FIRE-EXTINGUISHING POWDERS

by

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1. BACKGROUND

Many finely divided solids (nonflammable salts) have been used to quench hydrocarbon flames. Sodium bicarbonate was widely used into the 1950s as the primary fire-extinguishing powder. The U.S. Navy determined that potassium bicarbonate was superior to the sodium analog and subsequently changed its hand-held extinguishers from sodium bicarbonate to potassium bicarbonate. Other solids, such as Monex, have been proposed, but their fire-extinguishing ability is only marginally superior to potassium bicarbonate. Because of the expense, there has been resistance to a changeover.

It is widely believed that fireextinguishing powders can function as both energy-absorbing materials and solid surfaces on which free radicals can be destroyed. Heat may be absorbed by the heat capacity of the solid, the heat of fusion at the melting point, the heat capacity of the liquid, heat of dissociation from breaking of chemical bonds, and heat of vaporization. All of these contribute to the total endothermicity of the fireextinguishing powder (ref. 1).

From a chemical aspect (ref. 2.3). it has been found that potassium salts are more. effective than sodium salts, and iodide anions are more effective than chloride anions. Presumably, there is a catalytic path for destruction of free radicals, such as H, O, and OH, utilizing the potassium in the salts. It must be remembered that any powder that has a chemical fireextinguishing capability will also have a heat-absorbing (endothermic) capability.

Ewing (ref. 1) has shown that less weight of salt per unit volume of a fuel-air mixture is required for extinguishment if the salt is finely divided. Large particles may actually pass through the flame zone before they can reach flame temperature and, thus, not absorb as much heat as an equivalent mass of finer particles. Another way to look at it is that the time required for small particles to become effective is less than that for large particles. Thus, micron-sized solids are more efficient as fire-extinguishing powders than are larger particles. Large surface areas are important in both the heat absorption and the chemical interference mechanisms.

2. INTRODUCTION

In many cases, **there** is a hesitation to use conventional fire-extinguishing powders, such as **Purple** K, Monex, and sodium bicarbonate, which can be corrosive to metals, especially aluminum. Therefore, **aluminum** oxide powder, which is chemically unreactive, has been chosen for aircraft applications. This material has no ability to melt, vaporize, or undergo bond-breaking at the temperatures encountered in hydrocarbon flames. Yet, **tests** have shown that aluminum oxide powder is effective in extinguishing fires, even though it only has the heat capacity of the solid to serve **as** its heat sink. This fact prompted a decision to examine aluminum oxide powder in a scanning electron microscope (SEM) to determine if there was anything unusual about this material.

This, in *turn*, led to a decision to examine new types of micronized sodium bicarbonate powders that have recently become commercially available. These powders have been proposed for use in engine compartments of combat vehicles. In order to complete this study, other common fire-extinguishingpowders have also been examined. Since the expense of full-scale testing of all of the powders under consideration would have been prohibitive, a simple method of screening these powders for their effectiveness as fire-extinguishing agents was needed. From the physics of fire extinguishment, the following parameters were selected: particle-size distribution, degree of agglomeration, and appearance (amorphous or crystalline). **The** materials that were evaluated **are.** all currently accepted fire-extinguishing agents and, therefore, possess the quality, in various degrees. of endothermicity; obviously, they are also acceptable from the standpoint of toxicity. Interpretation of SEM and optical microscopy photographs was employed as the screening method in this study.

Obviously, powder fireextinguishing agents are not suitable for **use** in occupied (crew) spaces; however, they may find utility in unoccupied compartments (e.g., engine compartments). Even in this application, toxicity is of concern, and only recognized fire-extinguishing agents would be applicable.

It may be possible to use sprays of salt, dissolved in water, to obtain the effectiveness of a powder fire-extinguishing agent, but delivered as a liquid spray. Only in a flame zone, where the water would be vaporized from the droplets, would the powder salt be formed. This approach could allow the use of high-salt, water-based sprays as very efficient fire-extinguishing agents.

3. DESCRIPTION OF EXPERIMENTS

3.1 Samules. Thiieen types of fire-extinguishing powders were available for testing. Eight were samples of sodium bicarbonate from various manufacturers. Table 1 gives some details about the powders that were evaluated.

