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WESTINGHOUSE ELECTRIC CORPORATION
TRANSFORMER DIVISIONS

MATERIALS ENGINEERING DIVISION

Mats. Eng. Dept. Report #694
Fluid Insulation Section

Proprietary Class 1

July 25, 1969

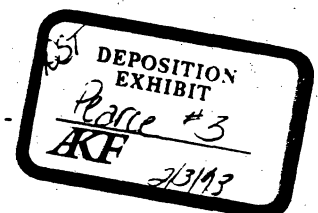
INVESTIGATION OF THE GASES PRODUCED
BY THE ELECTRICAL ARCING OF INERTEEN

I. Synopsis

INERTEEN 54201CM, which is AROCLOR 1242 and a small percentage of phenoxypropene oxide as a scavenger, produced sufficient combustible gases when arced to burn when those gases were mixed with air. Under similar tests, INERTEEN 54201KA, which is a mixture of 70% AROCLOR 1254 and 30% trichlorobenzene, produced only about 4% combustible gases, which was below the lower combustible limit of hydrogen-acetylene-air mixtures. The amounts of combustible gases produced when various combinations of the AROCLORS and chlorinated benzenes were mixed was dependent upon the ratio of chlorine to hydrogen in the molecules. Below a one to one chlorine to hydrogen ratio combustible gases were formed.

II. Introduction

INERTEEN is the Westinghouse trade name for a family of chlorinated hydrocarbon liquids which are non-combustible. The generic name for these materials is "askarel." Other manufacturers of electrical apparatus use various other trade names for this family of non-combustible insulating liquids. However, all of the trade marked brands of askarels contain AROCLOR which is the trade name of Monsanto Chemical Company¹⁶² for their series of chlorinated biphenyls and chlorinated polyphenyls. These compounds are chemically stable, fire-resistant, heat stable, and have high dielectric strength. Westinghouse has used various blends of the AROCLOR and chlorinated benzenes for many years. The most recent was INERTEEN 54201KA, which consisted of 70% AROCLOR 1254 (pentachlorodiphenyl) and 30% trichlorobenzene. A recent study of the properties and the economics of AROCLOR 1242 (trichlorodiphenyl), which is used in capacitors, brought about a change to 100% AROCLOR 1242 for use in transformers. AROCLOR 1242 was assigned the material number 54201CM. Both INERTEEN 54201KA and INERTEEN 54201CM have been approved by the Underwriters Laboratories³⁶⁴ for use in transformers.



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Concern arose as to whether the gases formed on arcing INERTEEN 54201CM were similar to the gases formed on arcing INERTEEN 54201KA due to the change in the amounts of chlorine and hydrogen present in the compounds. Table I was prepared to show the hydrogen and chlorine which can be present in chlorinated diphenyl and chlorinated benzene. From this it can be seen that in INERTEEN 54201KA the ratio of hydrogen to chlorine is 1 to 1, while in 54201CM it is 7 to 3. On arcing hydrogen and chlorine atoms are released. As long as there is an amount of chlorine equal to or in excess of the amount of hydrogen, there will be little or no free hydrogen resulting. When the ratio of chlorine to hydrogen falls below one to one, hydrogen will be found in quantities proportionate to the ratio. With INERTEEN 54201KA the formed gas should approach 100% hydrogen chloride, but in the case of 54201CM an excess of hydrogen approaching 40% should be present.

