

ALVAN SMALL, PRESIDENT
C. R. WELBORN, SECRETARY
H. F. DUNCAN, TREASURER

FOUNDED 1894

CHICAGO, 207 E. OHIO ST.
NEW YORK, 161 SIXTH AVE.
SAN FRANCISCO,
800 BANSOME ST.

Underwriters' Laboratories, Inc.

For Service - Not for Profit

SPONSORED BY

National Board of Fire Underwriters

207 EAST OHIO STREET, CHICAGO

Miscellaneous Hazard 2581

Application No. 3601794

February 18, 1937

REPORT

on

LIQUID DIELECTRIC AND COOLING MEDIUM
ADMIXED WITH SMALL AMOUNTS OF TRANSFORMER
OIL

General Electric Co.,
Schenectady, N.Y.

I N T R O D U C T I O N

In converting oil-filled transformers into Pyranol-filled transformers, the manufacturer has found that it is very difficult, if not impossible, to remove all traces of oil from the transformer with the practical methods available at the present time. The small quantity of oil remaining in the transformer becomes mixed with the Pyranol upon its addition to the transformer and it is, therefore, important to reduce such contamination by residual transformer oil to a point where the fire and explosion hazard of the Pyranol is not appreciably increased. Accordingly, this investigation was undertaken in order to obtain data as to the effect of the presence of small amounts of transformer oil on the fire and explosion hazards of Pyranol.

Our reports, Miscellaneous Hazard 2581, dated September 29, 1934 and April 14, 1936, respectively, describe the fire and explosion hazards of the liquid dielectric and cooling mediums known as Pyranol Nos. 1476, 1480, 1485, 1488, 1490, and 1491.

PLAINTIFF'S
EXHIBIT

472

D E S C R I P T I O NPRODUCTS COVERED BY THIS REPORT:

Liquid dielectric and cooling medium, "Pyranol No. 1488" admixed with small amounts of transformer oil.

P L A N O F I N V E S T I G A T I O N

The object of this investigation was to determine the fire and explosion hazard of Pyranol admixed with small amounts of transformer oil as compared with that of Pyranol containing no transformer oil.

In planning the investigation, consideration was given to the effect of the added transformer oil upon the flash point, fire point, ignition temperature and explosibility. The tests included flash point tests, fire tests, ignition temperature tests, and tests for flammability using specially-designed apparatus.

E X A M I N A T I O N A N D T E S T R E C O R D

DESCRIPTION OF SAMPLES

The manufacturer furnished a 10-gal sample of "Pyranol No. 1488" and a 1-gal sample of 10-C transformer oil. Samples of Pyranol-oil mixtures for the tests were made up containing 2, 3, and 5 per cent by volume of the transformer oil.

SPECIFIC GRAVITY TESTS:

METHOD

The specific gravity was determined by means of a pycnometer.

RESULTS

The specific gravity of "Pyranol No. 1488" was 1.5606 at $\frac{15.6C(60F)}{15.6C(60F)}$.

The specific gravity of 10-C transformer oil was 0.8845 at $\frac{15.6C(60F)}{15.6C(60F)}$.

FLASH POINT TESTS:

METHOD

The flash point was determined with the Pensky-Martens closed tester according to the method (D93-32) of the American Society for Testing Materials.

RESULTS

The results of the flash point tests are as follows:

<u>Sample</u>	<u>Flash Point</u> (1)
Pyranol No. 1488	118.3C (245F)
Pyranol-oil mixture containing 2 per cent by volume transformer oil	118.3C (245F)
Pyranol-oil mixture containing 5 per cent by volume transformer oil	118.3C (245F)
Transformer oil	126.7C (260F)

FIRE TESTS:

METHOD

The fire tests were made with the Cleveland open cup according to the method (D92-33) of the American Society for Testing Materials.

RESULTS

Pyranol-oil mixtures containing 3 and 5 per cent by volume transformer oil gave negative (2) results in the fire tests (3).

The transformer oil had a fire point of 154.4C (310F).

-
- (1) In this connection, see note 3.
 - (2) Intermittent flashes were obtained but the mixture did not continue to burn. The sample was heated to boiling point; the test was then discontinued.
 - (3) In view of the negative results obtained in the fire tests, it is clear that the flash point cannot be depended upon to give a true measure of the fire hazard of these mixtures. It was therefore necessary to conduct tests of the explosibility of the vapors of the mixtures in specially designed apparatus. See pages 6 and 7.

IGNITION TEMPERATURE TESTS:

METHOD

The apparatus consists essentially of a combustion chamber surrounded by a solder bath, which is heated at a constant temperature during the test by a bunsen burner. The temperature of the solder bath is measured by means of a calibrated thermocouple provided with a quartz tube to protect the hot junction.

The combustion chamber consists of a quartz or glass flask of conical form with flat bottom, 4-1/2 in. (11.4 cm.) in height, 2-3/8 in. (6.0 cm.) in diameter at bottom, and 1-1/8 in. (2.8 cm.) in diameter at top. It is of about 160 cc capacity (rated capacity 125 cc) having a ratio of surface area to volume of about 1.1.

Measured test samples in the liquid phase are introduced into the heated combustion chamber by means of a micro pipette. Different amounts of the sample are admitted to the chamber in successive tests in order to determine the minimum temperature at which the vapor of the liquid in any proportion with air will ignite. The residual vapors or gases in the combustion chamber are completely displaced by a stream of air in the interval between tests.

Ignition temperature tests were also conducted using a horizontal iron plate 10 in. square and 1/4 in. in thickness, heated by a gas burner. Flames and hot gases from the burner are deflected from the upper surface of the iron plate by a strip of sheet iron extending 10 in. beyond each side of the plate. The deflector is bolted to the edges of the plate, asbestos gaskets being provided at the joint. A calibrated chromel-alumel thermocouple (No. 14 Awg) connected with a potentiometer is used to measure the temperature of the plate, the hot junction of the thermocouple being brazed to the center of the upper surface of the plate. Check measurements of the temperatures of the plate are also made employing an optical pyrometer of the disappearing filament type.

In conducting tests, measured samples (up to 10 cc) were dropped on the center of the heated plate. A slow stream of air was applied to the evaporating sample in some of the tests. The minimum ignition temperature was determined by successive trial tests, during which the iron plate was maintained at progressively lower temperatures.

Miscellaneous Hazard No. 2581
Application No. 33C2060

September 29, 1934.

REPORT

on

LIQUID DIELECTRIC AND COOLING MEDIUMS

General Electric Co.,
Schenectady, N. Y.

D E S C R I P T I O N

PRODUCTS COVERED BY THIS REPORT:

Liquid dielectric and cooling mediums, "Pyranol
Nos. 1476, 1480, 1485, and 1488."

