Kendrick Lowe

REPORT NO. 2755

FINAL REPORT ON

HCl SCAVENGERS FOR TRANSFORMER FURANOLS.

JOB NO. 171-360

R. J. Good March 13, 1952

RESEARCH DEPARTMENT
Phosphate Division

2755 - HCl SCAVENGERS FOR FURANOLS - 1

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CHEMICALS - PLASTICS

Report No. 2755

FINAL REPORT ON

HCL SCAVENGERS FOR TRANSFORMER PYRANOLS

Job No. 171-360
File No. 141-32

Research Department - Phosphate Division
Anniston, Alabama.

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I. Introduction

Pyranol 1488, which is a mixture of trichlorobenzene (40%) and Aroclor 1260 (60%), is a very stable, non-flammable dielectric cooling and insulating medium for transformers. However, in the course of operation of a transformer, a power surge or prolonged overload may cause an arc to occur through the cooling liquid, and the transformer may fail. An electric arc, by reason of its high temperature, causes Pyranol 1488 to break down into carbon and HCl. The HCl attacks the paper insulation of the windings, weakening it or causing it to crumble, and also corrodes all metal parts of the transformer. Scavengers are added to the transformer liquid, to react with the HCl as soon as it is evolved and thus prevent or localize damage to the transformer. Tetraphenyl tin is the compound used for this purpose at present; it is covered by General Electric patents.

The object of this project was to find HCl scavengers that function at least as well as, and preferably better than, tetraphenyl tin. Patents in this field will greatly improve Monsanto's position if and when we start selling dielectrics directly to the transformer industry without subjection to G. E. patents.

II. Summary

A total of 73 new suggested compounds have been screened during the phase of the study reported herein. Of these, 16 were found to be as good as or better than tin tetraphenyl according to our tests. For the tabulated results, see Table 1 and Appendix A.

The protection from attack by HCl afforded by the proposed scavenger to paper of the type used as transformer insulation was taken as a criterion of effectiveness as an HCl scavenger. The tensile strength of test papers was measured, after a standard exposure to HCl dissolved in Pyranol containing the proposed scavenger. This was compared with the tensile strength of similarly treated papers protected by tin tetraphenyl.

The most satisfactory of the new scavengers were: poly (alkyl-alkoxy) tin compounds of the type of Advance Solvents Stabilizers Nos. 3 and 52, and Paraplex G-60. Samples of the two Advance Solvents stabilizers have been forwarded to the Westinghouse Electric Co. for their evaluation.

The Patent Department has expressed the opinion, (based on our observation that tetralauryl tin is completely inoperative as a scavenger under the test conditions) that the broad claim of the G. E. patent on tin tetraphenyl is invalid and will not dominate our patent on dibutyldiphenyl tin.

Westinghouse has expressed considerable interest in dibutyldiphenyl tin and phenoxy propene oxide. (These were found to be effective scavengers in previous work in this laboratory, reported in Interim Report No. 2353.)

A drum of Pyranol 1488 with 0.125% dibutyldiphenyl tin scavenger was sold to Westinghouse in 1950. A tank car of Pyranol 1488 with 0.205% phenoxypropene oxide scavenger (lot E-1) was shipped to them from the Wm. G. Krummrich plant on Jan. 4, 1952.

III. References

(A) Previous Monsanto Technical Reports
(1) Short Form Report No. 2052, Anniston, "Stabilization of Pyranol", E. F. Jackson, June 5, 1946
(2) Central Research Report No. 374, "Interim Report on Preparation of Organometallic Compounds to Test as Stabilizers for Polyvinyl Chloride", E. W. Gluesenkamp, April 16, 1945
(3) Central Research Report No. 503, "Fundamental Study of Stabilization of Polyvinyl Chloride", Miss Hogg, April 9, 1948
(4) Short Form Report No. 2209, Anniston, "HCl Scavengers for Pyranol. Testing Procedure", T. H. Cleveland, April 20, 1948
(5) Central Research Report No. 525, "Preparation of Organic and Metallic Organic Compounds Primarily for Test as Polyvinyl Chloride Stabilizers", E. W. Gluesenkamp, Oct. 1948
(6) Interim Report No. 2353, Anniston, "HCl Scavengers for Transformer Pyranols", R. R. Knight, May 2, 1949
(7) Short Form Report No. 2483, Anniston, "Purification of Organometallic Compounds for Pyranol Scavenger", H. Flores, May 5, 1950