III. Conclusions

1. Rapid burning or explosive mixtures resulted from mixing with air, gases that were produced by electrically arcing AROCLOR 1242 as indicated by Monsanto's test data shown in Table V.
2. The percentages of combustible gases resulting from the arcing of AROCLOR 1242 varied somewhat among the three locations, (Monsanto, Westinghouse Sharon, Westinghouse Canada) but allowing for small differences in techniques the agreement was good. A general average of the arced gases showed 39 to 48% combustible. (See Table IV).
3. Tests by Monsanto Company showed that the combustible limits of the hydrogen-acetylene-hydrogen chloride mixture were narrower than for hydrogen alone. For hydrogen and air the lower combustible limit is 4% hydrogen, and the upper limit is 75% hydrogen. The lower combustible limit of burning was 4.4% hydrogen but the upper limit was less than 20% because of the HCl present. (See Table VI).
4. Arcing tests made on INERTEEN 54201KA, (70% 1254 AROCLOR-30% trichlorobenzene) did not produce sufficient combustible gases needed to burn under various tests. The total combustible including hydrogen and acetylene were not greater than 4% on any of the tests. (See Table IV).
5. Monsanto's tests of a mixture of 80% AROCLOR 1242 and 20% tritetrachlorobenzene when arced produced hydrogen and acetylene in the amount of 16 hydrogen and 10 acetylene using a 1500 volt spark. Westinghouse tests made using a carbon arc from a welder showed 16% hydrogen and 4.5% acetylene. Both of these compositions will burn. (See Table II for the Westinghouse results and Table V for Monsanto results).
6. Canadian Westinghouse tests using a pressure sensing device showed that a spark in the gas space of a transformer with AROCLOR 1242 which had arced would produce significant pressures. A 10 pound diaphragm ruptured readily. Similar testings using INERTEEN 54201KA showed only a slight pressure rise with no rupture of a 10 pound diaphragm. (See Figure 3).
7. No measureable amounts of combustible gases were formed when either INERTEEN 54201CM or 54201KA was subjected to the corona type electrical discharges in the Merrell Test Cell or the Pirelli Test Cell.

IV. Recommendations

Due to the combustible gases which may be formed when INERTEEN 54201CM is subjected to an electric arc, it is recommended that investigations be conducted to determine the potential quantities of such gases which might be generated in a transformer and the probability of a resultant hazard thus occurring.

V. Experimental Procedure and Results

Samples of INERTEEN 54201KA and 54201CM were subject to an electric discharge in the Merrell Test Cell described in ASTM D-2298 for Insulating Oil. The sample was admitted under vacuum into the evacuated cell at room temperature and 10,000 volts were applied for 1000 minutes. Any evolved gas was collected in an evacuated glass sample container. These samples were then tested by Mass Spectrometer at the Westinghouse R & D Laboratory. The analysis of the gas collected from the discharge in both 54201KA and 54201CM showed approximately 80% nitrogen and 18% oxygen with no combustible gases being present.

Samples of both materials were then subject to electric stress in the modified Pirelli Test Cell. This test cell is so arranged that the electrical stress is applied at the interface of gas and liquid. The gas used in the test cell was nitrogen. The liquid was degassed by vacuum and heat followed by a period of gas saturation. The gas flow was then stopped and the interface chamber isolated from the atmosphere. A stress of 100 volts/mil was applied for one hour at the gas liquid interface. The resultant gas generated was collected in a glass sampling bottle. Both materials were stressed at 80°C and at 100°C. The collected gas samples were then analyzed at the Westinghouse R & D Laboratories using the Mass Spectrometer. In every case the analysis of the gas showed approximately 81% nitrogen and 18% oxygen with no combustible gases present.

The results of these tests made it apparent that a more intense electrical stress would be required to decompose these materials. Therefore, a setup was made using an arc between two carbon electrodes to breakdown the liquid samples. The carbon electrodes were 5 mm diameter with a gap set as large as possible, but small enough for spontaneous arcing, which was approximately 1/32". The gap could be adjusted by rotating the electrode supports consisting of a brass fixture supported by 1/4" brass rods mounted in Micarta spacers. The power was supplied by a Westinghouse 8N64 D. C. Welder. The voltage was 40 volts under load and the current was set at 45 amps. The gas generated was collected by displacing liquid in a glass tube on top of an inverted glass funnel located right above the arc. The test set-up is shown in Figure 1. Figure 4 shows the fixture ready for arcing and Figure 5 after arcing. Samples of gas thus generated were collected on breaking down INERTEEN 54201KA, 54201CM, and a mixture of 80% 54201CM and 20% tritetrachlorobezene. Samples of the gas from 54201KA and 54201CM were analyzed at Westinghouse R & D Laboratories using the Mass Spectrometer and samples of gas from 54201KA, 54201CM, and the mixture of 80% 54201CM and 20% tritetrachlorobezene were analyzed in our laboratory on the Gas Chromatograph. The Gas Chromatograph is a Burrell Corporation, Kromotog Model K-1. The results of these tests are recorded in Table II.

Samples of the gas generated from the breakdown of the three liquids were bubbled through a .097 N sodium hydroxide solution and the solution was then titrated with 0.1N hydrochloric acid solution to determine the amount of HCl in the gas sample. These results are recorded in Table III.