GENERAL CHARACTER AND USE:

The products which are the subject of this report are mixtures of chlorinated hydrocarbons in different proportions. They are pale yellow liquids differing markedly in respect to viscosity. They are intended for use as dielectric and cooling mediums in electrical apparatus.

"Pyranol No. 1476" is intended for use in cables and capacitors. Pyranol Nos. 1480, 1485, and 1488 are intended for use in transformers, Nos. 1480 and 1485 representing two extremes in the proportions of the chlorinated hydrocarbons and No. 1488 being the average.

MARKING:

"Pyranol Nos. 1476, 1480, 1485, or 1488" stencilled on containers.

C L A I M S M A D E F O R T H E P R O D U C T S

The manufacturer claims that the products are a distinct improvement in liquid dielectric and cooling media, are nonflammable at ordinary temperatures, and evolve non-explosive gaseous mixtures when decomposed by the electric arc.

The following claims are quoted verbatim:

"Pyranol is the trade name of the General Electric Company covering liquid dielectric and cooling media which are non-inflammable and non-explosive at ordinary temperatures and which even when decomposed by heat or the electric arc evolve only non-inflammable and non-explosive mixtures. The use of these improved liquid dielectrics effectively removes the danger from fire and explosion heretofore inevitably associated with the use of the inflammable and explosive oils in electric design.

"The Pyranols are chemically stable, non-acid-forming, non-sludging and of excellent dielectric properties. Being characterized by high dielectric strength and high dielectric constant, they are admirably suited for use in electrical apparatus. The dielectric constant of the Pyranols, being essentially of the same value as that of the solid insulation, insures a more equitable stress distribution when liquid ducts and solid insulation are arranged in series. The dielectric constant, being more than twice that of mineral oil, also insures a minimum of physical size per microfarad in capacitor design.

"The Pyranols have been in successful commercial service in increasing amounts during the past three years. The value of these liquids as non-inflammable and non-explosive dielectric and cooling media has been demonstrated.

"The first commercial use of the Pyranols in capacitor design was made in January, 1931. Commercial application of Pyranol capacitors has included the use of Pyranol in all types of service, including a-c power factor correction, use on direct current and high frequency circuits and other special applications well-suited to demonstrate the reliability and efficiency of the Pyranol capacitor. In the larger capacitor sizes a total of more than 8500 Pyranol-filled units with a

capacity in excess of 75,000 kva. have been manufactured and shipped in addition to a total of more than 250,000 small kva. Pyranol-filled capacitors for motor starting and motor running.

"The manufacture of Pyranol-filled transformers began in March, 1932 and has shown a steadily increasing volume. To date, more than 150 Pyranol-filled transformers have been shipped, totaling in excess of 27,000 kva.

"In the period during which commercial application of the Pyranols has been made, clear evidence has been obtained of their non-inflammable and non-explosive character, together with the advantages accruing therefrom. As examples, the following service experiences are cited, one illustration being taken from capacitor, and the other from transformer, experience.

"A 720 kva., 460 volt Pyranol capacitor was installed in a grain elevator. Dust accumulation between terminals of the controlling air circuit breaker eventually caused a severe arcover of considerable duration on the line side. Seven capacitor cases were melted open by the heat of the external arc. In twenty other cases the capacitor filling plug was melted off. In all cases the Pyranol was exposed to the high temperature and decomposition effects of the electric arc under the most favorable conditions for conflagration. In contrast to the behavior normally expected with mineral oil under similar conditions, the Pyranol did not burn nor evolve explosive gases.

"Experience has shown that an arc at the surface of the oil in an oil-filled transformer represents the most serious condition favoring fire and explosion. Routine examination of a service operating Pyranol-filled subway transformer showed clear evidence of such an arc having been present, yet not only had the transformer not exploded with resulting fire, but the transformer was still operating satisfactorily up to the time of the routine examination. The arc had burned completely away the insulation on the incoming cable terminal, the burning occurring at the surface of the Pyranol liquid, without affecting the service operation of the unit.

"The remarkable chemical and electrical stability of the Pyranols as evidenced by their successful commercial application in electrical design, together with the non-inflammable and non-explosive behavior of Pyranol-filled equipment under the most favorable conditions for fire and explosion, thoroughly substantiates the ten years' development and research program of which these products are the culmination."

P L A N O F I N V E S T I G A T I O N

The object of this investigation was to determine the fire and explosion hazard of the products.

In planning the investigation consideration was given to the General Nature of the products, their Fire and Toxic Hazard, Corrosive Action, Stability, and Uniformity. The method of investigation of each of these phases is given below.

Information as to the general nature of the products was obtained by means of Identification Tests.

The fire hazard of the products was investigated in respect to flammability, explosibility, ignition temperature, and decomposition temperature. The products of decomposition were investigated in respect to flammability and explosibility. Consideration was also given to the toxicity of the fumes produced on contact with hot metal surfaces and electric arcs. The tests included Flash Point Tests, Decomposition Temperature Tests, Ignition Temperature Tests, Tests for Flammability using specially designed apparatus, Explosive Range Tests, Analytical Tests of Decomposition Products in the presence of hot iron surfaces and electric arcs, and Tests of Transformers to Destruction.

Corrosion Tests of the products on metals commonly used in electrical apparatus were conducted.

Information bearing on the stability of the products was obtained from Decomposition Temperature Tests, Corrosion Tests, and consideration of the chemical properties of the products.

The process for manufacturing the products is subject to definite control, and a detailed investigation of factory process was not therefore considered necessary.

E X A M I N A T I O N A N D T E S T R E C O R D

DESCRIPTION OF SAMPLES

The manufacturer furnished 5-gal. samples of the following products: Pyranol Nos. 1476, 1480, 1485, and 1488.

IDENTIFICATION TESTS:

METHODS

Specific Gravity - The specific gravity was determined by means of a pycnometer.

Viscosity - The viscosity of Pyranol No. 1476 at 50 C (122 F) was determined by means of the Saybolt-Furol Viscosimeter using the method (D88-33) of the American Society for Testing Materials.

The viscosity of Pyranol Nos. 1480, 1485, and 1488 at 37.8 C (100 F) was determined by means of the Saybolt-Universal Viscosimeter using the method (D88-33) of the American Society for Testing Materials.

Distillation Test - A 100-g. sample was distilled using the method (D20-30) of the American Society for Testing Materials.

Acidity - Acidity was determined by mixing a 20-g. sample with 50 cc. of neutral ethyl alcohol and titrating with N/50 potassium hydroxide solution using phenolphthalein as an indicator. The acidity was calculated as per cent hydrochloric acid by weight.

Free Chlorides - A 50-cc. sample was agitated with 10 cc. of water in a separatory funnel. The aqueous extract was treated with aqueous silver nitrate solution and dilute nitric acid, the presence of chloride ions being indicated by the formation of a white precipitate of silver chloride.

