

Flammability of Metals and Other Elemental Dust Clouds

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This paper reports results from a U.S. Bureau of Mines study of the flammability of various metals and other elemental dusts dispersed in air. The data are useful for evaluating the explosion hazards in the minerals and metals processing industries. The dusts studied included boron, carbon, magnesium, aluminum, silicon, sulfur, titanium, chromium, iron, nickel, copper, zinc, niobium, molybdenum, tin, hafnium, tantalum, tungsten, and lead. The dusts were chosen to cover a wide range of physical properties—from the more volatile materials such as magnesium, sulfur, and zinc to the highly “refractory” materials such as carbon, niobium, molybdenum, tantalum, and tungsten. These flammability studies were conducted in the Bureau of Mines 20-L explosibility test chamber, using strong pyrotechnic ignitors. The parameters measured included the minimum explosible concentrations, maximum explosion pressures, and maximum rates of pressure rise. All of the elemental dusts ignited and burned as air-dispersed dust clouds except the nickel, copper, molybdenum, and lead. In general, the dusts with the highest explosion pressures and rates of pressure rise were also those with the highest calculated, adiabatic flame temperatures and/or the ones that vaporized most easily, but this was not true in all cases. The effect of particle size on flammability was studied for the aluminum and iron dusts. The minimum explosible concentrations were relatively independent of particle size below 30 μm , but the highest explosion pressures and rates of pressure rise were found at the finest sizes tested.

INTRODUCTION

An accurate knowledge of the explosibility behavior of materials is essential for a realistic safety evaluation of their use in manufacturing, handling, and processing. Various books such as references [1] through [6] have been published since 1980 on the general subject of the explosion hazards of dusts and powders. This paper will concentrate on the explosion characteristics of metal and nonmetal elemental dusts. These dusts are important from both the practical and fundamental points of view. These metal and nonmetal elements are widely used or occur in industry as powders or dusts, and an evaluation of their possible explosion hazards is important. In addition, the elemental dusts are ideal for studying the fundamental physicochemical processes occurring during combustion because they are pure, uniform substances with well-characterized phase transitions and thermodynamic properties. This is in marked contrast to the complex structures and heterogeneous chemistry associated with coal combustion. The elemental dusts also display a marked variation of reaction exothermicities in air and an enormous range in vapor pressures at their respective flame temperatures.

In the 1960's and earlier, the U.S. Bureau of Mines studied the explosibility of metal dusts using a 1.2-L Hartmann chamber [3, 7] with an electric spark ignition source; the results are summarized in references [8] and [9]. Recent Bureau research by the author and others used a 20-L chamber and much stronger pyrotechnic ignitors to study the explosibility of metal dusts [10–11]. The current paper is a continuation of these studies. The elemental dusts tested were boron (B), carbon (C), magnesium (Mg), aluminum (Al), silicon (Si), sulfur (S), titanium (Ti), chromium (Cr), iron (Fe), nickel (Ni), copper (Cu), zinc (Zn), niobium (Nb), molybdenum (Mo), tin (Sn), hafnium (Hf), tantalum (Ta), tungsten (W), and lead (Pb). The explosion characteristics measured for this report included minimum explosible concentrations (lean flammable limits), maximum explosion pressures and rates of pressure rise, and the effects of dust particle size. In this paper, the terms “flammability” and “explosibility” are used interchangeably to refer to the ability of an airborne dust cloud to propagate a deflagration after it has been initiated by a sufficiently strong ignition source.

The laboratory data in this paper were obtained in the Bureau of Mines 20-L chamber [12], which has been used extensively

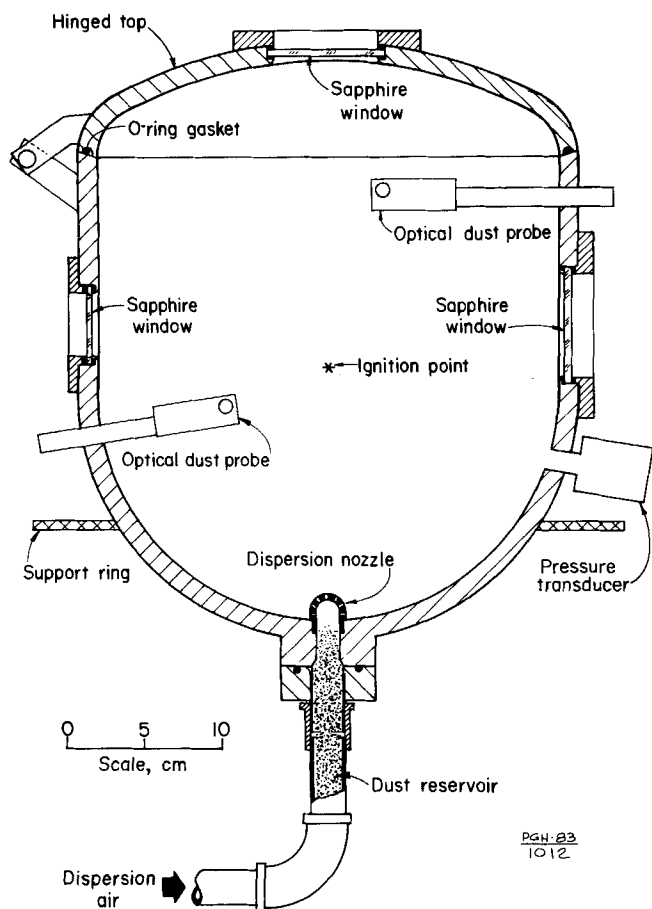


FIGURE 1. Vertical cross section of 20-L laboratory explosibility test chamber.