Similar Tests have been conducted by Linkert and Gray of Canadian Westinghouse⁵ and Dr. R. A. Munch of Monsanto Chemical Company. Table IV is a comparison of the results obtain by Westinghouse, Monsanto, and Canadian Westinghouse. The agreement among the various tests results was good. The Mass Spectrometer identified small amounts of various other gases which could not be identified with the Gas Chromatograph, but the primary interest was in the hydrogen and hydrogen chloride. The amount of hydrogen generated when the INERTEEN 54201CM was broken down quite high in comparison with the 54201KA and the percentage of hydrogen chloride was significantly lower. This confirms experimentally what was to be expected theoretically due to the imbalance of hydrogen and chloride in the INERTEEN 54201CM.

VI. Discussion

The experimental results and the theoretical considerations both agreed that in case of an electrical arc sufficient to break the carbon-hydrogen and carbon-chlorine bonds INERTEEN 54201CM will form gases containing a significant amount of hydrogen. The question then to be considered is the effect this would have on the use of INERTEEN 54201CM as an insulating liquid in transformers. It needs to be considered whether we have the nonflammability and safety expected.

Information in the Bureau of Mines Bulletin on "Limits of Flammability of Gases and Vapors"⁶ indicates that for hydrogen in air the lower explosive limit is approximately 4.1 percent hydrogen and the upper limit is about 74.2 percent hydrogen. From their information on flammability of hydrogen-oxygen ratio, we have plotted Figure 2, which indicates the range of gas mixtures which could cause problem if the INERTEEN were subjected to an electric arc.

Table V shows data collected by Monsanto using a modification of the apparatus used by the Bureau of Mines⁶ to determine the flammability of the gases generated by arcing AROCLOR 1242 and by arcing a mixture of 80% 1242 and 20% tritetrachlorobenzene.

Figure 3 is a sketch of the apparatus used by Canadian Westinghouse to compare the effect of a spark on the gases generated by arcing AROCLOR 1242 and AROCLOR 1254.

References

1. Monsanto Chemical Company, Askarel Inspection and Maintenance Guide, September 1963.

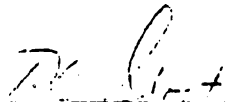
2. Monsanto Chemical Company, Technical Bulletin No. PL-306,
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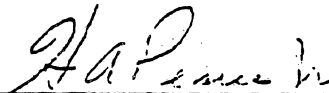
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5. Canadian Westinghouse Company Limited, Research and Development
Laboratories, Report No. 02021-350, "Chromatographic Analysis of the Gas
Produced by the Electrical Arcing of Aroclor 1242", by D. Gray, and W. G.
Linkert, September 20, 1968.

6. United States Department of Interior, Bureau of Mines, Bulletin
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Jones, 1952.



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TABLE I

Hydrogen - Chlorine Ratios in
Chlorinated Diphenyl and Chlorinated Benzene

<u>AROCLOR</u>	<u>Chlorinated Diphenyl</u>		<u>Number of Chlorine on Ring</u>
	<u>Number of Hydrogen on Ring</u>	<u>Percent Chlorine</u>	
	10	0	0
	9	18.9	1
1232	8	32.0	2
1242	7	42.0	3
1248	6	48.6	4
1254	5	54.3	5
1260	4	59.0	6
	3	63.0	7

<u>Chlorinated Benzene</u>		
<u>Number of Hydrogen on Ring</u>	<u>Percent Chlorine</u>	<u>Number of Chlorine on Ring</u>
6	0	0
5	31.6	1
4	48.2	2
3	58.5	3
2	65.8	4
1	70.8	5
0	74.8	6

	<u>Hydrogen</u>	<u>Chlorine</u>	<u>Ratio</u>
INERTEEN 54201KA	4.4	4.4	1-1
INERTEEN 54201CM	7.0	3.0	7-3
80% AROCLOR 1242-20% Tritetrachlorobenzene	6.1	3.1	2-1

TABLE II

Analysis of Gas Generated by an
Electric Arc in INERTEEN 54201KA and 54201CM

	<u>Gas Content</u>					
	Hydrogen %	Nitrogen %	Acetylene %	Carbon Dioxide & Carbon Monoxide %	Hydrogen Chloride %	Oxygen %
54201CM						
Mass Spectrograph	33	10	6		49	2
Gas Chromatograph	27	5	7	1	60*	
54201KA						
Mass Spectrograph	2	13	1		71	3
Gas Chromatograph	.3	4	.4	1	93*	1
80% 54201CM & 20 % Tritetrachlorobenzene						
Gas Chromatograph	16	5	4	1	73*	1

