
2A (As Rec'd)	60	112	165	0.68
1A (As Rec'd)	50	65.1	90.4	0.72
9A (38-63)	60	334	446	0.75

Average

0.72 ± 0.02

ⁿ Compositions and particle-size fractions for several of the substances are in Reference 1. Large particle fractions were subject to blowoff; measurements of effectiveness were made with mixtures incorporating 20 weight percent of a finely divided substance with known effectiveness.

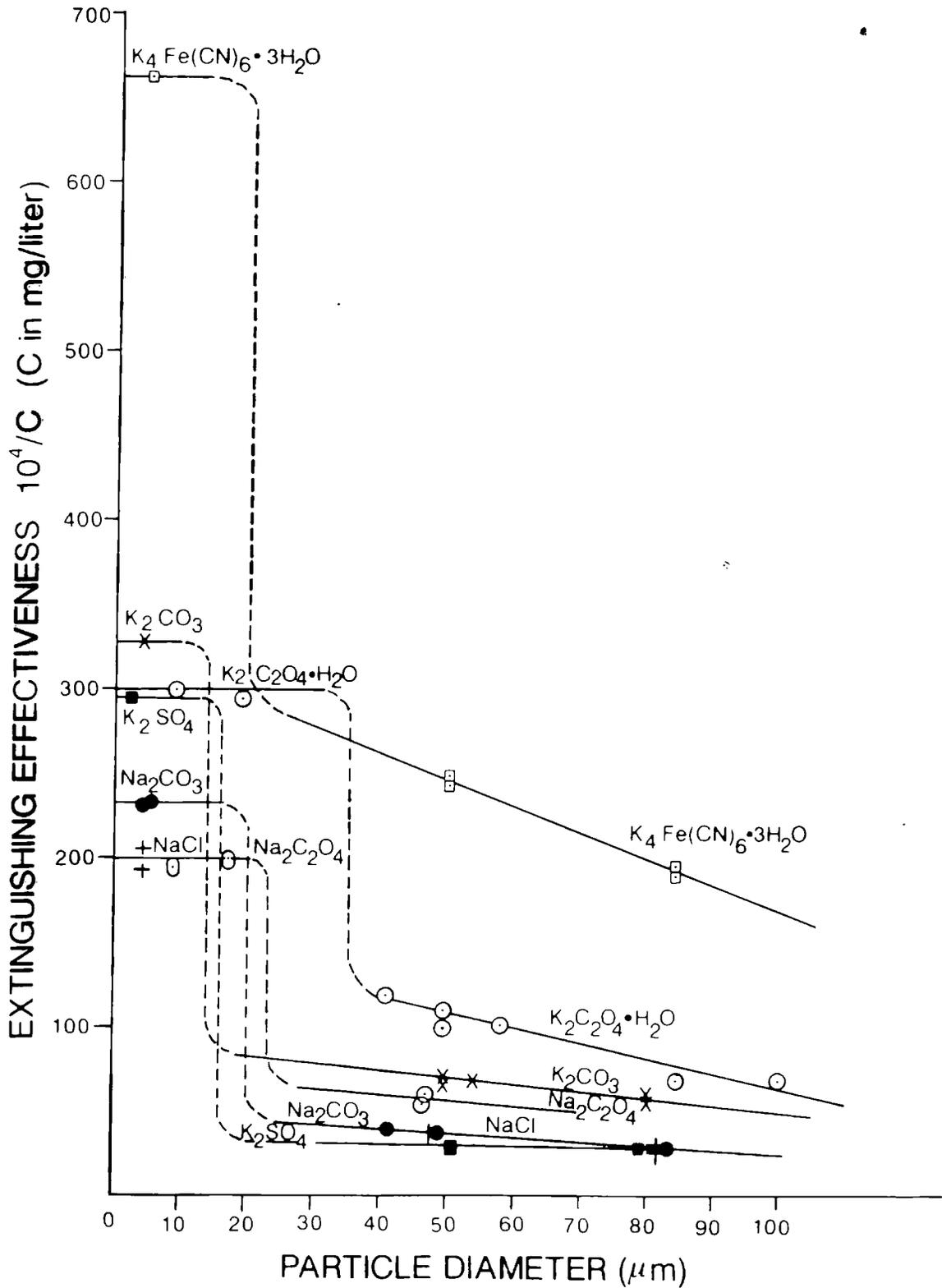


Figure 5. Flame extinguishing effectiveness ($1/C$) for the extinction of the n-heptane pan fire by dry chemicals; $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$, K_2CO_3 , $\text{K}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$, K_2SO_4 , Na_2CO_3 , $\text{Na}_2\text{C}_2\text{O}_4$, and NaCl.