Determination of Chlorine - The percentage by weight of combined chlorine was determined by the method of Carius.

RESULTS

The results of the identification tests are recorded in Table I.

FLASH POINT TESTS:

METHOD

The flash point was determined with the Pensky-Martens closed tester using the method (D93-32) of the American Society for Testing Materials.

TABLE I
RESULTS OF IDENTIFICATION TESTS

	Pyranol No. 1476	Pyranol No. 1480	Pyranol No. 1485	Pyranol No. 1488
Specific Gravity at 15.6 C (60 F) 15.6 C (60 F)	1.5481	1.5492	1.5817	1.5644
Viscosity: Saybolt-Furol at 50 C (122 F)	51.2	-	-	-
Saybolt-Universal at 37.8 C (100 F)	-	43.3	97.7	53.9
Distillation Test: Initial Boiling Point	352.2 C (666 F)	206.6 C (404 F)	207.7 C (406 F)	206.1 C (403 F)
Temperature Below 235 C (455 F)	amount distilled -	amount distilled 43.7% by weight	amount distilled 18.7% by weight	amount distilled 31.0% by weight
235 C (455 F) to 270 C (518 F)	-	5.1% " "	10.0% " "	9.7% " "
270 C (518 F) to 365.5 C (690 F)	72.1% by weight	0.14% " "	0.5% " "	0.4% " "
Above 365.5 C (690 F)	24.0% " "	46.6% " "	65.9% " "	54.8% " "
End Point	374.4 C (706 F)	394.4 C (742 F)	395.0 C (743 F)	396.1 C (745 F)
Residue	3.5% by weight	3.0% by weight	4.0% by weight	3.5% by weight
Distillation Loss	0.4% " "	1.2% " "	0.9% " "	0.6% " "
Acidity as HCl, Per Cent by Weight	0.0017	0.0018	0.0018	0.0011
Free Chlorides	absent	absent	absent	absent
Chlorine	(1) present	(1) present	(1) present	(1) present

(1) The percentage by weight of combined chlorine corresponds closely to data furnished by the manufacturer and held as confidential.

RESULTS

The results of the flash point tests are as follows:

<u>Sample No.</u>	<u>Flash Point</u> (2)
1476	232.2 C (450 F)
1480	115.6 C (240 F)
1485	118.3 C (245 F)
1488	115.6 C (240 F)

FIRE TESTS:

METHODS

The fire tests were made with the Cleveland open cup, using the method (D92-33) of the American Society for Testing Materials.

RESULTS

Sample Nos. 1476, 1480, 1485, and 1488 gave negative (3) results in the fire tests. (4)

IGNITION TEMPERATURE TESTS:

METHOD

The apparatus consists essentially of a combustion chamber surrounded by a solder bath, which is heated at a constant temperature during the test by a bunsen burner. The temperature of the solder bath is measured by means of a calibrated thermocouple provided with a quartz tube to protect the hot junction.

-
- (2) In this connection, see Note 4.
- (3) Intermittent flashes were obtained but the product did not continue to burn. The sample was heated to boiling point; the test was then discontinued.
- (4) In view of the negative results obtained in the Fire Tests, it is clear that the flash point test cannot be depended upon to give a true measure of the fire hazard of these products. It was therefore necessary to conduct tests of the explosibility of the vapors of the products in specially-designed apparatus. See page 10, et. seq.

The combustion chamber consists of a quartz flask of conical form with flat bottom, 4-1/2 in. (11.4 cm.) in height, 2-3/8 in. (6.0 cm.) in diameter at bottom, and 1-1/8 in. (2.8 cm.) in diameter at top. It is of about 160 cc. capacity (rated capacity 125 cc.) having a ratio of surface area to volume of about 1.1.

Measured test samples in the liquid phase are introduced into the heated combustion chamber by means of a micro pipette. Different amounts of the sample are admitted to the chamber in successive tests in order to determine the minimum temperature at which the vapor of the liquid in any proportion with air will ignite. The residual vapors or gases in the combustion chamber are completely displaced by a stream of air in the interval between tests.

Ignition temperature tests were also conducted using a horizontal iron plate 10 in. square and 1/4 in. in thickness, heated by a gas burner. Flames and hot gases from the burner are deflected from the upper surface of the iron plate by a strip of sheet iron extending 10 in. beyond each side of the plate. The deflector is bolted to the edges of the plate, asbestos gaskets being provided at the joint. A calibrated chromel-alumel thermocouple (No. 14 Awg) connected with a potentiometer is used to measure the temperature of the plate, the hot junction of the thermocouple being brazed to the center of the upper surface of the plate. Check measurements of the temperatures of the plate are also made employing an optical pyrometer of the disappearing filament type.

In conducting tests, measured samples (up to 10 cc.) were dropped on the center of the heated plate. A slow stream of air was applied to the evaporating sample in some of the tests. The minimum ignition temperature was determined by successive trial tests, during which the iron plate was maintained at progressively lower temperatures.

RESULTS

The results of the ignition temperature tests are tabulated below:

Sample No.	Ignition Temperature			Iron Plate
	Quartz Flask	(6)	(7)	
1476	571 C(1059.8 F)	Lag 3-4 sec.	754 C(1389.7 F)	
1480	553 C(1027.4 F)	" " "	714 C(1317.2 F)	
1485	539 C(1002.2 F)	" " "	714 C(1317.2 F)	
1488	553 C(1027.4 F)	" " "	716 C(1320.8 F)	

In the ignition tests using the heated iron plate the combustion was very weak and did not show any tendency to propagate beyond the vicinity of the heated iron surface. It will be noted that there was no confinement of the vapors in the tests with the heated iron plate.

-
- (5) The main value of the ignition test is to determine the minimum temperature required to produce ignition under the most favorable conditions in the absence of a flame or spark, including ratio of vapor to air and ratio of heated surface to volume of vapor-air mixture. Under less favorable conditions as when the liquid is applied to a hot plate a higher temperature for ignition is required. A limitation of the ignition test in a small vessel is that it does not show whether flame propagation for any material distance will occur. After determining the ignition temperature therefore it is necessary to obtain additional data having a bearing on flame propagation. These data are given by tests with hot plate and by flammability tests with specially-designed apparatus.
- (6) The term "lag" is used to denote the time interval between the introduction of the sample and the appearance of flame.
- (7) Within experimental error the optical pyrometer and the thermocouple gave the same values for the temperature of the iron plate.

FLAMMABILITY TESTS IN SPECIALLY-DESIGNED APPARATUS:

METHOD

The apparatus consists of a cylindrical steel vessel 6 in. in diameter (internal) and 26 in. long. It is provided with a small mica window and an outlet to the atmosphere. The apparatus is heated externally by gas burners. Openings are provided half way between the ends of the vessel to admit electrode terminals connected to an induction coil. The electrode terminals are spaced to give a spark gap of 1/4 in.

