

### Sensitivity of Explosives to Initiation by Electrostatic Discharges

It has long been recognized that there are static electrical hazards associated with the manufacture, handling, and use of explosives, particularly initiating explosives, but only within recent years has a systematic attempt been made to obtain quantitative data on such hazards. The Bureau of Mines has made and is continuing to make an extensive study of the static electrical hazards associated with the manufacture, handling, and use of explosives. Preliminary investigations on a number of explosives have been made.<sup>28/</sup> The results indicate that a considerable number of explosives, including primer, initiator, detonator, igniter, tracer, and incendiary types may be ignited by electrostatic discharge energies less than those that may be built up on and discharged from the human body. It was established that electrostatic energies accumulated on the body may readily reach values as high as 0.015 joules, and this value was accepted as a standard in determining for what explosives extra precautions must be taken against electrostatic discharges. This standard was accepted by the U. S. Army Ordnance in drafting their safety requirements for Ordnance plants manufacturing or handling explosives.

Further work on this subject has included investigations of electrostatic sensitivity of most commercial detonators manufactured in the United States. Marked differences in sensitivity have been found, depending on composition of ignition charges and on geometry of bridge wire and case of the detonator.

### List of Permissible Explosives

A permissible explosive is one that is similar chemically, physically, and in all other respects to a basic sample that has passed certain required approval tests of the Bureau of Mines. After an explosive or blasting device has passed all the required tests,<sup>29/</sup> it may be placed on the permissible list. This list is constantly being revised owing to additions of explosives and blasting devices that have passed the tests and to transfers between the active and inactive lists. As of June 30, 1946, the list contained the names of 180 explosives and 9 blasting devices, compared with the names of 178 explosives and 9 blasting devices on the lists as of June 30, 1945.<sup>30/</sup> Of the two new explosives added to the list, one was submitted for complete tests for permissibility and the other was an additional

<sup>28/</sup> Brown, F. W., Kusler, D. J., and Gibson, F. C., Sensitivity of Explosives to Initiation by Electrostatic Discharges: Bureau of Mines Rept. of Investigations 3852, 1946, 8 pp.

<sup>29/</sup> Bureau of Mines, Procedure for Testing Explosives (Including Sheathed Explosives) and Blasting Devices for Permissibility and Suitability: Schedule 1F, approved January 20, 1945, 15 pp. (Test conditions and procedure to follow in making application for tests are given.)

<sup>30/</sup> Tiffany, J. E., and Gaugler, Z. C., Active List of Permissible Explosives and Blasting Devices Approved Previous to December 31, 1945: Bureau of Mines Rept. of Investigations 3910, 1946, 20 pp.

name given to an explosive already on the list. The nine models of Cardox blasting devices remained the same as last year.

#### Consumption of Permissible Explosives

In blasting coal, only permissible explosives should be used; otherwise disastrous explosions may occur. Permissible explosives were first introduced in 1909, and their subsequent use has increased steadily. During the fiscal year 1946, the consumption of permissible explosives in coal mines amounted to almost 91 million pounds. In addition, there were used almost 34 million pounds of black blasting powder and slightly over 97 million pounds of high explosives other than permissibles. Thus, about 2.7 times as much permissible explosives as black blasting powder was used. There has been a steadily increasing ratio since the fiscal year 1940, the first year in which the consumption of permissible explosives exceeded that of black blasting powder.

Subsequent to the introduction of permissible explosives in 1909, more than 1-1/2 billion pounds of these explosives have been used in coal mines. When used in a permissible manner, they have never been known to be the cause of a mine explosion. In the few instances of explosions in which permissible explosives were involved, the fact has been established that the explosives were used in a nonpermissible manner. Even in recent years some mine disasters have been caused by the use of black blasting powder in mines that were definitely gassy. There can be no excuse for continuing the use of black blasting powder in coal mines. The conditions of use prescribed by the Bureau of Mines form an essential part of the requirements for permissibility, and failure to observe any of these conditions constitutes a violation of the requirements and renders the use of the explosive or blasting device nonpermissible.

#### Field Samples of Permissible Explosives

To continue to be permissible, an explosive or blasting device must be so manufactured that it will possess all the chemical and physical characteristics of the basic sample. To check these characteristics, samples are taken in the field and retested. Tolerances that are allowed when comparison is being made with a basic sample are set forth in Schedule 1F. These tolerances define the limits beyond which field samples cannot vary and still be considered permissible for use in coal mines. Thirty samples were collected during the fiscal year. Only one failed to pass gallery test 1, and all the other samples passed both gallery test 1 and 4, although 13 of these samples did not meet the tolerances for their chemical and physical characteristics. Safeguarding the quality of permissible explosives through field sampling has been an important factor in promoting safety in the coal-mining industry in the United States.