* By difference

TABLE III

Percent of HCl in Gas Samples

	<u>% HCl</u>
INERTEEN 54201CM	55%
INERTEEN 54201KA	82%
80% 54201CM + Tritetrachlorobenzene	62%

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TABLE IV

Comparison of Average Percentages of Hydrogen, Acetylene and Hydrogen Chloride
Obtained by Westinghouse, Monsanto and Canadian Westinghouse

	<u>Gas Content Percent</u>		
	<u>Hydrogen</u>	<u>Acetylene</u>	<u>Hydrogen Chloride</u>
INERTEEN 54201CM			
Westinghouse Mass Spectrograph	33	6	49
Westinghouse Gas Chromatograph	27	7	60
Monsanto Gas Chromatograph	24	14	62
Canadian W Gas Chromatograph	35	7	45
INERTEEN 54201KA			
Westinghouse Mass Spectrograph	2	1	71
Westinghouse Gas Chromatograph	.3	.4	93
Monsanto Gas Chromatograph	2.5	.3	96
Canadian W Gas Chromatograph	2	2	87

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TABLE V

Flammability Data From Monsanto

Monsanto broke down AROCLOR 1242 and a mixture of
80% AROCLOR 1242 and 20% Tritetrachlorobenzene
using a 240 volt arc and a 15000 volt spark

<u>Sample</u>	<u>Voltage</u>	<u>Gases Formed</u>		
		<u>Hydrogen</u>	<u>Acetylene</u>	<u>Hydrogen Chloride</u>
AROCLOR 1242	240 volt AC Arc 5 amps	20%	13%	67%
AROCLOR 1242	15000 volt spark	29%	17%	58%
80% AROCLOR 1242 20% TTCB	240 volt AC Arc 5 amps	16%	10%	75%
80% AROCLOR 1242 20% TTCB	15000 volt spark	13%	4%	83%

Using a modified Bureau of Mines Test using a 5cm
tube 5 ft. long synthetic gases were fed into the
tube with the balance air to determine minimum and
maximum combustible range.

Min. - Max. Combustible Range

<u>Percent Gas</u>			<u>Percent Air</u>	
<u>H₂</u>	<u>C₂H₂</u>	<u>HCl</u>	<u>Minimum</u>	<u>Maximum</u>
20	13	67	46	78
29	17	58	46	85
16	10	75	51	73
13	4	83	42	58

All of these gas mixtures were combustible when
mixed with percentages of air in the listed min. -
max. ranges.

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TABLE VI

Percentages of Hydrogen, Acetylene, and Oxygen in the
 Combustible Mixtures based on Monsanto Tests as per Table V

<u>Generated Gas</u>		<u>%</u>	<u>Composition of Combustible Mix</u>		
<u>H₂</u>	<u>C₂H₂</u>	<u>Air</u>	<u>H₂</u>	<u>C₂H₂</u>	<u>O₂</u>
20	13	46	10.8	7.0	9
20	13	78	4.4	2.9	15
29	17	46	15.6	9.2	9
29	17	85	4.4	2.6	17