to study to explosibility of coals and other carbonaceous dusts. Previous Bureau papers have discussed various aspects of explosibility that are also pertinent to the subject of metal and other elemental dusts. These include the ignition energy requirements for accurate measurements of flammability limits of dusts and gases [13-14], a volatility model for coal dust flame propagation [15], the effect of volatility on the explosibility limits of coals and other carbonaceous dusts [15-16], the effects of particle size [17-19], comparisons of data from 20-L and 1-m³ chambers [14, 18-19], and comparisons of laboratory and experimental mine data [18-21].

EXPERIMENTAL EQUIPMENT AND TEST PROCEDURES

The dust flammability experiments in this paper were conducted in the Bureau of Mines 20-L laboratory chamber [12] shown in Figures 1 and 2. This is the standard laboratory test chamber used at the Bureau for studying the flammability and inerting of combustible dusts. There is another style of 20-L chamber designed by R. Siwek [1, 5, 22-23] that is in wide use in Europe. The Bureau of Mines 20-L chamber is near-spherical in shape and made of stainless steel. It has a pressure rating of 21 bar, g. The chamber top is hinged and opens across the full chamber diameter (Figure 1), allowing easy access to the interior for positioning instruments and for cleaning. The hinged top is attached with six 3/4-in (19-mm) diameter bolts which are not shown on the drawings. Two optical dust probes [24-26] are used to measure the uniformity of the dust dispersion at the positions shown in Figures 1 and 2. The optical probes measure the transmission through the dust cloud. Thin jets of air keep the probe windows dust-free. For the majority of the measurements, one dust probe with a 38-mm path length

and a second dust probe with a 95-mm path length were used. The longer path length is more suitable for dusts with higher densities and larger particle sizes. References [12] and [14] contain examples of dust probe transmission measurements showing the dispersion uniformity in the 20-L chamber. The strain gauge pressure transducer measures the explosion pressure and rate of pressure rise. A multichannel infrared pyrometer [27-28] can be used to measure the explosion temperature by observing the flame radiation through the sapphire window. The data from the various instruments are collected by a high speed personal computer (PC) based data acquisition system. It can sample data from 16 channels at a maximum rate of 9 kHz if all channels are used or at even faster rates if fewer channels are used. Data are displayed on a color monitor immediately after each test.

The dust to be tested can be placed either in the dust reservoir or on top of the dispersion nozzle at the bottom of the chamber (Figure 1). After the dust and ignitor have been placed in the chamber, the top is bolted on and the chamber is partially evacuated to an absolute pressure of 0.14 bar, a. Then a short blast of dry air (0.3 s duration at 9 bar from a 16-L reserve tank) disperses the dust and raises the chamber pressure to about 1 bar, a. The ignitor is activated after an additional delay of 0.1 s. This results in a total ignition delay of 0.4 s from the start of dispersion until ignition. The experimental dust concentration reported for the 20-L chamber is the mass of dust divided by the chamber volume.

The Bureau has historically placed more emphasis on the measurement of minimum explosible concentrations (MEC) and rock dust inerting amounts rather than on the measurement of rates of pressure rise (which are used for vent sizing) because it is not possible to vent mine explosions. Therefore, the dispersion time is longer and the turbulence level is lower for the standard dispersion procedure in the Bureau of Mines 20-L chamber than for the Siwek 20-L chamber. This should mainly affect the rates of pressure rise (at high concentrations) and should not affect MEC measurements [14]. The rate of pressure rise data reported in this paper from the Bureau 20-L