An iron-constantan thermocouple connected to a potentiometer is used for rough measurements of the temperature of the vapor inside of the vessel.

Samples ranging in volume from 20 to 90 cc. were introduced into the cylinder which had previously been heated to a predetermined temperature. The outlet of the cylinder was closed with a loose asbestos plug. Sparks were passed between the electrode terminals at intervals of 1/2 min.

Residual gases and vapors were displaced from the cylinder by a stream of air in the interval between tests.

RESULTS

Sample No. 1476 - No propagation of flame occurred at temperatures up to 204 C (399.2 F). Flame propagation with weak pressure effects (just sufficient to push asbestos plug from outlet of cylinder) occurred at 208 C (406.4 F). Moderate pressure effects (asbestos plug thrown about 3 to 4 ft. horizontally from outlet of cylinder) were obtained at temperatures somewhat above 208 C (406.4 F).

Sample No. 1480 - No propagation of flame occurred at temperatures up to 108 C (226.4 F). Flame propagation with weak pressure effects occurred at 112 C (233.6 F). Moderate pressure effects were obtained at temperatures somewhat above 112 C (233.6 F).

Sample No. 1485 - No propagation of flame occurred at temperatures up to 110 C (230.0 F). Flame propagation with weak pressure effects occurred at 113 C (235 F). Moderate pressure effects were obtained at temperatures somewhat above 113 C (235.4 F).

Sample No. 1488 - No propagation of flame occurred at temperatures up to 110 C (230.0 F). Flame propagation with weak pressure effects occurred at 113 C (235.4 F). Moderate pressure effects were obtained at temperatures somewhat above 113 C (235.4 F).

EXPLOSIVE RANGE TESTS:

METHOD

The apparatus consists essentially of a glass chamber equipped with a spark gap and a stirrer. The chamber is cylindrical with the lower end hemispherical and is approximately 3 in. in diameter by 8 in. in height; it has a net volume of 1000 cc. The apparatus is provided with a glass lid supporting the stirrer and the leads to the spark gap near the bottom of the chamber. An opening in the lid is provided for introduction of the sample. The glass chamber is immersed in a molten solder bath to a depth of 6 in.

In conducting tests the solder bath was maintained at a constant temperature of 400 C (752 F), a measured quantity of the liquid to be tested was placed in the apparatus, and the vapors stirred. Sparks were then passed at the spark gap while observations were made for flame travel and pressure effects. Following the test the vapors were displaced by a slow stream of compressed air in preparation for the next test.

RESULTS

The results of the explosive range tests of Samples Nos. 1476 and 1480 in air at 400 C (752 F) are shown in Table II.

DECOMPOSITION TEMPERATURE TESTS:

METHOD

The apparatus described in connection with Ignition Temperature Tests was used in these tests. The vapors evolved on introducing samples into the heated chamber were tested with moist blue litmus paper, a change in the color of the paper from blue to red indicating decomposition of the product. The minimum temperature at which litmus paper showed an appreciable change in color within a short time (3 min.) was considered to be the decomposition temperature.

TABLE II
RESULTS OF EXPLOSIVE RANGE TESTS

Sample No.	Lower Limit			Upper Limit		
	Volume Used in Test CC.	Lb. Vaporized Liquid per 1000 Cu. Ft. of Air (Calculated)	Per Cent by Volume (Calculated)	Volume Used in Test CC.	Lb. Vaporized Liquid per 1000 Cu. Ft. of Air (Calculated)	Per Cent by Volume (Calculated)
1476	0.038	3.69	1.0	0.100	9.67	2.7
1480	0.042	4.09	1.6	0.105	10.18	3.9

Weak pressure effects were obtained in these tests, as would be expected for mixtures near the limits of flammability.

RESULTS

Results of the decomposition temperature tests are recorded in the following table.

<u>Sample No.</u>	<u>Decomposition Temperature</u>
1476	300 C (572.0 F)
1480	324 C (615.2 F)
1485	340 C (644.0 F)
1488	340 C (644.0 F)

ANALYTICAL TESTS OF DECOMPOSITION PRODUCTS:

METHOD

Hot Iron Surfaces - The cylinder previously described under Flammability Tests in Specially-designed Apparatus was also used for exposing vapor-air mixtures to hot iron surfaces. Connections for withdrawing samples of the decomposition products for analysis were inserted in the outlet pipe. The cylinder was externally heated to a temperature of 600 C (1112 F) by gas burners.

Samples of the product in the liquid phase were introduced into the heated cylinder at a uniform rate. Samples of the decomposition products were withdrawn from the outlet pipe and hydrochloric acid, free chlorine, phosgene, carbon dioxide, oxygen, carbon monoxide, gases absorbed by bromine, and methane and other paraffin hydrocarbon gases, were determined using the following methods.

Hydrochloric acid was determined by absorption with water and subsequent titration with standard alkali solution using methyl orange as an indicator. A seven-liter sample was drawn by a calibrated aspirator bottle through an absorption train consisting of three spiral form bubbling towers. Free chlorine interferes with the determination and is removed by mercury in contact with the water in the bubbling towers.

Tests for free chlorine were made by liberation of iodine from aqueous potassium iodide solution and subsequent titration with sodium thiosulphate solution using starch solution as an indicator. A seven-liter sample was drawn by a calibrated aspirator bottle through a train consisting of two spiral form bubbling towers containing potassium iodide solution.

Phosgene was determined by absorption in aqueous aniline solution. Phosgene reacts quantitatively with aniline to form diphenylurea, one molecule of phosgene being equivalent to one molecule of diphenylurea.

A 15-liter sample was drawn through a train of three bubbling towers containing freshly prepared aqueous aniline solution saturated with diphenylurea. Free chlorine interferes with the determination and was removed by granulated antimony contained in a tube through which the sample passed before it entered the bubbling towers. The precipitate of diphenylurea was separated from the aniline solution by filtration, washed with cold water, dissolved in ethyl alcohol, recrystallized, dried, and weighed.

Carbon dioxide, oxygen, carbon monoxide, gases absorbed by bromine, and methane, were determined in the Moorehead form of gas analysis apparatus after treating the sample with silver nitrate solution to remove hydrochloric acid.

Electric Arcs - The apparatus consists of a cylindrical steel vessel 10 in. in diameter (internal) and 18 in. high. It is provided with a small mica window and an outlet to the atmosphere. Openings are provided in the vessel to admit two electrode holders, one holder being fixed and the other movable. The electrodes are copper rods 1/2 in. in diameter; their arcing terminals are horizontal. A connection for withdrawing samples of decomposition products for analysis is inserted in the wall of the vessel. A small cylindrical settling chamber for the removal of solid products of decomposition is attached to the sampling connection.

