

THE EXPLOSIVE FLAMMABILITY OF LIQUID GRAIN FUMIGANTS

by

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## TABLE OF CONTENTS

INTRODUCTION AND REVIEW OF LITERATURE. . . . .	.1
MATERIALS AND METHODS. . . . .	.3
Chemicals. . . . .	3
Chemicals Used. . . . .	.3
Formulation. . . . .	.4
Laboratory. . . . .	.4
Location. . . . .	4
Floor Plan. . . . .	4
Control Section. . . . .	.4
Fume Hoods. . . . .	9
Constant Temperature Cabinet. . . . .	9
Electrical Apparatus. . . . .	14
General. . . . .	14
Explosion Vessel. . . . .	14
High Voltage. . . . .	.21
Control Panel. . . . .	24
Capacitor Panel. . . . .	29
Flask Aeration System. . . . .	.29
PROCEDURE. . . . .	.36
General Test Procedure. . . . .	36
Detailed Test Procedure. . . . .	40
Section 1, Low Voltage. . . . .	.40
Section 2, High Voltage direct current test sequence. . . . .	.40
Section 3, Steps to evacuate and purge explosion vessel. . . . .	41

Section 4, High voltage alternating current test sequence. . . . .	.42
Section 5, Steps to set direct current breakdown voltage. . . . .	43
Section 6, Procedure to ground capacitors. . . . .	43
Section 7, Hood, operation sequence before test. . . . .	.43
Section 8, Hood, operation sequence during test. . . . .	44
Section 9, Hood, operation sequence after test. . . . .	44
Section 10, Steps to set direct current breakdown voltage. . . . .	45
DISCUSSION AND RESULTS. . . . .	45
The Effect Of Altering The Electrical Parameters. . . . .	46
AC Versus DC Sparks. . . . .	46
Voltage, Capacitance, And Spark Gap. . . . .	46
The Effect of Environment, Technique and Procedure. . . . .	50
Laboratory Temperature. . . . .	50
Sample Temperature. . . . .	50
Bath Temperature. . . . .	50
Sample Size. . . . .	50
Stirring Time. . . . .	53
Method of Sample Introduction. . . . .	54
SUMMARY AND CONCLUSIONS. . . . .	57
ACKNOWLEDGMENTS. . . . .	61
LITERATURE CITED. . . . .	62
APPENDIX. . . . .	63

## INTRODUCTION AND REVIEW OF THE LITERATURE

Carbon disulfide ( $\text{CS}_2$ ) is one of the oldest grain fumigants. A serious limitation to its use is its extreme flammability. This property becomes increasingly important when it is realized that  $\text{CS}_2$  vapors are explosive over a very wide range. A concentration of  $\text{CS}_2$  in air varying from one to fifty percent will explode when subjected to a source of ignition. (Underwriters Laboratories' Inc., 1943). This fact renders  $\text{CS}_2$  very hazardous as a grain fumigant. In an early paper, Neifert et al, 1925, mentioned that a mixture of 75 percent carbontetrachloride ( $\text{CCl}_4$ ) and 25 percent  $\text{CS}_2$  (by volume) is highly flammable. At present, a formulation containing 80 percent  $\text{CCl}_4$  and 20 percent  $\text{CS}_2$  (by volume) with a fractional percentage of an additive to increase its flash point, is found to be relatively safe.

Some appraisal of the relative hazard of various grain fumigants was desired. The Underwriters Laboratories Inc. modified their procedures used to classify hazards of flammable liquids in order to enable them to classify grain fumigants. This procedure is given in Appendix I.

The explosive flammability<sup>1</sup> of the fumigant is tested as a part of the overall test procedure. In the opinion of the personnel at Kansas State University, a detailed study of this

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1. Explosive flammability is defined as flame propagation with pressure effects when a fumigant vapor is ignited.

test would afford a practical approach to a study of the flammability of liquid grain fumigants. Therefore, a research program was developed which would permit an investigation of this phase of the testing procedures.

An extensive study of the explosion test procedure used by the Underwriters Laboratories' Inc. revealed a list of possible factors which could effect the results of this test. A list of these factors which are studied in this paper are given below.

- I. Characteristics of the explosion apparatus.
  - A. Type of apparatus used, AC versus DC.
  - B. The voltage of the spark.
  - C. The capacitance of the circuit.
  - D. The width of the spark gap.
- II. Environment, Technique and Procedure.
  - A. Laboratory temperature.
  - B. Sample temperature
  - C. Bath temperature
  - D. Sample size
  - E. Stirring time
  - F. Method of Sample introduction

After compiling this list, a research program and experimental apparatus was developed which would permit investigations of the effect of each of these factors upon the explosive flammability of grain fumigants.

The apparatus currently being used to test the explosive flammability of grain fumigants lacked the flexibility and

controls which were necessary to conduct this investigation. Because of this fact, it was necessary to design an apparatus which could permit control of most of these factors so that each one could be studied separately. The apparatus was constructed in such a way as to afford the operator maximum safety along with the necessary controls.

This paper demonstrates how this apparatus and test procedure can be used to control and study the factors which effect the explosive flammability of liquid grain fumigants.

A search of the literature revealed no published work in the field of the explosive flammability of grain fumigants.

## MATERIALS AND METHODS

### Chemicals

#### Chemicals Used.

1. Chloroform ( $\text{CHCl}_3$ ).
2. Carbon Tetrachloride ( $\text{CCl}_4$ ).
3. Carbon Disulfide ( $\text{CS}_2$ ).

Formulation. All of the fumigants used in these experiments were formulated in our laboratory. Five hundred <sup>ml</sup> samples were prepared in a graduated cylinder and transferred to one quart, brown glass bottles fitted with screw caps. Bakelite caps with cork and tin metal foil liners were used to seal the bottles. This size sample gave sufficient uniformity of results and was easily formulated and stored. This volume was adequate to provide enough fumigant for ten tests. This minimized the alteration of the formulation due to evaporation since the

bottle was opened only ten times. In most instances, the samples were tested the same day they were formulated. If it was necessary to store samples for future tests, they were stored under refrigeration at about fifty degrees Fahrenheit.

### Laboratory

Location. A special laboratory was constructed for this project in order to afford both the operator and bystanders a maximum degree of safety. It was constructed in a trailer house, eight feet wide and twenty seven feet long, located on the grounds of the college apiary where few people would be exposed to the potential hazards of these tests. There were three potential hazards in conducting these experiments. First, the fumigants which were being tested or formulated were toxic to man, both acutely and chronically. Second, the high voltage used as a source of ignition was very dangerous.<sup>1</sup> Third, when a material like chloroform or carbon tetrachloride was burned, one of the products formed was phosgene gas.

Floor Plan. A floor plan of the trailer showing the location of the fume hoods, control section, and other facilities is given in Plate I.

Control Section. A picture of the control section is given in Plate II. This section enclosed all the electrical

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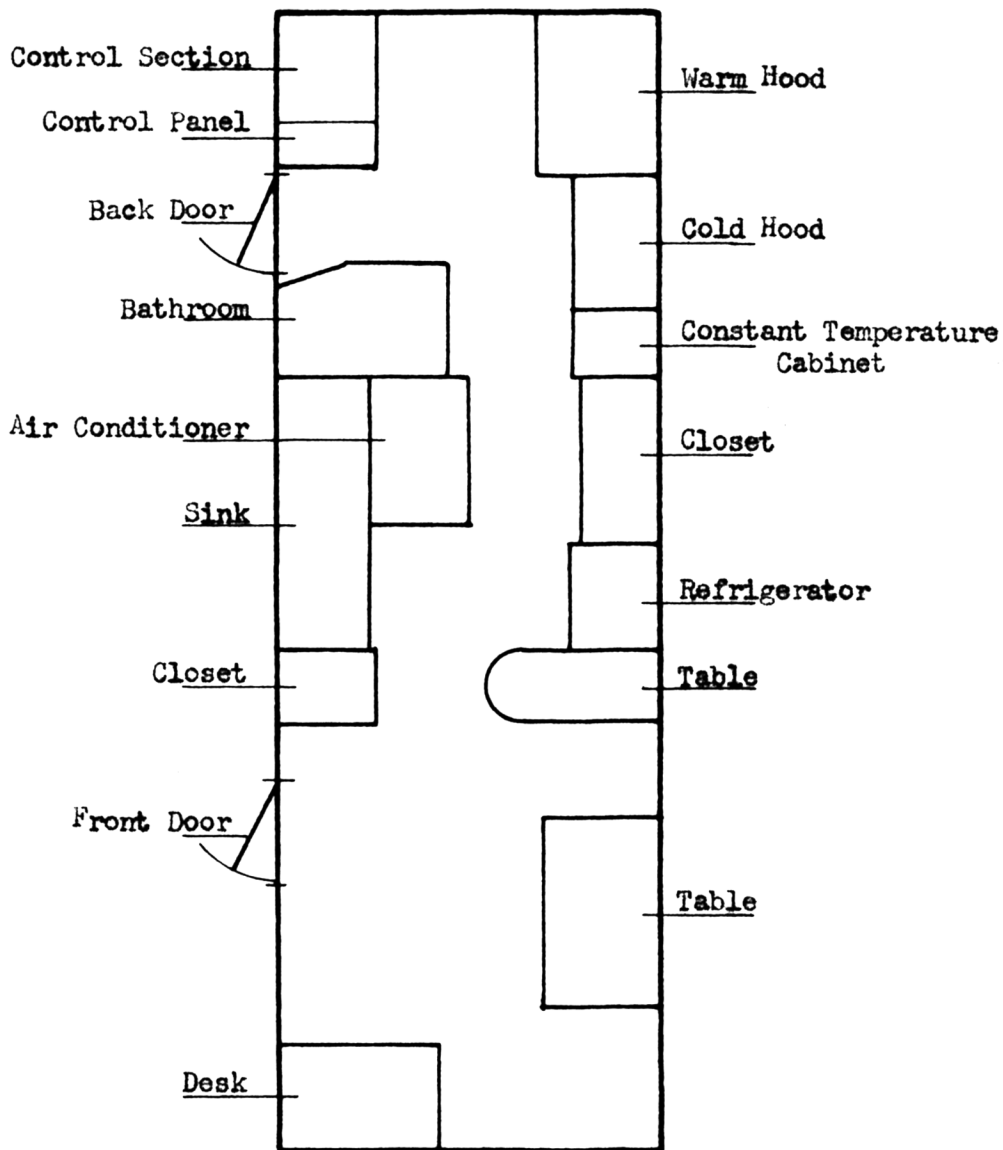
1. In a communication from General Electric it was pointed out that with the DC circuit used, the amperage at the electrode gap at the time of discharge could reach 1,000 amperes.

EXPLANATION OF PLATE I

Floor plan of trailer laboratory.