FIXTURE FOR ARCING LIQUIDS

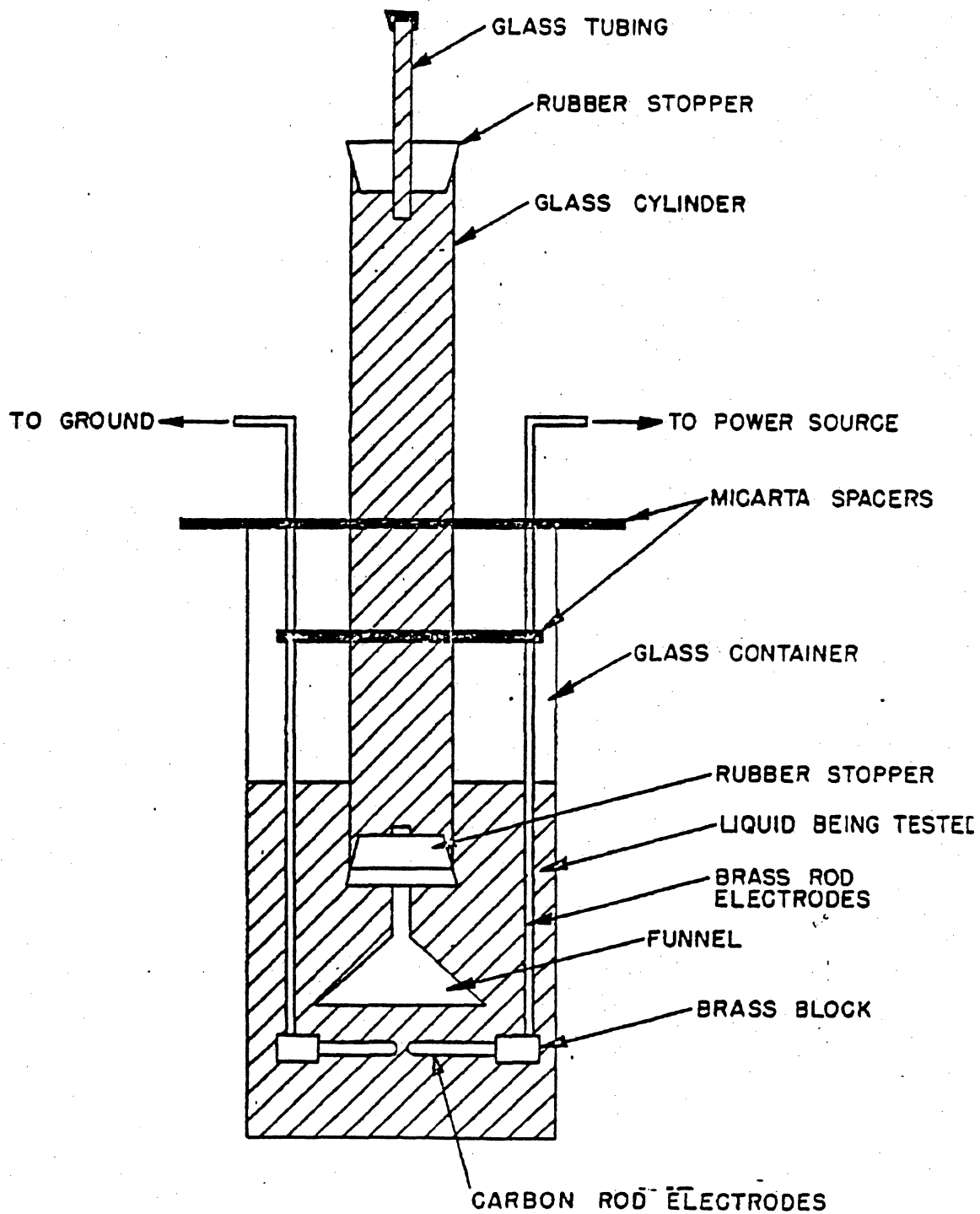
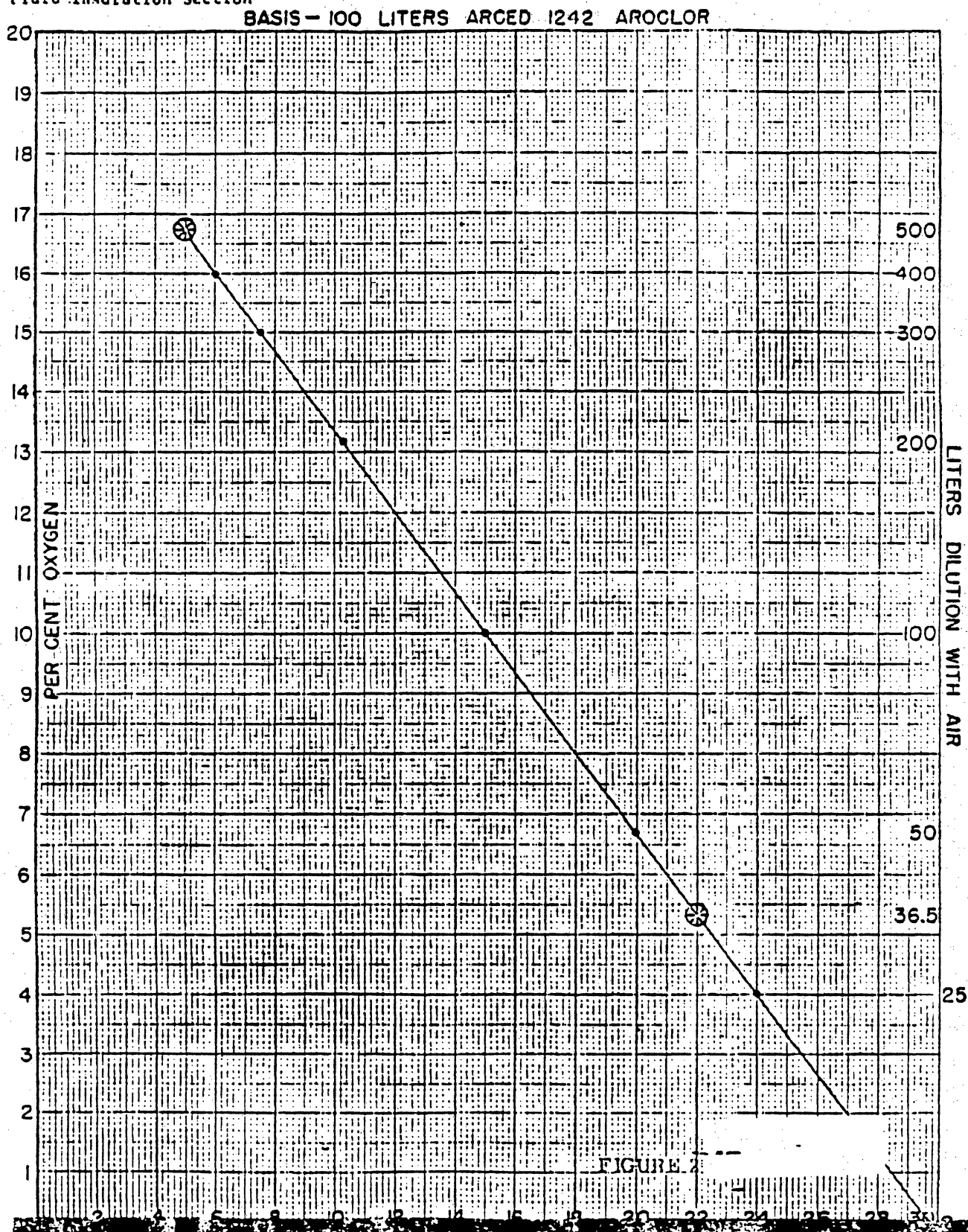