### Miniature-Cartridge Test for Detonators

The miniature-cartridge test<sup>31/</sup> was developed as a means of evaluating the relative initiating efficiency or strength of a detonator. This value is measured by the weight of sand crushed when the detonator under test is fired in a miniature cartridge of an insensitive mixture like TNT and iron oxide weighing 5 grams embedded in a weighed quantity of standard Ottawa sand and held in a bomb. From this weight of sand crushed is subtracted another weight of sand which is crushed when the same kind of detonator is fired embedded in a 5-gram charge of pure iron oxide. The value thereby derived represents the initiating efficiency of the detonator in comparison with values obtained from detonators with various weights of mercury fulminate used as the base charges.

Based upon the more recent tests, it is believed that the initiating efficiency of a detonator is improved (1) by substituting for a mixture of mercury fulminate-potassium chlorate (80-20) any one of the following compounds used as base charges (improvement follows in the order enumerated: (a) Tetryl, (b) PETN, (c) Cyclonite; (2) by using a reinforcing capsule for enclosing the priming charge; (3) by use of an aluminum shell instead of a gilding metal shell, and (4) by use of a small-diameter shell.

During the war, a large variety of detonators captured with enemy equipment was examined and tested. The detonators included those of German, Italian, and Japanese make. Most of the German detonators were loaded in aluminum shells charged with a base constituent of tetryl or PETN and had a priming charge of lead azide-lead styphnate enclosed in a reinforcing capsule.

### Technical Assistance and Services to Others

Assistance was given to the War and Navy Departments and other Federal agencies. This included consultations on matters pertaining to demolition explosives and equipment, safety inspections of the testing area of a military reservation, surveillance tests of propellants and explosives, and testing of a sample of red phosphorus for its sensitivity to friction on the Bureau of Mines' pendulum friction device.

### The Electronic Chronoscope

The Bureau of Mines is frequently consulted for recommendations on methods of improving performance and safety of explosives and for advice on explosives technology in general. This often requires short-term miscellaneous investigations. Such miscellaneous projects have included work on performance and safety of explosives using hydrogen peroxide as the oxidizing agent, liquid-oxygen explosives, and tetranitromethane-gasoline

<sup>31/</sup> Grant, R. L., and Tiffany, J. E., Factors Affecting Initiating Efficiency of Detonators: Ind. and Eng. Chem., vol. 37, July 1945, pp. 661-6.

mixtures; work on methods of measuring rates of detonation and evaluation of hazards associated with a number of specific operations in industry. One such investigation led to the development of an electronic chronoscope to determine velocities of detonation of explosives that is capable of measuring time intervals as small as 1 microsecond.<sup>32/</sup> This instrument is small, portable, and direct-reading and can be operated from stations quite remote from the explosive without transmission-line difficulties. It can be operated from the ordinary 110-volt AC circuit or can be adapted to battery operation. It can measure velocities of detonation over lengths as small as 1 centimeter of highly brisant explosives with an accuracy of approximately 5 percent. Figure 15 is a photograph of the instrument.

#### Ignition Temperatures of Compounds in Air and Oxygen

An apparatus consisting of a 50-pound, electrically heated, stainless-steel block, in which was enclosed a 125-cc. Pyrex Erlenmeyer flask as the ignition chamber, was used to determine the ignition temperatures of 21 different compounds that were determined in air and oxygen. This is a modification of the standard nitrate bath apparatus and served to avoid the hazards of flying glass when ignition occurred. The flask within the steel block simulates black-body conditions. The usual drop method was employed. Where the compound is a gas at ordinary temperatures, it was first cooled to the liquid state and the required amount was dropped into the apparatus. Minimum ignition temperatures determined in this modified apparatus and given in table 4 are usually only a few degrees lower than those obtained in the standard nitrate bath apparatus.