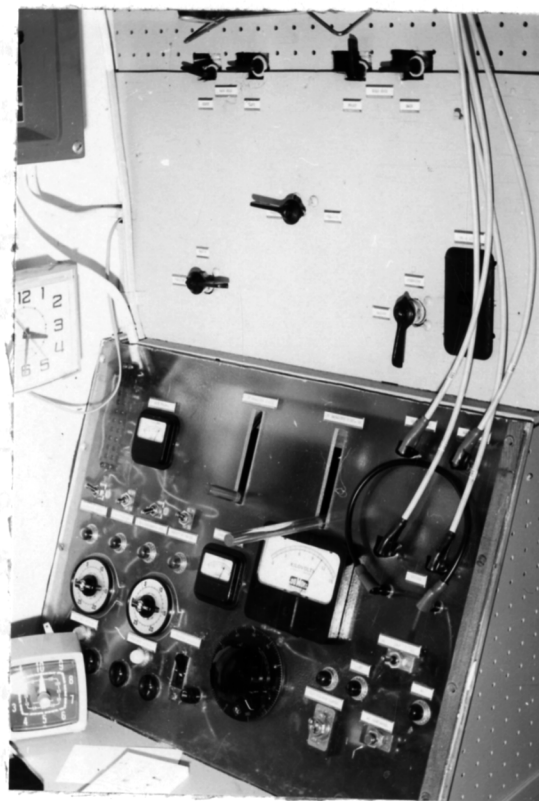
PLATE I



EXPLANATION OF PLATE II

Complete control panel showing electrical panel  
below and aeration control valves above

PLATE II



equipment and aeration system equipment. The electrical system was housed in the lower section of the panel and underneath the table. The aeration system was installed in the two sections above the electrical system.

Fume Hoods. Two fume hoods were constructed. One of these enclosed a refrigerated water bath which was used in the low temperature tests. The other was set up to conduct room temperature tests and to provide an area to prepare formulations. Each hood was fitted with a lattice work of rods to which the explosion vessels and stirring motors could be fastened. The hoods were lighted with fluorescent lights which were controllable from the instrument panel. The hoods were painted flat black to enable the observer to see the spark and flame in the flask more clearly. A kitchen exhaust with a 600 CFM capacity was used in the warm hood. The hoods were separated by a sliding panel which allowed the fans to evacuate both hoods. The hood doors were covered with clear plastic enabling the operator to observe the explosion vessel and afforded protection from possible flying glass. These hoods are pictured in Plate III and IV.

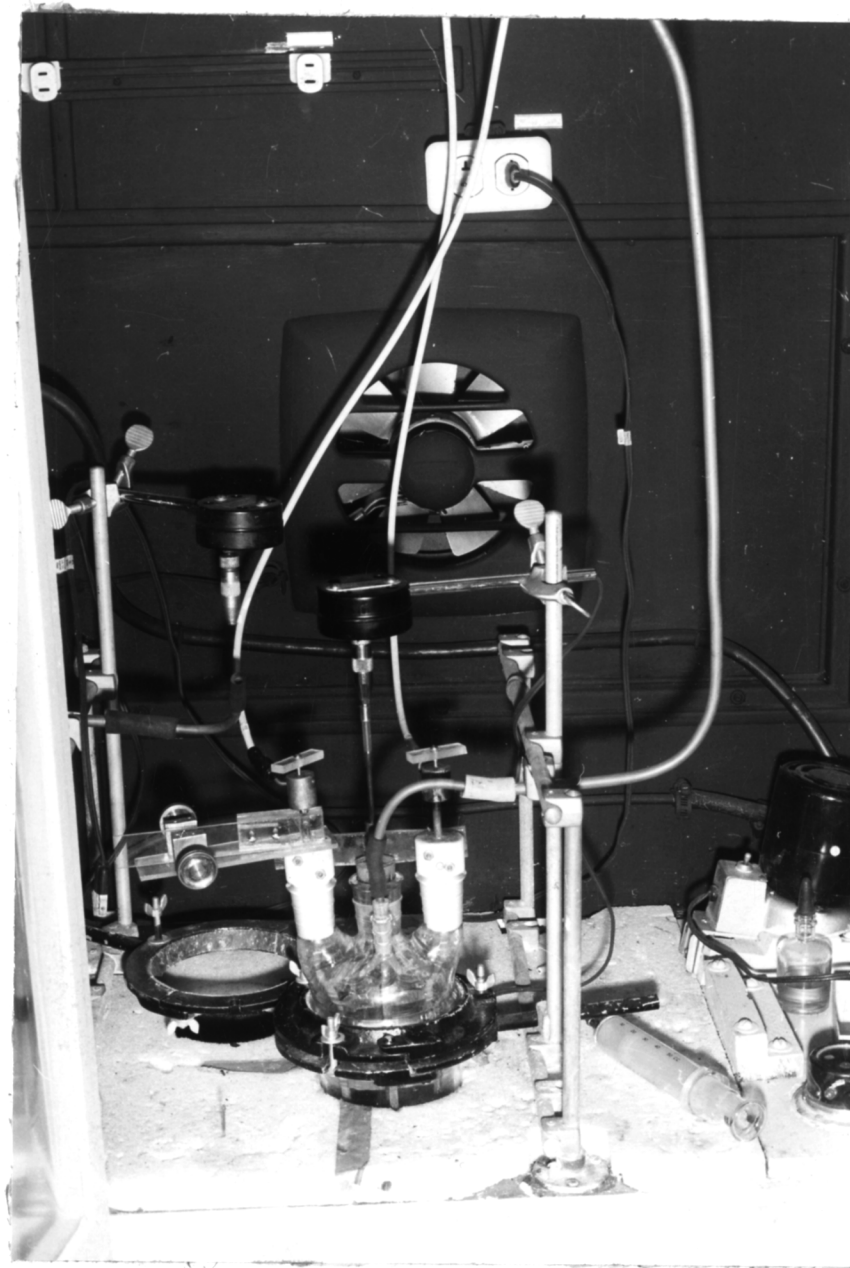
Constant Temperature Cabinet. The standard test procedure which was developed called for all fumigant samples to be at a temperature of 75 degrees Fahrenheit. To facilitate this procedure, a constant temperature cabinet was constructed from a closet in the trailer. The temperature was regulated by circulating water at 75 degrees Fahrenheit through a coil of 3/8

**EXPLANATION OF PLATE III**

The cold hood showing the arrangement of  
the explosion vessel with all attachments.

The top of the bath is insulated with one  
inch styrefoam.

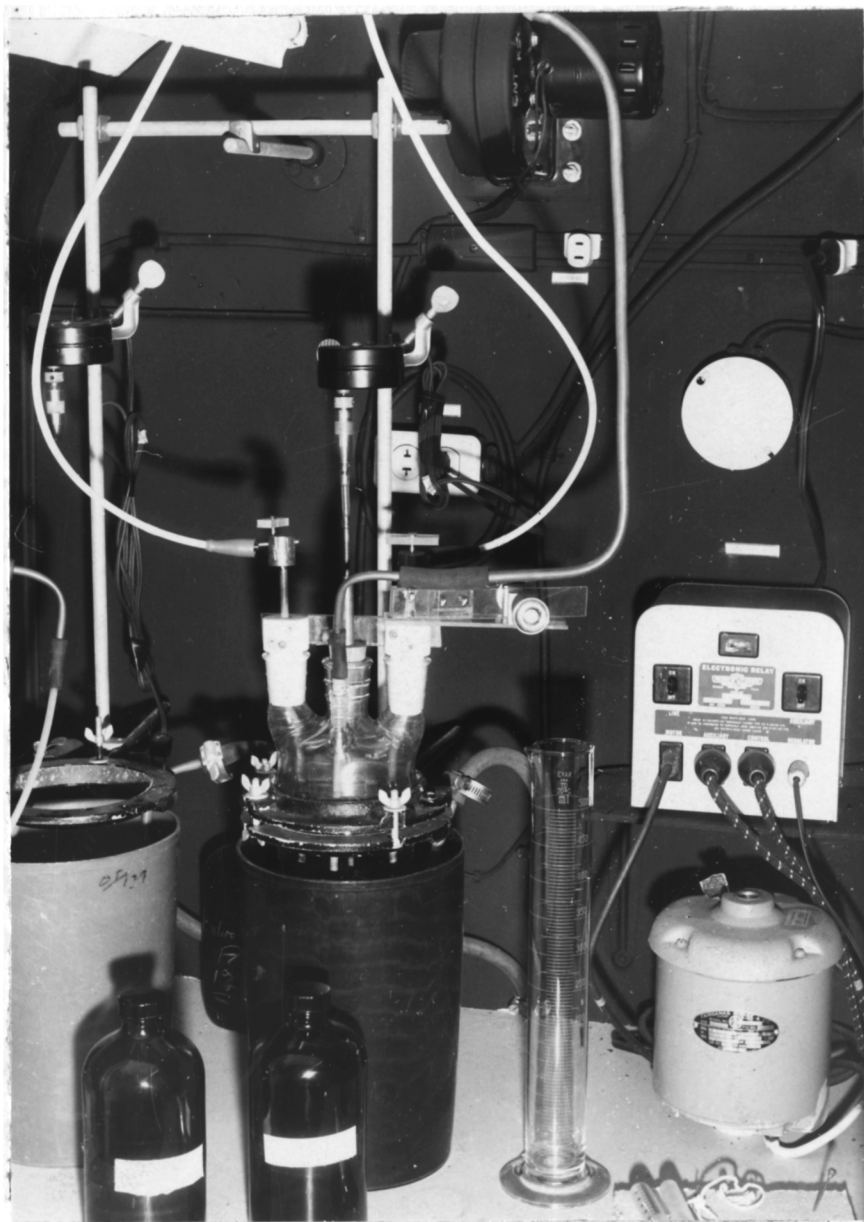
PLATE III



**EXPLANATION OF PLATE IV**

The warm hood showing the arrangement of the explosion vessel with all attachments. The motor and relay box on the right are part of the system used to regulate the temperature of the explosion vessel and the constant temperature cabinet.

PLATE IV





inch copper tubing which lined the walls of the closet. A thermostatically controlled water reservoir equipped with a circulating pump provided the source of 75 degree water. This same tank also served the water bath of the room temperature hood by circulating water through a coil immersed in the bath.

### Electrical Apparatus

General. The explosion apparatus consisted of the following: 1. An explosion vessel which was fitted with a pair of adjustable electrodes, a stirring assembly, and an aeration tube. 2. A source of ignition from a high voltage AC or DC spark. 3. A control panel.

Explosion Vessel. The explosion vessel was a two piece, two liter Pyrex reaction vessel. The bottom section was cylindrical. The top section was provided with four joints, three 29/42 and one 10/30. The electrodes were fitted through the 29/42 joints, on the sides of this top section. The stirring assembly was fitted through the 29/42 joint in the center. The flask aeration tube was fitted through the 10/30 joint on the side of the flask. A picture of the assembled flask and top assembly is shown in Plate V.

The center well was fitted with a cork stopper. This cork served two purposes. It supported the stirring shaft and acted as a pressure release and indicator during an explosion. The stirring shaft was a 3/16th inch steel rod approximately 18 inches long. A polyethylene paddle 1 1/2 x 2 1/2 inches was attached to the rod. The edges of the paddle were bent to form

EXPLANATION OF PLATE V

Fig. 1. The completely assembled explosion vessel.