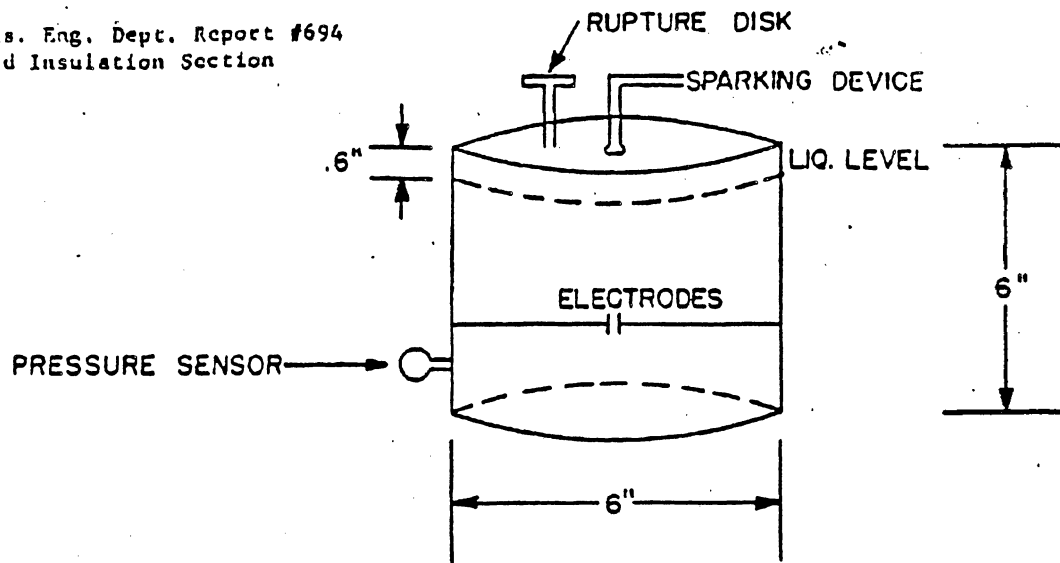
FIGURE 1

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1242

Arc created and pressure built up to 3# Gauge.
The gas was sampled and found to contain 6% hydrogen.
Spark created and pressure sensor rose to 43# in .03 seconds. Returned to 3# in 0.3 seconds. 150# rupture disk was stretched but not broken. 10# rupture disk substituted for 150# disk. Ruptured in 3 milliseconds after sparking.