The electrodes are connected to a 230-volt, d-c. test circuit, the current being controlled by resistors. An ammeter is connected in the circuit and a voltmeter is connected across the electrode terminals.

A sample of the product, about 15 lb., was placed in the vessel, the arcing terminals of the electrodes being partially immersed in the sample. The arcing terminals were located on the axis of the cylinder, 3-1/2 in. above the bottom. A continuous arc (170 amperes) was maintained between the electrodes until destruction of the arcing terminals (5 min.).

Samples of the decomposition products were withdrawn continuously during this period and tested for phosgene and chlorine using the methods previously described. Samples of the decomposition products were also collected in evacuated glass sampling tubes at the conclusion of the test and the chief constituents determined, employing the following methods. Hydrochloric acid was determined by absorption in water and titration with standard alkali solution. Carbon dioxide, carbon monoxide, oxygen, gases absorbed by bromine, and paraffin hydrocarbon gases were tested for, using the Moorehead apparatus after treating the sample with water to remove hydrochloric acid.

Tests were also conducted with the arcing terminals of the electrodes 2-3/4 in. below the level of the sample in the vessel. A 21-lb. sample of the product was used in these tests. The arcing terminals were located on the axis of the cylinder, 2 in. from the bottom. A continuous arc (125 to 190 amperes) was maintained between the electrodes until destruction of the arcing terminals. Samples of the decomposition products were withdrawn at intervals during the test (See Table V) and the chief constituents determined using the methods previously described.

RESULTS

Hot Iron Surfaces - The results of analytical tests of the decomposition products are shown in Table III.

Electric Arcs - The results of analytical tests of the decomposition products in the presence of an electric arc between terminals partially immersed in Sample Nos. 1476 and 1480 are shown in Table IV.

The results of analytical tests of the decomposition products in the presence of an electric arc between terminals immersed in Sample Nos. 1476 and 1480 are shown in Table V.

TESTS OF TRANSFORMERS TO DESTRUCTION:

METHODS

The following tests were conducted at the Pittsfield, Massachusetts, plant of the General Electric Company.

TABLE III
RESULTS OF ANALYTICAL TESTS OF DECOMPOSITION PRODUCTS IN PRESENCE OF HOT IRON SURFACES

					Sample No. 1476		Sample No. 1480	
					5 to 13 Min. after Start of Test		5 to 13 Min. after Start of Test	
Hydrochloric Acid	Per Cent by Volume				11.2		7.5	
Chlorine	" " " "				0.000		0.000	
Phosgene	" " " "				0.000		0.000	
					5 Min. after Start of Test	13 Min. after Start of Test	5 Min. after Start of Test	13 Min. after Start of Test
Carbon Dioxide	" " " "				27.6	20.2	15.2	15.6
Carbon Monoxide	" " " "				13.2	8.0	17.0	11.4
Oxygen	" " " "				1.0	1.0	2.0	0.4
Gases Absorbed by Bromine	" " " "				0.0	0.0	0.0	0.0
Methane and Other Gaseous Paraffin Hydrocarbons	" " " "				0.0	0.0	0.0	0.0

In addition to the above volatile decomposition products some finely divided carbon was formed.

TABLE IV
RESULTS OF ANALYTICAL TESTS OF DECOMPOSITION PRODUCTS IN THE PRESENCE OF
ELECTRIC ARCS BETWEEN TERMINALS PARTIALLY IMMERSED IN SAMPLES OF PYRANOL

		Sample No. 1476	Sample No. 1480
		5 Min. after Start of Test	5 Min. after Start of Test
Hydrochloric Acid	Per Cent by Volume	26.7	34.0
Carbon Dioxide	" " " "	1.3	0.7
Carbon Monoxide	" " " "	7.7	4.3
Oxygen	" " " "	7.7	10.0
Gases Absorbed by Bromine	" " " "	0.0	0.0
Methane and Other Gaseous Paraffin Hydrocarbons	" " " "	0.0	0.0
		Start of Test to 5 Min. after Start of Test	Start of Test to 5 Min. after Start of Test
Chlorine	" " " "	0.000	0.000
Phosgene	" " " "	0.000	(8) trace

In addition to the above volatile decomposition products a large amount of finely divided carbon was formed.

(8) Less than 0.001 per cent by volume.

KH2581

TABLE V

RESULTS OF ANALYTICAL TESTS OF DECOMPOSITION PRODUCTS IN THE PRESENCE OF ELECTRIC ARCS BETWEEN TERMINALS IMMERSSED IN SAMPLES OF PYRANOL

		Sample No. 1476			Sample No. 1480			
		2½ Min. after Start of Test	5 Min. after Start of Test	5½ Min. after Start of Test	5 Min. after Start of Test	7.5 Min. after Start of Test	10 Min. after Start of Test	11 Min. after Start of Test
Hydrochloric Acid	Per Cent by Volume	36.5	62.0	69.2	17.7	60.5	62.4	73.1
Carbon Dioxide	" " " "	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Carbon Monoxide	" " " "	0.8	0.5	0.4	0.5	0.2	0.2	0.2
Oxygen	" " " "	12.4	7.4	5.7	16.0	7.6	7.3	5.1
Gases Absorbed by Bromine	" " " "	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Methane and Other Gaseous Paraffin Hydrocarbons	" " " "	0.0	0.0	0.0	0.0	0.0	0.0	0.0
			Start of Test to 5½ Min. after Start of Test			Start of Test to 11 Min. after Start of Test		
Chlorine	" " " "		0.000 (9)			0.000 (9)		
Phosgene	" " " "		trace			trace		

In addition to the above volatile decomposition products a large amount of finely divided carbon was formed.

(9) Less than 0.001 per cent by volume.

- 18 -

Two transformers, rated 60 cycles, 5 kv-a., 2200-110 volts, were employed, the interiors being designed for use in Pyranol. Taps were brought out from the outer layer of the 122-volt winding, arranged in such a manner that an arc could be started between the coil and carbon blocks located on the core clamps. The carbon blocks were used so that the arc could be maintained more readily during the arcing test.

Steel subway tanks were used for these test transformers in order to provide sufficient strength to withstand the pressure generated during the transformer failures. Pressure-tight covers were provided with glass pressure relief diaphragms designed to break at not less than 10 to 12 lb. pressure per square inch. A visual pressure indicator was provided in the cover to show the pressure in the tank before the relief diaphragm was broken.

Pyranol No. 1488 was used in these tests.

Short Circuit Test - The first transformer was prepared with the arcing tips bent back clear of the core and was connected for test as shown in Fig. 1. The secondary winding was short-circuited externally and the primary winding was connected across a 12,000 kv-a. generator at 1500 volts.

Arcing Test with Arc from Coil to Core - The second transformer was prepared with the arcing tips bent so that they made light contact with the carbon arcing blocks and was connected for test, as shown in Fig. 2, with the primary and secondary windings in series. The core, tank, and the other high voltage lead were connected to ground. The 12,000 kv-a. generator was connected so as to apply 7500 volts between the ungrounded 122-volt lead and ground.