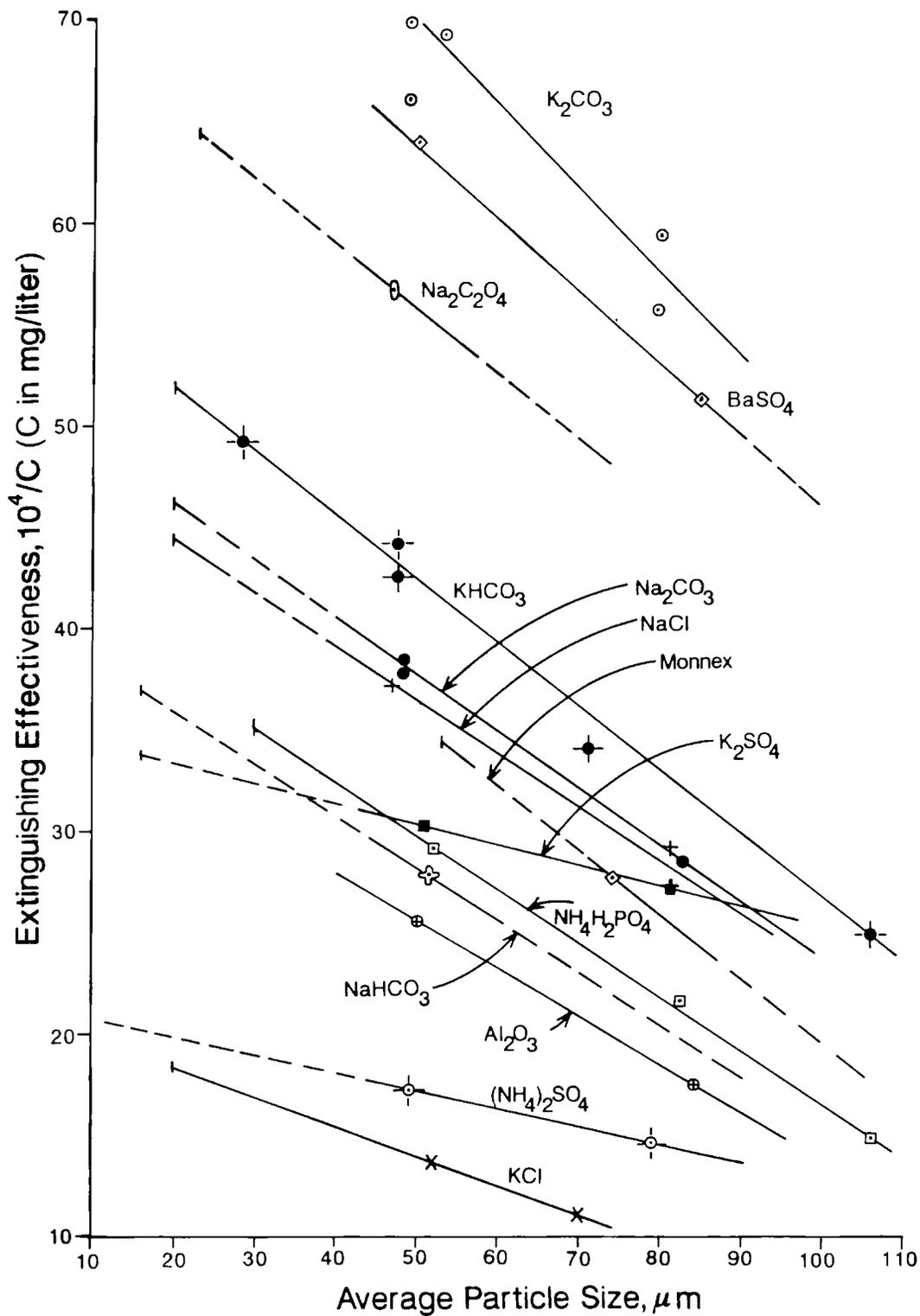


Figure 6. Latent flame extinguishing effectiveness ($1/C$) for the extinction of the n-heptane pan fire by large particle sizes of K_2CO_3 , BaSO_4 , $\text{Na}_2\text{C}_2\text{O}_4$, KHCO_3 , Na_2CO_3 , NaCl , Monnex, K_2SO_4 , $\text{NH}_4\text{H}_2\text{PO}_4$, NaHCO_3 , Al_2O_3 , $(\text{NH}_4)_2\text{SO}_4$, and KCl .

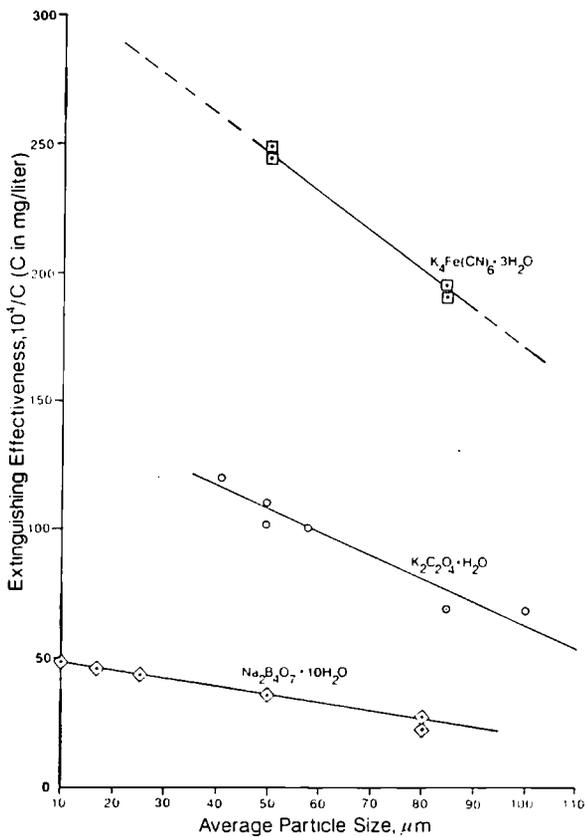


Figure 7. Flame extinguishing effectiveness (1/C) for the extinction of the n-heptane pan fire by large particle sizes of $K_4Fe(CN)_6 \cdot 3H_2O$, $K_2C_2O_4 \cdot H_2O$, and $Na_2B_4O_7 \cdot 10H_2O$.

S_L . These were used principally to define the effectiveness of the regions. In addition, effectiveness levels of the large particle sizes (greater than S_L) for fifteen substances are presented at expanded scales on Figures 6 and 7. Large particle fractions were subject to blowoff; measurements of effectiveness were routinely made with mixtures (and Equation 1) incorporating 20 weight percent of a finely ground substance at 0-38 μm with known effectiveness. All extinction results are reported as concentrations (based on Equation 3) so that they may be compared directly with results for the other substances in Reference 1 and with predictions from thermal mechanisms^{2,3}.

The limiting particle size, S_L , for each substance and the sharpness of its discontinuity were based on additional experimental data (Table 4) for samples with particle-size fractions overlapping both regimes. The final and selected value of S_L (Table 5) for each substance was

that which gave the highest degree of correlation of all the data (Table 4) with the mixture relationship (Equation 2).