Fig. 2. Top of explosion vessel showing electrodes  
and adjusting mechanism, aeration tube,  
and stirring assembly

## PLATE V

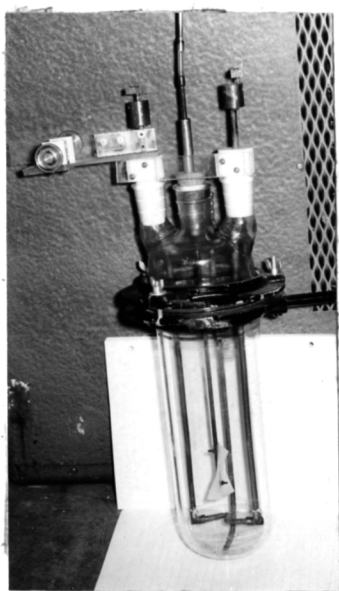


Fig. 1

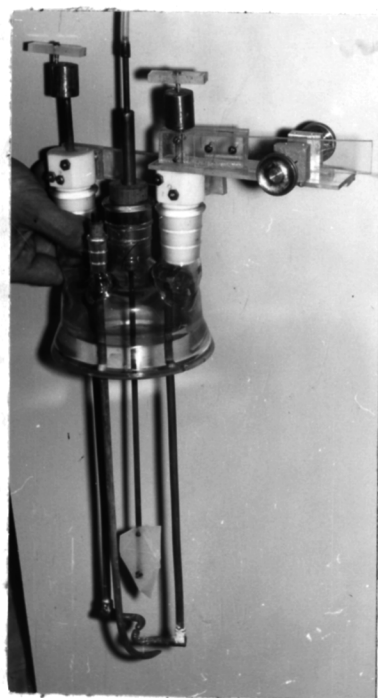


Fig. 2

a propeller like device, thus affording rapid distribution of the air in the closed flask. The stirring shaft ran through a 5 inch brass bushing which was inserted through the cork. This relatively long bushing prevented excessive wobbling of the long stirring shaft, and therefore allowed the use of a small, 1/1000th horsepower electric motor to power it. This bushing also made it easy to align the stirring shaft between the electrodes.

The electrodes were made from 1/4th inch copper rod and were inserted through teflon plugs which were machined to fit the side joints. The ends of the electrodes were about two inches above the bottom of the flask. Teflon stoppers were used because of their chemical inertness and machinability.

Modified brass T's were fitted to the bottoms of the electrodes. The shank of the T was soldered to the electrode, and the top of the T was threaded to permit short electrode tips to be screwed into position. One arm of the T was cut off to prevent the electrodes from touching the flask. This feature aided in the alignment of the electrode tips and permitted interchanging or replacement of the tips.

The electrode tips were designed to keep their rounded faces always opposite each other even when the moveable electrode was rotated to provide a quarter inch gap. This feature is illustrated in figure 1 of Plate VI.

One of the electrodes was securely fastened to the teflon stopper. The other was allowed to rotate within its supporting stopper permitting adjustment of the electrode gap. The device

## EXPLANATION OF PLATE VI

- Fig. 1. Close up of the tips of the electrode assembly. Shown in the figure are the specially curved electrode tips, the end of the aeration tube, and the stirring paddle.
- Fig. 2. A top view of the explosion vessel and electrode adjusting mechanism.
- Fig. 3. A front view close up of the electrode adjusting mechanism.

PLATE VI

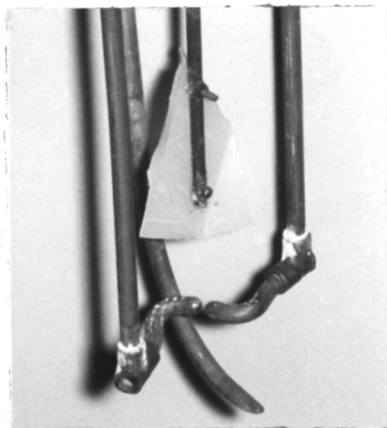


Fig. 1

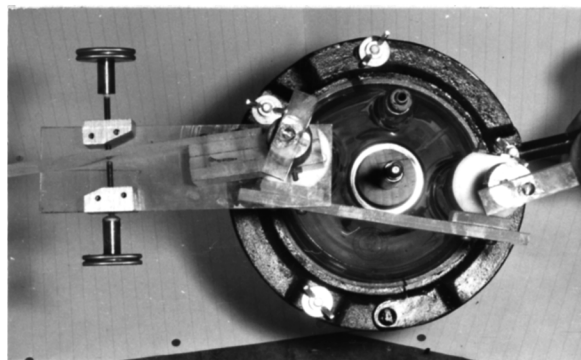


Fig. 2

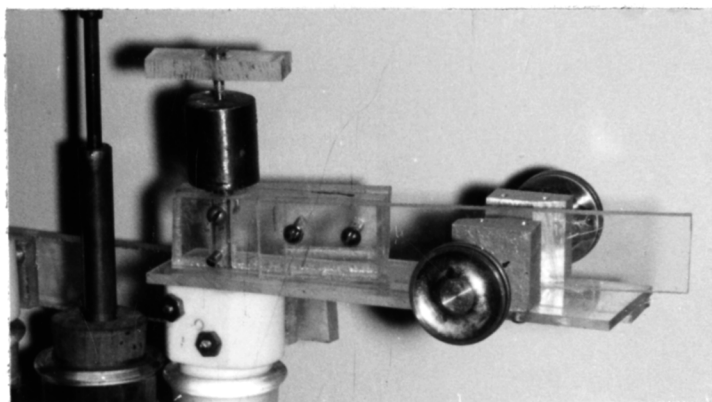


Fig. 3

used to rotate this electrode through a short arc is shown in figures 2 and 3 of plate VI. It consisted of a plexiglass lever attached to the electrode rod by small bolts. The position of this lever could be controlled by two opposed adjusting screws. Because of the excellent insulating properties of plexiglass this mechanism allowed the electrode gap to be adjusted while the electrodes were connected to a high voltage source. This permitted an accurate setting of the spark gap based on breakdown voltage.

The top of each electrode was fitted with a block of copper, drilled to permit insertion of the electrode lead, which was secured by a set screw.

A 1/4 inch copper tube was fitted through a small cork stopper in the 10/30 joint. The end section of this tube was curved to follow the contour of the flask with the end of the tube beveled so that it would fit nearly flush against the bottom of the flask. This tube was connected to the pressure vacuum system, which will be presented in detail later.

The resistance of this apparatus to explosive forces was inadvertently demonstrated in the following manner. A 50 ml sample of  $CS_2$  instead of a less explosive mixture was accidentally introduced into the test flask. After 30 seconds stirring the sample was sparked. The vapors detonated with excessive pressures, extremely sharp noise, and an unusually large volume of combustion products. These extreme forces did not rupture or even crack the explosion vessel.

High Voltage. The apparatus was designed to permit either AC or DC high voltage sparks to be used as the source of ignition. The circuits used to generate these sparks are diagrammed in plate VII along with the specifications of the equipment used. The AC circuit was identical to the one used by the UL. The DC circuit was similar to the one used by Swett (1949) and Laffitte (1953).

The AC circuit consisted of a transformer rated 115 volt AC for the primary and 23 m. amp. 10,000 volts for the secondary. A .01 microfarad (MFD) capacitor was placed in parallel circuit across the secondary, causing an intermittent discharge. A variable transformer (powerstat) was placed in the primary of the high voltage transformer to regulate the input voltage.

The input voltage was indicated on a volt meter. The secondary of the high voltage transformer was attached to the electrodes of the explosion vessel. A push button switch was placed in the circuit before the variable transformer which, when depressed momentarily, would cause a spark-like discharge at the electrode gap.

The spark producing system of the DC apparatus consisted of a condenser that could be charged and discharged across the spark gap in the explosion vessel. A transformer with a primary of 115 volts AC and a secondary of about 12,500 volts was the source of high voltage. The secondary of this transformer was rectified and switched into a capacitor panel where various capacitance could be inserted in parallel in the line. The

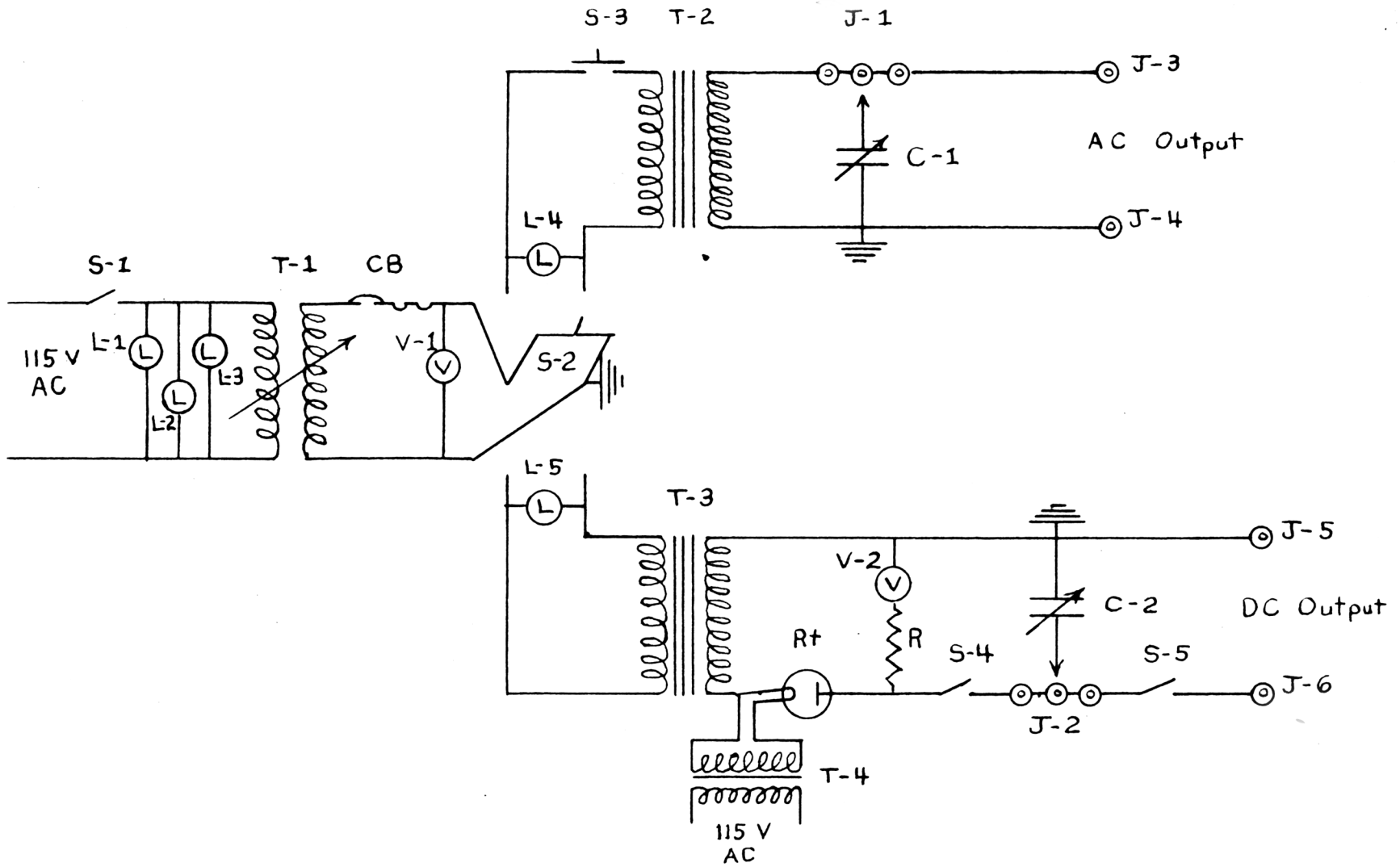


## EXPLANATION OF PLATE VII

Schematic diagram of the high voltage circuit.