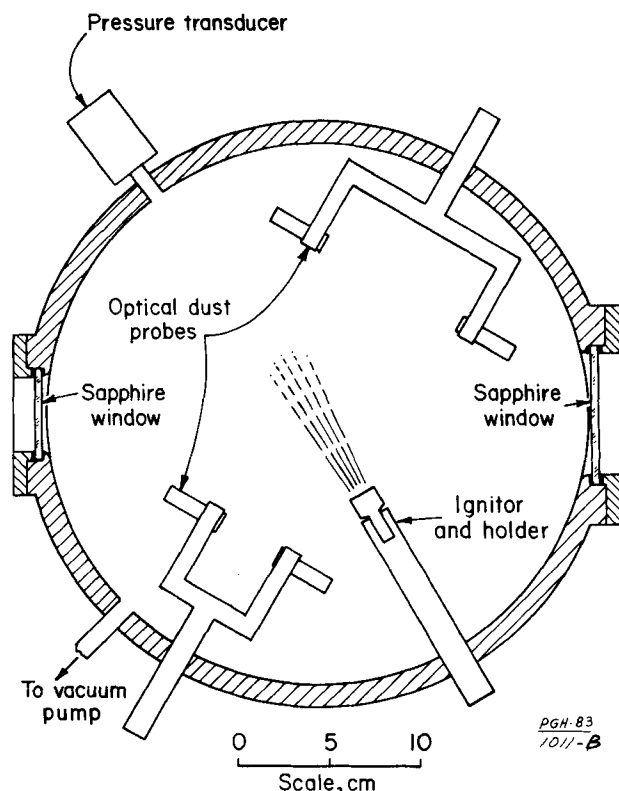


FIGURE 2. Horizontal cross section of 20-L laboratory explosibility test chamber.

PERIODIC TABLE OF THE ELEMENTS

FIGURE 3. Periodic table of the elements, highlighting the dusts tested

chamber should only be used as relative data for comparison of different dusts and should not be used for the sizing of vents according to ASTM Standard E1226, ISO Standard 6184/1, NFPA Guide 68, and VDI Standard 3673, which are based on the higher turbulence level of the Siwek 20-L chamber and the 1-m³ chamber [1, 5].

The ignition sources used for the 20-L tests were electrically activated, pyrotechnic ignitors manufactured by Fr. Sobbe* of Germany. These ignitors are composed of 40% zirconium, 30% barium nitrate, and 30% barium peroxide. They are activated electrically with an internal fuse wire and deliver their energy in about 10 ms. The Sobbe ignitors are available in various energies from 250 to 10,000 J. For the 20-L tests reported in this paper, 2,500- and 5,000-J ignitors were used. These energies are nominal calorimetric values based on the mass of pyrotechnic powder in each ignitor. The 2,500- and 5,000-J ignitors by themselves produce pressure rises of about 0.33 and 0.54 bar, respectively, in the 20-L chamber.

EXPERIMENTAL RESULTS AND DISCUSSION

The metal and nonmetal elemental dusts studied are shown in Figure 3, highlighted at their positions within the periodic table. Nineteen dusts were studied: 15 metals and 4 nonmetals. Table 1 lists the pertinent physical data for the dusts. The first column lists the atomic number and element symbol. The second column lists the name of the dust and denotes the sample number for elements tested at more than one particle size. The third column lists the density for each element. The fourth column lists the size range for each dust as observed with a scanning electron microscope (SEM). The fifth column lists the surface mean diameter as calculated [25] from transmission measurements made with the optical dust probes. The last column lists the median diameter as estimated from a combination of SEM, dust probe, and other size data (sieving and Coulter counter analyses).

Examples of absolute pressure versus time traces for typical dust explosions at a concentration of 600 g/m³ in the 20-L chamber are shown in Figure 4. The traces for aluminum (Al-1 in Table 1), magnesium, titanium, iron (Fe-1), zinc (Zn-1), and tantalum powders are compared with those for two carbonaceous dusts—polyethylene and a high volatile bituminous (hvb) coal. The relative reactivity of the dusts can be estimated from either the peak explosion pressure or the maximum rate of pressure rise. One of the reasons that the aluminum has such a high reactivity is that it is much finer in size than any of the other dusts in Figure 4. Next in order of reactivity is

Table 1. Physical data for elemental dusts

Element	Dust	Density, g/cm ³	D ₅₀ (SEM), μm	D ₅₀ (%T), μm	D _{med} , μm
5 B	Boron	2.35	0.5-10	2-6	~3
6 C	Carbon-1	2.25	0.2-2	≤2	≤1
	-2	*	4-10 f	3-6	~1
	-3	*	4-30 f	5-7	~4
	-4	*	10-200 f	15-22	~40
12 Mg	Magnesium	1.72	10-50 f	30-80	~16
13 Al	Aluminum-1	2.70	3-30 f	~2-4	~1
	-2	*	5-15	~10-14	~7
	-3	*	3-60	~40-70	~15
	-4	*	20-100 r	~60-180	~40
14 Si	Silicon	2.33	1-50	3-8	~4
16 S	Sulfur	2.07	~10-50	~60-100	~35
22 Ti	Titanium	4.5	10-60 r	~30-120	~25
24 Cr	Chromium	7.20	4-40	10-18	~10
26 Fe	Iron-1	7.86	1-8	4-11	~4
	-2	*	10-90	~60-160	~45
28 Ni	Nickel-1	8.90	3-8	~30-45	~6
	-2	*	20-40	~50-200	~30
29 Cu	Copper	8.92	10-50	~30-60	~30
30 Zn	Zinc-1	7.14	6-50 f	3-8	~4
	-2	*	10-100 r	~100-200	~45
41 Nb	Niobium	8.57	10-60	~50-100	~30
42 Mo	Molybdenum	10.2	3-6	10-23	~5
50 Sn	Tin	5.75	2-20	14-30	~8
72 Hf	Hafnium	13.31	4-30	~7-13	~10
73 Ta	Tantalum	16.6	4-30	~20-60	~15
74 W	Tungsten-1	19.4	≤1	1-3	≤1
	-2	*	5-25	~30-100	~10
82 Pb	Lead	11.3	20-60 r	~100-1000	~40

Note: For the SEM size listing, f denotes flake or plate-like particles and r denotes rod-like particles.

the Mg dust, followed by the two carbonaceous dusts. The polyethylene and coal have similar maximum pressures, but the polyethylene has a faster rate of pressure rise. The Ti dust has a lower explosion pressure than the carbonaceous dusts, and the Fe and Zn dusts are even lower. The dust with the lowest reactivity in Figure 4 is the Ta dust, which barely reaches its maximum pressure by 250 ms.