(B) Literature
(8) Clark, "Nonflammable Dielectric Organic Compounds", I. and E. Chem., 29, 698-702 (1937)
(9) Gilman and Towne, JACS 61, 739-43 (1939)
(10) Gilman, Ed. in Chief, "Organic Chemistry, an Advanced Treatise", Vol. I, pp. 1071-2, Wiley and Sons, Inc., New York, 1943.
(11) Clark, "Electrical Insulation, a Field for Chemical Exploitation", Chem. Eng. News, 25, 2976-8 (1948)
(12) "Stabilizers" (brochure), Advance Solvents and Chemical Corp., New York. 1950
(13) "Epichlorohydrin", Shell Chemical Corp. Technical Bulletin SC: 49-35 (This gives Shell's analytical method for determining epoxides.)

(C) Patents
(14) U. S. Pat. 1,931,373 and 1,931,455, "Dielectric Material for Electrical Devices", F. M. Clark, assignor to G. E., Oct. 17, 1933. These two patents cover mixtures of chlorinated biphenyl and chlorinated benzene as dielectric and coolant in transformers and capacitors.
(15) U. S. Pat. 2,468,544, "Stabilized Halogenated Compositions and Electrical Devices", F. M. Clark, assignor to G. E., April 26, 1949. This patent covers tin tetraphenyl as an HCl scavenger for Pyranol and its broad claim, if valid, would dominate our patent on dibutyl-diphenyl tin.
(16) British Patent 601,359, "Improvement in and Relating to Liquid Hydrocarbon Compositions" -- to British Thompson, Huston Co., May 4, 1948
(17) British Pat. 418,230, "New or Improved Compositions Comprising Chlorinated Organic Substance", to I. G. Farben, Oct. 22, 1934. British patent 601,359 covers phenoxypropene oxide as an HCl scavenger for Pyranol. British patent 418,230 is believed to have been cited against the corresponding application by G. E. in this country.
(18) U. S. Pat. 1,235,399, "Uninflammable and Electrically Insulating Liquid", Georges Lepine, July 31, 1917

(19) U. S. Pat. 1,696,641, "Stabilized Chlorinated Rubber", Carlton Ellis, assignor to Chadeloid Chemical Co., Dec. 18, 1928
(20) U. S. Pat. 1,944,274, "Process of Treating Chemical Compounds", P. L. Salzberg, assignor to du Pont, Jan. 23, 1934
(21) U. S. Pat. 2,036,274, "Insulating Liquid", H. D. Holler, assignor to Westinghouse, April 7, 1936
(22) U. S. Pat. 2,005,840, "Insulating Material", R. Engelhardt, assignor to I. G. Farben, June 25, 1935
(23) U. S. Pat. 2,073,009, "Fireproof Material", R. Engelhardt, assignor to I. G. Farben, Mar. 9, 1937
(24) U. S. Pat. 2,105,406, "Liquid Insulating Composition," F. M. Clark assignor to G. E., Jan 11, 1938
(25) U. S. Pat. 2,105,407, "Liquid Insulating Composition", F. M. Clark, assignor to G. E., Jan. 11, 1938
(26) U. S. Pat. 2,143,685, "Electric Device and Dielectric Materials Therefor", F. M. Clark, assignor to G. E., Jan. 10, 1939
(27) U. S. Pat. 2,116,604, "Stable Composition Comprising Chlorinated Substances", G. Meyer, assignor to I. G. Farben, July 18, 1939
(28) U. S. Pat. 2,169,872, "Liquid Halogenated Compositions", F. M. Clark et.al., assignors to G. E., Aug. 15, 1939
(29) U. S. Pat. 2,217,173, "Stabilized High Film Strength Lubricating Oil, B. H. Lincoln, assignor to Continental Oil Co., Oct. 8, 1940
(30) U. S. Pat. 2,377,630, "Stabilized Dieleotric Composition", J. L. Hyde, assignor to Sprague Specialties Co., June 5, 1945
(31) U. S. Pat. 2,388,529, "Apparatus for Absorbing Decomposition Products", F. M. Clark, assignor to G. E., Nov. 6, 1945
(32) U. S. Pat. 2,453,493, "Halogenated Hydrocarbon Composition", F. M. Clark, et.al., assignor to G. E., Nov. 9, 1948
(33) British Patent Application No. 12,969, "New Organo-Tin Compounds and Resins Stabilized Therewith", G. P. Mack, et.al; application, May 16, 1947

