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Inhibition and Extinction of Coal Dust and Methane Explosions

By Martin Hertzberg, Kenneth L. Cashdollar,
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INHIBITION AND EXTINCTION OF COAL DUST AND METHANE EXPLOSIONS

By Martin Hertzberg,[1] Kenneth L. Cashdollar,[2] Charles P. Lazzara,[1] and Alex C. Smith[3]

ABSTRACT

The Bureau of Mines 8-liter flammability system was used to study the effectiveness of a variety of powdered inhibitors in preventing the propagation of explosions of coal dust or methane in air. Over 35 different chemical additives were evaluated against Pittsburgh seam pulverized coal. The least effective inhibitors were the carbonates, which required mass additions in the range of two to three parts inhibitor to one part of coal dust in order to prevent propagation. The most effective inhibitors were the derivatives of ammonium phosphate, which were effective quenching agents at additions of only one part inhibitor to four parts of coal dust. Alkali halide powders were of intermediate effectiveness. These laboratory-scale results are in good agreement with full-scale mine experiments in all cases where detailed comparisons have been made.

Data were also obtained for the effectiveness of several of the same powdered inhibitors against methane-air explosions. Their relative order of effectiveness and the concentration ranges required for quenching the gas explosion are comparable to those measured for coal dust explosions. Data are also presented for the effectiveness of N_2 and CF_3Br addition.

Some preliminary data are also presented for powder addition to methane burner flames. Those data are compared with other burner data and evaluated in terms of their relevance to explosion tests.

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INTRODUCTION

Explosion disasters in American coal mines have killed about 12,000 miners since 1839. The fuels involved in those explosions were coal dust and/or methane. Although each disaster differs in its structural details from every other disaster, one can nevertheless distill a typical scenario from the evidence of postdisaster investigations (25).[4] One of the more usual disaster scenarios involves the following sequence:

1. The growth of a large, flammable methane-air zone near the face that is being mined. The flammable zone growth is the result of increasing methane emission. The mining process results in the rapid advance of the mine void into the fresh seam, which steepens the internal pressure gradient of the coal seam, which increases the flow of methane into the mine. If the ventilation is inadequate to dilute, render harmless, and to carry away that increased emission, significant flammable volumes are generated.

2. The ignition of that flammable volume by the frictional heating of cutting bits, by an electric or electrostatic spark, or by an explosives shot.

3. The development of a localized methane-air explosion, referred to as a "face ignition," and its outward acceleration from the closed-end or "face" of the mine entry.

4. The lifting of coal dust accumulations by the flows and pressures generated by the accelerating "ignition," and the mixing of that dust with air to create a flammable dust-air mixture.

5. The ignition of the dust-air mixture by the methane-air explosion.

6. The further turbulent acceleration of the flame front, which intensifies the aerodynamic disturbance, which lifts more coal dust mixing it with air throughout an increasingly lengthening zone in advance of the flame.

7. The propagation of a dust explosion throughout the mine.

In those mine explosion disasters where methane emissions were not significant, the dust was usually ignited directly by an explosives shot, or some other strong ignition source.

The annual fatality rate from such disaster scenarios, or their myriad variations, was about 400 men per year for the first decade of this century. The worst 1-year period on record involved about 1,000 explosion fatalities starting in December 1907. Over 700 of those fatalities occurred during that first month with some 362 killed in one explosion at Monongah, W. Va. on December 6, 1907 (25).

Subsequent Federal investigations into the causes of those disasters were conducted at the Bruceton (Pa.) Experimental Mine facility, which was first established in 1908 (39). In 1910, the Bureau of Mines was created by Congress and given specific authority to inquire into the causes of those disasters. It was also given general authority for promoting safety and health in the mining and minerals industries. Over the years, Bureau of Mines research led to the development of permissible explosives, the explosion-proofing of electrical equipment, the use of adequate ventilation, the monitoring of methane, the predrainage of methane, and the generalized rock dusting of mine entries. In recent years, emphasis has been placed on mandatory regulations, their enforcement, and on the proper training of miners and mine inspectors (44-45). Over the decades, as research results accumulated, preventive measures were introduced; and as regulations were enforced, the annual fatality rates from explosions declined slowly. From a peak value above 500 per year in the years around 1907, such fatalities dropped to

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[4]Underlined numbers in parentheses refer to items in the list of references at the end of this report.

about 300 per year in the 1920's, to about 100 per year in the 1930's, to about 90 per year in the 1940's to 35 per year in the 1950's, and to 25 per year for the 1960's decade (25, 35). For the most recent decade, that of the 1970's, the annual fatality rate from coal mine explosions was 7 per year (35).

As Bureau of Mines research on the explosibility of coal dust and methane progressed and the data were made available to the public, other industries experiencing similar problems with flammable gases or dusts sought the assistance of the Bureau. It was soon recognized that a realistic appraisal of the explosion hazards involved with any substance, whether it be in its mining, manufacture, transportation, storage or use, required an accurate knowledge of its limits of flammability. Such concerns motivated numerous studies of the flammability limits of natural substances, fuels, and synthetic products. The results of such studies for homogeneous gases and vapors have been collected, analyzed and summarized in a series of Bulletins (7, 47). For dusts of various kinds, the results were first reported in a series of Bureau reports (26-27, 36), which were subsequently summarized in a standard tabulation (37).

For gas mixtures, the data are sufficiently accurate and reproducible to generate a consensus. For example, the lean limit for methane in air is 5.0±0.1 vol-pct. By contrast, there had been a lack of consensus for dusts despite the large amount of data accumulated during this century. Even a brief review of the available literature revealed wide discrepancies and lack of reproducibility in the reported data for coals (20). This is not surprising when one considers the great difficulty in generating uniformly dispersed dust clouds as compared to premixed gases. Recently, more consistent and reproducible data have been obtained and an attempt has been made to resolve the earlier discrepancies (18, 20). There is now general agreement on a lean limit for Pittsburgh seam coal dust of 100±50 g/m^3, although the uncertainty in the value is still much larger than for the gases. Data by the authors for uniformly dispersed, Pittsburgh seam coal dust in an 8-liter flammability chamber with a strong ignition source indicates a lean limit of about 130 g/m^3 (18, 20-21). This is the value used in the present paper as a basis for evaluating the effects of various added inhibitors.

There was a similar lack of consensus with respect to the effectiveness of various powdered salt additives that were used to suppress or extinguish coal dust explosions. These inhibiting powders may be added initially to coal dust accumulations in order to inert the dust before it can be dispersed, or, they may be used in barriers that release the powder into a propagating dust explosion in an attempt to extinguish it. The best example of this lack of consensus with respect to such salts are the glaring discrepancies in the data obtained by various researchers for the relative effectiveness of Purple K (fluidized $KHCO_3$). This powder, which had been developed for extinguishing liquid fuel fires (29), is usually considered to be a "chemical" inhibitor. In laboratory scale tests with burners or ducts, Purple K appeared to be much more effective than a thermal inhibitor such as rock dust (13-14, 42). However, in full-scale tests in mines and galleries in which $KHCO_3$ was used, no such greater effectiveness was ever realized. In those full-scale tests, the so-called "chemical" inhibitor, Purple K, was no better than the thermal inhibitor, rock dust (12, 40). Recent data, including those to be presented in this report, give much better agreement between laboratory-scale studies and full-scale mine tests (18, 21, 40).

Currently, the main countermeasure for preventing dust explosions in most of the coal mines of the world is the practice of generalized rock dusting. All mining operations generate coal dust, and that dust inevitably accumulates on the interior surfaces of the mine in mass loadings that are flammable. These accumulations can be inerted by adding "stone dust" or "rock dust." However because rock dust is a "thermal" inhibitor, relatively large quantities are required. U.S. law (44-45) requires that the incombustible content of those dust accumulations be continuously maintained at at least 65 pct in most mine passageways. In return airways, the incombustible content attained by adding rock dust must be at least 80 pct. Still higher values are required if methane is present. These regulations and their enforcement by mine inspectors were probably responsible for the marked reduction in the fatality rate from major explosion disasters that was achieved in the decade of the 1970's. However, even the current rate of seven fatalities per year must be considered as unacceptably high. There were three major disasters from explosions in the 1970's. The one with the greatest number of fatalities involved the illegal use of nonpermissible explosives and the failure to adequately rock dust the underground mine entries (46). The other two disasters were caused by methane explosions in inadequately ventilated sections of coal mines. Thus the most recent fatality data for the decade following the passage of the Coal Mine Health and Safety Act of 1969 show clearly that generalized rock dusting, if it is properly practiced, is generally effective in preventing coal dust explosions. However, statistical data inevitably contain hidden variables, and one must be cautious in interpreting them. Major problems remain that require continual refinement of regulations and the development of new countermeasures, particularly as new mining technologies are introduced and as production rates are increased. There are several areas of current concern that are being addressed by research.

First, there is the continuing problem of gas explosions. There is no clear evidence that the current levels of rock dusting in mine entries has any demonstrable effect in preventing gas explosions. Current countermeasures against gas explosions emphasize the monitoring of methane, the use of adequate ventilation, the use of explosionproof or intrinsically safe equipment that will not ignite flammable mixtures, and the predrainage of methane. A parallel countermeasure which has been the subject of considerable research activity in both the United States and abroad involves the use of explosion barriers. Such barriers would extinguish developing gas explosions in mine entries or in the face areas (31). The size and performance of such barriers should be a strong function of the relative effectiveness of the inhibiting or extinguishing material that is dispersed by the barrier.

Secondly, there are many areas in a mine where it is difficult or virtually impossible to apply conventional rock dusting techniques to render the coal dust inert. Examples of such areas are conveyor belts that carry coal, the gob areas behind longwalls, the longwall faces themselves which extend for considerable distances, and the head and tail gate areas of such longwalls. A thoroughly documented, recent accident investigation (11) shows clearly how a gas ignition can be amplified by the dust accumulations in such areas of longwall developments. Similar hazards exist in surface facilities that handle or process coal and in utility powerplants that store, convey, pulverize, and pneumatically transport coal as a dust-air mixture to boiler furnaces in order to generate steam for the production of electricity. In recent years, considerable attention has been given to this problem of explosion prevention in those circumstances where generalized rock dusting is not possible. One countermeasure proposed for such cases is again the use of barriers that contain inhibiting or extinguishing agents, which when dispersed into the coal dust-air mixture near the flame front of the explosion, would extinguish it (32-34, 43).

Many types of inerting or extinguishing agents are being studied for use in such barriers. They may be pure substances in gaseous, liquid, or solid form; or they may be hybrid mixtures containing several phases (31). The effectiveness of these various agents against dust and gas explosions is being studied in full scale tests in surface galleries and in the

Bruceton (Pa.) Experimental Mine (33, 43). In addition to their use in explosion barriers, the solids being studied have the additional potential of being used as supplements to generalized rock dusting. There is, in addition, an economic interest in being able to develop inerting methods that are equally effective but less expensive than generalized rock dusting.

All such proposed methods must be tested in realistic mine experiments; however, the full-scale mine testing of inhibitors is costly and time consuming. Accordingly, even from the earliest days when testing in the Bruceton (Pa.) Experimental Mine was first initiated, Bureau of Mines scientists have tried to develop laboratory-scale tests that could reliably reproduce the results obtained in full-scale studies. It was realized that such small-scale experimentation could be an efficient and cost-effective complement and guide to the full-scale test program; however, the early results were inconsistent and of limited utility. In recent years, considerable progress has been made in understanding the causes of those inconsistencies and in correcting them. An apparatus and method have evolved that have generated data for pulverized coals, other dusts, and dust-gas mixtures that are internally and externally consistent, reproducible, and reliable (18, 20-21). Accordingly it was natural to consider the use of that same apparatus and method for evaluating various extinguishing agents that were being proposed for use in barriers to suppress gas and dust explosions.

This report will summarize the results for several years of such studies involving small-scale tests of a variety of different extinguishing powders mixed with Pittsburgh seam pulverized coal. In cases where comparable full-scale experiments are available, the two results are compared. Some preliminary data were reported earlier (4, 18, 33, 40); however, this report is more comprehensive in scope and presents the totality of those results. Also included in this report are additional studies of gaseous inhibitors as well as studies of the effectiveness of some powdered inhibitors against methane-air explosions.