In order to study the overall explosibility characteristics of dusts, tests are made over a range of concentrations. A summary of 20-L chamber explosibility data for three carbonaceous dusts (using 2,500-J ignitors) is shown in Figure 5. Only the average data curves are shown and not the individual data points for each test. The dusts include polyethylene ($D_{med} \approx 29 \mu m$), high volatile bituminous coal ($D_{med} \approx 48 \mu m$), and low volatile bituminous coal ($D_{med} \approx 50 \mu m$). In the bottom part of the figure, the pressure ratio (PR) is the maximum absolute explosion pressure (with the pressure rise of the ignitor sub-

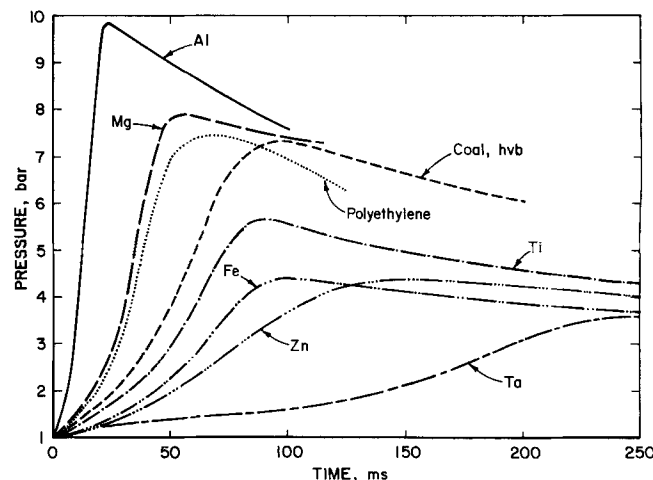


FIGURE 4. Pressure-time traces from 20-L chamber for explosions of six metal dusts, compared to two carbonaceous dusts.

* Reference to trade names does not imply endorsement by the Bureau of Mines.

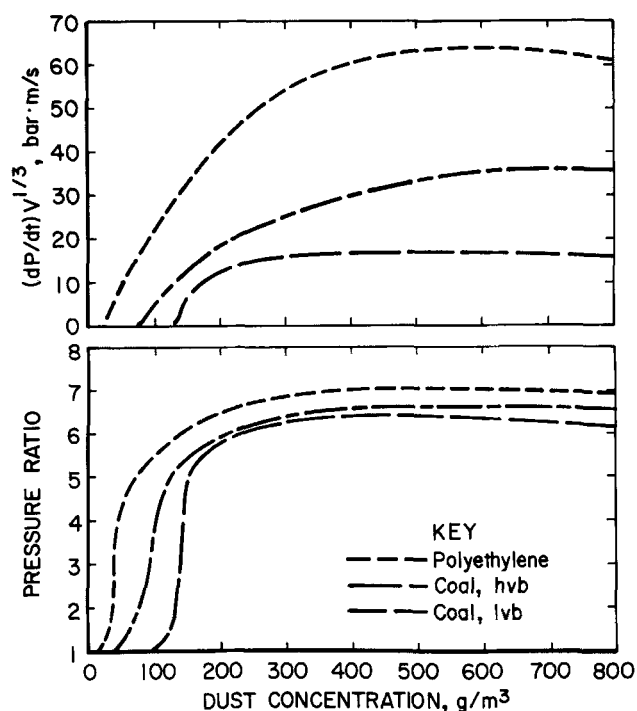


FIGURE 5. Explosibility data for three carbonaceous dusts in 20-L chamber.

tracted) divided by the pressure at ignition (about 1 bar,a). Therefore, the pressure ratio corresponds approximately to the absolute explosion pressure in atmospheres or bars. In the top part of the figure $(dP/dt)V^{1/3}$ is the size normalized maximum