TABLE 4. - Ignition temperatures

	Formula	Minimum ignition temperatures, °C.	
		In air	In oxygen
Ethane .....	C <sub>2</sub> H <sub>6</sub>	516	506
Propane .....	C <sub>3</sub> H <sub>8</sub>	493	468
1-3-butadiene .....	C <sub>4</sub> H <sub>6</sub>	418	335
n-butane .....	C <sub>4</sub> H <sub>10</sub>	408	283
iso-butane .....	C <sub>4</sub> H <sub>10</sub>	462	319
n-pentane .....	C <sub>5</sub> H <sub>12</sub>	290	258
iso-pentane .....	C <sub>5</sub> H <sub>12</sub>	420	294
2-3-dimethylbutane .....	C <sub>6</sub> H <sub>14</sub>	420	298
n-heptane .....	C <sub>7</sub> H <sub>16</sub>	230	214
n-octane .....	C <sub>8</sub> H <sub>18</sub>	218	208
2-2-4 trimethyl pentane.	C <sub>8</sub> H <sub>18</sub>	434	283
Dimethyl ether .....	(CH <sub>3</sub> ) <sub>2</sub> O	350	252
iso-phorone .....	C <sub>7</sub> H <sub>14</sub> O	462	322
n-propyl formate .....	C <sub>4</sub> H <sub>8</sub> O <sub>2</sub>	455	312
iso-propyl formate .....	C <sub>4</sub> H <sub>8</sub> O <sub>2</sub>	485	412
n-propyl acetate .....	C <sub>5</sub> H <sub>10</sub> O <sub>2</sub>	457	-
iso-propyl acetate .....	C <sub>5</sub> H <sub>10</sub> O <sub>2</sub>	476	448
1-2-dichloro-n-butane ..	C <sub>4</sub> H <sub>8</sub> Cl <sub>2</sub>	276	250
Monomethylamine .....	CH <sub>3</sub> NH <sub>2</sub>	430	400
Dimethylamine .....	(CH <sub>3</sub> ) <sub>2</sub> NH	402	346
Trimethylamine .....	(CH <sub>3</sub> ) <sub>3</sub> N	190	175

<sup>32/</sup> Nisewanger, C. R., and Brown, F. W., Electronic Chronoscope for Measuring Velocities of Detonation of Explosives: Bureau of Mines Rept. of Investigations 3879, 1946, 18 pp.

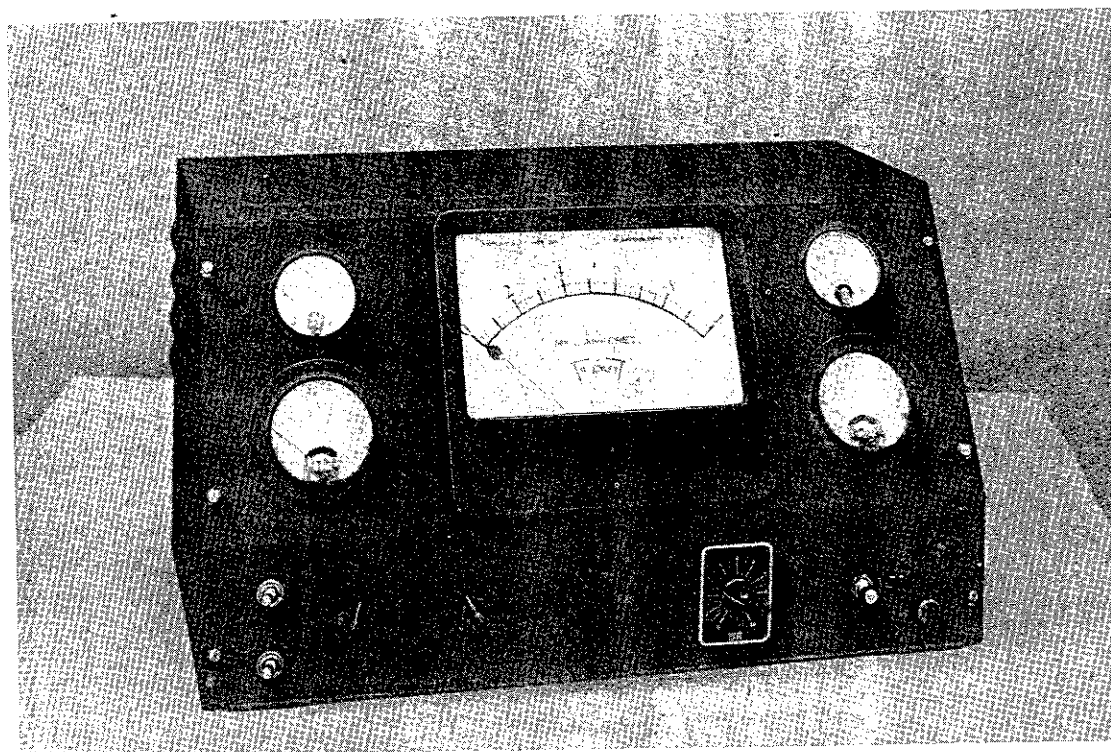


Figure 15. - Electronic chronoscope for measuring velocities of detonation.