3.2 Samule Preparation for SEM Observation. The instrument used was an ISI model Super III-A SEM. Cylindrical aluminum pedestals ½ in **x** ½ in were used in this instrument for sample mounting. **A** small piece of double-sticky tape was placed on the upper flat surface to accept the sample powder. The powder was lightly stirred to bring some of it up from beneath the surface, to promote a more representative sample selection, and a small spatula was used to extract a very small amount of powder from the container. The spatula was held a few centimeters above **the** pedestal and gently tapped until the desired amount of powder had fallen onto the pedestal. The pedestal was in turn tapped in various places to distribute the powder more

Table 1. Listing of Samples That **Were** Investigated

Powder Type	Description	Source
Amerex	Sodium Bicarbonate	ATC
Ansul + 50	Sodium Bicarbonate	ATC
Ansul + 50C	Sodium Bicarbonate	ATC
Arm & **Hammer** Baking Soda	Sodium Bicarbonate	K-Mart
Dessicarb Regular	Sodium Bicarbonate	ATC
DXP Clone Dessicarb	Sodium Bicarbonate	ATC
BSC Siliconized	Sodium Bicarbonate	ATC
Aluminum Oxide	Fire-Extinguishing Grade	Alcoa Composites
Aluminum Oxide	Anhydrous	Phaltz & Bauer
MAP[b]	Monoammonium Phosphate	Local Fire Department
Monex	Condensation product of urea and potassium bicarbonate plus 15% excess potassium bicarbonate	ICI
Purple K	Potassium Bicarbonate plus a purple dye	Automated Protection Systems

[a] ATC - **Aberdeen** Test Center
[b] MAP - Monoammonium Phosphate

uniformly over the surface area. The sample was then sputtered with a gold-palladium alloy for 2 min at 15-pa current and 75-pm **Hg** pressure to ensure uniform conductivity and to prevent sample charging during exposure to the electron beam. The sample, prepared in this manner, was then inserted into the SEM sample holder and photographed at several magnifications. Operator bias can enter the procedure here in the choice of sample region to study and analyze; therefore, the two methods, SEM and optical microscopy, were employed.

3.3 Sample Preparation for Optical Microscopy. Optical photo microscopy was also done on all **of** the previously mentioned samples, using a Nikon Optiphot binocular optical microscope. The microscope slides were cleaned and then coated with a very thin film of silicone grease. The grease was necessary to keep the powder in place on the slides during handling and observation. A small quantity, approximately 1 g of the powder as received, was placed into an evaporating dish, and a stream of air was directed onto it from an atomizing squeeze bulb. The aerosolized powder was allowed to fall onto the microscope slide. Care was taken to ensure that the microscope slide was approximately in the center of the footprint of the falling powder. To avoid observational **bias.** each slide **was** observed in the microscope at the same five coordinate locations (Figure 1).

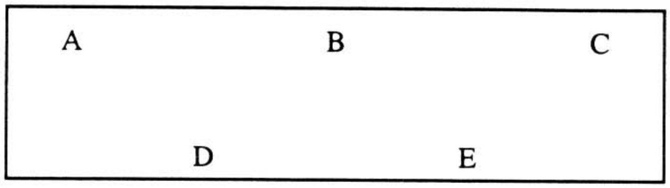

Figure 1. Coordinate Locations Used for Optical Microscope Observations.

The method of obtaining samples for SEM observation was considered to produce valid representations of particle-size distributions, whereas the aerosolization method used to make samples for optical microscopy may not have produced samples that were as independent of particle size. However, with care and practice, the authors think that valid samples were obtained.

3.4 Assessment Criteria for SEM Samples. Several characteristics are relevant to the evaluation of powders as potential fire-extinguishing agents. Those used in this study are: (1) size in two dimensions of the median particle, and of the largest and smallest particle found; (2) particle-size distribution; (3) degree of agglomeration; (4) appearance; and (5), for certain samples, surface texture.

3.5 Assessment Criteria for Optical Samples. Particle-size distribution and both average and median particle sizes were used to predict the effectiveness of the powders as fire-extinguishing agents. Photographs of each slide were taken at the five predetermined positions. Particle size was determined as follows. All particles, except "dust,"[*] were treated as two-dimensional rectangular particles. A photograph of a calibrated scale with 1-µm subdivisions was used for size reference. Each particle (above the arbitrary cutoff of 7 µm for the largest dimension) was measured for the maximum dimension and its corresponding dimension, 90° from the maximum (treated as a rectangle). The calculated area of each particle was determined by multiplying the two dimensions. The square root of this "area" was taken and called the "characteristic dimension" of the particle. The areas were used to calculate the average and median particle sizes at each of the five locations on each slide. The characteristic dimension of the average particle was used as a measure of the size of the fire-extinguishing powder. The particle-size distribution was used as an indication of the quality control during manufacture and packaging/distribution.

4. RESULTS

4.1 SEM. The SEM photographs were analyzed for what appeared to the analyst to be the largest, smallest, and median particle sizes. Appearance and surface texture were also observed and recorded. Table 2 presents these data for the thirteen powders analyzed.