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EIGHT-LITER APPARATUS AND EXPERIMENTAL METHOD

Test Chamber and Instrumentation

The majority of the data in this report were obtained using the 8-liter flammability chamber shown in figure 1. The chamber has been used previously to study coal dust flammability as reported in references 18 and 20. The experimental method for testing dust flammability is described in reference 20. The present report will describe the method for testing gases and gas-inhibitor mixtures, as well as a brief review of the method for testing dusts.

The chamber shown in figure 1 has a volume of 7.8 liters and its dust dispersion system is similar to that of the original 1.2-liter Hartmann chamber (10). Instrumentation includes a pressure transducer, an oxygen sensor, and an optical dust probe. The pressure transducer is based on the strain gage principle and has a listed time response of 1 msec for 90 pct of the full-scale reading. It is used to measure partial pressures when mixing gases and also to measure the explosion pressures after ignition.

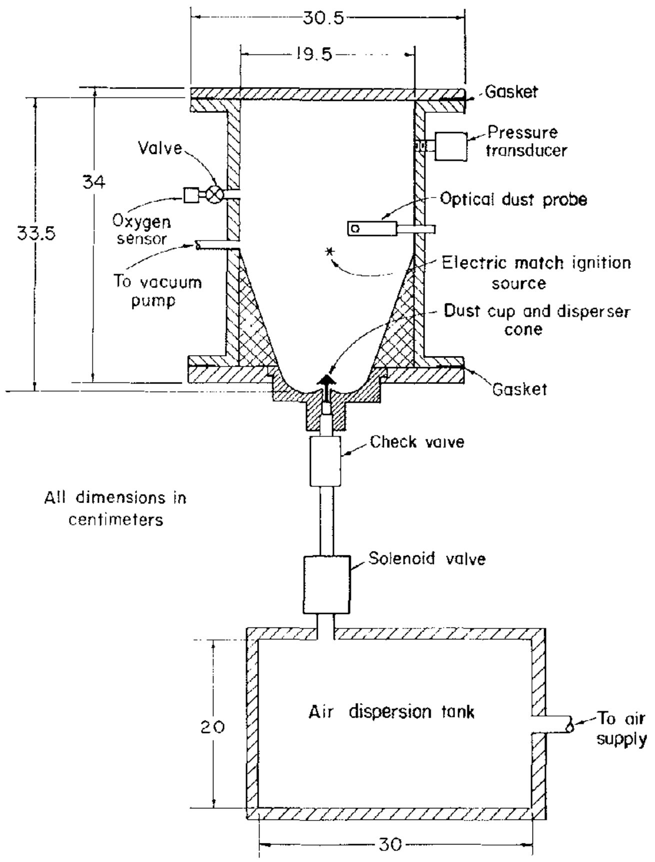

FIGURE 1. - Eight-liter flammability chamber.

The oxygen analyzer uses a polarographic method to measure the partial pressure of O_2. It is initially calibrated for 20.9 pct O_2 in ambient air at atmospheric pressure. The sensor is isolated from the chamber by a valve during the actual explosion tests. After the test is over and the product gases have cooled to ambient temperatures, the valve is opened and the oxygen content is measured at a pressure of 1 atm. The intrinsic response time of the sensor is 20 sec for 95 pct of full-scale response, but several minutes are required for mixing between the small dead volume at the sensor and the main chamber volume before an accurate O_2 measurement can be made.

The optical dust probe (5, 20, 30) is used to study the dust dispersion by measuring the attenuation of near-infrared light at 0.95-µm wavelength. It consists of a gallium-arsenide light-emitting diode (LED) and a silicon photodiode detector. The probe windows are kept dust free by narrow jets of air passing over the windows. The probe measures the light attenuation by the airborne dust in the 3.8-cm path between the LED and detector. Data from the pressure transducer and dust probe are recorded on a high-speed strip chart recorder with a measured response time of 20 msec for 90 pct of full-scale response.

The average particle sizes of the coal and inhibitor dusts studied were determined from Coulter Counter[5] size analyses in which the dust was dispersed in a liquid electrolyte. The sizes are only for comparison because the actual sizes of the dusts dispersed in air are larger due to agglomeration (5, 20).

Gas Explosion Test Methods

Two test methods were used for the gas explosion studies. In the first, the 8-liter chamber was evacuated, methane was added until a predetermined partial pressure was reached, and then air or some other O_2-N_2 mixture was added, bringing the chamber pressure to 1 atm absolute. If an inhibitor gas was used, it was added after the methane and its concentration was controlled by its measured partial pressure. After reaching a final pressure of 1 atm, the total gas mixture was stirred for several minutes with an internal fan. A delay of 1 min before ignition allowed the fan-generated turbulence to subside. Ignition was by a high voltage electric spark or an electrically activated, high temperature, pyrotechnic match (20).

A second test method was used in those experiments where it was necessary to disperse inhibitor dust in a methane-air mixture. Examples of several test runs for such mixtures are shown in figure 2. An initial run for pure methane-air without dust is shown in figure 2A. Initially, the chamber was evacuated and methane was added slowly until the desired partial pressure was reached. Then some air was also added slowly until the chamber

[5]Reference to trade names does not imply endorsement by the Bureau of Mines.

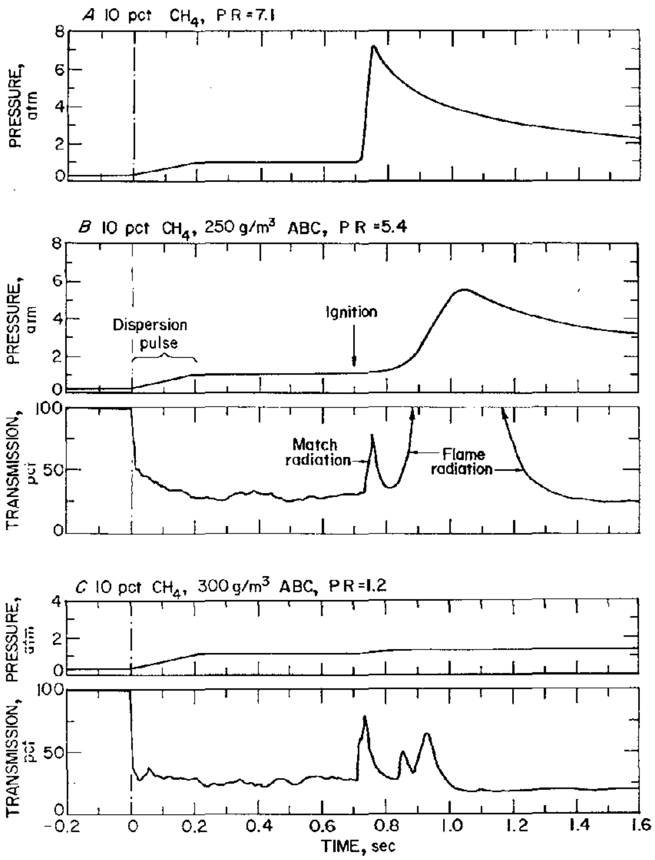

FIGURE 2. - Recorder traces of absolute pressure and dust probe transmission for flammability tests of pure methane in air and methane in air with added inhibitor dust.

pressure reached about 0.27 atm. Finally, a short (0.2 sec) pulse of high-pressure air (from the dispersion tank) was added through the disperser cone at the bottom of the chamber. This short, intense air pulse mixed the gases and raised the pressure to 1 atm. The delay before ignition was 0.5 sec. This was enough time for the turbulence to diminish so that the test results were comparable to data obtained with the first test method.

For the methane gas and powdered inhibitor in air tests shown in figures 2B and 2C, this second test method was used. The inhibitor powder was placed in the dust cup around the disperser cone prior to evacuation of the chamber. Methane was again added first, but now the air pulse not only mixed the gases but also dispersed and mixed the dust. By using optical dust probes at various positions in the chamber, it was found that the air pulse effectively dispersed the dust into a fairly uniform cloud. Details of these uniformity measurements are found in references 5 and 20. Figures 2B and 2C show data for near-stoichiometric methane-air tests with added powdered inhibitor. After the methane and a small amount of air were added to raise the chamber pressure to 0.27 atm, a "start" switch was pushed resulting in the automatic operation of the timed air dispersion pulse and the timed delay before ignition. The transmission signal measured by the optical dust probe showed that the dust was dispersed very quickly. The transmission reached a steady value even before the end of the 0.2-sec dispersion pulse. This steady-state value was maintained until ignition at 0.5 sec after the end of the dispersion pulse. In figure 2B, the added 250 g/m^3 of ABC powder (fluidized $NH_4H_2PO_4$ with a surface mean particle diameter, $\bar{D}_s$ = 7 µm) was not enough to inert the gas mixture and the pressure after ignition rose from 1 atm to a peak of over 5 atm. The pressure data for each test was recorded as a pressure ratio (PR) which was the peak pressure divided by the initial pressure (about 1 atm), corrected for the small pressure rise due to the match ignition source. The detector in the optical dust probe also observed the match radiation and flame radiation from the hot particles, which in this probe design prevents the measurement of transmission after ignition.

In figure 2C, it can be seen that 300 g/m^3 of ABC powder was enough to inert the near-stoichiometric methane-air mixture. The measured pressure ratio was 1.2 which corresponds to a pressure rise of only 0.2 atm above the ambient pressure at ignition. This slight pressure rise was probably due to some small amount of burning in regions close to the ignition source, but there was no propagation beyond the source. The optical dust probe shows the match radiation and a very small amount of flame radiation.

Dust Explosion Test Method

The method for testing coal dusts or coal dust and powdered inhibitor mixtures was previously described in reference 20 and was similar to the second method for gas-inhibitor mixtures except that no methane was added. The dust mixture was placed in the dust cup around the disperser cone, the chamber was partially evacuated to 0.2 to 0.3 atm, and then the air pulse from the dispersion tank (at 6 atm absolute) dispersed the dust and raised the chamber pressure to 1 atm. The dispersion pulse is about 0.2 sec and there is a 0.1-sec delay before ignition by the electrically activated matches.

Figure 3 shows typical test runs for pure coal and coal with added limestone ($CaCO_3$) rock dust. The coal dust used had a broad distribution of particle sizes with a surface mean diameter, $\bar{D}_s$ = 23 µm. The rock dust also had a broad distribution of sizes with $\bar{D}_s$ = 10 µm. Recorder traces for pressure and dust probe transmission are shown for pure coal dust explosions at two different concentrations in figures 3A and 3B. At the lower coal dust concentration in figure 3A, the peak pressure was lower and the time to peak pressure was longer. The optical dust probe transmissions are consistent with the values expected for the different dust concentrations. When rock dust was added to the same coal