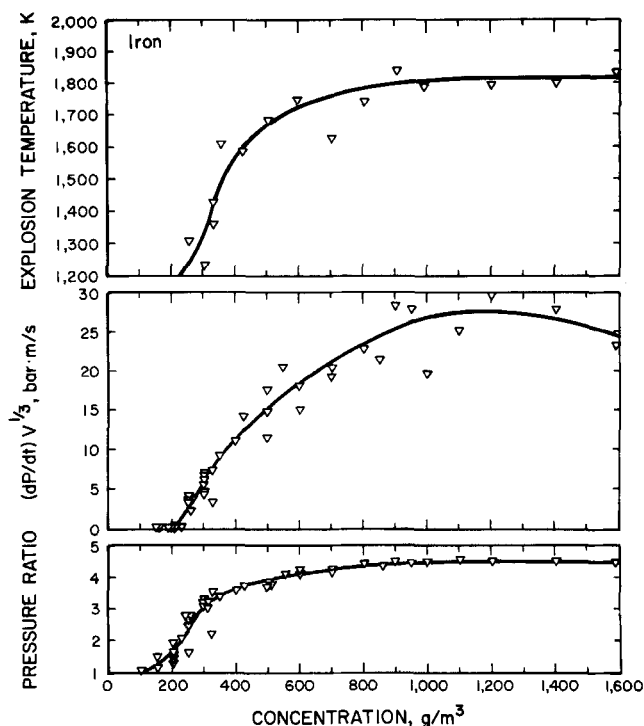


FIGURE 7. Explosibility data for iron dust.

rate of pressure rise for each explosion test. Note again that the turbulence level is lower in the Bureau's 20-L chamber, and therefore the $(dP/dt)V^{1/3}$ data are not recommended for vent sizing calculations. The data are, however, useful as a relative measure of explosion hazard. At the higher turbulence level recommended in ASTM Standard E1226, the maximum $(dP/dt)V^{1/3}$ data for the hvb coal would be roughly three times higher. For each dust in Figure 5, the explosibility data show that explosions are not observed below a certain dust concentration. This is the minimum explosible concentration (MEC) or lean flammable limit (LFL). However, the data in Figure 5 show no evidence of a "normal" rich limit as would be observed for hydrocarbon gases [9, 17]. At the higher concentrations, the maximum explosion pressure, P_{max} , and $(dP/dt)_{max}V^{1/3}$ level off as all of the oxygen in the chamber is consumed. Additional tests [20] at even higher concentrations have shown no evidence of a rich limit for coal or polyethylene out to concentrations as high as 4000 g/m³. This agrees with older full-scale experimental mine data for coal [29]. The normal rich limit observed for hydrocarbon gases is not observed for the dusts. One explanation of this effect, at least for many carbonaceous dusts, is that the solid phase fuel must first devolatilize before it can mix with the air [15]. As soon as sufficient volatiles are generated to form a stoichiometric concentration in air, the flame front propagates rapidly through the mixture before excess fuel volatiles can be generated.

Figure 6 shows explosibility data for an aluminum dust (Al-2 in Table 1) tested in the 20-L chamber, using 2,500-J ignitors. In this case, the data points for the individual tests are shown. The shapes of the curves are similar to those for the carbonaceous dusts in Figure 5, but P_{max} and $(dP/dt)_{max}V^{1/3}$ are higher than for the carbonaceous dusts, showing that the aluminum is more reactive. For aluminum in air, the stoichiometric concentration is $C_{stoich} = 310$ g/m³. P_{max} and $(dP/dt)_{max}V^{1/3}$ are found at concentrations considerably above C_{stoich} . As was found for the carbonaceous dusts, there is no evidence of any "normal" rich limit behavior at concentrations in excess of C_{stoich} . In determining the minimum explosible concentration (MEC) from the data in Figure 6, the criteria for significant flame propagation (previously developed for carbonaceous dusts in

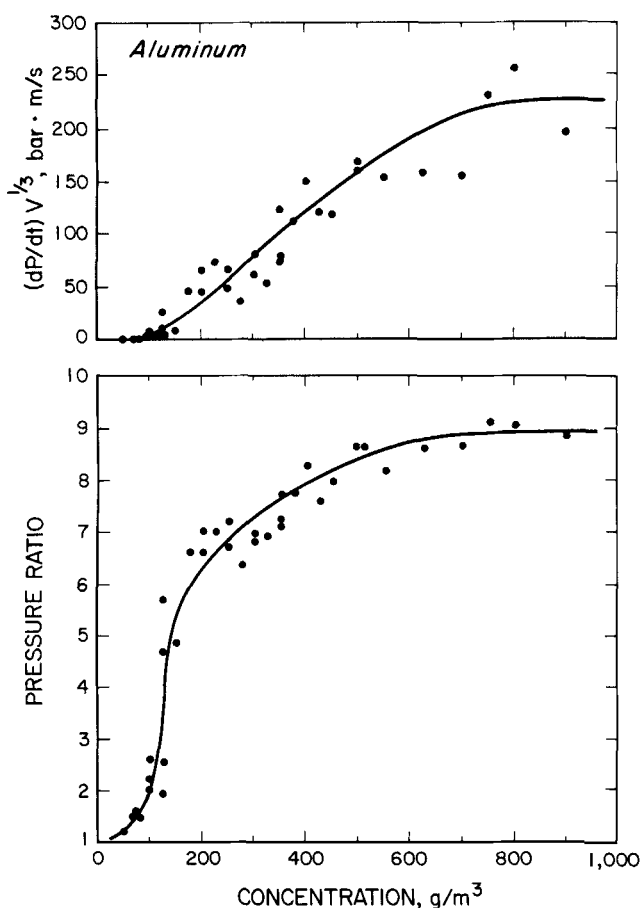


FIGURE 6. Explosibility data for aluminum dust.