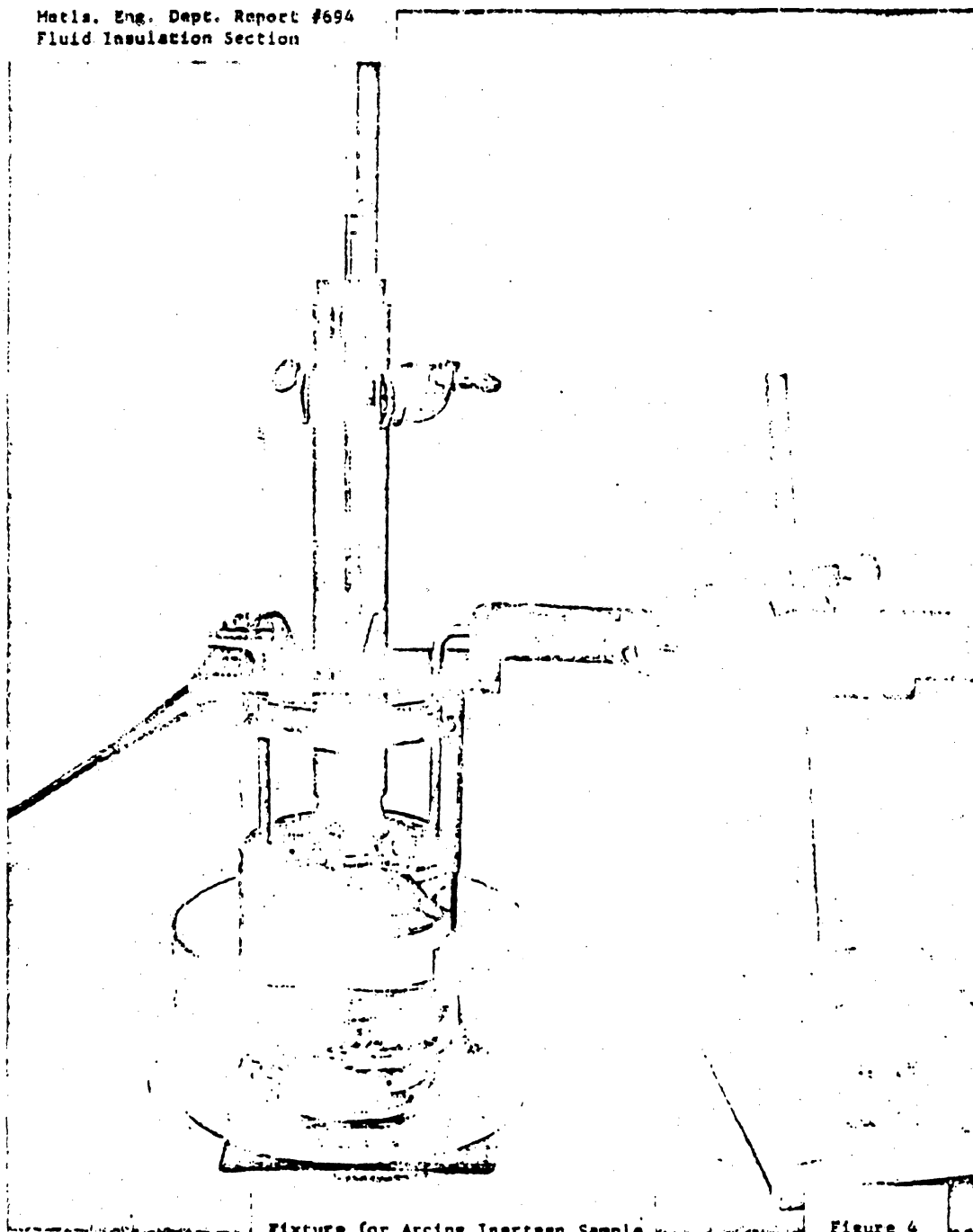
1254

Arc repeated to 3# Gauge. Sparked and pressure sensor rose to 4#. 150# rupture disk replaced with 10# paper disk. No rupture occurred on subsequent trials.