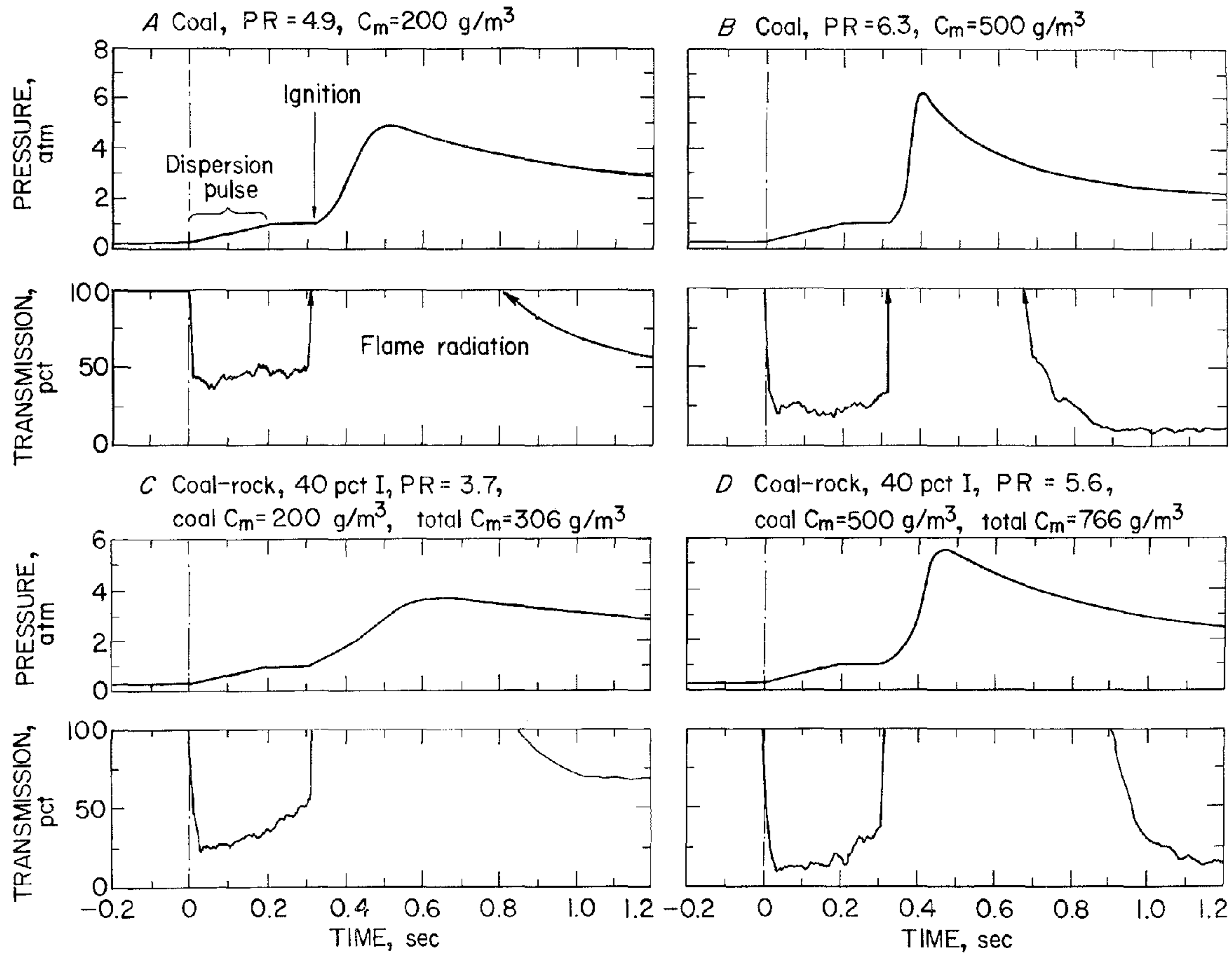

FIGURE 3. - Recorder traces of absolute pressure and dust probe transmission for flammability tests of pure coal dust and a coal and rock dust mixture.

dust concentrations (figs. 3C-3D), the peak pressures declined and the time to peak pressure increased for both coal concentrations. In these two coal-rock dusts runs, a premixed amount of coal dust and rock dust was placed in the dust cup before dispersion. The mixture was 65 wt-pct coal dust and 35 wt-pct rock dust. The rock dust combined with the nominal 8-pct ash and moisture in the coal gives an incombustible (I) content of 40 pct. The added rock dust in figures 3C and 3D did not totally inert the mixture, but it did reduce the intensity of the explosion.

These data (figs. 2-3) are characteristic examples of the kinds of raw data that are used to evaluate effectiveness of various inhibitors. It is necessary now to consider the way in which such raw data are used to determine the point at which an inhibitor completely suppresses an explosion. That point is determined by the criterion for flame propagation, and that criterion is essentially the same one used to define the normal limits of flammability for any substance or mixture of substances.

EIGHT-LITER INHIBITION AND EXTINCTION DATA--GASES

Limit Criteria for Methane in Air

The initial motivation for conducting preliminary experiments with gas mixtures was the desire to "calibrate" the 8-liter flammability chamber with fuels whose limits had already been carefully established by prior research (7, 47). It was felt that such calibrations were essential in order to establish the reliability and consistency of the data being accumulated for the flammability limits of various dusts (18, 20-21). The calibration gas used first was methane, since its flammability limits have been most extensively studied. The explosion data for various methane-air compositions in the 8-liter chamber are shown in figure 4. The data are for initially quiescent mixtures, ignited with one pyrotechnic match (20). In figure 4A, the measured peak explosion pressure ratios are shown and compared with calculated adiabatic values for constant volume combustion. The residual oxygen contents after the explosions were also measured in some experiments, and those data are presented in figure 4B. The decimal fraction of oxygen consumed is shown; and, as expected, as stoichiometric mixtures are reached, virtually all the oxygen is consumed. However, because of various heat losses due to nonadiabatic processes, the measured explosion pressures shown in figure 4A are inevitably lower than the adiabatic values. These loss processes involve radiative and convective heat losses to the container walls and are discussed in detail elsewhere (15). For lean mixtures there is a relatively sharp increase in measured peak pressures as the composition exceeds 5 pct methane. That near discontinuity

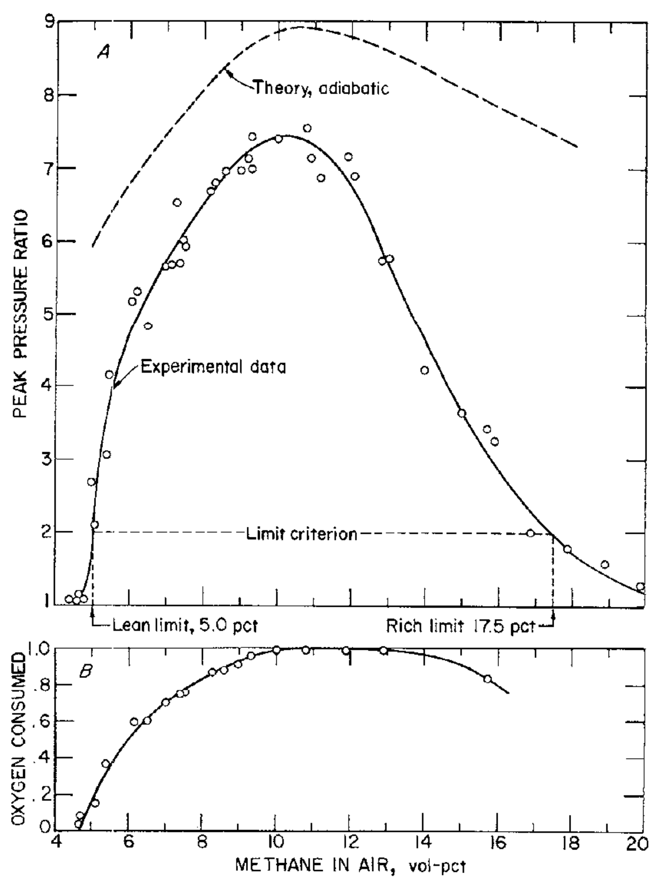

FIGURE 4. - Flammability data for methane-air mixtures.

in the peak pressure ratio gives a fairly well-defined lean limit of 5.0 pct methane that is not very sensitive to the exact criterion chosen to define the limit. On the other hand, the pressure decrease that occurs for rich mixtures is more gradual; and the exact value of the rich limit is more sensitive to the limit criterion chosen.

What then is a realistic criterion for defining the limit of flammability in such constant volume experiments? This question has been considered in some detail in an earlier publication that dealt with coal dust data (20). It is somewhat more of a problem for dusts than it is for gases. In the conventional or "standard" limit of flammability apparatus (7, 47), experiments are conducted at constant pressure in a tube, and the limit criterion is the visual observation of flame propagation through the full length of a long tube. The data in figure 4A for a closed chamber suggests that a pressure ratio of 2.0 is a realistic choice for the limit criterion. It gives a lean-limit value of 5.0±0.1 pct methane, which is in good agreement with the "standard" value obtained for upward flame propagation in a tube (7, 47). For central ignition in the 8-liter chamber, the pressure ratio of 2.0 corresponds to the consumption of about 20 pct of the oxygen; and in the ideal case, this would correspond to upward flame propagation at a cone half-angle of about 30° from the vertical. Using that same pressure ratio criterion of 2.0 gives a rich limit of 17.5±0.5 pct methane. This value is significantly higher than the 15-pct methane value that is generally reported for the flammability tube method. This difference for rich mixtures is significant and real, and not some artifact of the limit criterion chosen. Earlier data (with spark ignition) for radiances and temperatures of methane-air explosions at compositions between 15 and 17 pct methane have already been reported (23-24). The significance of such observations of real flame propagation at compositions beyond the conventionally accepted rich limit has also been discussed earlier (24). The totality of data suggests that the "accepted" value of 15 pct methane may be too low, at least for constant volume chambers. The difference may be due to a weaker ignition source or higher heat losses for the flammability tube data.

Limit Criteria for Hydrogen in Air

Similar data for H_2-air mixtures with the same 8-liter apparatus were reported elsewhere (15). For lean hydrogen mixtures, the process of selective diffusion (17) generates cellular flame structures which complicate the problem of choosing consistent and realistic limit criteria. The cellular structures are noncontiguous flame fronts with large "holes" or "dark spaces" within them. For upward propagation in lean H_2-air mixtures, buoyancy and selective diffusion are mutually supportive and flame propagation is confined to sharply curved flamelets that occupy only a small fraction of the premixed volume. That complication requires a substantial adjustment in the pressure ratio criterion for constant volume combustion in order for it to be consistent with the visual observation criterion that is used in the conventional method. In the latter case, any propagation reaching the top of the tube, regardless of its "quality," is considered to indicate that the mixture is flammable (7, 47).

Methane in Air With Added Nitrogen

For any fuel-air mixture, the simplest inerting substance that can be considered is the inert additive that is already present in air, namely nitrogen gas. If one adds excess nitrogen to a fuel-air mixture, or dilutes any exothermic fuel gas with nitrogen, the mixture is eventually rendered nonflammable. The nonflammable condition is reached because dilution causes the oxygen level to be reduced below some critical value and/or because the same dilution causes the overall mixture's exothermicity to be reduced to below some critical value. That critical value is determined by flame stretch losses induced by buoyancy (16).

For hydrocarbon fuels, the corresponding heating value is the range of 10 to 12 kcal/mole of total gas mixture (16, 21).

The 8-liter chamber data for the effect of nitrogen addition on the flammability limits of methane-air mixtures is shown in figure 5. The data points shown are for experiments in which methane was mixed with various O_2-N_2 mixtures containing oxygen concentrations below that of normal air. The amounts of methane and added nitrogen for each data point can be read directly from the axes, and the amount of air can be calculated as shown in the key by subtracting the "pct methane" and "pct added nitrogen" from 100 pct. Those limit data points were obtained from peak pressure ratio data similar to those shown in figure 4A, but at reduced oxygen levels. The ignition source was one pyrotechnic match. The pressure ratio criterion of 2.0 was used to define the limit concentrations. These data are compared with the flammability tube data from Bulletin 627 (47).

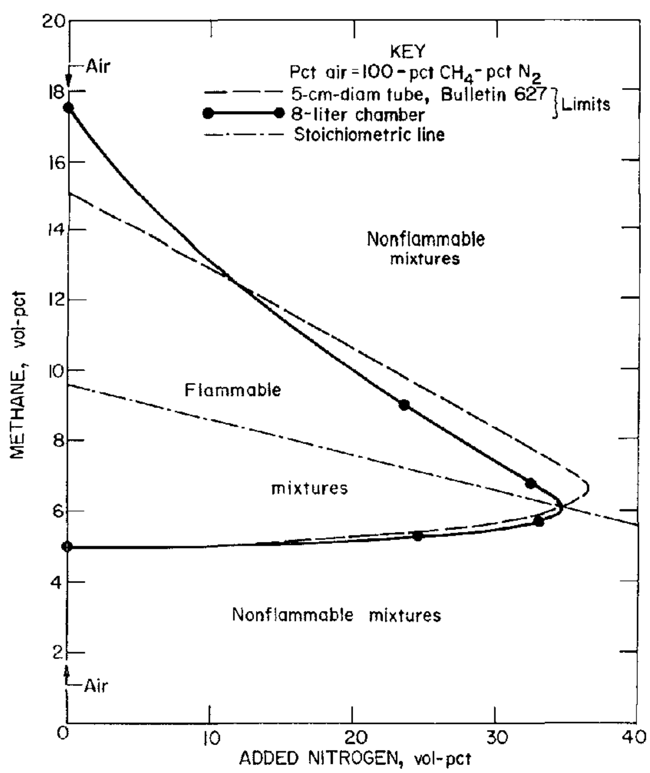

FIGURE 5. - Flammability diagram for methane-air with added nitrogen.

There is good agreement for the lean mixtures, and the data near the nose of the flammability curve may agree within experimental error. In any case, the "nose" of the flammability domain corresponds to a minimum oxygen concentration of about 12 pct which corresponds to an added nitrogen concentration of 35 to 37 pct. This volume percent of additional nitrogen corresponds to a mass concentration of 400 g/m^3 of added nitrogen. Thus a mixture containing a stoichiometric ratio of methane in air requires the addition of 400 g/m^3 of additional nitrogen gas in order to be rendered inert.