Limits of Inflammability of Substances in Air

Determinations of lower and upper limits of inflammability were made of a number of combustible vapors and liquids in air. Table 5 contains a summary of the values.

TABLE 5. - Limits of inflammability in air

Compound	Formula	Limits of inflammability, percent by volume	
		Lower limit	Upper limit
iso-pentane .....	$C_5H_{12}$	1.35	7.60
n-octane .....	$C_8H_{18}$	1.00	-
2-2-4 trimethyl pentane ..	$C_8H_{18}$	.98	5.23
Ethyl benzene .....	$C_8H_{10}$	.98	-
n-butyl formate .....	$C_5H_{10}O_2$	1.73	8.10
Isophorone .....	$C_{11}H_{20}O$	.84	3.80
Monomethyl amine .....	$CH_3NH_2$	4.95	20.75
Dimethylamine .....	$(CH_3)_2NH$	2.80	14.40
Trimethylamine .....	$(CH_3)_3N$	2.00	11.60

Extinction of Gasoline Flames by Inert Gases

Gasoline is one of the chief contributors to the causes of fires and explosions, which take an enormous yearly toll in property damage and cause considerable loss of life. Its widespread use makes it important to discover ways of eliminating or at least mitigating the explosion hazards of this substance. Accordingly, a study was made of the effects of various inert gases having different chemical compositions on the extinction of gasoline flames, the results of which should find considerable application.<sup>33/</sup> The substances investigated were nitrogen, carbon dioxide, automobile exhaust gas (85 percent  $N_2$  + 15 percent  $CO_2$ ), dichlorodifluoromethane ( $CCl_2F_2$ ), known as Freon-12, trichloromonofluoromethane ( $CCl_3F$ ), known as Freon-11, and dichloromonofluoromethane ( $CHCl_2F$ ), known as Freon-21.

Gasolines may have rather wide variations in chemical and physical properties. They may also contain small amounts of other substances to enhance their anti-knock properties, engine-operating characteristics, and to increase their stability during storage, transportation, and use. The results given in the report show, however, that the inflammable properties of different gasolines at normal atmospheric temperatures are influenced largely by the more volatile hydrocarbons containing 5, 6, and 7 carbon atoms in the molecule, and that the heavier constituents of higher molecular weight have a minor influence under these conditions.

<sup>33/</sup> Jones, G. W., and Gilliland, W. R., Extinction of Gasoline Flames by Inert Gases: Bureau of Mines Rept. of Investigations 3871, 1946, 14 pp.

Three types of gasolines were investigated having octane ratings of 75, 92, and 100 and specific gravities at 60/60°F. and vapor pressures, in mm. Hg at 25°C., of 0.7136, 0.7061, and 0.7161, and 200 mm., 182 mm., and 168 mm., respectively. The limits of inflammability of the gasolines in air, in percent by volume of gasoline vapor, were determined to be 1.50, 1.50, and 1.40 for the lower limit and 7.60, 7.60, and 7.40 for the upper limits in an open tube ignited by a flame. Slightly smaller values were found for both limits in a closed tube ignited by a spark. These results show that both limits of inflammability for the three different gasolines are almost identical, using a particular method. The average lower limit of inflammability of gasoline may be taken as 1.40 percent by volume in dry air and the average upper limit at 7.40 percent.

Results of tests with all possible mixtures of gasoline-air-nitrogen in a closed tube and with ignition by a high-voltage spark indicate that the addition of nitrogen had no appreciable effect upon the lower limit of gasoline vapor until 20 or more percent of nitrogen is added, whereas the upper limit was reduced in direct proportion to the amount of nitrogen added. At least 42.4 percent of nitrogen must be present to render all mixtures with air noninflammable.

Similar tests with gasoline-air-carbon dioxide mixtures showed generally the same results, except that the extinctive effects of carbon dioxide were found to be greater than equivalent amounts of nitrogen, as is to be anticipated qualitatively from the greater heat capacity of carbon dioxide. Only 28.9 percent of carbon dioxide is required to render all gasoline-air mixtures noninflammable.