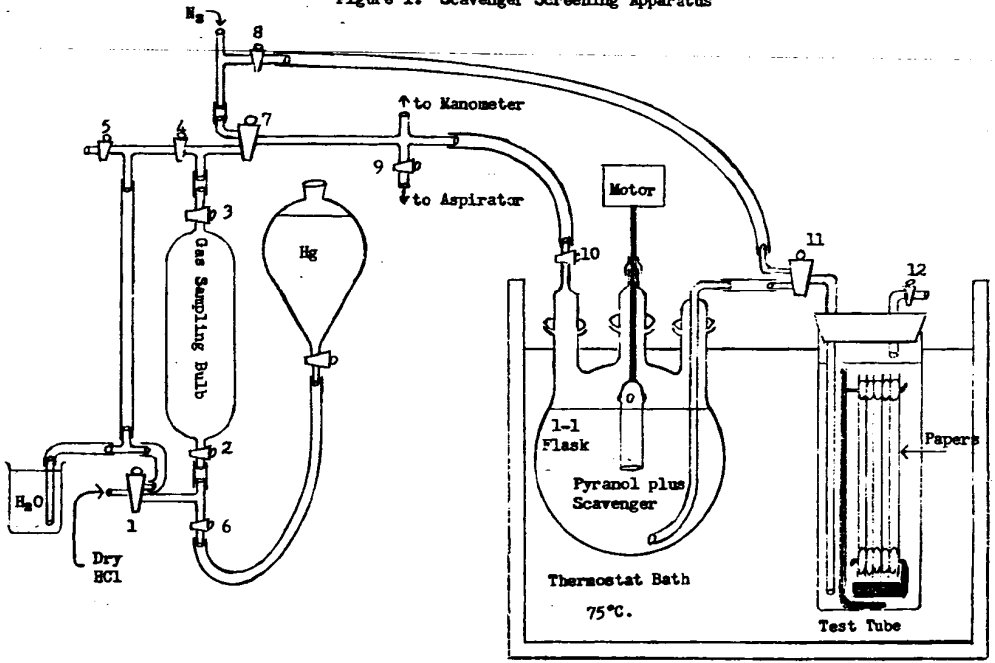
IV. Experimental Work:

A. Apparatus Used, and Methods

(1) Tensile strength screening test. See Figure 1, sketch of apparatus for treatment of papers for tensile strength test. The gas buret and manifold on the left was the means of admitting reproducible quantities of dry HCl to the system. The solution of the scavenger under test, in Pyranol 1488, was contained in the three-necked flask, and there treated with HCl. After a fixed reaction time, the Pyranol was blown over into the test tube containing the papers. The papers were in the form of strips 1" X 7", with the ends punched, and they were hung on the rack in the test tube, separated by glass spacers.