- L-1,4,5 Pilot lights; L-2,3 Warning lights on hoods.
- S-1 High master, dpst.
- S-2 Selector switch, dpdt center off.
- S-3 AC discharge, spst push button.
- S-4 DC capacitor charge, modified spst knife switch.
- S-5 DC capacitor discharge, modified spst knife switch.
- T-1 Power-stat variable transformer, 0-140v, 3A.
- T-2 High voltage, 115 to 10,000 V, 23 ma. Jefferson Electric.
- T-3 High voltage, 115 to 15,000 V, 30 ma. Jefferson Electric.
- T-4 Filament transformer, DC operating 12 KV, Peak 35 KV, Prim. 5v, 10A.
- V-1 Powerstat output, 0-150V AC.
- V-2 15 KV DC with external resistance, 1,000 ohms/volt, 1 ma. Roller-Smith.
- R Voltage multiplier, 15 megaohms.
- CB Circuit breaker, 3A. Heinemann #AM 12M 63-3-10, Through Herbach and Rademan.
- Rt Rectifier, Kentron tube, 371B, VT 166.
- C-1 Plug in capacitors, .01 Mfd and less. Chicago Condenser Corp. and Aerovox Corp.
- C-2 Plug in capacitors, .1, .1, and .2 Mfd. Gugeman, and Aerovox Corp. Through Herbach and Rademan.
- J-1 & J-2 Three tip jacks, for tip plugs on capacitor hot leads.
- J-3 AC high voltage outlet, tip jack for tip plugs on electrode leads.
- J-4 & J-5 High voltage ground tip jack for electrode leads.
- J-6 DC high voltage outlet, tip jack for top plugs of electrode leads.

PLATE VII



charge on the capacitor was read on a voltmeter. This meter was supplied with sufficient external resistance to permit direct readings in thousands of volts. Two specially insulated knife switches were used in the circuit. One was used between the capacitor and the voltmeter in order to prevent the charged capacitor from discharging to ground through the meter. The other switch was placed between the capacitor and the electrode lead which connected to the explosion vessel. This switch, when closed, released the charge of the capacitor across the electrode gap in the explosion vessel.

Control Panel. All of the controls necessary to operate and regulate these high voltage circuits plus the controls of various accessory devices were located on a 1/4 inch plexiglass sheet. A photograph of this control panel and a sketch identifying the controls appears in Plate VIII. The panel controls fall into two categories. The first includes all the controls used to produce and control the high voltage spark. The second includes all the accessory controls necessary to conduct a test. Each section will be discussed separately by describing its parts and their functions. Each section of the panel was served by a separate line in order to divide the load and stabilize the voltage.

The high voltage controls will be presented first. The line circuit fed into a master switch which controlled all the items on that section. This switch also controlled three pilot lights. One was on the panel and the other two were placed over each hood in order to warn the operator that the

## EXPLANATION OF PLATE VIII

Fig. 1. Electrical control panel.

Fig. 2. Sketch of control panel identifying its components.

S-1	Auxillary master	V-1	Line voltage
S-2	Hood blowers	V-2	Powerstat output
S-3	Pressure-vacuum pump	V-3	DC Kilovolts
S-4	Rectifier heater	O	115 v, AC outlets, controlled by time switch
S-5	Timer, Switch, stirrer	T	Powerstat
S-6	Timer, Switch, stirrer	L	Pilot lights
S-7	High voltage master	J-1	DC secondary output
S-8	AC DC selector	J-2	AC secondary output
S-9	AC discharge	J-3	Flask electrode, ground
S-10	DC capacitor charge	J-4	Ground to clear cap
S-11	DC capacitor discharge	L-1	Leads to explosion vessel
CB	Powerstat breaker	L-2	Lead to ground capacitors



circuit was on and could be dangerous. The circuit went from this switch to a powerstat which controlled the input voltage to the high voltage transformers, and thus controlled their output voltage. The powerstat was protected by a three ampere circuit breaker placed on its output side. The output of the powerstat lead to a double pole double throw center off switch which served as a selector switch. One position of the switch activated the AC circuit, the other the DC circuit. Each of the on positions controlled a pilot light which identified the high voltage circuit being used.

The leads from the AC side of this switch are attached to a push button switch before being attached to the primary of the AC high voltage transformer. When this switch was pushed momentarily the high voltage transformer became activated causing a spark to pass across the electrode gap. The secondary of the high voltage transformer was connected to the capacitor panel. The function of this panel will be discussed later. The hot lead from the capacitor panel was connected to a specially insulated jack on the control panel. If AC was to be used in a test, the lead which was attached to the explosion vessel in either the room temperature hood or the cold hood, was plugged into this jack.

The leads from the DC side of the selector switch were attached directly to the primary terminals of the DC high voltage transformer. The output of this transformer was then rectified. The switch which controlled the filament transformer for the rectified. The switch which controlled the filament transformer

for the rectifier tube was located in the controls on the low voltage side of the control panel. A voltmeter was attached at this point to indicate the output of the transformer and the charge on the capacitor. Two knife switches were controlled on the panel. One appeared between the capacitor panel and the voltmeter. When this switch was closed the capacitor in the circuit could be charged, and when it was opened the charge on the capacitors would not ground out through the voltmeter. The second knife switch was on the output side, of the DC section of the capacitor panel. This knife switch when closed released the capacitor charge across the electrode gap. The knife switches were mounted behind the control panel and were controlled by a half inch polystyrene rod which were bolted to the knife blade and protrudes through a slit in the control panel.

The hot lead from this second switch was attached to a jack identical to that used in the AC side.

The accessory controls consisted of a series of six switches and a voltmeter. Each switch was equipped with a pilot light. The first was on the incoming line circuit which fed all the accessory controls. A voltmeter was placed just beyond this switch to permit a continual check of the line voltage. The second switch controlled the hood blowers. The third switch controlled the pressure-vacuum pump which aerated the explosion vessel. The fourth switch supplied the filament transformer for the rectifier tube in the DC circuit. The fifth and sixth are switching timers used to control the electric stirring motors of the explosion vessel.

Capacitor Panel. The capacitor panel consisted of a series of six different capacitors which could attach in parallel across either the AC or DC circuits. The capacitors used were: 0.2-MFd, 0.1 MFd, 0.1 MFd, 0.01 MFd, 0.01 MFd, and a variable capacitor consisting of a board on which various small capacitors could be added. Plate IX shows the capacitors and the board where they were plugged into the circuits. To the hot terminal of each capacitor, a lead was attached. A plug was attached to the other end of this lead. When this plug was inserted in the proper jack in either the AC or DC circuit, this capacitor was in parallel in the line. Three plugs were provided in each circuit. The 0.1 and 0.2 MFd capacitors were used in the DC circuit and the one hundredth and smaller were used in the AC circuit.

#### Flask Aeration System

The type of explosion vessel used made it necessary to devise a method of removing the unevaporated liquid from the vessel after a test and to purge the flask with dry air before the next test. A system of three three-way valves used in conjunction with a pressure-vacuum pump, a liquid trap, a scrubber, a dryer, and manifold was designed to permit the use of the single tube in the explosion vessel for both vacuum and pressure. The section of the control panel which contained these controls is shown in Plate II. A line diagram of the air system, and pictures of the trap, scrubber and are given in Plate X and XI respectively. The pump was a



## EXPLANATION OF PLATE IX

- Fig. 1. Capacitor panel partially removed from apparatus. The plastic plate in center contains jacks and plugs used to place capacitance in the circuits. The plate containing the two terminal strips is the capacitor board to which small capacitors can be attached.
- Fig. 2. Capacitor panel, top view, showing large, oil filled, high voltage capacitors.

PLATE IX

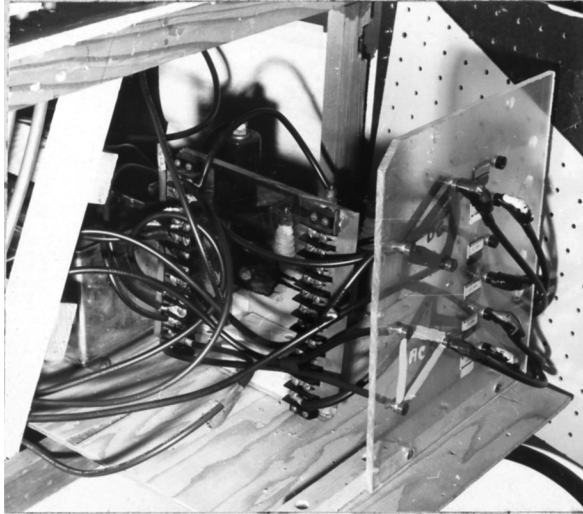


Fig. 1

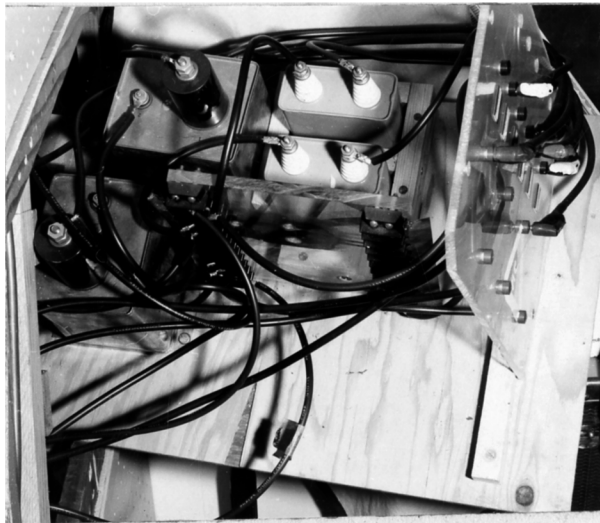
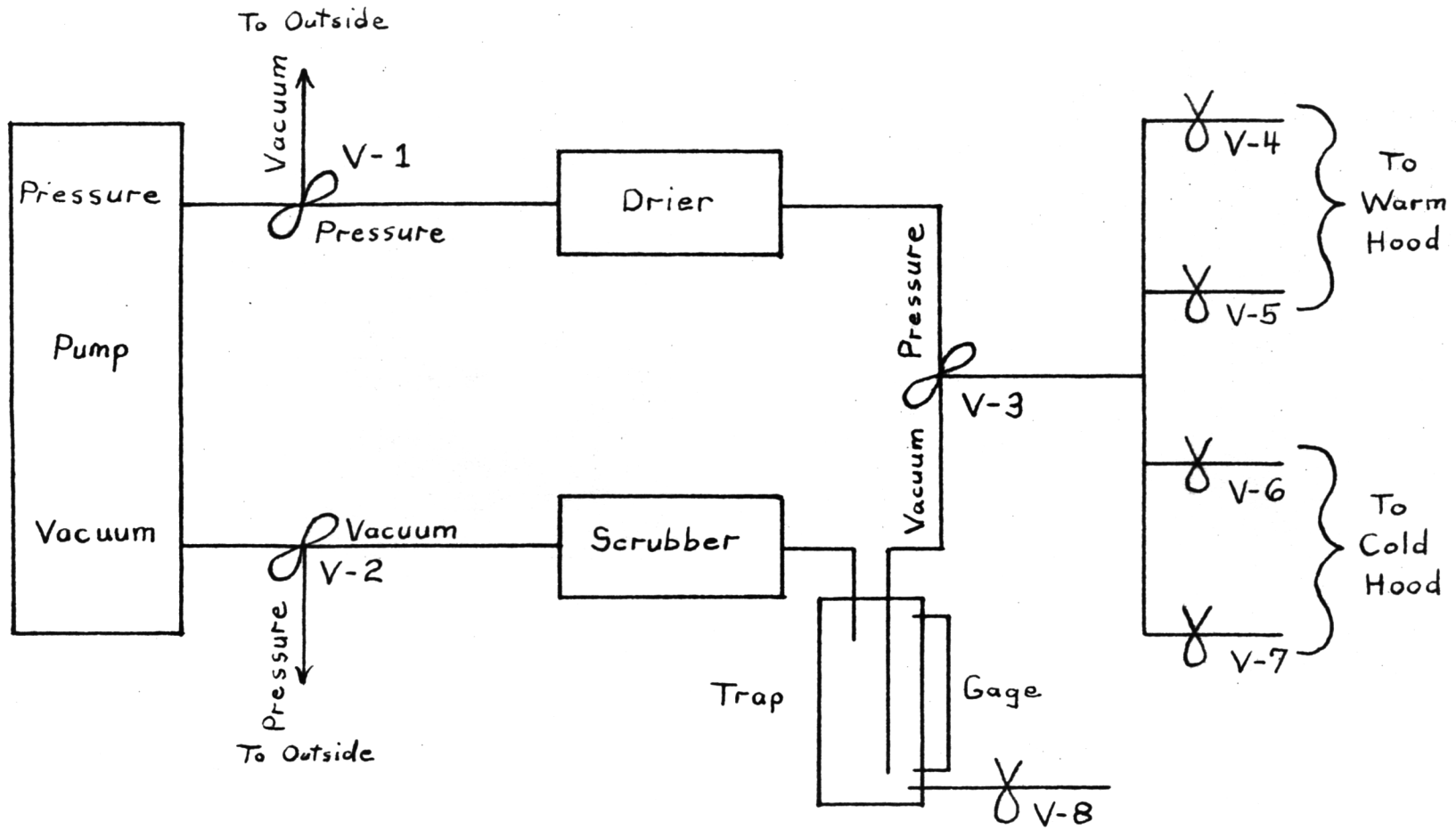