Methane in Air With Inhibitor Dusts

The amounts of inert or inhibiting dusts that are required to extinguish stoichiometric methane-air mixtures are shown in figure 6. The measured peak pressure ratios in the 8-liter vessel are shown as a function of added dust concentration. The data were obtained with one pyrotechnic match as the ignition source. The previously presented nitrogen data are also shown on the same scale for comparison purposes. The addition of dust, like the addition of more nitrogen, results in a reduction of the peak explosion pressure until at some level the explosion is completely extinguished. Using the same pressure ratio of 2.0 as the limit criterion for extinction, the concentrations of the various additives required to inert a stoichiometric methane-air mixture are shown in the second column in table 1. For the dusts, the relative order of effectiveness is $NH_4H_2PO_4$ > $KHCO_3$ > Al_2O_3 ≃ $CaCO_3$. However, the impression that nitrogen appears to be more effective than $KHCO_3$ is somewhat misleading. It must be remembered that gas addition substantially reduces both the methane and the oxygen concentration of the initial mixture, but the addition of a solid-phase dust leaves the initial fuel and oxygen contents essentially unchanged. The addition of 400 g/m^3 of nitrogen gas reduces the methane concentration to 6 vol-pct and the oxygen content to 12 vol-pct. The addition of a solid dust at the same mass

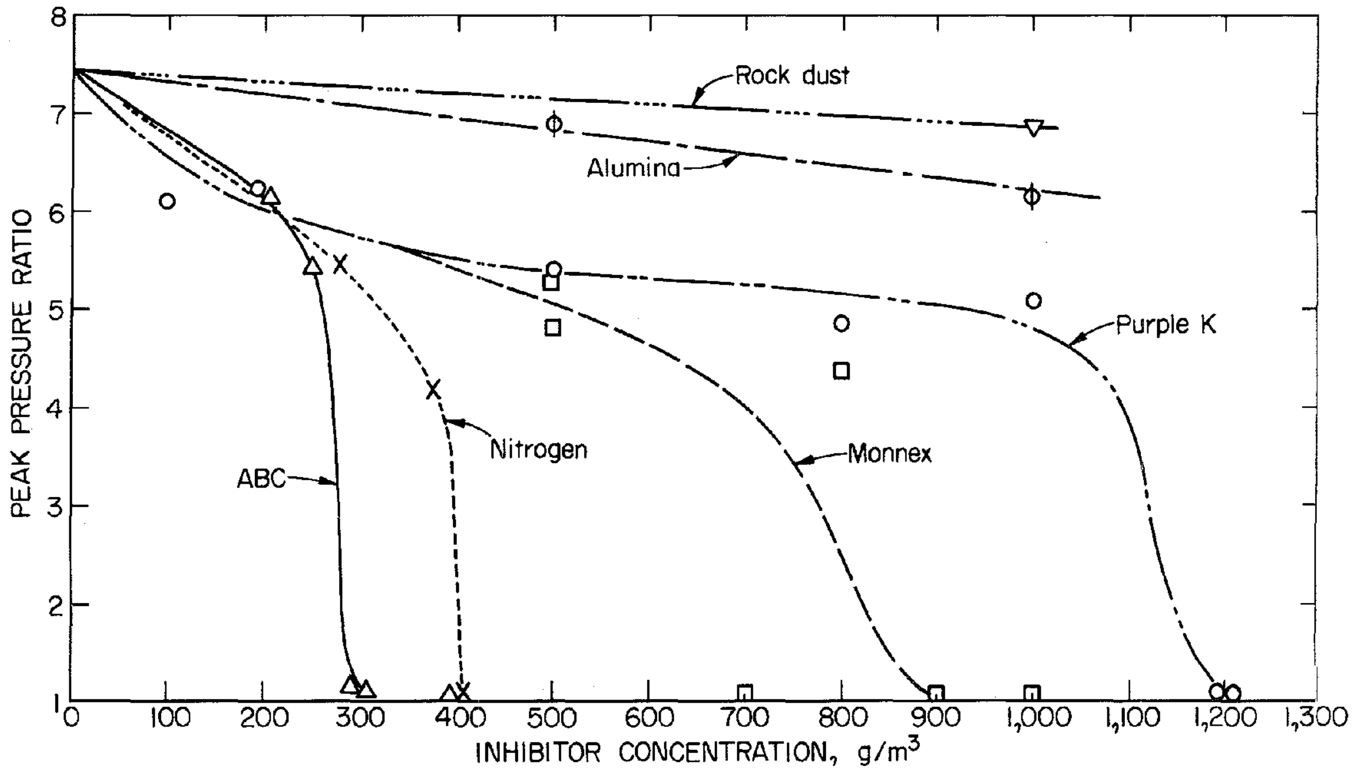

FIGURE 6. - Effect of added inhibitor dusts on explosion pressures of stoichiometric methane-air.

concentration level leaves the methane concentration unchanged at 10 vol-pct and the oxygen concentration similarly unchanged at 19 vol-pct.

TABLE 1. - Inhibitor concentrations required to inert a stoichiometric methane-air mixture

Inhibitor	Inerting concentration	
	g/m^3	wt-pct
ABC ($NH_4H_2PO_4$)...	290	81
Nitrogen gas (N_2)	400	86
Monnex ($KHCO_3$+urea)...	~800	92
Purple K ($KHCO_3$).	1,150	95
Alumina (Al_2O_3)..	>1,200	>95
Rock dust ($CaCO_3$)	>1,200	>95

In order to account for this effect when comparing powdered inhibitors with gaseous inhibitors, it is convenient to express the inhibitor concentration as the percent by weight of the incombustible substance that must be added to the pure fuel in order to completely inert it when mixed with air in a stoichiometric ratio. The third column of table 1 expresses that inhibitor concentration as the weight-percent of inhibitor in the inhibitor-fuel mixture. Clearly, if nitrogen is classified as a "thermal" inhibitor for methane-air explosions, then the bicarbonates must also be considered thermal for that case. Only the ammonium dihydrogen phosphate is significantly more effective than the thermal inhibitors.

Methane in Air With Halon

Data were also obtained with Halon 1301, CF_3Br, as an inhibiting additive and are shown in figure 7. Conventionally quoted values for the concencentration of CF_3Br required to inert a stoichiometric methane-air mixture are in the range of 4 to 5 pct (28, 38). The data in figure 7 are for two types of ignition sources: the first was a spark source with an effective ignition energy of at most several tenths of a joule (20), and the second was a single pyrotechnic match ignition source with an effective energy

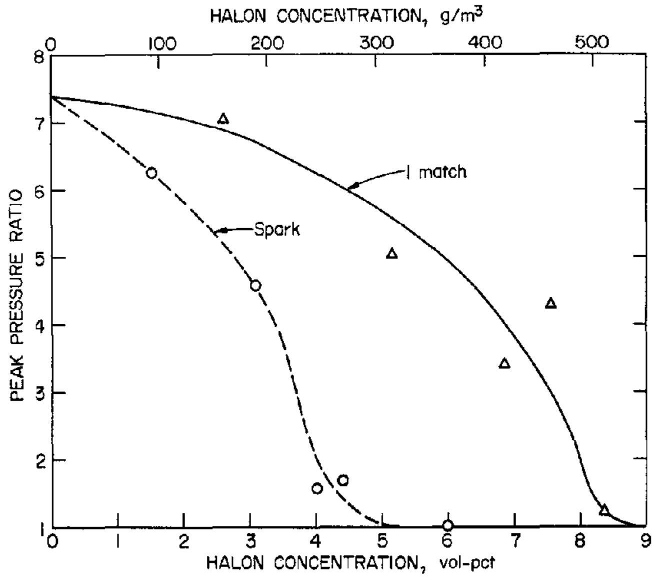

FIGURE 7. - Effect of added Halon 1301 on stoichiometric methane-air explosions.

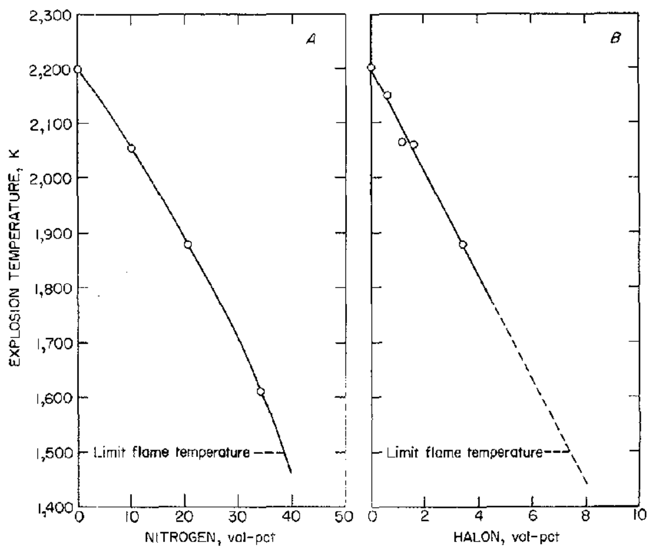

FIGURE 8. - Reduction in explosion temperature of stoichiometric methane-air with added nitrogen and Halon 1301.

of about 35 joules. These effective or $V\Delta p$ energies were computed from the measured pressure rise, Δp, in a chamber of known volume, V. The data show clearly that the conventional value in the 4- to 5-pct CF_3Br range is obtained only with the weaker ignition source. Clearly 4 pct CF_3Br is the amount of Halon required to prevent ignition with a spark source but is not sufficient to prevent propagation once ignition is obtained. The 4 pct CF_3Br is thus only an ignitability limit and not a true flammability limit. The true limit with a strong ignition source appears to be in the range of 8 pct CF_3Br. On a mass concentration basis, 8 pct CF_3Br corresponds to an inert concentration of about 500 g/m^3, or to an incombustible content of 88 pct of the fuel-Halon mixture. The CF_3Br is thus about as effective on a mass basis as nitrogen in its ability to inhibit or extinguish a methane-air explosion. However, on a volume basis it is much more effective than nitrogen.

Additional support for the 8-pct CF_3Br value as the true limit comes from earlier data (22) on measured explosion temperatures. These data for stoichiometric methane-air mixtures inerted with N_2 and CF_3Br are shown in figure 8. The explosion tests were made in a large, 3.7-m-diameter sphere and the temperatures were measured with an infrared spectrometer (22). For nitrogen addition, the measured temperatures are quite consistent with the flammability domain depicted in figure 5. For no nitrogen dilution in figure 8A, the stoichiometric mixture has a measured flame temperature of 2,200 K, which is very close to the calculated adiabatic flame temperature for constant volume combustion. As nitrogen is added, one moves down the stoichiometric line toward the nose of the flammability curve, and the measured temperature decreases continuously with dilution. At the nose of the flammability curve, with 37 pct added nitrogen, the measured flame temperature is 1,500 K. That value is consistent with the limit flame temperatures for the combustion of saturated hydrocarbons (16). Note, however, that the flame temperature in figure 8B for the addition of 4 pct CF_3Br is much higher, about 1,800 to 1,900 K. The temperature data does not extend beyond 4 pct CF_3Br because only spark ignition was used in those experiments. However, the data in figure 7 show clearly that the use of a pyrotechnic match ignitor would have given temperature data at Halon 1301 concentrations above 4 pct. Furthermore, a simple extrapolation of the measured temperatures in figure 8B to the normal limit flame temperature of 1,500 K would predict that the real inerting concentration should be 8 pct CF_3Br. Thus the temperature data also support the argument that the 8-pct value is the true inerting limit, and that 4 pct is only an apparent value, limited by the inadequacy of the ignition source. There is also substantial independent experimental evidence supporting the higher CF_3Br value in a variety of practical studies with other saturated hydrocarbon fuels (6).

This problem of ignition energy requirements is one major cause of past uncertainties and contradictions between the various studies of inhibition and extinction. In earlier studies (18, 20) relating to the limits of flammability of dusts, it was clearly shown that spark energies in the 0.1- to 1.0-joule range, although adequate for igniting most gaseous hydrocarbons in air, are not adequate for dusts. True limits of flammability for dusts are attained only when the limit values are independent of ignition energy. For coal dusts, ignition energies in the range of hundreds of joules are necessary (18, 20). Clearly the data in figures 7 and 8 show that this spark energy is also inadequate for Halon-containing mixtures. Apparently, in the case of halogenated compounds, their strong electron affinity and high electron capture probability causes them to interfere directly with the electron-avalanche processes in the spark discharge. Accordingly, they selectively suppress the ignition process at a lower concentration than that required for true extinction of the propagating flame (2). A similar effect has been reported recently for pure methylene chloride vapor in air (3). Although it appears to be nonflammable even for moderate spark energies, it is actually nonignitable. However, at high spark energies its true flammability limits can be measured.