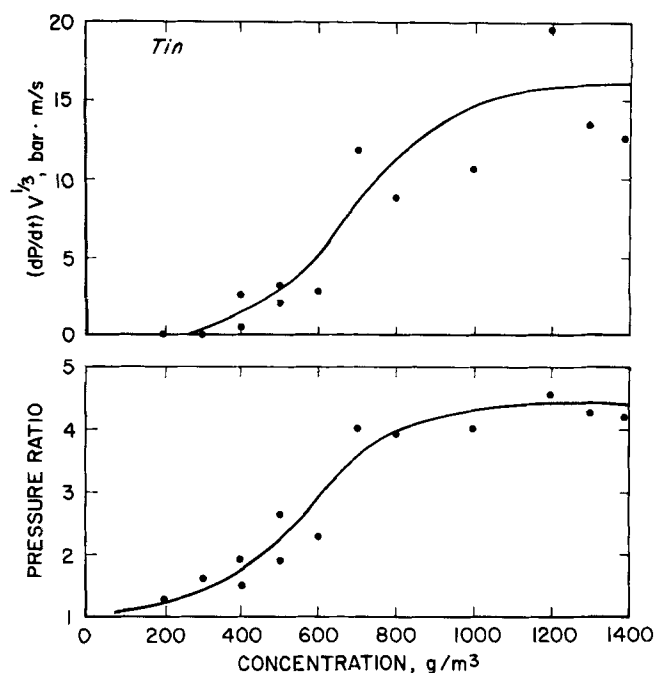


FIGURE 8. Explosibility data for tin dust.

reference [13] are a pressure ratio $PR \geq 2$ and a measurable value for $(dP/dt)V^{1/3}$ beyond that of the ignitor. This is the same test method for measuring the MEC as in ASTM Standard E1515. Using these propagation criteria, the MEC for this aluminum dust is $\sim 90 \text{ g/m}^3$.

Explosibility data for an iron dust (Fe-1) as a function of concentration are shown in Figure 7. In addition to the explosion pressure and rate of pressure rise data, the measured explosion temperatures are shown at the top of the figure. These measurements were made using the Bureau's six-wavelength infrared pyrometer [27-28], which viewed the developing dust explosions through the sapphire window at the top of the 20-L chamber. The pyrometer observed the continuum radiation from the particles, and temperatures were calculated from the best Planck curve fit to the infrared radiance data using a multiplicity of wavelengths [27-28]. The maximum measured particle temperatures in Figure 7 are $\sim 1,800 \text{ K}$, well below the maximum calculated adiabatic temperature, $T_{ad,max} = 2250 \text{ K}$, for ideal combustion [11]. However, these experimental temperatures are only those of the particles in the explosion, and the gas temperatures may have been somewhat higher. From the data in Figure 7, the MEC for this iron dust is about 230 g/m^3 , using the 2,500-J ignitors, but there

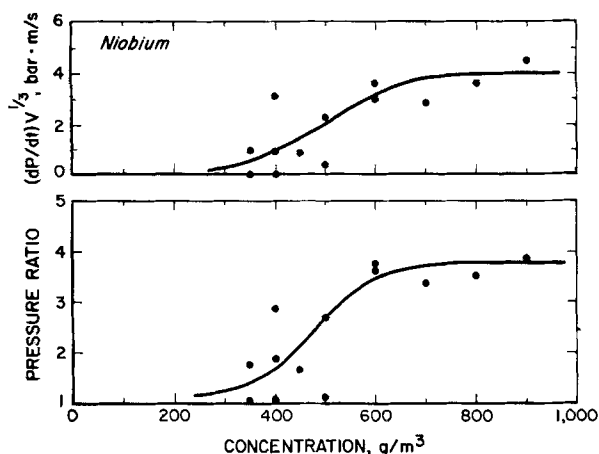


FIGURE 9. Explosibility data for niobium dust.