Sodium tetraborate and ammonium sulfate were both relatively ineffective in extinguishing the small pan fire. The tetraborate, based on the experimental data, was thermally stable at all particle sizes (Figure 7). Ammonium sulfate exhibited only a limited increase in effectiveness at very small particle sizes (Table 4).

DISCUSSION

Limit Size, Residence Time, and Flame Temperature

The limit size for a dry-chemical powder is that below which all particles are completely decomposed. The authors recognize that the limit will depend on residence time and flame temperature. The limits reported are for saturated hydrocarbon-air diffusion flames. They do appear to be independent of the type of powder application. Limits for total flooding conditions¹ are the same as those obtained by nozzle application in this article. The authors have shown in work to be published⁵ that the limit sizes reported are valid for most pressurized nozzle applications where pressure levels are high enough to generate latent effectiveness values. However, one would expect higher limits for hydrocarbon-oxygen flames and for fire or flame sizes where residence times would be expected to be higher.

Comparison of Results with Those in the Literature

It is difficult, and often impossible, to compare extinction quantities observed by different investigators. Part of this stems from the lack of distinction between real and latent extinction quantities. The authors have shown in a concurrent paper⁵ that the real extinction weight required to penetrate and extinguish higher velocity flames can be 2 to 4 times higher than the corresponding latent quantity. There are also problems comparing latent quantities. The latent extinction weight for a given powder sample depends on the type of fuel and on its burning rate⁵. It was shown earlier that burn-

Table 4.
OBSERVED EFFECTIVENESS CONCENTRATIONS FOR NINE ADDITIONAL SUB-
STANCES; PARTICLE-SIZE FRACTIONS BELOW S_L AND FRACTIONS WITH PARTICLE
SIZES ABOVE AND BELOW S_L

<u>Class Number</u>	<u>Substance</u>	<u>Particle Size Distribution</u>	<u>Conc. mg/liter</u>	<u>Conc. Index ($10^4/C$)</u>
37A	K_2CO_3	0-20	30.5	328.
		0-38	44.0	227.
		As Rec'd	57.9	173.
36A	K_2SO_4	0-10	33.9	295.
		0-20	43.2	232.
		0-63	80.0	125.
		As Rec'd	97.0	103.
36B	K_2SO_4	0-38	43.33	231.
		0-63	121.8	82.
38A	NaCl	0-20	51.8	193.
		0-20	48.7	205.
		0-38	70.2	143.
		0-38	71.6	140.
		0-63	72.7	138.
40A	Na_2CO_3	0-20	43.05	232.
		0-20	42.63	235.
		0-63	48.0	208.
		As Rec'd	52.2	192.
34A	$Na_2C_2O_4$	0-20	50.4	199.
		0-38	51.4	195.
		0-53	57.6	174.
		As Rec'd	60.6	165
33A	$K_2C_2O_4 \cdot H_2O$	0-20	33.3	300.
		0-38	33.9	295.
		0-106	52.9	189.
		As Rec'd	90.8	110.
39A	$K_4Fe(CN)_6 \cdot 3H_2O$	0-20	15.1	662.
		0-38	17.9	559.
		0-63	24.1	414.
		As Rec'd	32.5	308.
35A	$(NH_4)_2SO_4$	0-20	218.	45.9
		0-38	240.	41.7
		0-38	239.	41.8
		0-63	322.	31.0
		As Rec'd	404.	24.8

Table 5.

EXPERIMENTAL LIMITING PARTICLE SIZES, S_L

Substance	Limiting Size, S_L , μm	
	14.7 cm diffusion flame	25.5cm diffusion flame
$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$		< 10
$(\text{NH}_4)_2\text{SO}_4$		(30) ^c
K_2CO_3		14
NaHCO_3	16	
K_2SO_4		16
KHCO_3	22	20 ^e
NaCl		20
Na_2CO_3		20
KCl	20	
$\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$		20
NaC_2O_4		23
$\text{NH}_4\text{H}_2\text{PO}_4$	33	29 ^e
$\text{K}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$		35
Monnex	52	51 ^e

c A limiting diameter of 30 μm was determined for $(\text{NH}_4)_2\text{SO}_4$ in a crib study⁶. Since the limiting sizes of $\text{NH}_4\text{H}_2\text{PO}_4$ and KCl were found to be about the same for crib and pan fires⁶, the value of 30 μm is taken as the limit size of the sulfate for the extinguishment of the small pan fire.