EIGHT-LITER INHIBITION AND EXTINCTION DATA--DUSTS

Pittsburgh Seam Coal Dust in Air With Added Nitrogen

Detailed data on the limits of flammability of pure coal dust-air mixtures, and the effects of particle size, have been presented previously (18, 20-21). To summarize those results briefly, they indicate that the lean limit of flammability for Pittsburgh seam coal dust in air is 130 g/m^3, independent of particle size below 50 µm diameter. The majority of the inhibition data to be reported here are for a broad size distribution of Pittsburgh pulverized coal (PPC) with a surface mean diameter $\bar{D}_s$ = 27 µm and a mass mean diameter $\bar{D}_w$ = 45 µm. Pittsburgh seam coal has a volatility of about 36 pct by the ASTM D3175 test.

It is instructive to contrast the data for pure Pittsburgh seam coal dust with data for other carbonaceous dusts and methane as shown in figure 9. The flammability limits measured in the 8-liter chamber are plotted as a function of the oxygen concentration for various oxygen-nitrogen mixtures. The dusts span the extremes of carbonaceous dusts from polyethylene (a completely volatilizable, solid alkane) with a hydrogen-to-carbon ratio, H/C, of 2.0 to the normally nonvolatile allotropes of pure carbon, graphite and diamond dust. For air, at 21 pct O_2, the lean limits vary inversely with volatility. In particular, the limit combustible volatile contents are constant at 40 to 60 g/m^3, despite the wide variation in the lean limit concentration of the total dust (18). Note, for example, that the gravimetrically measured lean limit value for polyethylene [C_nH_{2n+2} ($n \rightarrow \infty$)] in air is virtually identical to the accepted volumetrically measured value for alkane vapors of high molecular weight (47). Additional discussion on the significance of the data in figure 9 is found in reference 18.

Most of the inhibitor-effectiveness data reported in this paper were obtained with the broad distribution of Pittsburgh pulverized coal, but the data in figure 9 were for a narrow distribution with

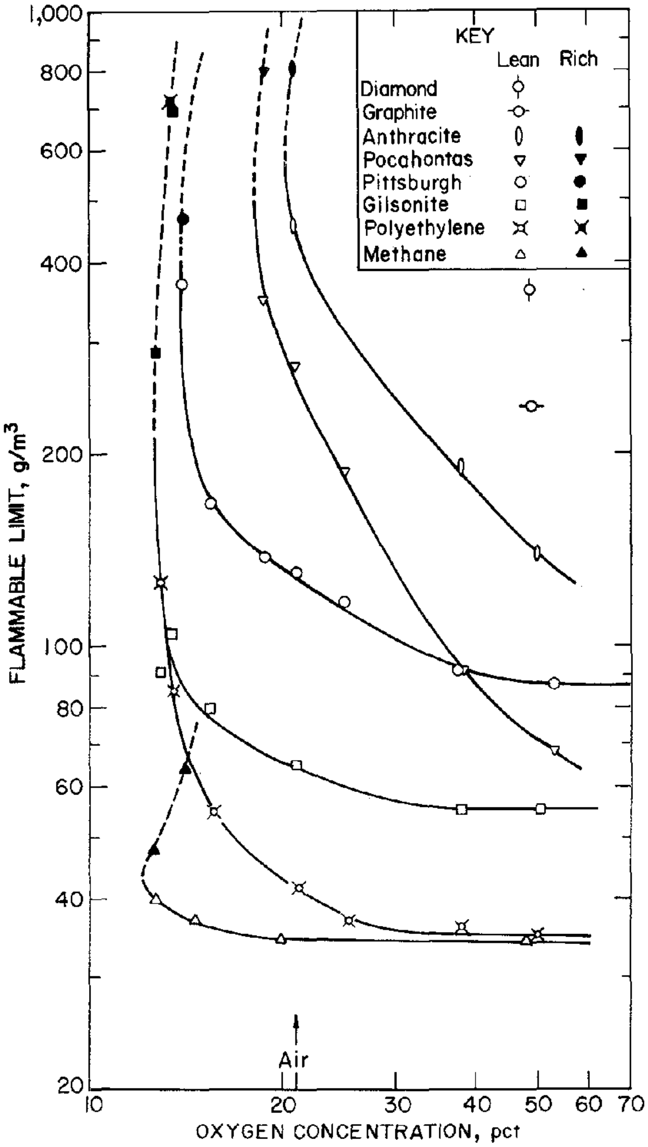

FIGURE 9. - Flammability limits for seven dusts and methane at varying oxygen concentrations.

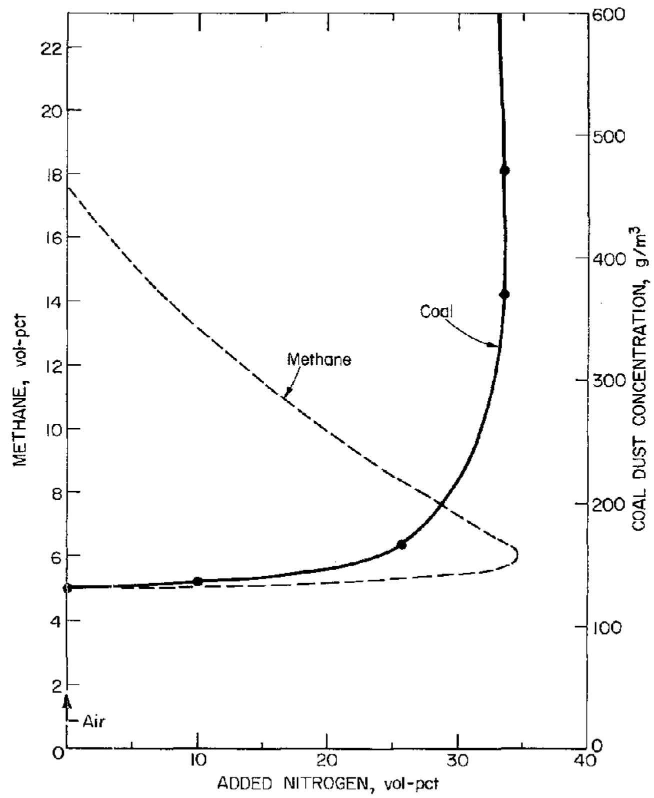

FIGURE 10. - Flammability diagram for coal and methane with added nitrogen.

$\bar{D}_s$ = 5 µm and $\bar{D}_w$ = 7 µm. As with methane, the simplest inerting substance that can be studied is nitrogen, the inert gas already present in air. The data in figure 9 for oxygen concentrations below 21 pct essentially show the effect of added nitrogen as an inhibitor. It is more instructive, however, to convert the coal dust and methane data to the more typical type of flammability diagram used in the Bureau of Mines Bulletins (7, 47) and in figure 5. This comparison between methane and coal dust is shown in figure 10, where the flammability domains are shown as a function of added nitrogen. For the methane, the flammable domain is the triangular region to the left of the dashed curve. The nose of the methane flammability curve occurs at 35 pct added N_2, 6 pct CH_4, and 59 pct air. The nose, therefore, corresponds to a minimum O_2 concentration of about 12 pct. The coal dust concentration scale on the right side of figure 10 has been normalized so that its 130-g/m^3 lean limit in pure air coincides with the 5-pct lean limit value for methane on the left. Note the contrast between the methane curve and the coal dust curve. For coal dust, the flammability domain is the region to the left and above the solid curve. It does not display a clearly definable "nose" as the methane curve does. Instead the "nose" is replaced by a broadly shaped, blunt "brow" that extends to very high dust concentrations. For coal dust, as one approaches the minimum O_2 concentration, the curve steepens and becomes almost vertical. The measured coal dust rich limit for 26 pct added N_2 was 3,600 g/m^3; and for air or zero added N_2, the rich limit exceeds 4,000 g/m^3.

From figure 10, the amount of added N_2 necessary to inert Pittsburgh coal dust is 34 pct, or the minimum oxygen concentration is about 13.5 to 14.0 pct. The "brow" occurs at a concentration of about 420 g/m^3, which is much higher than would normally be expected for gaseous hydrocarbon fuels. The nose of the flammability curve for gases (47) normally occurs along the stoichiometric line (fig. 5). For methane, for example, the nose occurs at a methane to oxygen ratio of 1:2, which is a stoichiometric ratio (usually the most reactive mixture). By contrast for coal dust, the most reactive mixture appears to be at a dust concentration of 400 to 450 g/m^3 which is a rich concentration even with respect to the normal volatile content of the coal. The reason for such behavior is related to the more complex mechanism of dust flame propagation. Premixed gases involve only the normal gas-phase kinetic sequence of flame propagation reactions; whereas dust flames require several additional processes: particle heating, devolatilization, and mixing of volatiles in the space between particles. These additional processes cannot only limit the rate of flame propagation but also limit the amount of volatiles that are generated in the finite time available for flame front passage. Thus, although the most reactive coal dust flame is probably propagating through a near-stoichiometric mixture of volatiles, only part of each dust particle is able to devolatilize rapidly enough to contribute to that flame. Even for high dust loadings, the flame front will always manage to devolatilize just enough of the coal dust to propagate in a near-stoichiometric mode. The front rides the crest of the most reactive mixture, much as a surfer rides the crest of an ocean wave. That is also the reason why rich limits occur only at very high dust loadings. If one loads the system down with more dust, the flame adjusts by feeding on the smaller particles, the sharpest corners, or thinner layers at the surface of each particle; and thus the flame front passes before a fuel rich concentration of volatiles can be generated (4, 18, 21).

In any case, the data show clearly that the most reactive mixture for Pittsburgh coal dust contains about 400 to 500 g/m^3; and accordingly, for inhibition measurements to be realistic and conservative enough, they should be made at coal dust concentrations that are at least that high.

Pittsburgh Seam Coal Dust in Air With Inhibitor Dusts

The pressure data for explosion tests with several inhibitor dusts are shown in figure 11. The data were obtained in the 8-liter flammability chamber with an ignition source consisting of four pyrotechnic matches. The data for the inhibitors in figures 11B, 11C, and 11D are to be compared and contrasted with the data for pure coal dust in figure 11A. The coal dust used was the broad size distribution of Pittsburgh pulverized coal (PPC) with $\bar{D}_s$ = 27 µm and $\bar{D}_w$ = 45 µm. The added inhibitor curves are identified by the weight-percent of inhibitor dust in the total dust mixture. The measured peak explosion pressure data in figure 11A is the normal curve for pure coal dust. Using a pressure ratio of 2.0 as the limit criterion, the lean limit is 130 g/m^3.

The effect of adding various concentrations of Purple K (fluidized $KHCO_3$) dust is shown in figure 11B. Additions in the range of 13 to 35 wt-pct of the powder raise the lean limit only slightly. Very high concentrations of the inhibitor, about 80 wt-pct, are necessary to completely inert the coal dust and Purple K mixture. The effect of the addition of BCD (fluidized NaCl) powder is shown in figure 11C. It is significantly more effective than Purple K. The addition of 35 wt-pct of BCD powder raises the lean limit from 130 to 270 g/m^3 of coal dust. The addition of 46 vol-pct BCD raises the lean limit to 450 g/m^3, and a slightly higher concentration would inert the mixture completely.