Fig. 2

#### EXPLANATION OF PLATE X

Flow plan of aeration system. V-1, V-2, and V-3 are three way valves. V-4 through 8 are single valves which control the flask being aired.

PLATE X



## EXPLANATION OF PLATE XI

- Fig. 1. View of top section of control panel with cover removed, revealing drier, top tube; scrubber, bottom tube; and the air lines leading from the four manifold valves.
- Fig. 2. Side view of air system components showing the liquid trap with its gauge and drain valve, (lower right corner).

## PLATE XI

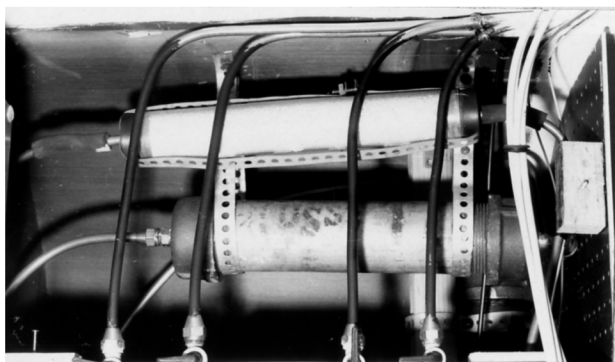


Fig. 1

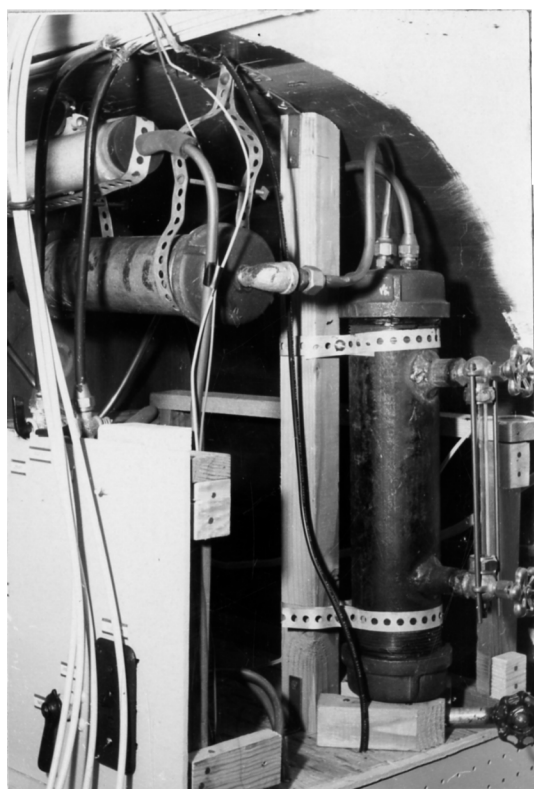


Fig. 2

Fisher Scientific Pressure vacuum pump with a capacity of 1.3 CFM free air and 27 in. mercury. The operation procedure of this device is described under Detailed Procedure, Section 3.

With this flask aeration system a 50 cc sample could be removed from the flask and the flask aired sufficiently to permit a new sample to be introduced within three minutes. This cleared the flask so that there was no apparent interfering vapor residue from previous tests. The waste fumigant in the trap was drained outside the Laboratory at the end of each day. Indicating Drierite was used in the drying tube and was changed as necessary. The vapor scrubber used to protect the vacuum pump was filled with activated charcoal and changed when necessary.

## PROCEDURE

### General Test Procedure

The test procedure used by the U.L. is presented in Appendix I. This procedure is very long and time consuming; therefore a much more abbreviated procedure was used to conduct these experiments. A detailed step by step procedure for setting up and conducting an experiment is given under Detailed Procedure. The general steps in conducting a test on a fumigant containing  $CS_2$  will be presented in this section.

First the equipment was assembled and adjusted. The explosion vessel was immersed in a constant temperature bath filled with water and ethylene glycol. The temperature of this bath usually 32 F. It was important that the temperature

of the explosion vessel be adjusted to a constant value before a test is run.

The parameters of the test to be conducted are recorded on a data card before the test is conducted. This is explained in Plate XII.

The electrical parameters are usually the following:

DC, Spark-11 KV, capacitor - 0.2 MFD, gap breakdown - 7 KV.<sup>1</sup> These conditions are kept constant for all tests except those where the effect of AC versus DC sparks, voltage, capacitance, and electrode gap are studied.

A 50 cc sample of the fumigant to be tested is measured into a 50 cc syringe fitted with a 15 gauge needle. The sample is introduced into the explosion vessel by lifting the center cork stopper and spraying it rapidly down the side of the flask. Immediately after the sample is introduced, the stirrer is started and the time noted. The hoods are closed, and the hood lights turned off. The capacitor is charged. After 30 seconds the stirrer is stopped, and the capacitor charge is released across the spark gap. At this instant the operator watches for a flame traveling rapidly up through the flask and listens for the pop of the center cork caused by the pressure build up due to an explosion. In some cases just a slow moving flame is observed without pressure. If no flame or flame propagation with pressure effect is observed, the operator

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1. Break-down voltage is the minimum voltage which will jump a given electrode gap with dry air in the flask.



## EXPLANATION OF PLATE XII

## Explanation of data cards and table notation.

- KSU-46. This is the fumigant identification number.
- A. The date and also the time is recorded here.
  - B. The temperature in the laboratory.
  - C. Records the relative humidity inside/outside.
  - D. The volume of sample introduced into the explosion flask.
  - E. The temperature of sample at the time of introduction.
  - F. The length of time the air-gas mixture above the liquid is stirred.
  - G. The temperature of the water bath in which the explosion flask is immersed.
  - H. The type of electrical spark used to ignite the gas-air vapor.
  - I. With DC the entry indicates the number of kilo-volts in the spark discharge. With AC the entry indicates the voltage introduced into the primary of the high voltage transformer.
  - J. The amount of capacitance in MFD's in the circuit.
  - K. The length of the spark gap 7KV. This indicates the air gap between the electrodes broke down and allowed a spark to jump at 7000 volts. For AC gap distance is  $\frac{1}{4}$  inch.
  - L. & M. Fl stands for a visable flame. Pr stands for pressure effect.  
A ( ) sign indicates a positive reaction, A (-) sign no reaction.
  - N. Used for other notes, like whether the air in the flask was dry, and to note how the sample was introduced.

PLATE XII

I.D. No.		Formulated by										Card No.		of		Cards											
Date		Laboratory		Sample		Bath		Electrical			Results		Remarks														
		Temp	RH %	Vol. ml.	Temp	Stir Time	Temp	Type	Kilo V.	Cap.	GAP	Fl.	Pr.														
6-5-60	1036	75	34/45	50	72	1/2	32	DC	11.0	.2	7 KV	-	-	Dry													
6-5-60	1042	75	34/45	50	72	1/2	32	AC	115	.01	1/4 in	-	-	Dry													
														A	B	C	D	E	F	G	H	I	J	K	L	M	N

UNISORT ANALYSIS CARD STD. FORM Y9 THE TODD COMPANY, INC. - CHARLES R. HADLEY DIVISION - PRINTED IN U.S.A.

resparks the vapor. After 5 sparks there is little chance of igniting the vapor with continued sparking.

After the flask is sparked, the unvaporized liquid in the flask is removed and the flask is aired 2 minutes to remove vapors and combustion products.

The flask is then ready for another test run. After 10 to 15 explosions the break-down voltage is rechecked. When this is no longer constant, it is necessary to remove the electrode assembly and clean it.

#### Detailed Test Procedure

The following is a step by step outline of the test procedure used with this apparatus. This procedure is set up for two operators, one at the control panel the other at the fume hoods. Sections 1-6 cover the steps used by the control panel operator, and sections 7-10 cover the steps used by the hood operator.

##### Section 1, Low Voltage.

1. Turn on auxiliary master switch, S-1. (See Plate VIII)
2. Turn on hood switch, S-2.
3. Switch on rectifier heater, S-4.
4. Check line voltage, V-1.
5. Check pressure-vacuum system, S-3.

##### Section 2, High voltage direct current test sequence.

1. Open capacitor discharge switch, S-11.
2. Ground capacitors, (See section 6).
3. Place proper capacitor in circuit.

4. Plug hood electrode leads (L-1) into output jacks, J-1 & 3.
5. Move selector switch to d.c., S-8.
6. Close capacitor charge switch, S-10.
7. Turn powerstat(T) to zero or leave at preselected position.
8. Clear hoods, except when setting electrode gap breakdown, (See section 5).
9. Start timer switch (S-5 or 6) for stirrer when directed by hood operator, and note time. (THE EXPLOSION IF ANY WILL OCCUR IN 30 SECONDS).
10. Turn on high voltage master switch, S-7.
11. Adjust power stat until KV meter (V-3) indicates desired voltage.
12. When proper stirring time has elapsed turn off stirrer.
13. When stirrer stops, open capacitor charge switch and rapidly close capacitor discharge switch, while observing explosion vessel for spark or explosion. If no explosion or flame occurs spark the vapors again. Open capacitor discharge switch and close capacitor charge switch. As soon as the high voltage meter indicates the proper voltage, repeat step 13. After five sparks with no explosion or flame, continue stirring or clean flask.