The series of operations was as follows:

Figure 1. Scavenger Screening Apparatus



(1) Dry HCl (from a H_2SO_4 drying train) was swept through the 273 ml bulb, with the exit gas being passed into the beaker of water, until the lack of bubbles in the beaker indicated that all air had been swept out. At the same time, the space above the Pyranol was evacuated several times and nitrogen admitted. Also a slow sweep of nitrogen was passed through the test tube containing the papers, at a reproducible rate and for a reproducible length of time.

(2) The HCl was diverted from the sampling bulb, (at stopcock 1) and then turned off. The flask was evacuated, and then with stopcocks 4, 9 and 11 closed the line was opened from the bulb to the flask. Stopcock 6 was opened, and the mercury was used as a piston to displace the HCl from the bulb. (The mercury was allowed to rise only to stopcock 3, which was then closed, as was stopcock 7.)

(3) The high-speed agitator motor was started. The Hoesch-type impeller gave very rapid absorption of the gaseous HCl. Nitrogen was admitted via stopcock 7 to keep the internal pressure up to atmospheric pressure. If the nitrogen was admitted intermittently, and the seal on the agitator was tight, it was possible to follow qualitatively the rate of absorption of the HCl by the drop in pressure indicated by the manometer. This gave a qualitative indication of the rate of reaction of the scavenger with HCl.

(4) After 20 minutes agitation, the motor was turned off and enough Pyranol was blown over into the test tube to cover the paper strips completely. The papers were allowed to soak in the Pyranol for 1 1/2 hours. They were then removed from the Pyranol, soaked 15 minutes in benzene followed by 15 minutes in methanol, and placed on a paper towel to dry. When dry, 1/2 inch was cut from each end, leaving a strip 1" x 6".

The tensile strength of the strips of paper were determined for us at the Southern Research Institute, Birmingham, Ala. A Scott IP2 Serigraph was employed, having a jaw separation of 3 inches and a rate of travel of 34.5 seconds for a load of 40 lb. Those papers that did not break under 40 lb were cut to a narrower width and a suitable correction factor applied. Before testing, the papers were humidified at 65% R.H. and 70°F for a minimum of 48 hours. Since papers were treated in sets of six, the tensile strengths reported are the average of six breaks.

In the earlier work of R. R. Knight, the gas buret and manifold on the left of figure 1 were omitted, and only the nitrogen inlet, the vacuum line and manometer were employed. In the schedule of operations, after the flask was evacuated nitrogen was admitted to a predetermined pressure (30 cm Hg below atmospheric pressure). Dry HCl was then admitted until the pressure in the flask was the same as atmospheric. The valves were closed and the agitator started. There was one other difference in the procedure, in that the nitrogen sweep of the test tube containing the papers was omitted.

The gas buret and manifold were added to the system because it was felt that with the method formerly employed, the variable rate of absorption of HCl into the Pyranol was causing different total quantities of HCl to be drawn into the system in different runs. In particular, scavengers which affected the surface tension would affect the rate of absorption. Also, scavengers that were particularly rapid in their action would cause more rapid absorption, and would thus be exposed to a greater quantity of HCl; they would consequently be penalized in comparison to slower-acting scavengers.

The nitrogen sweep of the test tube was added because it was deemed illogical to take pains to remove oxygen from the space above the Pyranol in the flask, and do nothing about the oxygen in the test tube. The nitrogen sweep was found to have a very marked effect, (higher tensil strengths were obtained) but it was later found that an oxygen sweep had the same effect. It was eventually decided that the variation in tensile strength with gas sweep of the test tube was probably due to the drying of the papers by the stream of gas. Water adsorbed on cellulose fibers might be expected to catalyze the degradation reaction, both chemically and by promoting adsorption of HCl molecules on the cellulose. No specific experiments were preformed to test this hypothesis, however.