A cheap and convenient supply of inert gas may be obtained for flame-quenching purposes by utilizing the exhaust gases from internal-combustion engines, provided the fuel-air ratio is adjusted to produce an exhaust gas containing maximum percentages of carbon dioxide and a minimum of carbon monoxide and residual oxygen. Under certain conditions, an exhaust gas containing 85 percent nitrogen and 15 percent carbon dioxide can be made, and this was used. As expected, tests with gasoline-air-exhaust gas yielded results that lie between those of nitrogen and carbon dioxide. Thirty-six percent of exhaust gas was required to be added to render all mixtures noninflammable.

Tests with the three Freons show that their flame-quenching efficiencies are much greater than other inert gases like nitrogen and carbon dioxide. Both the lower and upper inflammable limits are affected materially by additions of small percentages of these substances, causing a marked decrease in the range of inflammability. The extinction effect increases in the order  $\text{CHCl}_2\text{F}$ ,  $\text{CCl}_2\text{F}_2$ ,  $\text{CCl}_3\text{F}$ . The amounts of these substances that will render all mixtures of gasoline-air-freon noninflammable are 15.6 percent, 12.4 percent, and 11.1 percent, respectively.

It is of interest to note that all hydrocarbon-air mixtures from methane through hexane and gasoline will be free of explosion hazards at

normal temperature and pressure if the atmosphere contains 44 percent or more of nitrogen or 31.5 percent or more of carbon dioxide.

It is sometimes more convenient to control the explosion hazards of the mixtures by means of the oxygen concentration. This is accomplished by diluting with inert gas until the oxygen concentration falls to some critical value (which varies with the inert gas added), below which the mixtures become noninflammable. These critical oxygen concentrations for the inert gases nitrogen, carbon dioxide,  $\text{CHCl}_3$ ,  $\text{CCl}_2\text{F}_2$ , and  $\text{CCl}_3\text{F}$  are 11.6, 14.4, 17.2, 17.6, and 17.9 percent, respectively. A comparison of the critical oxygen values for different hydrocarbons from methane to hexane and gasoline reveals that they do not differ very much for a given inert gas. Thus, when nitrogen is used, the oxygen values range from 11.0 to 12.1 percent, and if the oxygen is kept below 11.0 percent all of the indicated hydrocarbons are noninflammable in any concentration. More oxygen can be tolerated if judicious corresponding changes are made in the gasoline concentrations which the results of the investigation allow to predict.

The use of inert gases to dilute explosive atmospheres and thereby dilute the air or oxygen concentration to a point where the mixtures become noninflammable has found numerous applications in recent years. Information of the type just given has proved of great benefit to industry. By applying these data, combustible mixtures containing gasoline can be removed safely from containers and equipment, or the mixtures may be introduced into such vessels originally containing air without running the risk of explosion, provided the proper concentrations of inert gases are present.

#### Limits of Inflammability and Ignition Temperature of Naphthalene

Information concerning the German chemical industry and in particular the utilization of naphthalene has brought this substance to the fore as a chemical of commercial importance. Its potential fire and explosion hazards have therefore been studied.<sup>34/</sup> The immersion method for determining the limits of inflammability of vapors was employed.<sup>35/</sup> The limits determined are temperatures between which air saturated with naphthalene vapor is explosive when the barometric pressure is 747 mm. mercury. The lower limit was found to be 77.8°C. and the upper limit 121.8°C. Converted to concentration limits, from the vapor pressures of naphthalene at these temperatures, the lower limit becomes 0.88 percent by volume of naphthalene vapor in air and the upper limit becomes 5.9 percent of naphthalene vapor in air. The ignition temperature of naphthalene was determined by dropping a small crystal of naphthalene onto the bottom of a flask immersed in a nitrate bath. In air, the ignition temperature was found to be 587°C.; in oxygen it was 560°C.

<sup>34/</sup> Jones, G. W., and Scott, G. S., Limits of Inflammability and Ignition Temperatures of Naphthalene: Bureau of Mines Rept. of Investigations 3881, 1946, 5 pp.

<sup>35/</sup> Jones, G. W., Inflammation Limits and Their Practical Application in Hazardous Industrial Operations: Chem. Rev., vol. 22, No. 1, Feb. 1938, pp. 1-26.