Section 3, Steps to evacuate and purge explosion vessel.

1. Open capacitor discharge switch.

2. Turn off high voltage master switch.
3. Open valve in manifold to proper flask. (See Plate X)
4. Turn valves 1, 2, and 3 to vacuum position.
5. Turn on pressure-vacuum pump switch.
6. After all the liquid has been evacuated, turn valves 1, 2, 3, to pressure position and air for prescribed time.
7. During the pressure cycle, more efficient aeration will be obtained if the aeration tube in the explosion vessel is lifted slightly to raise its tip off the bottom of the flask.

Section 4, High voltage alternating current test sequence.

1. Ground capacitors at A.C. secondary outlet, J-2.
2. Plug in hood A.C. electrode leads, L-1.
3. Place proper capacitors in circuit.
4. Set selector switch to A.C.
5. Turn power-ostat to preselected value, check power-stat output voltmeter.
6. Clear hoods.
7. Start stirring timers when directed.
8. Turn on high voltage master switch.
9. When stirring stops push A.C. discharge button momentarily. If no explosion, repeat 5 times. If explosion, clear flask. If none, either clean flask or continue stirring.
10. To clean flask see Section 3.

Section 5, Steps to set direct current breakdown voltage.

1. DANGER HIGH VOLTAGE.
2. After hood operator has set an approximate spark gap and cleared hood, connect proper hood electrode leads.
3. Turn powerstat to zero.
4. Set selector switch to d.c.
5. Turn on high voltage master switch.
6. Increase powerstat voltage desired for breakdown as indicated on KV meter.
7. The hood operator will adjust the gap, if necessary, until a spark passes about every second.

Section 6, Procedure to ground capacitors.

1. Turn off high voltage master switch.
2. Open D.C. capacitor discharge switch.
3. Disconnect hood electrode leads.
4. Plug ground jumper lead into D.C. secondary outlet jack.
5. Close capacitor discharge switch.
6. When KV meter to 0, open capacitor discharge switch.
7. Plug ground jumper lead into A.C. secondary outlet jack.
8. Disconnect ground lead.
9. The capacitor panel is now safe.

Section 7, Hood, operation sequence before test.

1. Check for high voltage warning light.

2. Check to see if reaction vessels and electrode assemblies are clean and dry.
3. Place electrode assemblies on flask and tighten clamps.
4. Attach pressure-vacuum line, seat tube firmly.
5. Attach, align, and plug in stirring motor.
6. Attach electrode leads. Ground (Black tip) to adjustable electrode. Hot (Red tip) to rigid electrode.
7. Gap electrodes.
  - A.C. - about one fourth inch, as marked.
  - D.C. - set for 7 KV breakdown. (See Section 10)

Section 8, Hood, test operation sequence during test.

1. Measure sample to be tested in a fifty ml syringe.
2. After measuring sample, place thermometer in sample bottle.
3. Introduce sample.
4. Reset and check stirrer alignment rapidly.
5. Tell panel operator to start stirrers. (THE EXPLOSION IF ANY, WILL OCCUR IN 30 SECONDS).
6. Dismantle syringe and place on fiberboard to dry; read temperature of sample.
7. Close hood doors.
8. Tell panel operator you are clear, and give the sample temperature.

Section 9, Hood, test operation sequence after the test.

1. Do not open hood unless high voltage indicator light is off.

2. If the sample exploded, let the hood air for one minute.
3. After the light is off open the hood and prop open the stirrer stopper.
4. When panel operator is finished with the vacuum cycle loosen pressure-vacuum tube to allow flask to air.
5. While flask is airing prepare next sample.

Section 10, Steps to set the direct current gap breakdown voltage.

1. Close electrodes completely.
2. Open to about one eighth inch.
3. Attach electrodes.
4. Tell panel operator to check breakdown.
5. Adjust electrodes by turning the adjusting screw on the electrode assembly until sparking stops- close electrode until a sparking starts. Lock the electrodes. Be especially careful and handle only the adjustment knobs.

DISCUSSION AND RESULTS

A list of factors which can effect the explosive flammability of grain fumigants containg CS<sub>2</sub> was given in the Introduction. An apparatus was constructed which could control the electrical parameters and a procedure was developed to minimize the effect of the factors created by environment, technique and procedure.



The effect of each of these factors upon a basic fumigant formulation will be presented in the following paragraphs. This basic fumigant contained 78 percent chloroform and 22 percent CS<sub>2</sub> (by volume). The test parameters were: Temperature °Fahrenheit; Laboratory 75-80, Sample 68-73, Bath 32. Sample volume: 50 ml.; stirring time 30 seconds. Electrical; DC. spark: 11 KV.; gap breakdown: 7 KV. Capacitance: 0.2 MFD. These parameters were kept constant throughout all these tests except when a specific factor was being studied.

#### The Effect of Altering the Electrical Parameters

The source of ignition used in these tests was an electrical spark. The ability of a spark to ignite a fumigant vapor depends upon the energy it possesses. With this fact in mind, an apparatus was designed which would generate a spark with a fairly constant energy. It is described in Materials and Methods, Electrical Apparatus, High Voltage.

AC versus DC Sparks. A DC spark, produced by discharging a 0.2 MFD capacitor, charged to 11 KV, across the electrode gap, was much more capable of igniting a fumigant being tested than an AC spark generated by a momentary discharge of a 10KV transformer with a 0.01 MFD capacitor in parallel with the secondary.

Voltage, Capacitor and Spark Gap. The ability of a DC spark to ignite a fumigant vapor is dependent upon the energy the spark possesses. The energy of the spark produced by the apparatus described in this paper is dependent primarily

upon three things: its voltage, the capacitance in the circuit, and the electrode gap.

Table 1 shows the effect of varying the indicated voltage and the circuit capacitance, while maintaining a constant spark gap, upon the explosive flammability of a fumigant composed of 78 percent chloroform and 22 percent CS<sub>2</sub> (by volume). From this table it is readily seen that as the capacitance in the circuit is increased the voltage necessary to produce ignition is reduced.

The effect of electrode gap upon the ability of a spark to ignite a specific formulation is demonstrated in table 2. It should be noted that an electrode gap of less than 3KV breakdown was too narrow to allow ignition. Once the gap was increased to 4KV breakdown or greater, a spark of less energy was capable of igniting the vapors.

It is extremely difficult to properly study the effect of spark gap because of the problem encountered in setting a gap of less than 4KV breakdown. Because of this, a gap setting of 7KV breakdown was adapted for the standard test procedure.

Table 1. The effects of varying the indicated voltage and circuit capacitors on the explosive flammability of a fumigant composition composed of 78 percent Chloroform and 22 percent CS<sub>2</sub> (by volume).<sup>1</sup>

Voltage KV	:	Capacity MFD	:	Results	
				Propagated Flame	Pressure
6		0.4		NO	NO
7		0.4		YES	YES
7		0.3		NO	NO
7		0.3		YES	YES
8		0.3		NO	NO
10		0.2		NO	NO
11		0.2		YES	YES

1. Test Parameters. Temperatures ° Fahrenheit, Laboratory 75-80, Sample 68-73, Bath 32. Sample volume 50 ml. Stirring time 30 seconds. Electrical, DC. Spark KV-as indicated. Gap breakdown 3KV. Capacitance - as indicated.

Table 2. The effects of varying the spark voltage and gap breakdown voltage upon the explosive flammability of a fumigant composition composed, of 78 percent Chloroform and 22 percent CS<sub>2</sub> (by volume).<sup>1</sup>

Spark Voltage KV	Gap Breakdown Voltage-KV	Results	
		Propagated Flame	Pressure Effect
11.0	1	NO	NO
11.0	2	NO	NO
11.8	3	NO	NO
8.0	4	NO	NO
9.0	4	YES	YES
8.0	6	NO	NO
9.0	6	YES	YES
7.0	7 <sup>2</sup>	NO	NO
8.0	7	YES	YES

1. Temperature ° Fahrenheit; Laboratory 75-80, Sample 68-73, Bath 32. Sample volume 50 ml. Stirring time 30 seconds. Electrical DC. Spark KV- as indicated. Gap breakdown - as indicated. Capacitance - 0.2MFD.

2. No spark.

## The Effect of Environment, Technique and Procedure

Laboratory Temperature. The laboratory temperature can be an important factor in a test of this type. If no provisions are made to regulate the temperature of the fumigant samples being tested, their temperature will be controlled by the laboratory temperature. The effect of sample temperature is discussed next.

Sample Temperature. Table 3 illustrates the effect of varying the sample temperature upon the explosive flammability of a fumigant composed of 78 percent chloroform and 22 percent CS<sub>2</sub> (by volume) when tested at two bath temperatures. At a bath temperature of 32° Fahrenheit, the sample temperature did not effect the explosive flammability; however, at a bath of 0° Fahrenheit, the sample temperature had a considerable bearing upon the explosive flammability.

Bath Temperature. The temperature of the bath in which the explosion vessel was immersed had a marked effect on the flammability of the fumigant tested. Table 4 shows how the explosive flammability of a fumigant consisting of 78 percent chloroform and 22 percent CS<sub>2</sub> (by volume) was altered by testing it at different bath temperatures. From this data, it is apparent that the critical test temperature for testing a fumigant mixture containing CS<sub>2</sub> was around 32° Fahrenheit.

Sample Size. The amount of fumigant introduced into the explosion vessel can have a bearing upon the flammability of a fumigant. The effect of sample size upon the explosive

flammability of a fumigant composed of 78 percent chloroform and 22 percent CS<sub>2</sub> (by volume) is shown in Table 5.

Table 3. The effect of varying the sample temperature at the indicated bath temperature on the explosive flammability of a fumigant compound of 78 percent chloroform and 22 percent CS<sub>2</sub> (by volume).

Sample Temperature ° Fahrenheit	Bath ° Fahrenheit	Results	
		Propagated Flame	Pressure Effects
68	32	YES	YES
32	32	YES	YES
68	0	NO	NO
84	0	YES	YES
100	0	YES	YES

1. Test Parameters. Temperatures ° Fahrenheit; Laboratory 75-80, Sample - as indicated, Bath - as indicated, Sample volume 50 ml. Stirring time 30 seconds. Electrical, DC. Spark - 11.0KV, Breakdown - 7KV, Capacitance - 0.2MPd.

Table 4. The effect of bath temperature on the explosive flammability of a fumigant composed of 78 percent chloroform and 22 percent CS<sub>2</sub> (by volume).

Bath Temperature ° Fahrenheit	Results	
	Propagated Flame	Pressure Effect
0	NO	NO
10	NO	NO
32	YES	YES
50	YES	NO
75	NO	NO

1. Test Parameters.

Temperature ° Fahrenheit; Laboratory 75-80, Sample 68, Bath - as indicated. Sample volume - 50 ml. Stirring time 30 seconds. Electrical, DC. Spark 11.0KV, Breakdown 7KV, Capacitance, 0.2Mfd.

Under the conditions stated in the table, a sample of this formulation of greater than 15 ml must be used in order to explode the vapors.

Table 5. The effect of the size of sample upon the explosive flammability of a fumigant composition composed of 78 percent chloroform and 22 percent CS<sub>2</sub> (by volume<sup>1</sup>).