(2) Electrical equipment
- (a) General Radio Capacitance Bridge type 716-C
- (b) General Radio Megohm Bridge type 544-BS4
- (c) General Electric resistivity test cell for liquids
- (d) Balsbaugh dielectric test cells
- (e) Fischer Isotemp oven
- (f) Dielectric Strength test equipment, consisting of the following:
  - (1) X-ray transformer, 8 KVA, 140 KV secondary voltage, 220 V. primary
  - (2) Sensitive circuit breaker
  - (3) General Radio Variac, type 50B
  - (4) General Electric Liquid Testing Receptacle, Catalogue No. 2248-09. Electrodes 1" diameter, 0.100" gap.
  - (5) General Electric A. C. voltmeter, type AR-2Y53.

Electrical tests were made on materials that gave favorable results in the tensile strength screening.

B. Results:

(1) Tensile Strength Screening Tests

Table 1 lists compounds found to be as good as or better than tetraphenyl tin, or for which quantitative proof was desired that the compound was inoperative. Compounds that were inferior to tetraphenyl tin are listed in Appendix A. The sources of the materials are given in Appendix C.

Tensil strength data are reported as per cent loss in tensile strength.

TENSILE STRENGTH SCREENING TEST

Table I-a

Scavenger	Source	Conc.,%	% loss in tens.str.	Remarks	Test No.	NB p.
Tetraphenyl tin	MT	0.05	93		139	67636
"	"	0.125	82		140	"
"	"	0.50	42		141	"
"	"	0.05	98	No H_2 sweep	144	"
"	"	0.125	50	of test tube	143	"
"	"	0.50	12	containing papers	142	"
"	"	1.00	0			
"	"	0.1	28	1/2 hr agitation in flask	22	59822
"	"	0.1	95	5 min " " "	45	65003
"	"	0.1	77		46	"
"	"	0.125	73		64	65004
					86	65004

Table I-b

Tetra-α(-thienyl tin	MD	0.1	38	Tests by R. H. Knight;	5	53229
Di-α(-thienyl tin	MD	0.1	79	used old method:	6	"
p-aminoazobenzene	EK	0.1	79		28	"
Carbide and Carbon G-18	CC	0.1	69	HCl admitted by	10	"
Meta-toluene-bis-ethylene ureа	MK	0.1	85	manometer pressure not gas buret.		
Ethyl orthosilicate	F	0.1	68		24	"
Tetraphenyl tin, ave. of 5 runs	MT	0.1	87		31	"
Advance Solvents Stabilizer P-1276	A	1.0	0	Very rapid HCl		
" " "	"	0.1	1	absorption, as	150	67636
" " " 3	"	1.0	4	indicated by	151	"
" " " "	"	0.1	94	manometer.	115	67635
" " " 52	"	1.0	29		103	"
" " " "	"	0.1	92		107	"
Tetra-2-furyl tin	MD	0.1	48		104	"
Dibutyl tin diethylate	MT	0.1	10	Very rapid action	122	67635
α-butyl glycydyl thioether	MD	0.1	27		74	65004
Paraplex G-60	RH	0.1	73	Very rapid action	44	65003
" "	"	1.0	4		75	65004
Carbide and Carbon A-5	CC	0.1	77		124	67635
Advance Solvent Stabilizer MSB	A	0.1	82		81	65004
" " "	"	0.1	76		106	67635
" " "	"	1.0	33		105	"
					108	"

Table I-c

Scavenger	Source	Conc.%	% loss tens.str.	Remarks	Test No.	NE #.
Tetralauryl tin	MT	0.05	105		131	67635
" "	(Also	0.5	90		129	"
" "	AL)	0.5	110		133	"
" "	"	1.0	98		109	"
" "	"	1.0	100		114	"
" "	"	1.5	74		130	"
Diphenyl tin dichloride	MT	0.05	102		136	67636
" " "	"	0.50	100	Pressure drop indicated some reaction with the HCl	134	67635
" " "	"	1.0	121		111	"
" " "	"	1.5	109		135	"
" " " no HCl	"	1.0	0		152	67636
Dibutyl tin dichloride	MT	1.0	118		112	67636
" " "	"	1.0	104		138	67636
" " "	"	1.0	0		148	67636