e Accurately determined by graphical procedure (Figures 2-4).

ing rates and corresponding extinction weights for a small pan fire can vary significantly, depending on the preburn period and on other experimental conditions. Therefore, a valid comparison of latent quantities from diffusion studies is possible only where preburn times and/or radiometer control for dispensing powder is stable and reproducible and where well-characterized powders with known particle-size distributions are measured to provide reference to extinction quantities under a standard set of conditions.

Measurements of the effectiveness of dry chemicals in the extinguishment of premixed flames are available^{7,8}. These also provide a type of "standard" since latent extinction concentrations are measured. Rosser *et al.*⁷ studied the inhibition of a stoichiometric premixed methane-air flame by finely divided metal salts (particle sizes below 10 μm). For five of the same salts included in the present study, they reported flame velocities for a

very low salt concentration to one approaching flame extinction. Velocity is not linear with concentration for the salts. It has already been shown³ that the correct extinction concentration is not that obtained by a linear extrapolation of initial velocity effects, but it is that concentration directly observed at the point of flame extinction. Therefore, extinction concentrations observed either in this study or in Reference 1 are compared in Table 6 with the highest concentrations directly observed by Rosser *et al.* as the flame approaches extinction. The agreement is surprisingly good, confirming the magnitude of the results reported in this study.

Fisher *et al.*⁸ used a premixed methane-air burner and measured extinction concentrations for five dry chemicals. The consistency shown between their results and those observed with the chamber¹ helps to confirm the sharpness of the discontinuities and the relative magnitudes of the results reported here.

Table 6.

**COMPARISON OF MINIMUM EXTINCTION CONCENTRATIONS FOR FIVE
SUBSTANCES AS OBSERVED IN THIS STUDY WITH THOSE OBSERVED
BY ROSSER *et al.*⁷**

<u>Substance</u>	<u>Extinction Concentrations, mg/liter</u>	
	<u>This Study</u>	<u>Rosser <i>et al.</i>^α</u>
K ₂ SO ₄	34	34
NaCl	50	39
K ₂ CO ₃	31	35
KHCO ₃	35	34
NaHCO ₃	46	49

^α The extinction concentration for any given extinguishant powder as observed for a n-heptane diffusion flame was shown with heat-balance calculations to be theoretically 1.53 times larger than that for a stoichiometric premixed methane-air flame^{2,3}. Therefore extinction concentrations observed by Rosser *et al.* are multiplied by 1.53 for comparison.

Decrepiation, Particle Reaction, and Limiting Particle Size

Decrepiation as used in this study is defined as the breaking up or blowing apart of particles as they are heated due to fracturing pressures from gas-liquid inclusions, water, or other mechanisms. This phenomenon and other possible reaction schemes were discussed in a previous paper³. However, with the experimental information on the additional substances, we now believe that the size of the limit, S_L , the maximum size which completely reacts in the flame, is generally controlled by flame temperature, residence time, and thermal rates of decomposition and/or vaporization. We recognize that decrepiation in NaCl^{9,10} and in the calcining of minerals⁸ is well documented. However, one would not expect all dry chemicals, as normally prepared, to have the large number of inclusions which would be required for decrepiation control over the limit size.

Monnex, potassium oxalate, and other dry chemicals have been reported to decrepitate into sub-micron particle sizes^{11,12}. This has generally been based on observations of particle-size change when particles are passed through furnaces or flames. However, the existence of decrepiation cannot be confirmed from these measurements since any of the dry chemicals at selected small particle sizes would completely

react and, regardless of whether or not decrepiation occurs, this would be interpreted as severe decrepiation.