FIGURE 3

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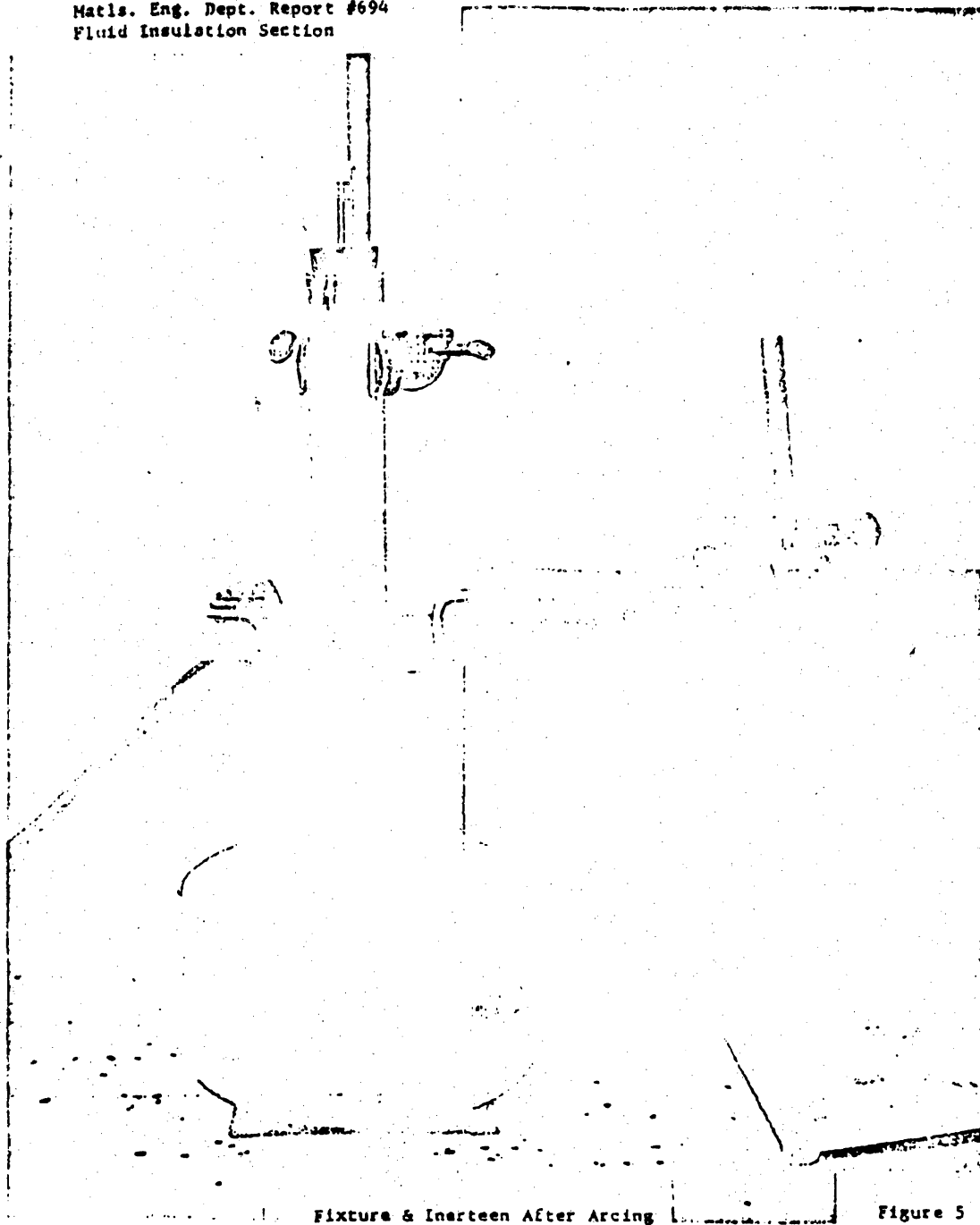
Fixture for Arcing Inerteen Sample

Figure 4

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Fixture & Inerteen After Arcing

Figure 5

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