Table I-d

Dibutyl diphenyl tin	MT	0.125	77		85	65004
Tetraphenyl tin	MT	0.125	73		86	65004
Phenoxypropene oxide	S	0.10	51		66	"
Aluminum isopropylate	TEC	0.1	32	Very rapid action	61	"
" "	"	0.05	77		60	65003
Acridine	E (Also	0.1	77	Rapid action	47	"
"	EE)	0.1	42		54	"
"	"	0.075	103		52	"
"	"	0.05	125		49	"
"	"	0.05	113		51	"

Let a = tensile strength of papers after exposure to Pyranol containing no scavenger, but which had been treated with HCl.

Let b = tensile strength of papers after exposure to pure Pyranol which had not been treated with HCl.

Let x = tensile strength of papers which had been exposed to Pyranol containing the stated concentration of the scavenger under test, and which had been treated with HCl.

$$\% \text{ loss in tensile strength} = 100\,\frac{(b-x)}{(b-a)}$$

This method of treating the data applies equally well to the data obtained by Knight (with admission of HCl by manometer pressure instead of by gas buret). The only difference is that the correct value for the constant a was not so certain as when the gas buret was used. Also, the statistical fluctuations in a, and the systematic trends over a period of months, appear to have been more pronounced with the earlier method.

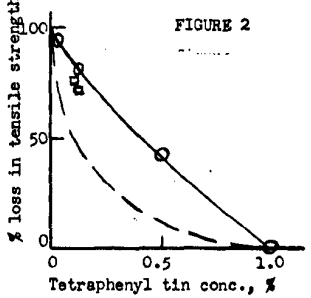
The tensile strength tests may be divided into 4 groups of experiments: (1) To establish the method, Table 1(a) (2) To discover new scavenger, (a) the earlier work of Knight; (b) the tests of the author; both in Table 1 (b) (3) To prove the broad claims of the O. E. patent on tin tetraphenyl to be invalid, Table 1 (c). (Negative results in this phase of the study are listed in Appendix B.) (4) To verify and extend previous results (e.g. on dibutyl diphenyl tin). Groups 2, 3 and 4 will be discussed under V, "Discussion".

(a) Estimate accuracy and significance of the method.

It is estimated that the precision of the tensile strength results in the middle range, as expressed in the table, is about 5 to 15%. (In the earlier work, the precision may have been about 20 to 40%.) Near 0 and 100% on the scale, the precision is better, probably about 3 to 5%. The term "accuracy" has little meaning in these tests except as to comparative values. In the comparison of results on different materials, particularly when the runs were near together in time, the accuracy is probably about 5%.

Figure 2 shows the data on loss in tensile strength vs. concentration of tin tetraphenyl, when the nitrogen sweep was employed and when it was not employed. (Data are from Table 1, tests 139 to 144). It is obvious that the type of curve obtained with the N_2 sweep, which is nearly linear, is much nicer for the comparison of compounds.

FIGURE 2



At 0.5% tin tetraphenyl, the actual tensile strengths were very nearly the same in tests with and without the N_2 sweep. The percent loss was much lower when the N_2 sweep was omitted, because the value of a (the no-scavenger tensile strength) was very much lower, 3.5 lb, vs. 25.5 lb when the N_2 sweep was employed. (The value of b ranged from 51 to 53 lb.) It is not worth while to attempt at present to explain the difference between the curves in figure 2, since a variety of unknown effects are certainly involved -- such as the rate reaction of scavenger with HCl, and the mechanism of attack of HCl on the cellulose.

A 30 minute sweep of N_2, with back pressure 2 cm, was adopted as the standard. A shorter sweep gave intermediate results. From figure 2 it may be seen that results depended strongly on N_2 sweep; it is thought that small fluctuations in the flow, whether or not they showed up in the back pressure, were probably responsible for most of the statistical fluctuations in the tensile strength results.