Size of Sample ml	Results	
	Propagated Flame	Pressure Effect
10	NO	NO
15	NO	NO
20	YES	NO
25	YES	YES

1. Test Parameters

Temperatures ° Fahrenheit; Laboratory 75-80,  
Sample 73, Bath 32. Sample volume- as indicated.  
Stirring time - 30 seconds, Electrical, DC.  
Spark - 11.0KV, Gap breakdown - 7KV, Capacitance  
0.2 MFD.

Stirring Time. The length of time that the air in the explosion vessel is stirred before the vapor is sparked appears to have little bearing upon the explosive flammability of a fumigant composed of 78 percent chloroform and 22 percent CS<sub>2</sub>. The test parameters were: Temperature in ° Fahrenheit; Laboratory 75, Sample 73-75, Bath 32. Electrical DC. Spark - 11.0 KV, Gap breakdown 7KV, Capacitance 0.2MFD, Sample Volume 50 ml.

Samples were stirred 2, 5, 10, 15, 20 minutes and all exploded.



Method of Introducing Sample. The manner in which the sample to be tested is introduced into the explosion vessel can have a tremendous effect upon the samples explosive flammability. If the sample is introduced by squirting it down the aeration tube or by pouring it into the vessel through a funnel, the sample will not explode. If the sample is squirted down the side of the vessel from a 50 ml syringe, the sample will explode. A fumigant containing 78 percent chloroform and 22 percent CS<sub>2</sub> was used in these tests under the following parameters: Temperature ° Fahrenheit; Laboratory 75, Sample 75, Bath 32. Electrical-DC, Spark-11.0KV, Gap Breakdown-7KV, Capacitance-0.2Mfd, Sample size-45m., Stirring time-30 seconds.

All of these factors which fall in the category of technique and procedure interact to effect the vapor pressure of the sample being tested. They can therefore, alter the ratio of flammable components to nonflammable components in the fumigant vapor in the flask, and in so doing, cause this vapor to be either flammable or nonflammable.

Once the effect of the two major groups of factors, electrical and procedural technique, was known, then a study of the explosive flammability of various fumigants could be undertaken with confidence.

One such test undertaken was to study the percentage of CS<sub>2</sub> which chloroform and carbon tetrachloride would carry and not explode. Table 6 shows the effect of varying the concentration of CS<sub>2</sub> and chloroform upon the explosive flammability under standard test conditions. Table 7 shows the effect of

varying the concentration of CS<sub>2</sub> and carbon tetrachloride upon the explosive flammability under standard test conditions.

Chloroform will carry 16 percent by volume CS<sub>2</sub> safely while carbon tetrachloride will carry 19 percent by volume.

Table 6. The effect of varying concentrations of CS<sub>2</sub> and chloroform on the explosive flammability under standard test conditions.<sup>1</sup>

Percent Concentration by Volume		Results	
Chloroform	Carbon Disulfide	Propagated Flame	Pressure Effect
84	16	NO	NO
83	17	YES	NO
82	18	YES	NO
81	19	YES	YES
80	20	YES	YES
79	21	YES	YES
78	22	YES	YES

1. Test Parameters

Temperatures ° Fahrenheit; Laboratory 75-80,  
 Sample 68-73, Bath 32. Sample volume 50 ml.  
 Stirring time 30 seconds. Electrical DC. Spark  
 11.0KV. Gap Breakdown 7KV. Capacitance 0.2 MFD.

Table 7. The effect of varying concentrations of  $CS_2$  and carbon tetrachloride upon the explosive flammability under standard test conditions.<sup>1</sup>

Percent Concentrations by volume		Results	
Carbon Tetrachloride	Carbon Disulfide	Propagated Flame	Pressure Effect
82	18	NO	NO
81	19	NO	NO
80	20	YES	NO
78	22	YES	YES

1. Temperature ° Fahrenheit; Laboratory 75-80, Sample 68-73, Bath 32. Sample Volume 50ml. Stirring time 30 seconds. Electrical DC. Spark 11.0 KV. Gap. Breakdown 7KV. Capacitance 0.2 MFD.

## SUMMARY AND CONCLUSIONS

The explosive flammability of a grain fumigant containing carbon disulfide, when tested with the apparatus and procedure described in this thesis, is governed by the interaction of numerous factors. The effects of a number of these factors on the explosive flammability of a fumigant formulation composed of 78 percent chloroform and 22 percent carbon disulfide have been evaluated.

These factors include the following:

- I. Characteristics of the Explosion Apparatus.
  - A. Type of apparatus used, AC versus DC.
  - B. The voltage of the spark.
  - C. The capacitance in the circuit.
  - D. The width of the spark gap.
- II. Environmental, Technique, and Procedure.
  - A. Laboratory temperature.
  - B. Sample temperature.
  - C. Bath temperature
  - D. Sample size.
  - E. Stirring time.
  - F. Method of sample introduction.

The first group of factors all effect the energy of the spark used as the source of ignition. The control and measurement of these factors is an essential element in developing a consistent and reproducible test.

The second group of factors all have either direct or indirect effect upon the vapor pressure of the fumigant being

tested. Since the composition of the fumigant vapor is a function of vapor pressure, and since the explosive flammability of this vapor is being tested, it is essential that a standard test procedure be used to keep the effects of these factors constant.

The apparatus and test procedure used to obtain the results presented in this paper provide adequate control for the above mentioned factors so as to permit fumigants containing  $CS_2$  as their principle flammable ingredient to be evaluated in a reproducible manner. The test parameters used were: Electrical DC, Spark 11.0KV, Gap breakdown 7 KV. Temperatures ° Fahrenheit; Laboratory  $75 \pm 5$ , Sample  $70 \pm 5$ , Bath 32. Sample volume 50 ml, Stirring time 30 seconds.

These parameters were arrived at after an evaluation of the results obtained while studying the effects of the previously mentioned factors upon the explosive flammability of grain fumigants. The conclusions reached regarding the effect of these factors are as follows:

AC vs DC Sparks. Using the apparatus as described in this thesis, it was found that the DC spark was more effective in igniting the fumigant vapors being tested.

The Voltage of the Spark. To make certain that the electrode gap would always breakdown, causing a spark, when a potential was applied, the capacitor was charged to 11 KV. This value was sufficiently larger than the 7 KV gap breakdown voltage loss due to closing the capacitor discharge switch (200-700 volts), and to overcome the insulating effect of the

fumigant vapors which possessed greater dielectric properties than the dry air in which the electrode gap was set (1-1.5 KV).

The Width of the Spark Gap. As was mentioned in the previous conclusion on spark voltage, a 7 KV gap breakdown voltage was used to set the electrode gap. This value was significantly above the minimum gap which would permit ignition, as determined in this thesis. The reason for using a higher value was to insure that the energy of the spark would be more constant therefore improving the reproducibility of the apparatus.

The Capacitance in the Circuit. A 0.2 microfarad capacitor when charged to the above mentioned 11 KV produced a spark of sufficient energy to insure consistent results.

Laboratory Temperature. A laboratory temperature of  $75^{\circ} \pm 5^{\circ}$  F was used since it was easily maintained and was close to the proper sample temperature.

Sample Temperature. A sample temperature of  $70^{\circ} \pm 5^{\circ}$  F. was used since it produced uniform results at the bath temperature used ( $32^{\circ}$  F). If a colder bath temperature were used ( $0^{\circ}$  F) a sample temperature of  $80^{\circ}$  F should be used.

Bath Temperature. A bath temperature of  $32^{\circ}$  F is the most stringent one used to test  $CS_2$  containing fumigants.

Sample Size. A sample size of 50 ml offered assurance of testing the fumigant under the most stringent conditions.

Stirring Time. Since a 30 second or greater stirring time had little effect upon the explosive flammability of the fumigant tested, a time of 30 seconds was arrived at since

this was the minimum time in which a test could be properly conducted.

Method of Sample Introduction. The only method of introduction which produced consistent results was to use a 50 ml syringe and squirt the sample down the side of the flask.

Through the use of the test parameters arrived at in these conclusions, a rapid and reproducible test method was developed.

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## LITERATURE CITED

Kenaga, E.E.

An evaluation of the use of sulfur dioxide in fumigant mixtures for grain treatment. Jour. Econ. Ent. 49(6): 723-729. 1956.

Laffitte, P. and R. Delbourgo

Ignition by condenser sparks. Regions of flammability of ethane, propane, n-butane and n-pentane. Fourth Symposium on Combustion, Combustion and Detonation waves. The Williams & Wilkins Company, Baltimore, Md. 926 p. 1953.

Neifert, I. E., F. C. Cook, R. C. Roark, W. H. Tonkin, E. A. Back, and R. T. Cotton.

Fumigation against grain weevils with various volatile organic compounds. U. S. Dept. Agric. Bulletin No. 1313. 1925.

Peters, Clayton.

2,913, 371 Fumigant composition and method. U.S. Patent Office. 1959.

Swett, Clyde C. Jr.

Effect of gas stream parameters of the energy and power dissipated in a spark and on ignition. Third Symposium on Combustion and Flame and Explosion Phenomena. The Williams & Wilkins Company, Baltimore, Md. 748 p. 1949.

Underwriters' Laboratories, Inc.

Bulletin of research, No. 29. 1943.

**APPENDIX**

## Underwriters' Laboratories, Inc.

Subject 340

July 20, 1955

TEST METHODS FOR CARBON BISULFIDE-CARBON  
TETRACHLORIDE BASE FUMIGANTS

Underwriters' Laboratories, Inc.'s classification of the fire hazards of carbon bisulfide-carbon tetrachloride base fumigants is based on performance tests relating to their combustion characteristics, as discussed below.

Where carbon bisulfide-carbon tetrachloride base mixtures containing relatively low amounts of carbon bisulfide have no true flash point when tested in conventional apparatus, the flash point test does not furnish conclusive information relating to the fire hazard. In order to evaluate the fire hazards of such products, including the temperature level at which they form flammable vapor-air mixtures, it is therefore necessary to conduct tests for the explosiveness of the vapor-air mixtures. Where a definite flash point (closed cup) is obtained, this generally establishes the hazard with respect to temperature level at which flammable vapor-air mixtures may be formed.

To obtain additional information on combustion characteristics, ignition temperature tests, and tests of the fumigants in the presence of heated surfaces are also conducted, but in the case of products which do not form flammable vapor-air mixtures the results of such tests are of less significance.

FLASH POINT TEST:

Flash point tests of carbon bisulfide-carbon tetrachloride base fumigants are usually conducted in a closed tester of the Elliot type. The Tag closed tester may also be employed.

TESTS FOR EXPLOSIVENESS OF VAPOR-AIR MIXTURES:

The explosion vessel used for determinations of the explosiveness of the vapors of the fumigant when mixed with air consists essentially of a spherical flask of Pyrex glass having a nominal capacity of two liters. The spherical diameter of the vessel is 6-3/8 in. (16 cm). It is provided with a vertical neck, 1-7/8 in. (4.8 cm) in diameter and 2-7/8 in. (7.3 cm) in length, the outlet of this neck being closed by a stopper having an inlet for introduction of samples of the fumigant in the liquid phase. A paddle-type stirrer,

1-5/8 by 2-1/4 in., for mixing vapors from the fumigant with air within the vessel, is located about 2-1/2 in. above bottom, this stirrer being driven by an external air motor with shaft passing through a tightly fitted sleeve in the stopper for the vessel. The stirrer does not make direct contact with the unevaporated sample of the fumigant.