Table 2. Explosibility data for elemental dusts

Dust	MEC, g/m^3		P_{max} bar, a	$(dP/dt)_{max} V^{1/3}$ bar·m/s	C_{stoich} g/m^3	$T_{ad,max}$ K
	@ 2500 J	@ 5000 J				
5 B	~ 110	~ 80	7.0	35	125	2850
6 C-1	90	90	5.5	~ 10	105	2320
-2	F	70	~ 5	~ 6	*	*
-3	NF	NF	1.1	~ 0	*	*
-4	—	NF	1.1	~ 0	*	*
12 Mg	55	50	8.5	130	420	3100
13 Al-1	85	~ 70	9.4	~ 290	310	3550
-2	90	~ 80	9.0	220	*	*
-3	90	—	7.5	~ 70	*	*
-4	120	90	6.6	24	*	*
14 Si	200	180	7.7	~ 56	240	2870
16 S	~ 100	—	5.0	28	280	1915
22 Ti	70	60	5.7	35	420	3450
24 Cr	$\sim F$	~ 600	~ 3	~ 3	600	2840
26 Fe-1	220	~ 160	4.5	29	650	2250
-2	~ 500	~ 300	3.1	3	*	*
28 Ni-1	—	NF	1.0	~ 0	1020	2240
-2	—	NF	1.0	~ 0	*	*
29 Cu	—	NF	1.0	~ 0	1100	1510
30 Zn-1	300	230	4.4	~ 17	1140	1860
-2	NF	~ 1400	~ 2	~ 2	*	*
41 Nb	~ 420	~ 350	~ 4	~ 4	650	3060
42 Mo	—	NF	1.0	~ 0	560	—
50 Sn	~ 450	~ 350	4.3	~ 16	1030	—
72 Hf	~ 180	—	5.2	~ 40	1550	4120
73 Ta	~ 400	~ 250	~ 4	~ 7	1260	3290
74 W-1	~ 700	~ 550	~ 3.3	~ 5	1070	2670
-2	—	NF	1.0	~ 0	*	*
82 Pb	—	NF	1.1	~ 0	3600	1660

Notes: NF means the dust was nonflammable or nonignitable.

F means the dust was flammable but the MEC could not be determined.

is considerable uncertainty in this value, due to the scatter in the data. For the iron, the stoichiometric concentration (for formation of Fe_2O_3) is $C_{stoich} = 650 \text{ g/m}^3$, and the pressure at C_{stoich} is almost at its maximum value. However, $(dP/dt)V^{1/3}$ at C_{stoich} is considerably less than its maximum value. Both P_{max} and $(dP/dt)_{max} V^{1/3}$ are significantly lower for the iron dust than for the aluminum dust, showing that the iron is less reactive.

Figures 8 and 9 show explosibility data for tin and niobium dusts. The maximum explosion pressure measured for the tin is about the same as for the iron, but $(dP/dt)_{max} V^{1/3}$ is lower for the tin than for the iron. For the niobium dust in Figure 9, P_{max} is slightly less than that for the tin and $(dP/dt)_{max} V^{1/3}$ is considerably lower than that for the tin. The MEC values for the tin and niobium are both about 450 g/m^3 with the 2,500 J ignitors, much higher than the MEC for the aluminum in Figure 6 or even the MEC for the iron dust in Figure 7.

Table 2 summarizes the explosibility data for the elemental dusts tested, based on the data curves of Figures 6 through 9 and similar data for the other elemental dusts. The first column of the table lists the dust by atomic number and symbol. The second and third columns list the MEC as measured in the 20-L chamber using 2,500- or 5,000-J ignitors, respectively, based on ASTM Standard E1515. Although data for both ignitors are listed, there is some evidence [14] that the 5,000-J ignitor may overdrive the 20-L chamber somewhat, at least for some dusts. The fourth column lists the maximum absolute explosion pressure in bars. The fifth column lists the size-normalized rate of pressure rise $(dP/dt)_{max} V^{1/3}$. Note again that these values are lower than those that would be obtained at the higher turbulence level of ASTM Standard E1226, perhaps by a factor of three or four. The sixth column lists the stoichiometric concentration, C_{stoich} , for reaction of the dust with air to form its most common oxide. The last column lists the maximum adiabatic temperature, $T_{ad,max}$, calculated for ideal constant pressure combustion [11].

Four of the elemental dusts (Ni, Cu, Mo, and Pb) listed in Table 2 could not be ignited, even with the 5,000-J ignitor. It is not surprising that the Cu and Pb did not ignite because their C_{stoich} values are high and their $T_{ad,max}$ values are probably too low to sustain flame reaction. There were insufficient thermodynamic temperature coefficient data available to calculate a $T_{ad,max}$ value for the Mo dust. The Ni has a reasonably high

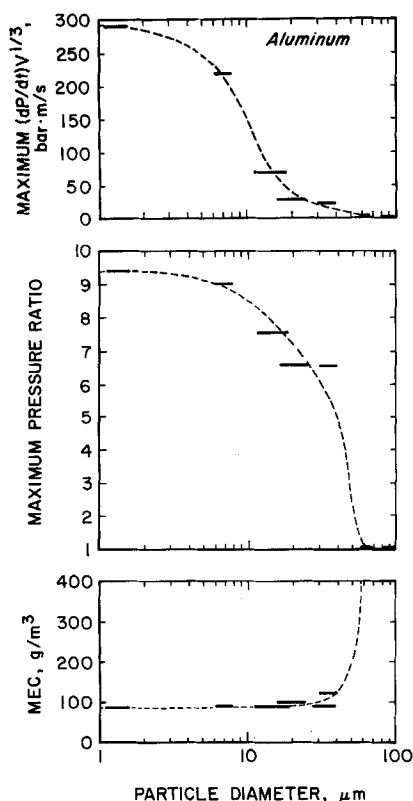


FIGURE 10. Explosibility data for aluminum dust as function of median particle diameter.