The transformers before test are shown in Figs. 3 and 4.

RESULTS

Short Circuit Test - No appreciable change in pressure within the tank was noted for approximately 2 min. after current was supplied to the transformer. The pressure increased fairly rapidly from thereon, and approximately 15 sec. later the pressure relief diaphragm ruptured at a pressure of about 12 lb. per sq. in. Current was applied to the transformer for approximately 1/2 min. after the diaphragm ruptured.

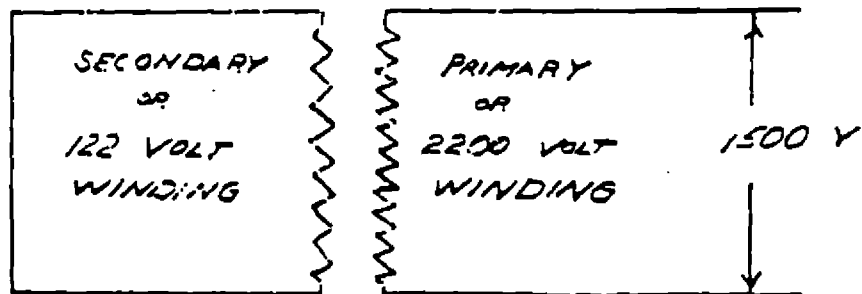


FIG. 1

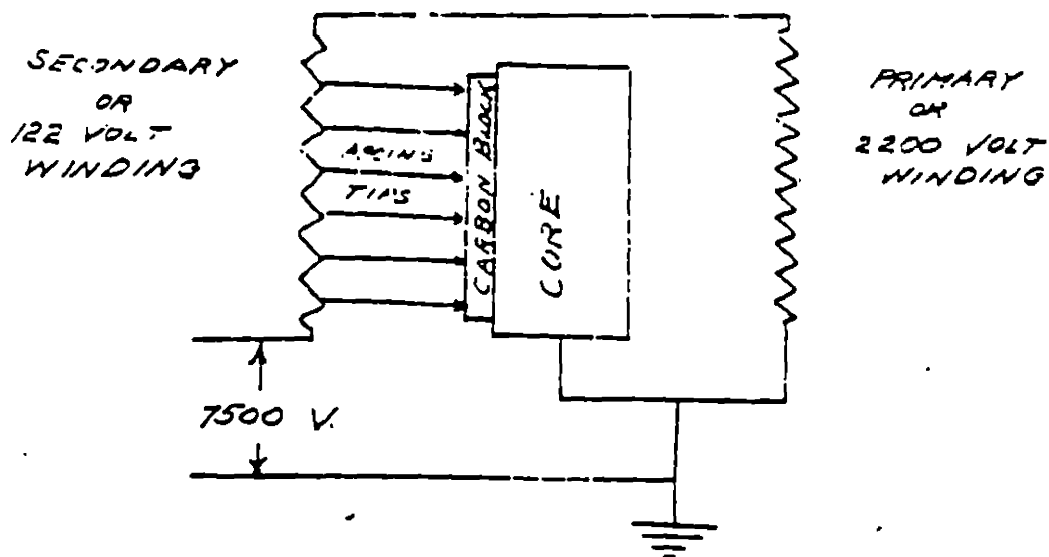


FIG. 2

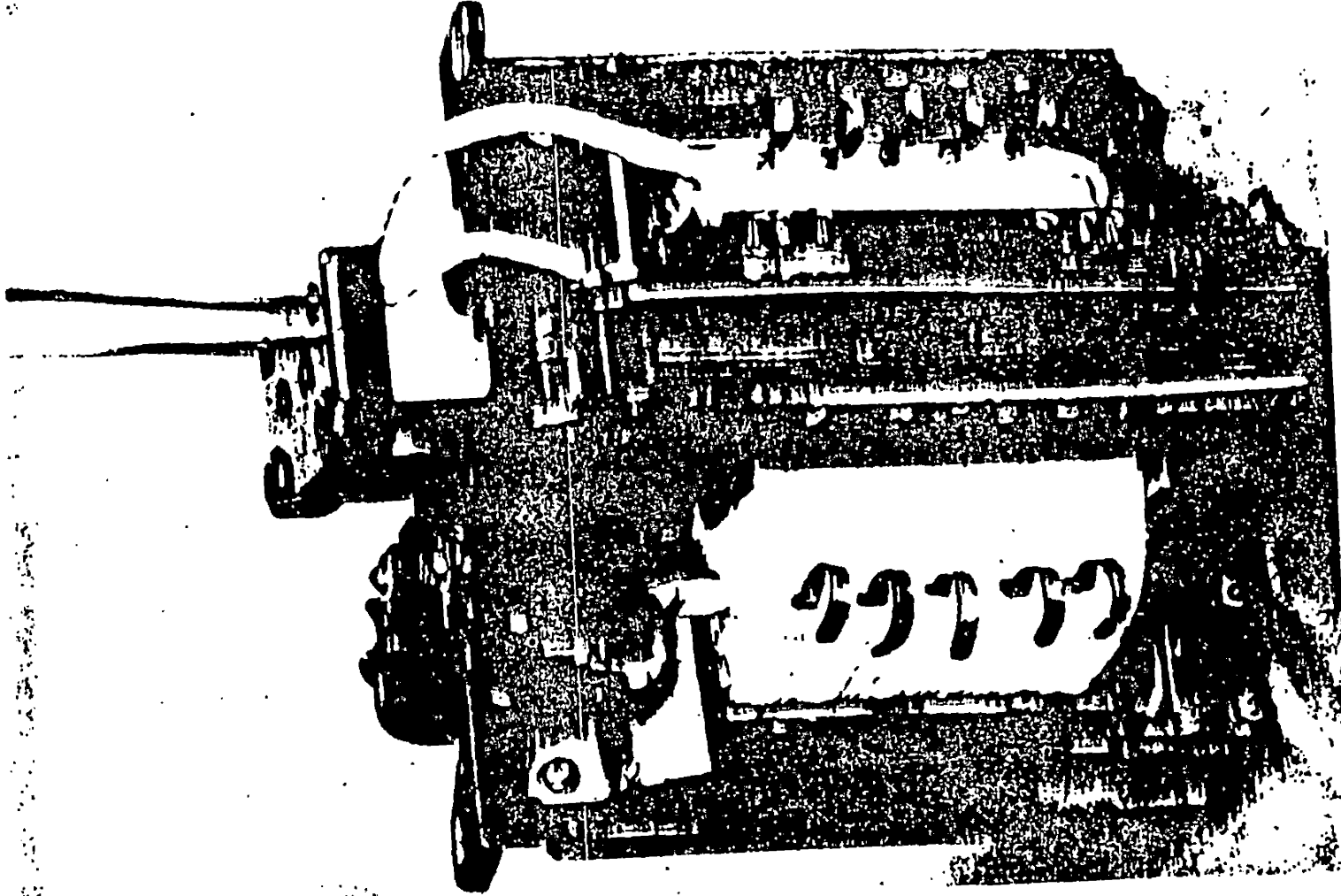


FIG. 3

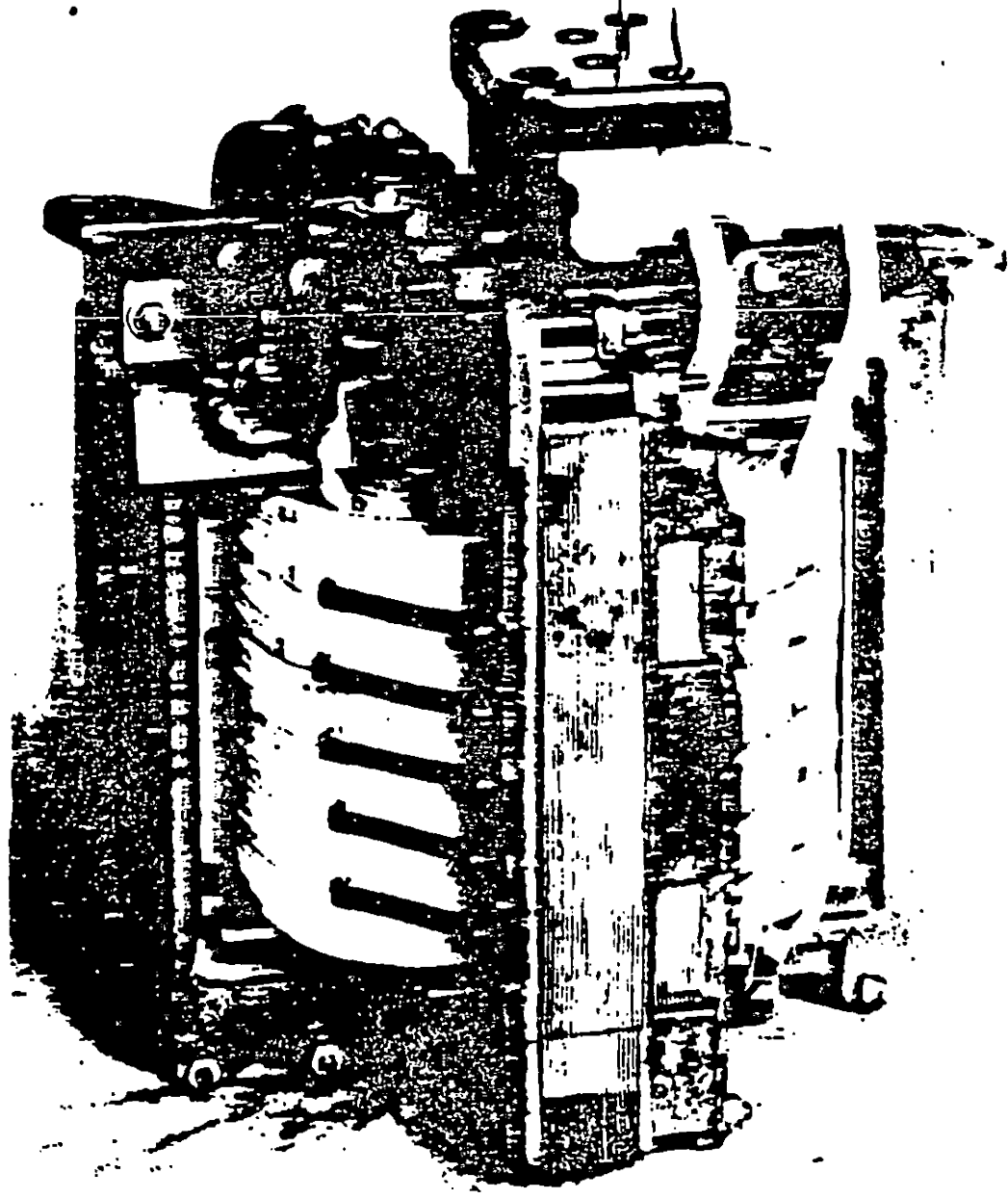


FIG. 4

A large volume of gases was liberated during the test. These gases did not ignite upon application of a test flame.

Upon examination of the transformers after the test, the coils were found to be severely burned.

Arcing Test with Arc from Coil to Core - No appreciable change in pressure within the tank was noted for approximately 2 min. after current was supplied to the transformer. From then on the pressure increased slowly to about 8 lb. per sq. in. and then increased rapidly to about 16 lb. per sq. in. before the pressure relief diaphragm ruptured. The arcing stopped shortly after the diaphragm ruptured. Current was supplied to the transformer for about 1/2 min. after the diaphragm ruptured.

A large volume of gases was liberated during the test. These gases did not ignite upon application of a test flame.

Upon examination of the transformer after the test, it was found that arcs had been established between the arcing tips and the core. There was no evidence of arcing along the face of the coil.

CORROSION TESTS:

METHOD