The two points in figure 2 indicated by circles, (tests 64 and 86) were obtained with the N_2 sweep. This indicates the range of uncertainty, referred to above, in the comparisons of tests run at relatively far apart times. We may take it that a scavenger that gave, at 0.1% concentration, a tensile strength loss less than 75%, was better than tetraphenyl tin. If the loss was above 85%, the scavenger was poorer.

A number of different three-necked flasks were used for the 1-l flask containing the Pyranol. In the earlier work of R. R. Knight, no effort was made to use flasks of matched volumes. In the first work of the author, the same flasks were used, but in all the runs listed in Table 1 (except those of Knight), matched flasks were used, having the same volume within about 5 cc. The diversity of volumes of the flasks led to a much greater per cent variations in the volume of the gas space above the Pyranol, and hence larger variations in the partial pressure of HCl from the solution. This contributed some uncertainty in the constant a, and decreases the quantitative value of the early experiments.

The quantity of Pyranol employed was in most cases 1400 g.
This quantity was chosen as standard because it gave the minimum gas space above the liquid, and hence caused the largest fraction of the HCl to dissolve in the Pyranol. 1000 g. was used in the first experiments (and a few of the later tests when the quantity of scavenger was very limited) and several tests were run with 1300 g. Qualitative comparisons of loss in tensile strength are valid as between runs using different quantities of pyranol; but quantitative comparisons of active scavengers should be made only with reservations. This is chiefly because of the question of molar excess: at a given scavenger concentration (say 0.1%), the HCl might be in a molar excess when 1000 g. of Pyranol, containing 1.0 g. of scavenger, was used; while the scavenger would be in excess when 1400 g. (i.e. 1.4 g. of scavenger) was used. This would not necessarily be automatically taken into account when the per cent tensile strength loss was calculated. (The difference between 1300 and 1400 g. of Pyranol is probably not serious.)

Tests 45 and 46 in Table 1, show the effect of the time of agitation of the Pyranol solution after admission of the HCl. Evidently the reaction of tetraphenyl tin is very far from instantaneous. Consequently, for slow-acting scavengers, the time of agitation plays a part in determining the precise value of the tensile strength result. This factor was probably one of the lesser sources of error.

(2) Electrical tests

The results of the various electrical tests that were made on these materials are shown in Table 2.

(a) The significance of the tests per se is as follows:

Dielectric strength is the measure of the ability of the fluid to prevent an arc between charged or current carrying components of the transformer. The precision of this test is relatively poor, and variations of 5 to 10 kv on a single sample are not uncommon. The mechanism of dielectric breakdown of liquids is very poorly understood at present. It is known that a large number of factors are involved, such as the rate of voltage rise, and the spacing, configuration, surface preparation, etc., of the electrodes. The effects of ionic contaminants, surface active agents, etc., are no doubt great, but there is little real knowledge.

In the tests listed in Table 2, only ethyl silicate can be regarded as at all significantly different from the other four materials; and it is not significantly different from the specification value, 35 kv. (See Appendix D)

Resistivity is the measure of the specific DC resistance of the fluid. It is in roughly an inverse relation to power factor (PF), which measures the AC conductivity. The inverse relationship actually holds only when the conduction is due to ionic contaminants, and when the ionic materials are of the same kind in the different samples compared. When the ions are different (and of course each different additive brings its own type of contaminant), all one can say is that an increase in PF generally accompanies a decrease in resistivity.

Low resistivity (or high PF) is harmful in a transformer because it leads to excessive heating of the fluid. In addition to specific electrode action, thermal degradation of the liquid and solid insulating material occurs, leading to yet lower resistivity and eventual arcing and failure.

The accuracy of PF and resistivity measurements is probably better than 5%. The measurements after 96 hr. at 100° (see Appendix D) are quite significant. Pyranol itself always increases in resistivity (possibly because of water being driven off). A lowering of the resistivity shows that the additive will be degraded by heat. This would lead to loss of the protecting power of the scavenger and more important, the further loss of resistivity in service, mentioned above.