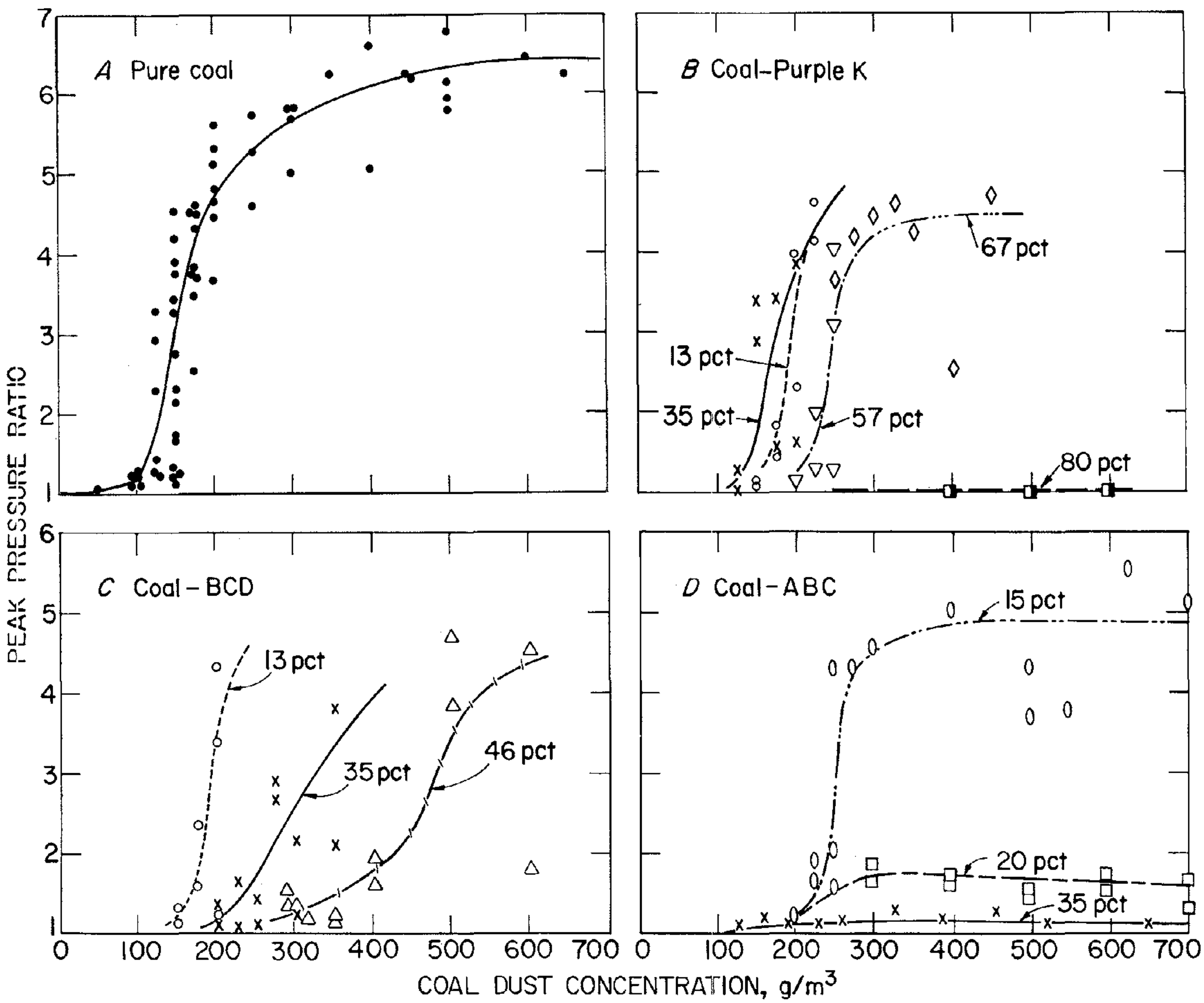

FIGURE 11. - Effects of added inhibitor dusts on explosion pressures of coal-air mixtures.

The most effective inhibitor studied was ABC (fluidized $NH_4H_2PO_4$) powder, and the data are shown in figure 11D. The addition of 15 wt-pct of ABC raises the lean limit from 130 to 240 g/m^3 of coal. With 20 wt-pct added ABC, the mixture is virtually completely inerted, with pressure ratios less than 2 for coal concentrations up to 700 g/m^3.

The data for limestone rock dust ($CaCO_3$) are shown in figure 12. Initial experiments were performed with normal rock dust, and the data are shown in figure 12A. Since that rock dust was not fluidized, there was some concern about a fair comparison of its effectiveness relative to the fluidized inhibitors. It was, in fact, surprising that rock dust should appear to be more effective than Purple K. Since the rock dust was not fluidized, it was suspected that the dispersion characteristics of the dust mixture were influencing the results. The unfluidized mixture is more difficult to disperse, especially at the high total dust concentrations required to study the less effective inhibitors. Accordingly, additional experiments were performed with fluidized rock dust and those data are presented in figure 12B. The data seem to show that the dispersion characteristics do indeed influence the results. However, even the fluidized $CaCO_3$

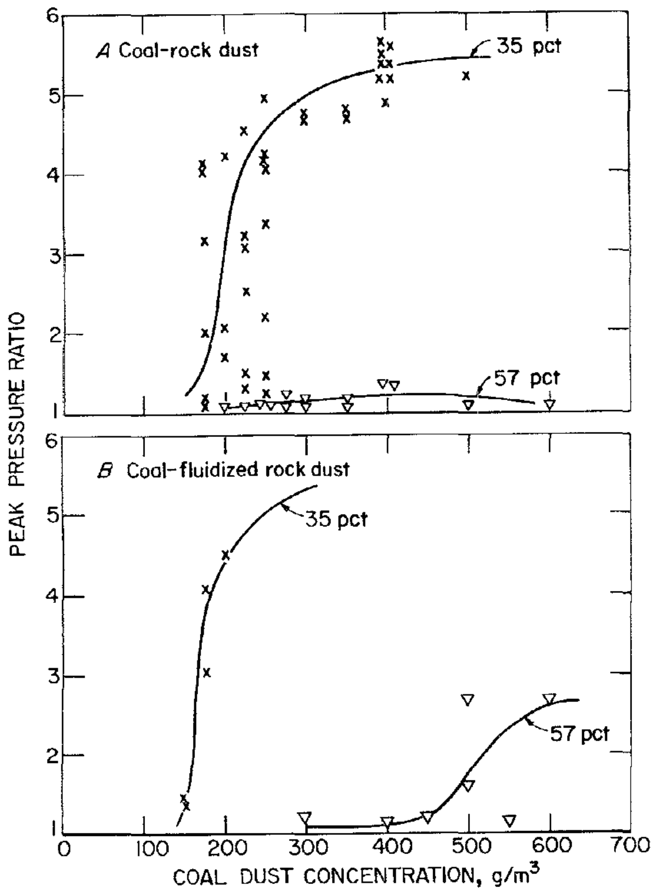

FIGURE 12. - Comparison of regular and fluidized limestone rock dust as inhibitors for coal dust in air explosions.

is somewhat more effective than fluidized $KHCO_3$. Concentrations of added, fluidized rock dust of about 60 wt-pct or about 63 pct incombustible (including ash in coal) would be necessary to inert the coal-rock mixture. This value is in reasonably good agreement with the data from full-scale mine tests which were the basis for the mining regulations (44-45).

The final results for all four inhibitors are summarized in figure 13. Using the standard limit criterion (measured pressure ratio of 2.0), the measured lean limit coal dust concentration is plotted as a function of the inhibitor content of the dust mixture. The inert content is shown both as the weight-percent of added inhibitor dust in the total mixture and as the weight-percent of incombustible, which includes the nominal 8 pct ash in the coal. All curves originate at 130 g/m^3 for zero added inhibitor content, which nevertheless contains 8 pct incombustible from the ash content of the pure coal dust. The lean limit increases with increasing inhibitor content. For the more effective inhibitors, the increase is marked; whereas, for the less effective inhibitors the increase is initially quite small. All curves essentially reach a vertical asymptote at the point where the mixture is rendered completely inert by the addition of the inhibitor dust. Once the lean limit has been raised as high as 400 to 600 g/m^3 of coal dust, one has usually just about reached that asymptote. This observation is quite consistent with the data for pure coal dust in figure 10, which indicated that the most reactive mixtures were at those concentrations.

The data in figure 13 show that the order of effectiveness of these four inhibitors is $NH_4H_2PO_4$ > NaCl > $CaCO_3$ > $KHCO_3$. The most effective, ABC ($NH_4H_2PO_4$) powder, is capable of inerting Pittsburgh seam coal dust at a concentration of only one part inhibitor to four parts coal dust; that is, only one-fourth as much inhibitor dust as coal dust. By contrast, the least effective inhibitor, Purple K ($KHCO_3$) powder, requires four times as much inhibitor as coal dust. BCD (NaCl) requires about equal parts of inhibitor and coal dust; whereas rock dust ($CaCO_3$) requires the standard amount: two parts incombustible to one part coal dust (44-45).

In addition to the inhibitors shown in figure 13, a variety of other chemical powders were studied. Various combinations of anion and cation salts were studied in a somewhat systematic way in the hope of finding the most effective inhibitor. Also studied were several refractory oxides and carbides of varying density. The results of those investigations are summarized in table 2. The inhibitors studied are tabulated in order of their increasing effectiveness. For each coal-inhibitor mixture, the lean limit in grams per cubic meter of coal

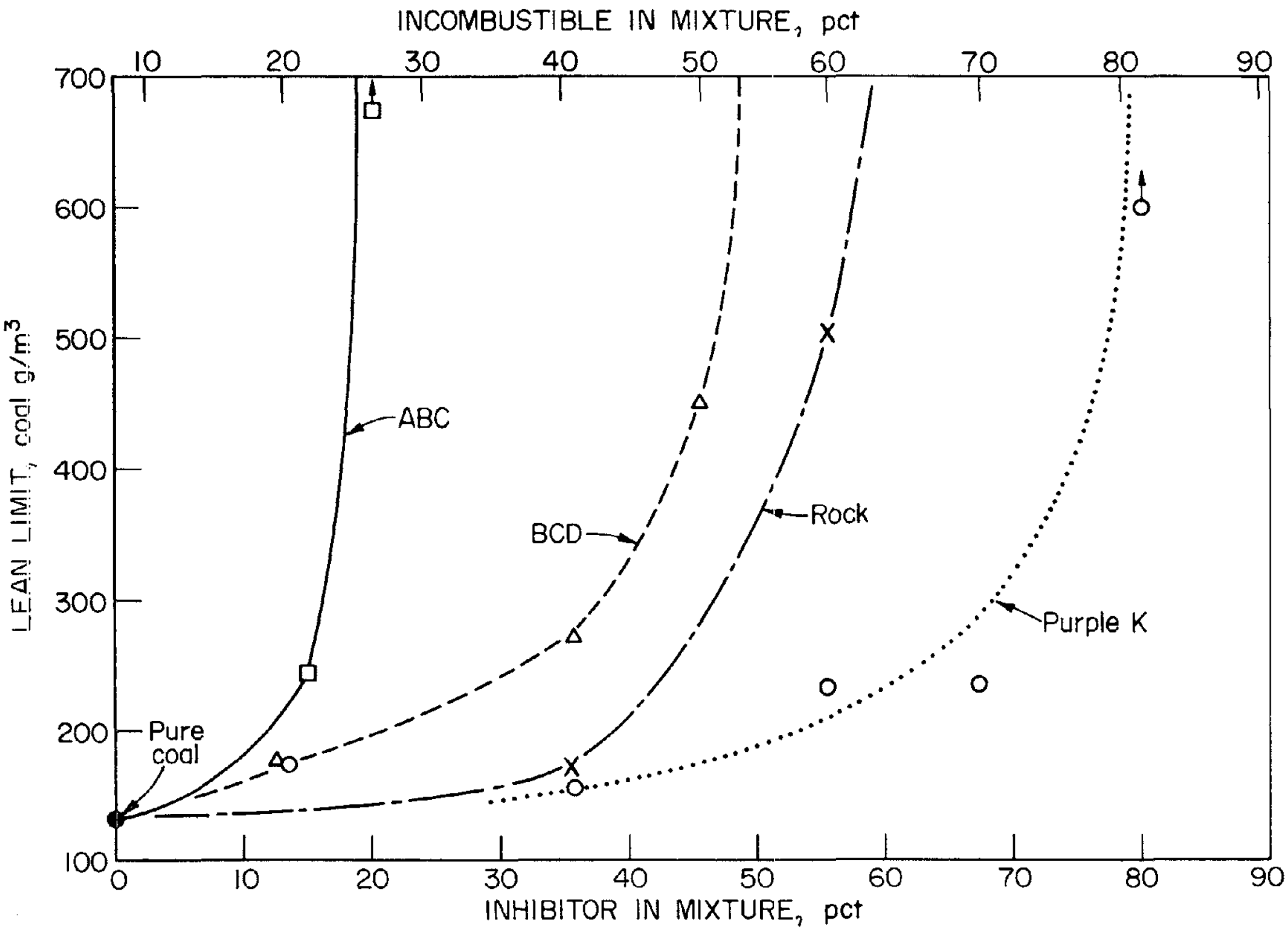

FIGURE 13. - The effect of added inhibitor dusts on the flammability limits of Pittsburgh seam coal.

is listed. Nonflammable mixtures are denoted by NF in the table. The amount of inhibitor dust required to totally inert the coal-inhibitor mixture is listed both as the weight-percent of that inhibitor and as the weight-percent of total incombustible, which includes the ash and moisture in the coal. The average particle sizes are from Coulter Counter size analyses.