Thermal mechanisms^{2,3} can be used to predict the flame extinguishing effectiveness of a dry chemical where particles are assumed to completely react or to only partially react. The effectiveness levels observed for the large particle sizes of K₄Fe(CN)₆ · 3H₂O and K₂C₂O₄ · H₂O (Figures 5 and 7) are too high to be attributed to a heat-capacity sink³, to the bulk loss of hydrated water, or to a combination of both. However, the level of effectiveness for each substance can be accounted for by surface decrepiation or spalling, evidently due to the hydrated water, followed by subsequent reaction of the spalled pieces. To account for the level of effectiveness exhibited by the substances, a 4 μm spalling depth would be required for large particles (60-100 μm) of K₄Fe₃(CN)₆ · 3H₂O and a 2 μm depth for those of K₂C₂O₄ · H₂O. It is also logical to conclude that the slightly higher than average effectiveness exhibited by large particles of several other substances – K₂CO₃, Na₂C₂O₄, etc. – may be due to spalling depths of 1 μm or less.

Substances like Al₂O₃ (Figure 6) which are thermally stable to high temperatures have effectiveness levels that one would expect from their heat-capacity sinks. Effectiveness versus

particle size curves are linear and do not exhibit discontinuity.

Sodium borate decahydrate was observed to be thermally stable in the small diffusion flame at all particle sizes studied (Figure 7). However, the low effectiveness observed for this hydrate with ten molecules of water and with dehydration temperatures near 100°C is difficult to understand. If all water is vaporized, thermal mechanisms^{2,3} would predict an effectiveness ($10^4/C_{XT}$) of over 120 for small particle sizes. The observed effectiveness is less than half of this. Ammonium sulfate has low effectiveness at small particle sizes tested (Table 6) and limited potential as an agent on Class B fires.

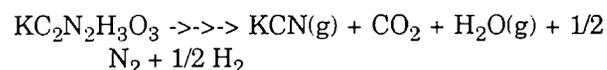
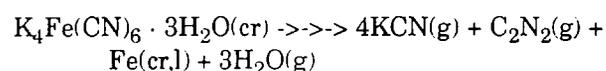
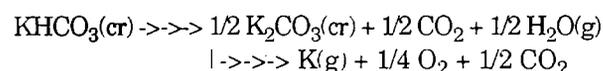
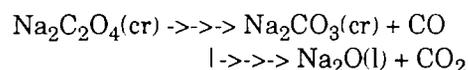
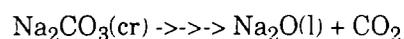
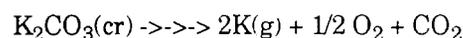
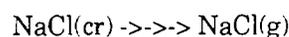
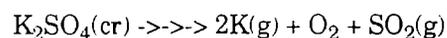
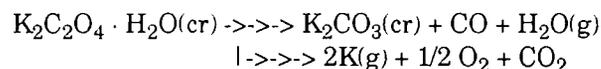
We can readily predict the small-particle effectiveness of most dry-chemical substances; but we have not been able to predict or significantly alter limit sizes or to predict the effectiveness levels of substances at large particle sizes. However, the effectiveness levels of large particles of $K_4Fe(CN)_6 \cdot 3H_2O$ are higher than the maximum observed for small particles of most dry chemicals. This suggests that the phenomenon of decrepitation and of other properties contributing to the usually high effectiveness are certainly worthy of additional study. There is a good probability that acquired knowledge in these areas would lead to dry chemicals with significantly higher flame extinguishing effectiveness.

Thermal Mechanisms: a Major Role in the Extinguishment of Flames

Latent extinction weights were measured at fine particle sizes (where particles completely react) for ten substances in order to further validate the thermal mechanisms concept. Corresponding minimum concentrations were obtained with Equation 3. These are reported in Table 7 and are compared with values predicted thermally from the heat-balance equation^{2,3}. The agreement for all substances except potassium ferrocyanide is good. We believe it has been experimentally demonstrated that the extinguishing effectiveness of a dry-chemical substance is generally related to the size of its heat-extraction sinks.