The metals used in the corrosion tests were copper, yellow brass, iron, tin-lead solder, copper and tin-lead solder, and copper and iron coupled. Test specimens, 3/4 in. wide and 6 in., long were cut from sheets of the metals. The specimens were buffed, measured, cleansed with soap and water, washed with ethyl alcohol and ethyl ether, dried, and weighed.

Each specimen was immersed for half its length in a sample of the product contained in a glass tube provided with a cork stopper. The tubes were heated to a temperature of 90 C in an electrically-heated oven controlled by a thermostat.

The samples were examined visually at weekly intervals during the test for evidences of corrosion. At the conclusion of the test, the specimens were cleansed, dried, weighed and the change in weight per square centimeter of surface area calculated.

RESULTS

When heated in glass tubes containing Sample No. 1476, 1480, 1485, or 1488 of the products at 90 C for 1608 hr., specimens of copper, yellow brass, copper and tin-lead solder, and copper coupled with iron showed no visible evidence of corrosion except for a slight discoloration of the surfaces above the liquid. Specimens of iron, iron coupled with copper, and tin-lead solder showed no change in appearance. The change in weight of the specimens was very small (less than 0.1 mg. per sq. cm.).

R E C O R D I N S E R V I C E

These materials have been in commercial service in increasing amounts during the past three years. The value of these liquids as dielectric and cooling media has been demonstrated.

T H E S U B M I T T O R

The manufacturer, the General Electric Company, Schenectady, New York, is experienced in the manufacture of electrical apparatus and related products, many of their products being listed by Underwriters' Laboratories.