The explosion vessel, except for the upper part of the neck, is immersed in a water bath maintained at a predetermined constant temperature. When working at temperatures below that of the laboratory, the explosion vessel is immersed in a mixture of brine and ice in suitable proportions to maintain the low temperature.

The electrical discharge from a transformer rated 110 v, ac for the primary and 23 ma, 10,000 v for the secondary is used as a source of ignition for the vapor-air mixtures. A 0.01- $\mu$  f capacitor is connected across the secondary of the transformer.<sup>1</sup> Electrodes, connected to the secondary, terminate within the explosion vessel at its vertical axis, 1 in. above bottom. The air gap between these electrodes is 1/4 in.

In conducting tests of the explosiveness of the vapors of the fumigants, a measured sample of the product in the liquid phase is introduced into the explosion vessel maintained at predetermined temperature, and the inlet to the vessel closed thereafter. The stirrer is operated to obtain rapid mixing of the vapor evolved by the sample with the air in the test vessel. At intervals of 1/4 or 1/2, 3/4, 1, 2, 3, 5, 10, 15, and 20 minutes after introduction of the sample, stirring is discontinued, and the electrical discharge from the transformer is passed momentarily across the air gap between the electrodes. Observations are made for flame propagation, with pressure effects, in the vapor-air mixture during application of this source of ignition.

Because of the difference in the relative volatility of carbon bisulfide and carbon tetrachloride, the vapors from the partially evaporated fumigant may be more hazardous, particularly when the liquid is at somewhat below ordinary room temperature. Tests are therefore conducted with the explosion vessel at ordinary room temperatures and at temperatures down to -15°C ( 5°F), 5.0°F ( 9°F). The measured samples of the liquid product introduced into the vessel range up to about 50 ml. Stirring of the vapor-air mixture in the explosion vessel, with intermittent application of the source of ignition

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1. Transformer, Cat. No. 63871, manufactured by the Jefferson Electric Co., Bellwood, Ill., and capacitor, Cat. No. ALX-100-0.01, manufactured by the Solar Manufacturing Corp., Paterson, N. J., or their equivalent.

(transformer discharge), is continued for a duration of at least 20 minutes, unless complete evaporation of the sample occurs in a shorter time with the smaller samples. When definite flame propagation, with pressure effects, occurs during the tests, it is not considered necessary to complete the full series of tests over the range with respect to volume of sample and initial temperature of the explosion vessel.

Following each test the unevaporated sample, if any, is removed from the explosion vessel, and the vessel purged of residual gases and vapors in preparation for the next test.

It will be noted that the ratio of the sample to the volume of the explosion vessel in these tests extends beyond the proportions used for fumigation in practice, and provides a margin of safety. Our tests indicate that the hazards of these fumigants are not increased by selective absorption when in contact with grain.

#### IGNITION TEMPERATURE TEST:

The apparatus consists essentially of a combustion chamber of glass surrounded by a molten alloy bath heated by a special electric furnace having low resistance, rod-type heating elements and thermostatic control. The alloy bath may also be heated by a gas burner. The temperature of the bath is measured by a calibrated thermocouple with a quartz tube for protection of the hot junction.

The combustion chamber is a flask of conical form with flat bottom, 11.4 cm in height, 6.0 cm in diameter at bottom, and 2.8 cm in diameter at top. It is about 160-ml capacity (rated capacity 125 ml), having a ratio of surface area to volume of about 1.1.

In conducting the test, measured samples of the fumigant in the liquid phase are introduced into the heated combustion chamber by a micropipette or graduated hypodermic syringe. Different amounts of the product are admitted to the chamber in successive trials at progressively lower temperatures, in order to determine the minimum temperature at which the vapors, in proportion with air, will ignite without application of a spark or flame. After each trial, the combustion chamber is purged of residual gases and vapors by means of a slow stream of air.

### TESTS OF BEHAVIOR IN THE PRESENCE OF A HEATED SURFACE:

The apparatus consists of a steel-surfaced electrically-heated hot plate, 7 in. in diameter. The temperature of the horizontal steel surface, in the test area at the center of the plate, is measured by an iron-constantan thermocouple (No. 30 Awg wire), the hot junction of this thermocouple being peened into a bottomed hole in the steel. The temperature of the steel surface is controlled by adjusting the electrical input to the hot plate by means of a variable transformer.

In conducting the tests, various amounts of the fumigant are applied to the steel surface heated to a predetermined temperature. Observations are made as to the combustion of the vapors and the extent of the flame propagation, if any, beyond the vicinity of the heated surface. Different amounts of the fumigant are applied to the heated steel surface in successive trials at progressively lower temperatures, to determine the minimum temperature at which the vapors undergo combustion (indicated by characteristic pale violet-colored flames or glowing).

### SPECIFIC GRAVITY AND DISTILLATION TESTS:

To obtain information on the general nature of the products, specific gravity and distillation tests are also conducted, but no attempt is made to verify the complete statement of composition furnished by the manufacturer, or appearing on containers for the products.

### CLASSIFICATION OF FIRE HAZARD:

The classification of the fire hazards of carbon bisulfide-carbon tetrachloride base fumigants is determined by the performance of these products in the tests relating to combustion characteristics described in the foregoing. The fire hazards are rated in accordance with Underwriters' Laboratories, Inc.'s Standard of Classification of the Hazards of Liquids in which

Ether rates	100
Gasoline rates	90-100
Alcohol (ethyl) rates	60-70
Kerosene (100 F flash) rates	30-40
Paraffin oil rates	10-20

Listed carbon bisulfide-carbon tetrachloride base fumigants rated in respect to fire hazard 1 to 5, in a class less hazardous than paraffin oil, may show localized burning of vapors in the vicinity of the test flame in Flash Point Tests, but are required to show no true flash point. It is required that the vapors of these products show no propagation of flame, in the presence of the source of ignition, when mixed with air at initial temperatures as low as  $-15^{\circ}\text{C}$  ( $\pm 5^{\circ}\text{C}$ ),  $5^{\circ}\text{F}$  ( $\pm 9^{\circ}\text{F}$ ), in tests for Explosiveness of Vapor-Air Mixtures. The vapors mixed with air may ignite weakly at the bottom of the combustion chamber at temperatures not lower than  $125^{\circ}\text{C}$  ( $257^{\circ}\text{F}$ ) in Ignition Temperature Tests, but it is required that there be no propagation of flame throughout the mixture. When applied to a steel surface heated to  $150^{\circ}\text{C}$  ( $302^{\circ}\text{F}$ ), or higher, in Tests of Behavior in the Presence of a Heated Surface, the products upon evaporation may undergo very weak combustion, but it is required that the pale violet-colored flames show no tendency to travel beyond the vicinity of the heated surface.

Carbon bisulfide-carbon tetrachloride base fumigants which do not comply with the above requirements may have definite explosion hazards which are reflected in a fire hazard classification rating considerably greater than 1 to 5. It appears that listing of these more hazardous fumigants by the Laboratories will generally be of little advantage to manufacturers or other interested parties.

**THE EXPLOSIVE FLAMMABILITY OF LIQUID GRAIN FUMIGANTS**

by

**CARL SIGVOLD BULGER**

**B. S., Kansas State University, 1958**

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**AN ABSTRACT OF A THESIS**

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The explosive flammability of a grain fumigant containing carbon disulfide, when tested with the apparatus and procedure described in this thesis, is governed by the interaction of numerous factors. The effects of a number of these factors on the explosive flammability of a fumigant formulation composed of 78 percent chloroform and 22 percent carbon disulfide have been evaluated.

These factors include the following:

- I. Characteristics of the Explosion Apparatus.
  - A. Type of apparatus used, AC versus DC.
  - B. The voltage of the spark.
  - C. The capacitance in the circuit.
  - D. The width of the spark gap.
- II. Environmental, Technique, and Procedure.
  - A. Laboratory temperature.
  - B. Sample temperature.
  - C. Bath temperature.
  - D. Sample size
  - E. Stirring time.
  - F. Method of sample introduction.

The first group of factors all effect the energy of the spark used as the source of ignition. The control and measurement of these factors is an essential element in developing a consistent and reproducible test.

The second group of factors all have either direct or indirect effect upon the vapor pressure of the fumigant being tested. Since the composition of the fumigant vapor is a

function of vapor pressure, and since the explosive flammability of this vapor is being tested, it is essential that a standard test procedure be used to keep the effects of these factors constant.

The apparatus and test procedure used to obtain the results presented in this paper provide adequate control for the above mentioned factors so as to permit fumigants containing  $CS_2$  as their principle flammable ingredient to be evaluated in a reproducible manner. The test parameters used were: Electrical DC, Spark 11.0KV, Gap breakdown 7 KV. Temperatures ° Fahrenheit; Laboratory  $75^{\circ} \pm 5^{\circ}$ , Sample  $70^{\circ} \pm 5^{\circ}$ , Bath  $32^{\circ}$ . Sample volume 50 ml. Stirring time 30 seconds.

These parameters were arrived at after an evaluation of the results obtained while studying the effects of the previously mentioned factors upon the explosive flammability of grain fumigants. The conclusions reached regarding the effect of these factors are as follows:

AC vs DC Sparks. Using the apparatus as described in this thesis, was found that the DC spark was more effective in igniting the fumigant vapors being tested.

The Voltage of the Spark. To make certain that the electrode gap would always breakdown, causing a spark, when a potential was applied, the capacitor was charged to 11 KV. This value was sufficiently larger than the 7 KV gap breakdown voltage. The reason for this difference was to overcome the voltage loss due to closing the capacitor discharge switch (200-700 volts), and to overcome the insulating effect of the fumigant vapors

which possessed greater dielectric properties than the dry air in which the electrode gap was set (1-1.5 KV).

The Width of the Spark Gap. As was mentioned in the previous conclusion on spark voltage, a 7 KV gap breakdown voltage was used to set the electrode gap. This value was significantly above the minimum gap which would permit ignition, as determined in this thesis. The reason for using a higher value was to insure that the energy of the spark would be more constant therefore improving the reproducibility of the apparatus.

The Capacitance in the Circuit. A 0.2 microfarad capacitor when charged to the above mentioned 11 KV produced a spark of sufficient energy to insure consistent results.

Laboratory Temperature. A laboratory temperature of  $75^{\circ} \pm 5^{\circ}\text{F}$  was used since it was easily maintained and was close to the proper sample temperature.

Sample Temperature. A sample temperature of  $70^{\circ} \pm 5^{\circ}\text{F}$  was used since it produced uniform results at the bath temperature used ( $32^{\circ}\text{F}$ ). If a colder bath temperature were used ( $0^{\circ}\text{F}$ ) a sample temperature of  $80^{\circ}\text{F}$  should be used.

Bath Temperature. A bath temperature of  $32^{\circ}\text{F}$  is the most stringent one used to test  $\text{CS}_2$  containing fumigants.

Sample Size. A sample size of 50 ml offered assurance of testing the fumigant under the most stringent conditions.

Stirring Time. Since a 30 second or greater stirring time had little effect upon the explosive flammability of the fumigant tested, a time of 30 seconds was arrived at since this was the minimum time in which a test could be properly conducted.

Method of Sample Introduction. The only method of introduction which produced consistent results was to use a 50 ml syringe and squirt the sample down the side of the flask.

Through the use of the test parameters arrived at in these conclusions, a rapid and reproducible test method was developed.