One should be cautious in attributing small differences in effectiveness to chemical effects exclusively. There were significant differences in particle size and degree of fluidization for the various powders studied, and these variables could have important effects on the apparent order of effectiveness. Preliminary data has shown that, for particle diameters less than 20 µm, variation in particle size has a relatively minor influence on an inhibitor's effectiveness. Three narrow distributions of alumina, Al_2O_3, dust ($\bar{D}_s$ = 4, 8, and 14 µm) were tested with Pittsburgh coal dust. At 35 pct inhibitor, the same coal lean limit was measured with all three sizes. At 56 pct inhibitor, the smaller sizes were only slightly more effective than the largest dust tested. Several narrow and broad distributions (with mean diameters of from 5 to 30 µm) of Phos-Chek P/30, $(NH_4PO_3)_n$, were also tested with Pittsburgh coal dust. At 13 pct inhibitor, the smaller sizes were somewhat more effective in raising the coal dust lean limit. The amount of Phos-Chek necessary to totally inert the coal-inhibitor mixture ranged from 13 wt-pct

TABLE 2. - Effectiveness of various inhibiting dusts against Pittsburgh seam coal dust explosions, as shown by the increase in the coal lean flammability limit with added inhibitor

Inhibitor	Particle diameter, µm		Lean limit coal dust concentration, g/m^3, at inhibitor content of--					Amount required to inert completely, wt-pct	
	$\bar{D}_s$	$\bar{D}_w$	13 pct	15 pct	35 pct	46 pct	56 pct	Inhibitor	Total incombustible
$LiC_5H_7O_2$ (lithium acetyl acetonate)..					85				
$C_3N_6H_6$ (melamine)...					120				
$K(CH_3COO)$...........					130				
$Na_3PO_4 \cdot 12H_2O$........					~130				
KNO_3................			140						
$KHCO_3$+urea (Monnex)[1]	12	19			140				
$NaHCO_3$ (BCS)[1].......	8	14			145				
$KHCO_3$ (Purple K)[1]...	11	22	180		155		230	78	80
NH_4HCO_3.............					~150				
Li_3PO_4..............	28	59			~160				
$(NH_4)_2SO_4$...........					165				
KBr................					165				
$(NH_4)_2C_2O_4 \cdot H_2O$......	16	23			170				
Al_2O_3..............	4	5			190		~400		
$CaCO_3$ (rock dust)[1]..	14	15			165		~500	60	63
$CaCO_3$ (rock dust)...	10	28	150		~180		NF	56	60
KCl (Super K).......	8	15			180	~300		~54	~58
NaF................					185				
KI.................					190				
B_2O_3...............	(2)	(2)			190				
WC.................					200				
Phosphate rock......	14	28			200	300		~53	~57
K_2HPO_4..............	90	120			210				
$CaC_2O_4 \cdot H_2O$..........	9	13			225				
NH_4Cl...............					225				
$Na_2B_4O_7$.............	40	60			225				
NaCl (BCD)[1].........	9	19	175		270	450		48	53
$Ca_2P_2O_7$............	11	16			290				
BN.................	8	11			390				
MgO................	8	10			~480		NF	39	44
$Ca_3(PO_4)_2$...........	8	12	200		~450			39	44
$CaHPO_4 \cdot 2H_2O$.........					NF			35	40
$NH_4H_2PO_4$............	11	16		180					
$NH_4H_2PO_4$ (ABC)[1].....	7	10		240	NF			20	26
$C_3N_6H_7 \cdot H_2PO_4$ (melamine phosphate)....	7	13	230		NF				
H_3BO_3...............	28	40	240		NF				
$(NH_4PO_3)_n$ (Phos-Chek P/30).............	22	33	~280	~450	NF			18	24

NF Nonflammable. [1]Fluidized powders. [2]Large.

NOTE.--No entry indicates that data were not collected or flammability teats were not performed.

for the smallest size to 18 wt-pct for the largest size. Therefore, variations in particle size below about 20 μm would probably not significantly affect an inhibitor dust's position in table 2. However, for the inhibitor dusts in the table with much larger mean diameters, the inhibitor's position in the table could improve significantly if a smaller size were tested.

In summary, the data suggests that the effectiveness of the inhibiting salts correlates better with their anion rather than with their cation components. The approximate order of anion effectiveness is phosphates > halides > carbonates. The most effective of the phosphates appears to be the ammonium salt, which has the lowest decomposition temperature of the phosphates studied. A more detailed discussion of these results will be presented later in this report.

COMPARISON OF SMALL-SCALE AND LARGE-SCALE DATA

Premixed Coal and Inhibitor Dusts

As discussed in the introduction, some early laboratory-scale tests (13-14, 42) were in total disagreement with mine tests (12, 40) on the relative effectiveness of Purple K and limestone rock dust as inhibitors against coal dust explosions. The data from the 8-liter flammability chamber, however, show good agreement with the mine tests as seen in table 3. The 8-liter data are compared with data from a 2-m-diameter by 28-m-long gallery, open at one end, and with data from the Bruceton (Pa.) Experimental Mine. In all tests the inhibitor and coal dust were premixed, and a strong ignition source was used. The values listed in the table are the amounts by weight of inhibitor necessary to totally inert the mixture. (Note that the weight-percent does not include the intrinsic ash and moisture in the coal.) The order of effectiveness for the five inhibitors is the same in both the small-scale laboratory chamber and in the large-scale gallery and mine. Also, the absolute amounts necessary to inert are in reasonably good agreement in the three test methods. Since inhibitors can be more easily tested in the laboratory-scale 8-liter chamber and since it gives good agreement with full-scale mine tests, it can be used as a screening device to test potentially effective inhibitors before the more costly full-scale tests are conducted.

TABLE 3. - Inerting requirements for Pittsburgh seam coal with various powdered inhibitors, small-scale and large-scale data

Inhibitor	Weight-percent required to inert		
	8-liter chamber	2-m-diameter gallery	Experimental mine
$KHCO_3$ (Purple K)....	75-80	70-75	67-73
$CaCO_3$ (Rock dust)...	~60	65-70	67-70
KCl (Super K).......	50-55	20-30	35-40
NaCl (BCD)..........	45-50	18-24	35-40
$NH_4H_2PO_4$ (ABC)......	18-20	10-15	18-24

Inhibitors in Triggered Barriers

Bartknecht (3) has studied the problem of extinguishing dust and gas explosions in enclosures of fixed volume by the rapid release of various inhibiting powders into the enclosure. The effectiveness of such triggered barriers were evaluated in terms of the number of containers, each containing a given mass of powder, that were required to suppress the explosion. Ammonium phosphate based powders proved to be the most effective inhibitors. That observation agrees with the data reported here in tables 1 and 2 and in figures 6 and 13. Since the barriers contained a given mass of powder and were dispersed into a known volume, the approximate mass concentration required for extinguishment can be estimated. For the large explosion vessels of 20 to 50 m^3, the concentration of ammonium phosphate required for extinguishment by triggered barriers was in the range 1,200 to 1,800 g/m^3. That value is considerably higher than the values observed in the present studies with methane gas (table 1) and with coal dust (table 2). In the 8-liter studies, the inhibitor was predispersed with the dust or gas prior to ignition; whereas, in the triggered barrier studies by Bartknecht, the inhibiting dust was dispersed only after an explosion had already been initiated. The higher concentrations required in the latter case suggest that these barriers' effectiveness may still be largely limited by the rate of discharge of the extinguishant and/or its dispersion and mixing requirement within the volume.

In Bureau studies in the 2-m-diameter gallery and in the Bruceton (Pa.) Experimental Mine, Liebman and Richmond (33) tested inhibitors in triggered barriers in addition to the premixed coal-inhibitor tests discussed in the previous section. They also found that ammonium phosphate (ABC powder) was the most effective inhibitor against coal dust explosions. Water was almost as effective and Purple K was again much less effective.

INHIBITION AND EXTINCTION IN A METHANE BURNER FLAME

In addition to the constant volume explosion tests, a variety of experiments were performed with a methane burner system. The system was constructed to deliver and measure the concentration of powdered inhibitors needed to quench a low-velocity, flat, methane-air burner flame. Data were obtained on the effectiveness of ABC, Purple K, and alumina.

Burner and Dust Feed System

The burner (fig. 14) was designed to generate a stable, flat flame and at the same time to minimize the resistance to powder flow into the flame front. The burner was oriented so that the inlet gases flowed downward. Accordingly, the flame propagation direction was upward with the upward laminar burning velocity balanced against the downward gas flow velocity. The grid that laminarized the flow profile was made of stainless steel with open mesh dimensions of 1.6-mm square cross sections. The wall thickness of the stainless steel elements that

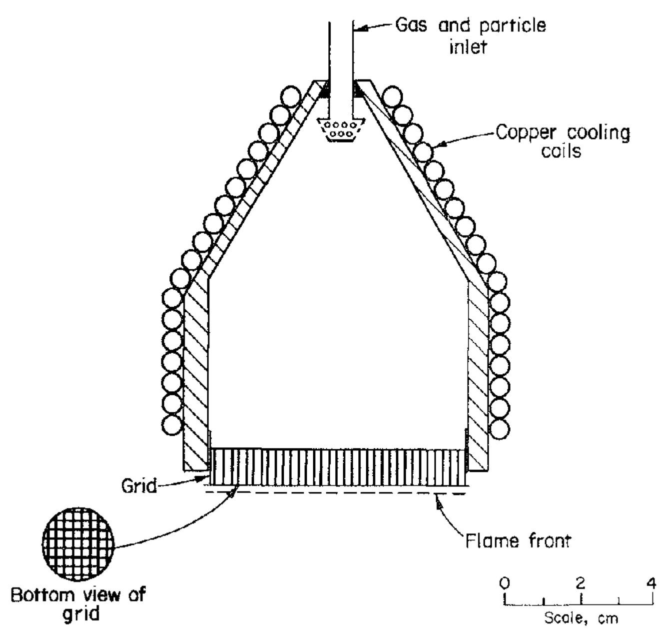

FIGURE 14. - Schematic of flat-flame gas burner.

formed the grid was 0.8 mm and the grid height was 16 mm. The grid was adjusted so that it protruded some 6 mm below the main body of the burner. The powder feeder system is similar to the one described by Altenkirch, Peck, and Chen (1). The feeder operates on the principle of a pressure difference which induces a powder flow from the fluidized bed (fig. 15) through an orifice in the 1-mm-ID stainless steel offtake tube positioned 6 cm above the fritted glass disk. The orifice is 0.06 mm in diameter and is located in the wall near the center of the tube. A metered air flow through the offtake tube controls the output powder concentration by defining the pressure differential between the bed and tube. The relationship of the combined powder feeder and burner system is shown in figure 16.

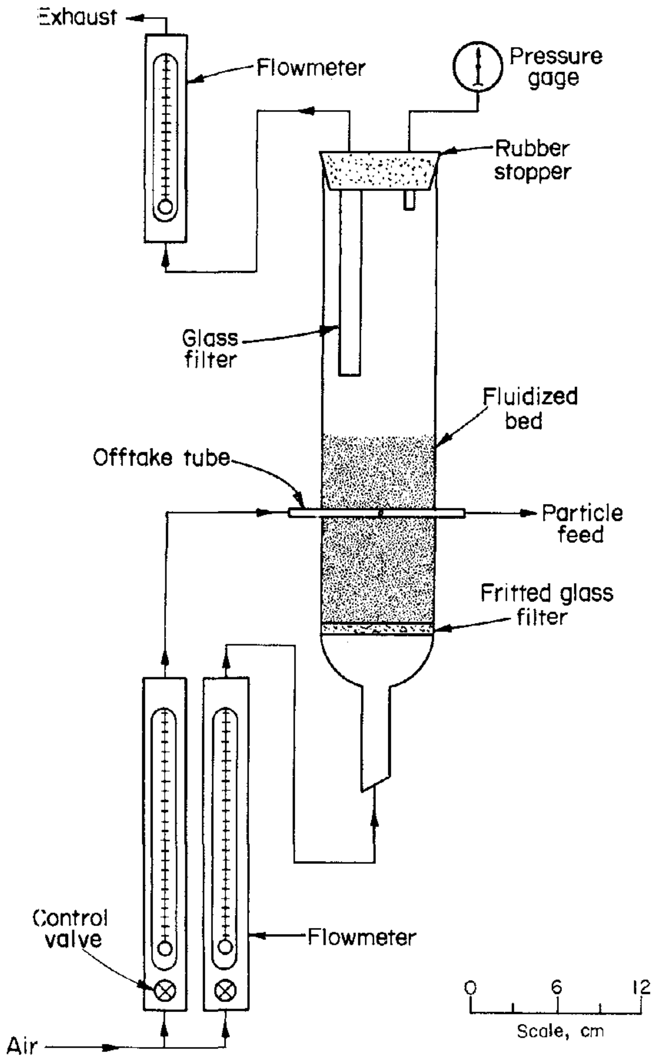

FIGURE 15. - Fluidized bed, dust feed system for the gas burner.