4.2 Optical Microscopy. Each of the thirteen powders was observed and analyzed at the five predetermined positions. There was very little overlap of particles in the photographs of each position. Data on average and median particle sizes, of concern when these powders are used as fire- extinguishing agents, are presented in Table 3. Appropriate comments and observations on degree of agglomeration are included.

The largest particle found on each of the thirteen slides is also reported in Table 3. The BSC siliconized sodium bicarbonate had the largest particle found, with a characteristic dimension of 132 µm. There were no other particles of BSC material with a characteristic dimension above 73.6 µm. It is felt that the one very

[*] "Dust" was defined as any particle whose largest dimension was less than 7 µm. This screen was used only for optical samples. The dust was excluded because the aerosolizing technique suspended the fine particles more efficiently than the larger particles. It was thought that the smaller particles were overrepresented on the microscope slide collectors.

Table 2. Observed Characteristics of Powders Analyzed by SEM

Material	Largest Particle In Picture (µm)	Smallest Particle In Picture (µm)	Median Particle Size (Judgement) (µm)	Appearance
Amerex	63 × 40	3 × 1.9	17 × 14	Amorphous; little dust; not much agglomeration.
Ansul + 50	93 × 30	5.8 × 1.8	[illegible]1 × 27.6	Little dust on particles; discrete particles, no agglomeration; lumpy particles; continuous particle-size distribution.
Ansul + 50C	77 × 63	9.5 × 4.6	29 × 21	Lumpy; some dust on large particles; not much agglomeration
Arm & Hammer Baking Soda	70 × 45	14 × 5	[illegible] × 2[illegible]	Extreme clumping; not much dust; some obvious crystalinity, but generally, irregular shapes; may need more drying agent, or already be too dry so that electrostatic attraction causes clumping.
DSP Desicarb Regular	114 × 90	2.4 × 2.4	20 × 14	Amorphous; lots of dust; no agglomeration.
Desicarb Clone Lot BNPP-079b	124 × 84	2.9 × 1.9	16 × 14	Sharp edges; some dust; much agglomeration.
Kiddie	95 × 66	3.9 × 2	42 × 26	Clumped; some dust; some agglomeration.
BCS Lot BNWQ-241	139 × 46	0.8 × 0.6	25 × 17	Amorphous; some dust; no agglomeration.
Fire-Extinguishing Al_2O_3	41 × 29	[illegible] × [illegible]	13 × 10	Little dust on surfaces of larger particles; lumpy, rounded shapes; some rods; few platelet particles; fewer sharp edges than anhydrous material.
Anhydrous Al_2O_3 Chemical Grade	133 × 83	13.9 × 9.6	80 × 40	No dust; all particles consist of aggregated platelets; sharp edges.

Table 2. Observed Characteristics of Powders Analyzed by SEM (continued)

Material	Largest Particle In Picture (μm)	Smallest Particle In Picture (μm)	Median Particle Size (Judgement) (μm)	Appearance
MAP	152 × 164	9 × 9	23 × 16	Individual particles with little dust; jagged, random shapes; wide range of particles sizes; distribution continuous, except for few very large particles.
Monex	44 × 34	4 × 4	17 × 11	Small particles are clumped together; large particles have dust on them; there are large, single particles; most large particles are agglomerates; distribution appears bimodal.
Purple K ($KHCO_3$)	81 × 59	3 × 3	23 × 13	Few median-size particles (appears to have bimodal distribution); generally smooth surfaces; some dust clinging to particles.

Table 3. Observations on Powders Using Optical Microscopy

Powder Type	Largest Particle Size (Characteristic Dimension) (μm)	Average Particle Size (Characteristic Dimension) (μm)	Median Particle Size (Characteristic Dimension) (μm)	Agglomeration Observed	Comments
Ammerex Sodium Bicarbonate	74 × 74 (74)	24 × 18 (21)	21 × 14 (17)	Little	Poor picture resolution.
Ansul + 50	86 × 49 (65)	29 × 21 (25)	26 × 19 (22)	None	
Ansul + 50C	67 × 42 (53)	21 × 14 (17)	19 × 12 (15)	None	
Arm & Hammer Baking Soda	146 × 56 (90)	58 × 31 (42)	51 × 21 (38)	Some	As many large particles as small particles.
Desicarb	85 × 58 (70)	30 × 20 (24)	26 × 15 (20)	Little	
DXP Desicarb Clone	90 × 70 (79)	26 × 18 (22)	20 × 14 (17)	Almost none	Small sample size.
Kidde Sodium Bicarbonate	46 × 32 (38)	28 × 20 (23)	23 × 16 (19)	None	Small sample size.
BSC[b] Siliconized Sodium Bicarbonate	260 × 67 (132)	43 × 24 (32)	37 × 26 (31)	None	
Aluminum Oxide, Fire-Extinguishing Grade	56 × 37 (46)	15 × 10 (12)	12 × 9 (10)	Possibly high	Irregularly shaped particles; clumping could be high.
Aluminum Oxide, Anhydrous	88 × 60 (73)	44 × 34 (39)	44 × 36 (40)	Little	Particles appear "hairy"; possible clumps of small particles.