SUPERVISION OF PRODUCTS BY UNDERWRITERS' LABORATORIES:

The products will be placed under Reexamination Service.

C O N C L U S I O N SGENERAL NATURE:

These products are mixtures of chlorinated aromatic hydrocarbons.

The results of the Identification Tests indicate that the products are mixtures containing combined chlorine in amounts corresponding closely to those stated by the manufacturer.

FIRE AND TOXIC HAZARD:

These products are nonflammable at ordinary temperatures. They are capable of forming moderately combustible and explosive mixtures with air under laboratory test conditions at higher temperatures, beginning at a temperature level of 112 C (233.6 F) to 113 C (235.4 F), in the case of Pyranol Nos. 1480, 1485, and 1488, and 208 C (406.4 F) in the case of Pyranol No. 1476, but under practical conditions formation of combustible or explosive mixtures is regarded as extremely unlikely. The fire hazard is very small.

It will be noted that the flash points of the products are comparatively high, and that a so-called "fire point" was not obtained. While intermittent flashes occurred in this test, the products did not continue to burn. The flash point and so-called "fire point" tests, particularly the latter, in the case of chlorinated hydrocarbons are of limited value as a measure of fire hazard but are useful for purposes of identification. The practical significance of the above tests in the case of the products in question is that their fire hazard is of a low order.

As shown by the results of Flammability Tests in Specially-designed Apparatus vapors of Pyranol No. 1476 failed to ignite or explode in tests at 204 C(399.2 F) but weak combustion occurred in tests at 208 C(406.4 F). Vapors of Pyranol Nos. 1480, 1485, and 1488 failed to ignite or explode in tests at 108 to 110 C(226.4 F to 230.0 F) but weak combustion occurred in tests at 112 to 113 C(233.6 F to 235.4 F). Moderate explosions were obtained in tests at temperatures somewhat above these minimum values. At a temperature of 400 C(752 F) the lower limits of flammability (upward propagation) of the vapors of Pyranol Nos. 1476 and 1480 were found to be 1.0 per cent and 1.6 per cent by volume in air respectively and the corresponding upper limits of flammability (upward propagation) were found to be 2.7 per cent and 3.9 per cent by volume. It will be noted that these are comparatively narrow explosive ranges.

The minimum ignition temperatures of the products were found to be 571 C(1059.8 F), 553 C(1027.4 F), 539 C(1002.2 F), and 553 C(1027.4 F) for Pyranol Nos. 1476, 1480, 1485, and 1488 respectively as recorded in the results of Ignition Temperature Tests.

In the ignition tests using the heated iron no ignition occurred at plate temperatures below 714 C. At higher temperatures the combustion was very weak and did not propagate beyond the vicinity of the heated iron surface.

In the tests with electric arcs the gases liberated, carbon monoxide and hydrochloric acid, were in such proportions as to be nonflammable alone or mixed with air. It will be noted that in the case of mineral oil under similar condition, highly explosive gases would be formed.

In the Tests of Transformers to Destruction under both short-circuit and arcing conditions, with Pyranol No. 1488 as the dielectric medium, the gases liberated were practically nonflammable.

The gases or fumes produced by burning or decomposition of the products by hot metal surfaces or electric arcs include hydrochloric acid, carbon monoxide, and in some cases a small amount of phosgene. This will ordinarily constitute a toxic hazard only where the conditions are such as to cause confinement of the fumes as in a closed room in which combustion or decomposition of the products is maintained by fire, highly heated surfaces, or electric arcs.

It is to be noted in this connection that oils in common use at present as the dielectric medium for electrical apparatus are readily combustible and when burning under conditions of restricted air supply form carbon monoxide in dangerous concentrations.

While phosgene is poisonous, our data indicate that the concentrations likely to result in the failure of a transformer or other electrical apparatus containing these products are not liable to endanger life.

The resulting concentration of hydrochloric acid in air when failure of a transformer or other electrical apparatus containing these products occurs will depend largely upon the conditions. It will constitute a toxic hazard only where the conditions are such as to cause a high concentration of the fumes as in a closed room.

The exceedingly unpleasant and irritating fumes from the decomposition of these products even in concentrations of a very low order act not only to give warning of their presence but to prevent dangerous exposure of persons. While carbon monoxide is odorless and toxic its formation from these products is always accompanied by the simultaneous formation of hydrochloric acid gas which gives adequate warning of its presence as brought out above.

It will be noted that combustion and decomposition of the products was maintained by heated surfaces (600 C, 1112 F) or by an electric arc in carrying out the analytical tests of the decomposition products. As shown by the results of the Decomposition Temperature Tests, the products were not appreciably decomposed at temperatures below 300 C (572 F).

CORROSIVE ACTION:

The products do not corrode the metals commonly used in electrical apparatus.

No corrosion occurred in the tests conducted on representative metals and alloys as recorded under Corrosion Tests.

It will be noted from the results of Analytical Tests of Decomposition Products that appreciable amounts of hydrochloric acid are formed on combustion or decomposition of the products in the presence of hot metal surfaces or electric arcs.

STABILITY:

The products are reasonably stable and in use are unlikely to undergo decomposition resulting in an increase in fire hazard.

In the Decomposition Temperature Tests the products did not undergo appreciable decomposition at temperatures below 300 C (572 F). Considerations of the chemical structure and properties of the products also indicate that they are reasonably stable.

UNIFORMITY:

Considering the general process of manufacture, it appears to be practicable to maintain a high standard of uniformity on a commercial scale.

R E C O M M E N D A T I O N

TO THE ELECTRICAL AND FIRE COUNCILS OF UNDERWRITERS'
LABORATORIES:

We recommend promulgation of the following notice
to subscribers and the action indicated thereby:

Guide No. 540 I4 September 29, 1934 - Laboratories' File
MH2581

General Electric Co., Mfr.,
1 River Road, Schenectady, N. Y.

Dielectric Mediums

Synthetic liquids intended for use as dielectric and cooling
mediums in electrical apparatus, particularly transformers,
cables, and capacitors.

Nonflammable and nonexplosive at ordinary temperatures.

Marking: "Pyranol Nos. 1476, 1480, 1485, or 1488."

Listed by Report - Further information is contained in a re-
port dated September 29, 1934, copy of which may be ob-
tained either from the manufacturer or from Underwriters'
Laboratories.

Listed - Reexamination Service.

See description of Reexamination Service on guide card.

Tests by:

A. H. Nuckolls
R. E. Dufour
C. C. Clogston

Report by:

R. E. Dufour
Asst. Chem. Engr.
C. C. Clogston
Physical Chemist

Reviewed by:

A. H. Nuckolls
Asso. Chem. Engr.

SUBMITTED

A. H. Nuckolls
Chemical Engineer.

The foregoing Recommendation has been accepted

UNDERWRITERS' LABORATORIES

W. P. Anderson
Secretary

RED:BIS