$T_{ad,max}$ value, similar to that of the Fe, but the rate of reaction may be too low to sustain flame propagation. The dusts with the lowest $T_{ad,max}$ values that produced explosions were the Zn with $T_{ad,max} = 1860$ K and sulfur with $T_{ad,max} = 1915$ K. Both of these elements are easily vaporized at these flame temperatures [11].

The elemental dusts (B, Mg, Al, and Si) with the higher P_{max} and $(dP/dt)_{max} V^{1/3}$ values were also those with high adiabatic flame temperatures, with $T_{ad,max} > 2800$ K. The Ti and Hf had intermediate P_{max} and $(dP/dt)_{max} V^{1/3}$ values although they also had $T_{ad,max} > 2800$ K. Some elemental dusts (Cr, Nb, and Ta) with $T_{ad,max} > 2800$ K had low P_{max} and $(dP/dt)_{max} V^{1/3}$ values. This may be due to their low volatilities and/or their low intrinsic reaction rates.

Some data on the effect of particle size for carbon are in Table 2. Only the finest two sizes could be ignited. However, there was also a wide variation in the physical structure of the carbon dusts. The C-1 was an amorphous lampblack, C-2 and C-4 were graphite flakes, and C-3 was described by its manufacturer as an amorphous graphite.

Data showing the effect of particle size for aluminum dust are shown in Figure 10. The data are shown as bars rather than points because the median particle diameters are somewhat uncertain. The MEC-values in the bottom section of the figure are relatively independent of particle size for the finer sizes. At the larger sizes, above $40 \mu m$, the MEC-values increase with particle size until a size is reached that can not be ignited. The top two sections of Figure 10 show that the maximum pressures and rates of pressure rise are found at the finest sizes tested. Both the pressures and the pressure rise rates decrease with increasing particle size. At some size above $60 \mu m$, the dust can no longer be ignited. The data for P_{max} versus particle diameter are similar to those of Ogle *et al.* [30] over the size range of 7 to $28 \mu m$, but they did not test larger sizes. The data in Figure 10 are typical for narrow size distributions of dusts. The largest sizes examined were sieved between two

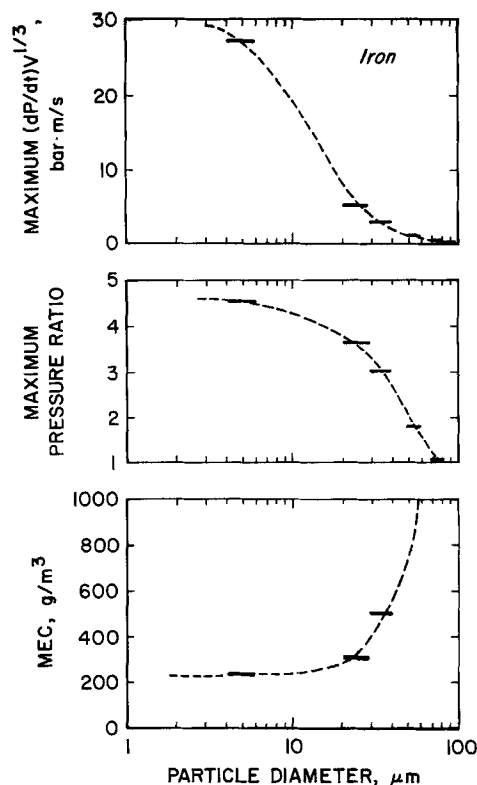


FIGURE 11. Explosibility data for iron dust as function of median particle diameter.

screens and therefore had the fine particles removed. A broad size distribution is just a combination of narrow distributions, and these data show that it is the finer particles in a broad distribution that contribute the most to its hazard. If broader size distributions (containing some fines) were used for the tests on particle size effects, the median size dust that could be ignited would be larger than that shown in Figure 10.

Data showing the effect of particle size for iron dust are shown in Figure 11. The explosion data are similar to those for the aluminum. The maximum values for pressure and rate of pressure rise are found at the finest particle size. The MEC values are relatively size-independent at the finer sizes and increase above $30 \mu m$ until a size is reached that can not be ignited.

Additional data for these elemental dusts, including measured temperature data, will be in a future Bureau report [31]. For additional interpretation of the data, including the mode of combustion, see references [11] and [31].

The results reported in this paper provide some general information on the flammability characteristics of nineteen metal and nonmetal elemental dusts. However, because of the particle size effects shown here, it is important to test the particular size of dust that occurs at a particular industrial plant. The best safety data would be based on tests of a sample of the actual dust encountered in the plant rather than trying to extrapolate from other test data for a different size of the same material.

ACKNOWLEDGMENTS

The author thanks I. A. Zlochower of the Bureau of Mines for the thermodynamic calculations of the maximum adiabatic temperatures in Table 2. The authors also acknowledge the assistance of G. M. Green of the Bureau in the collection of the experimental data.

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This paper (8c) was presented at the 28th Annual Loss Prevention Symposium which was held during the AIChE Spring National Meeting in Atlanta, GA, April 17-21, 1994.