Powder concentrations were measured with a collection system consisting of a vacuum cleaner and a large funnel with glass fiber filter paper. The concentration was determined by the mass of powder collected on the filter paper in a given time interval relative to the volumetric gas flow in the same time interval. Flame temperatures in the burner were measured using a 1-mil (25 µm) platinum-rhodium type S thermocouple.

Inhibitor Data

The data obtained with the methane-air burner flame are summarized in table 4. The data differ significantly from those obtained in the 8-liter constant volume chamber and in the large-scale gallery and mine. Purple K, which was relatively ineffective in those studies, appears to be the most effective powder in the burner test. Because of the apparent contradiction, these burner tests do not appear to be reliable indicators of extinguishant behavior in real explosions. However, the reasons for this contradiction are not entirely known.

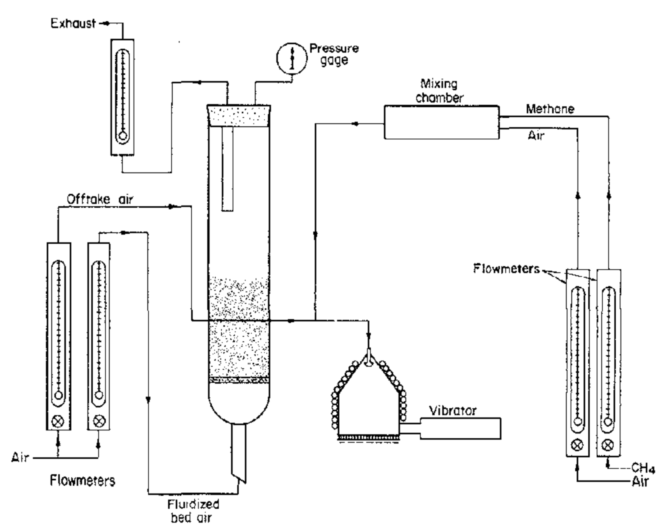

FIGURE 16. - Gas burner, dust feed system, and associated instrumentation.

TABLE 4. - Concentrations of added inhibitor dusts required to extinguish a burner-stabilized stoichiometric methane-air flame

Flame velocity, cm/sec	Measured, burned gas flame temperature, K	Extinguishing concentration, g/m^3		
		Purple K	ABC	Alumina
4.4......	1,730	1.6	41	>1,150
5.7......	1,760	1.1	94	>1,150
6.3......	1,780	2.0	168	>1,150

A clue that may lead to a resolution of the problem comes from the relatively low flow velocity and flame temperature for the uninhibited methane-air flame. The normal burning velocity for a stoichiometric methane-air flame is about 45 cm/sec and its adiabatic flame temperature is 2,200 K. Yet the burner flames shown in table 4 had burning velocities of only 4 to 6 cm/sec and flame temperatures 400 to 500 K lower than normal. Clearly, the flames were highly quenched by heat losses to the top of the burner system even before the powdered extinguishants were added. This is quite apparent from the ABC data, where a small increase in burning velocity from 4 to 6 cm/sec had a large effect on the concentration required to extinguish. In order for these data to be consistent with the data for the explosion studies, an even more dramatic increase (about two orders of magnitude) would have to appear for the Purple K data at the higher burning velocities.

Comparison With Other Burner Data

An early study of the effect of powdered additives on premixed flames was reported by Dolan (9). He measured the concentration of various powders required to extinguish a stoichiometric methane-air flame propagating upward in a 7-cm-diameter tube. For closed-end ignition, the concentrations of NaCl and $NaHCO_3$ powders (2 to 5 µm in diameter) required to extinguish the flame were 280 and 66 g/m^3 respectively. For open ended ignition, suppression occurred at considerably lower concentrations.

Dewitte, Vrebosch, and Van Tiggelen (8) measured the concentrations required to extinguish methane flames on a downward flowing burner flame in which the flame was propagating mainly upward. The flames were slightly enriched in oxygen; however, the measured critical dust concentrations for extinguishment were shown to scale with the square of the burning velocity. For the burning velocity corresponding to a stoichiometric methane-air mixture, the critical dust concentration for 3 to 5 µm K_2SO_4 was in the range of 200 to 250 g/m^3. The powder K_2CO_3 was somewhat more effective, requiring concentrations of 150 to 175 g/m^3, whereas Na_2CO_3 required concentrations of 500 to 600 g/m^3. An even more effective inhibiting powder K_2CrO_4 required about 100 g/m^3, whereas the alkali halides required concentrations that were a factor of two to three higher.

Rosser, Inami, and Wise (41) measured the effect of the addition of inhibiting powders on the upward propagation velocity of stoichiometric methane-air flames in a 2-cm-diameter tube. The dust was injected near the bottom of the tube in an upward flowing stream; however, the gas flow was stopped for an unspecified period of time just prior to ignition with an electric spark. Some powders such as $CaCO_3$ were not very effective in reducing the flame velocity, but several others appeared to be quite effective and were categorized as showing "chemical interference with the combustion process." For the more effective compounds there was a very rapid reduction in burning velocity with increasing dust concentration, dropping from 70 cm/sec to about 15 cm/sec. Below 15 cm/sec all additives showed a leveling off in apparent effectiveness. The dust concentration at which the curve broke or "leveled off" was considered to be a measure of inhibitor effectiveness. For the more effective dusts, the break occurred at concentrations as low as 10 to 20 g/m^3. It may, however, not be coincidental that the curves break at a common velocity of 15 to 20 cm/sec. That velocity is about equal to the rate of rise of a buoyant ignition kernel, at the limit flame temperature, in a 2-cm-diameter tube (16, 19). There are more uncertainties in the test procedure that cast suspicion on the validity of the low concentrations inferred at the break. First there is the unspecified delay between the stopping of the flow and the initiation of the spark. Dust particles in a static gas will settle by gravity generating a concentration distribution that can change markedly during the delay, especially near the ignition region at the bottom of the tube. Any downward velocity for the particles relative to the gas into an upward propagating flame causes the flame front to experience a dynamic dust concentration that can be markedly higher than the static concentration in the tube. In addition, the spark ignition source may not have been adequate to insure the reliable ignition of the mixture. Thus the data may, in reality, reflect only the effectiveness of the various powders in preventing ignition with a relatively weak source and not the amount required to extinguish a fully developed combustion wave. The situation may be similar to that described earlier for the halogenated compounds. In any case, the concentrations reported by Rosser, Inami, and Wise at the break of the propagation velocity curve for the addition of K_2SO_4, Na_2CO_3, and the alkali halides are at least an order of magnitude lower than the extinction concentrations reoprted by Dewitte, Vrebosch, and Van Tiggelen (8). Rosser, Inami, and Wise did, however, observe good correlation between the relative effectiveness of the various powders studied and the ease of volatilization. The ineffective additives were those that were nonvolatile at the flame temperatures encountered, whereas the effective powders had high volatilities at those temperatures.

Smoot and Horton (42) studied the effectiveness of various powdered additives in extinguishing burner-stabilized flames of methane-air and coal dust-air. A downward flowing system was used in an enclosed burner in which a 10-cm-diameter flat flame was stabilized in upward propagation toward a flow-smoothing, flame holder screen. Data were obtained for the concentrations of added powders required to reduce the burning velocity of stoichiometric methane-air from its normal value of 45 cm/sec to an extinction limit value near 5 to 8 cm/sec. The required concentrations were as follows: 20 g/m^3 for 18 µm $K_2C_2O_4$, 20 g/m^3 for 4 µm $KHCO_3$, 80 to 120 g/m^3 for 14 µm $KHCO_3$, 100 to 120 g/m^3 for 19 µm KBr, 400 to 500 g/m^3 for 22 µm KNO_3, 1,100 g/m^3 for 13 µm $CaCO_3$, and 1,300 g/m^3 for 12 µm Al_2O_3. For Pittsburgh seam coal dust-air flames, concentrations in the range 10 to 15 wt-pct of 19 µm $KHCO_3$ were sufficient to extinguish the most flammable coal dust concentration.

In summary, the more adiabatic burner flames gave better agreement with the 8-liter data; but there is still a contradiction for Purple K. Smoot and Horton's data for the thermal inhibitors, $CaCO_3$ and Al_2O_3, were somewhat in agreement with the 8-liter data from figure 6 and table 1. The reason that Purple K appears to be a more effective inhibitor against burner flames of methane and coal dust and against the vertical duct flames (13-14) is still not completely understood. Continued study of burner flames may be interesting from a purely scientific viewpoint. However, the final evaluation of the effectiveness of inhibitors against methane or coal dust flames should always be made in full-scale tests; and the laboratory-scale method (8-liter chamber) that gives best agreement with the full-scale tests is the one that should be used for preliminary testing and screening of inhibitors.

DISCUSSION AND INTERPRETATION

As shown earlier in table 2, the data for the inhibitor compounds indicate an effectiveness ranking according to their anion moiety. It is unclear why they should rank themselves according to their anion content. It is possible that that ranking merely reflects the ease of devolatilization or decomposition. The phosphates are generally more easily volatilized than the halides or carbonates. On the other hand, some easily decomposible substances such as NH_4HCO_3 were relatively ineffective. The data in table 2 suggest, in addition, a chemical role being played by some phosphorus bearing intermediates of the thermal decomposition of the phosphates studied. The observed effectiveness increases more or less monotonically with the phosphorus content of the inhibitor, except for Li_3PO_4 which is larger in particle size and melamine phosphate $C_3N_6H_7 \cdot H_2PO_4$ which is very effective with a low phosphorus content.

As discussed earlier in the section on the 8-liter data for coal and inhibitor dusts, some limited results were obtained for various particle sizes of a given inhibitor. In the case of very fine Al_2O_3 and $(NH_4PO_3)_n$, particle size variations did not seem to have a large effect below about 20 µm in diameter. Although all the inhibitor dusts studied were generally quite fine in size, they were of varying sizes. Accordingly, one should be cautious in attributing small differences in behavior of the various compounds studied to their chemical composition solely. Some particle size effects, especially for the coarser powders studied, may be hidden in the data. Better control of inhibitor sizes is desirable in future studies.

Another hidden variable discussed earlier is the state of fluidization. It is probably desirable to fluidize all inhibitors used in future studies, but it is especially necessary when dealing with the less effective substances such as $CaCO_3$. If large inerting quantities must be added to the most reactive coal dust concentration (400 to 600 g/m^3), then the total dust concentration being dispersed becomes quite large. In such cases, the degree of fluidization can markedly affect the dispersibility of the mixture. The data showed that fluidized rock dust appeared to be somewhat less effective as an inhibitor than unfluidized rock dust. This is probably because the unfluidized rock dust prevented the coal dust from being effectively dispersed. Accordingly, the most flammable coal dust concentration was not attained and a lower inerting level appeared to be effective. If the dust is fluidized, the dense mixture is more easily dispersed, the optimum coal dust concentration is readily attained, and a larger inerting level is required. Naturally, it is the latter value that correctly represents the true inerting requirement.

For methane-air extinction data there is no dispersibility requirement for the fuel. In that case, fluidization enhances the dispersibility of the inhibitor only and the fluidized powders could appear more effective than their unfluidized counterparts. This fluidization-dispersibility factor is measurable but small and tends to be confined to the less effective inhibitors. Because of the differences in fluidization for the compounds studied in table 2, one must be similarly cautious in attributing small differences in effectiveness to chemical effects only. As with particle size control, it is probably desirable to fluidize all the inhibitors studied to insure that the nominal mass loadings used correspond to the real concentrations that are dispersed.

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