Table 3. Observations on Powders Using Optical Microscopy (continued)

Powder Type	Largest Particle Size (Characteristic Dimension) (μm)	Average Particle Size (Characteristic Dimension) (μm)	Median Particle Size (Characteristic Dimension) (μm)	Agglomeration Observed	Comments
MAP	108 × 84 (95)	35 × 27 (31)	28 × 23 (25)	None	Several large particles on slide, but not at any of the five positions.
Monex	142 × 46 (81)	38 × 27 (32)	27 × 19 (23)	None	Small number of particles; may not represent true conditions.
Purple K					Al sm

large particle is an anomaly, not representative of the BSC siliconized sodium bicarbonate sample. The Purple K, however, with a maximum characteristic dimension of 109 pm had many large particles.

The powder with the smallest average characteristic dimension was the fire-extinguishing grade of aluminum oxide. Its average (characteristic dimension) was 12 µm. The only other powder with an average characteristic dimension under 20 pm was Ansul + 50C, with a value of 17 pm.

The traditional fireextinguishing powders, MAP (31 µm), Monex (32 µm), and Purple K (35 pm) had larger characteristic dimensions than most of the sodium bicarbonate powders. All the sodium bicarbonate fire extinguishing powders except the BCS (32 µm) had average characteristic dimensions of 25 pm or less.

As would probably be expected, the Arm & Hammer Baking Soda (sodium bicarbonate) and the anhydrous aluminum oxide had relatively large, average characteristic dimensions of 42 pm and 39 pm, respectively. Small particle size is not a requirement for these powders.

5. DISCUSSION

Neither optical nor SEM techniques provide the "better" data; they complement each other. The SEM photos yield a better view of surface texture than can be seen on the optical photos. Yet, there is a good chance the operator's attention will be drawn to interesting parts of the field of view in the cathode ray tube. Thus, the SEM results may not be truly representative of the powder, since there is operator input in deciding what to emphasize.

It was relatively easy to make the optical data free of bias by observations of predetermined sections of the microscope slides. This approach was not true of the SEM data.

An advantage of the optical analysis was a limited number of particles above dust size. This allowed measurements of every particle (excluding dust). In general, there was no overlap of particles on the slides, in contrast to a great deal of overlap of particles in the SEM photos.

In many cases, there were significant differences in the characteristic dimension of the median particle size from SEM and optical data. It is felt that the optical data is more reliable, since it does not involve operator judgement in selecting the site to be evaluated. It was also found to be quite difficult to pick the median particle size from the SEM photos, since there were many overlapping particles in the photos.

It is felt that the fire-extinguishing effectiveness of the MAP, Monex. and Purple K powders could be enhanced if their average characteristic dimensions were as small as that of most of the sodium bicarbonate fireextinguishing powders. It is possible, in the case of Monex, that what was observed on the optical photos was a small number of clumps of particles. If true, these clumps might break up upon activation of a fire extinguisher. It was noted, by examining Material Safety Data Sheets (MSDSs), that Ansul + 50 contains double the drying agents that Monex has. An increase in the amount of drying agent may prevent clumping of the Monex.

The fireextinguishing grade of aluminum oxide with the smallest average characteristic dimension of 12 µm is used in powder panels. In this application, the powder is released at the fuel source, which is the fire site. Thus, the smallest particles are not required to travel through the air from a pressurized extinguisher to the fire site. Large aerodynamic drag on small particles is not a problem when powder panels are used. However, when fireextinguishing particles are released from a pressurized extinguisher and must travel through several feet of air to the fire site, aerodynamic drag is important. The optimal size of the particles is a function of both the aerodynamic drag and the surface area presented to the fire. This value of the average characteristic dimension will have to be determined for individual applications.

CONCLUSIONS

The following conclusions were drawn.

(1) All of the sodium bicarbonate fire-extinguishing powders, with the possible exception of the BSC siliconized sodium bicarbonate, are similar enough in particle size that particle size should not be an issue.

(2) Even powders that must be driven through the air can have characteristic dimensions of 25 pm or less.

(3) Manufacturers of fire-extinguishing powders should produce agents with small (25 pm or less) characteristic dimensions.

(4) Large amounts of drying agents (8 to 10%) may be required to ensure good flow characteristics and absence of clumping in fire-extinguishing powders that normally tend to absorb water.

(5) Powders that do not have to be driven through air (aluminum oxide in powder panels) can be manufactured with very small characteristic dimensions (12 µm).

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