The decompositions and vaporizations which

fine particles of the dry chemicals (Table 7) are believed to undergo in the heptane-air flame are listed below. The modes of decomposition are generally known, but the dissociation or vaporization of each agent (or product) and its final physical state were defined by thermodynamics using a particle temperature of 1900 K and free energies from JANAF¹³. The heat sinks used for the thermal calculations are specified by the equations listed below.



The minimum extinction concentrations given for $K_4Fe(CN)_6 \cdot 3H_2O$ in Table 7 at particle sizes below 20 μm were measured with two pan sizes; 15 mg/liter was obtained with the 25.5 cm pan and 19 mg/liter with a 0.61 m pan⁵. The results for the iron-containing ferrocyanide are interesting. This is the only substance studied for which there is a possibility of significant chemical effects operative at the time of flame extinguishment. The decomposition of the ferrocyanide has not been characterized at 1900 K and that shown represents only one thermodynamic possibility. The minimum extinction concentration predicted for the decomposition was 43 mg/liter. This is significantly larger than either of the observed concentrations and differences are well outside expected error limits. Either the degree of decomposition or surface spalling must be much greater than that expected or iron must act as a catalyst for radical scavenging or recombination reactions. The extinguishment poten-

Table 7.

**COMPARISON OF EXPERIMENTAL EXTINCTION CONCENTRATIONS FOR
DRY-CHEMICAL SUBSTANCES WITH THOSE PREDICTED FROM
THERMAL MECHANISMS^{2,3}**

<u>Extinguishant</u>	<u>(C_{XT})</u>	<u>Thermal Mechanisms</u>
K ₂ C ₂ O ₄ · H ₂ O	33	33
K ₂ SO ₄	34	29
NaCl	50	50
K ₂ CO ₃	31	31
Na ₂ CO ₃	43	41
Na ₂ C ₂ O ₄	50	43
KHCO ₃	35	35
NH ₄ H ₂ PO ₄	54	50
K ₄ Fe(CN) ₆ · 3H ₂ O	15 (19)	46
Monnex	44	41 ^h
(NH ₄) ₂ SO ₄	(218)	{?}

^h Decomposition has not been characterized, and two possibilities are slightly exothermic.

tial of chemical kinetic effects, if present, would be equal to or double that which would be expected from thermal sinks.

The value of 216 mg/liter given for the minimum extinction concentration of (NH₄)₂SO₄ in Table 7 is consistent with the data in Table 4 and the limiting diameter of 30 μm (Table 5). This sulfate has a complex and poorly characterized decomposition. It is reported¹⁴ to decompose at about 357°C losing ammonia gas and forming an equilibrium melt consisting of (NH₄)HSO₄ or H₂SO₄ with itself. The decomposition mode – (NH₄)₂SO₄ → H₂SO₄(l) + 2NH₃(g) – has an exothermic heat of decomposition of –1 kcal/mole and the other mode – (NH₄)₂SO₄ → NH₄HSO₄(l) + NH₃(g) – has an exothermic value of –35 kcal/mole. One would therefore expect a C_{XT} value in the range of those observed for large non-reactive particles. The value of 218 mg/liter is in this range.

SUMMARY

Latent extinction quantities are the reference levels from which the scaling and prediction of real effectiveness on large pans can be made. This is described in detail in the concurrent paper⁵. We

now have reliable latent extinction information as a function of particle size for fifteen different extinguishants and carriers. The large pan n-heptane effectiveness in gm/m² of fuel surface can now be predicted for almost any combination of substances and/or particle-size distributions⁵.

We have also reaffirmed in this study that the flame extinguishing effectiveness levels of dry-chemical substances are not related to the specific surface area they present to the flame¹ nor to the chemical activities they exhibit at lower inhibitor concentrations³. However, effectiveness can be correlated and predicted from the reactivity of particles in flames and from the heat-absorption sinks contributed by them. We believe that substantial new evidence has been presented to support the proposition that heat extraction is the principal mode by which dry chemicals, halons², and other substances extinguish flames.

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