Table 2

Electrical Tests

Scavenger	Conc. %	Dielectric Strength, KV	Resistivity, ohm-cm x10⁻⁹	PF at 60 Cycles %	After 96 hrs. at 100° Resistivity	After 96 hrs. at 100° PF	Remarks	MB p.
None			1900					50407
Tetra-4-thienyl tin	0.1	46						54310
Di-4-thienyl tin	0.1	42						"
Stabilizer G-12	0.1	51						" &
Ethyl Silicate	0.1	34	1950	0.65	950	3.4	Pyranol lot T-2 used for resistivity tests	65044
Tetraphenyl tin	0.1	51						54310
Phenoxypropene oxide	0.2		1800					50407
" "	0.2		1400					"
" "	0.4		530					50420,3
None (Lot T-2)			6300	0.65	11000	0.50		61580
Dibutyldiphenyl tin, pract.	0.125		80	27				59834
" " " distilled	.125		9100	0.77				"
" " " "	.125		3400	0.81			This material was shipped to Westinghouse	61560
1st cut from dibutyldiphenyl tin distillation	.125			12				59838
Acridine	0.1		300	6.0	210	9.0	Solution developed a slight yellow color on heating.	61572
Paraplex G-60	0.14			2.1	1480	2.0	Heated only 72 hrs.	64375
"	0.1		2250	1.75				65005
"	0.1		1970	2.2			Scavenger treated with attapulgus earth before mixing.	66711
Stabilizer No. 21	0.1		15		7.7			66225
" " E6B	0.1		566		554			"
" " 3	0.1		22		5.1			"
" " 52	0.1		53		45			"
Aniline	0.1		380	12.7				69637
None			4970	1.7				74822-6
Advance Solvents Stabilizers								
3	0.1		20.7	4.4				"
3, solution earth-treated	0.1		1760	3.8				"
3	1.0		1.6	—				"
3, solution earth-treated	1.0		1035	2.8				"
52	0.1		21	59				"
52, solution earth-treated	0.1		215	5.8				"
52	1.0		1.9	—				"
52, solution earth-treated	1.0		8.3	—				"

While the resistivities listed in Table 2 are generally far above G. E. specifications (of Appendix D), it should be noted that the observed resistivities of Pyranol 1467 have ranged from barely-meeting-specification (100×10^9 ohm-cm.) to above $10,000 \times 10^9$ ohm-cm. It is clear that scavengers that are more harmful to the resistivity will have less of a chance of finding acceptance.

(3) Hydrolysis tests of Organometallic Compounds

Very rough tests were made of the susceptibility to hydrolysis, on several scavengers. Information was desired on this point because transformer fluids are ordinarily exposed to some moisture in handling; it would be very undesirable to have to insist on special precautions against moisture.

Solutions of about 0.1 to 1% concentration of scavenger in Pyranol were exposed, in open test tubes, to air of about 45% and 60% RH. This was quite a mild test, so in addition, in separate tests a drop of water was added to about 5 or 10 cc of solution and the tube shaken. The tubes were examined for signs of a "skim" on the surface, or a precipitate.

Scavengers found highly susceptible to hydrolysis:

Dibutyl tin diethylate	Tetrabutyl titanate
Diphenyl tin dibutylate	Tributyl borate
Aluminum butoxide	

Scavengers only slightly to very slightly susceptible to hydrolysis:

Tetraethyl silicate	Diphenyl tin diethylate
Advance Solvents Stabilizer 3, 21 and 52	Aluminum isopropylate

It is thought that the lower susceptibility of diphenyl tin diethylate and aluminum isopropoxide may be related to their low solubility. The homologues in the first list were procured in hopes that they would be as rapid scavengers, and soluble as well. Rapid they were, but also hydrolyzable. The Advance Solvents stabilizers 3 and 52 are polymers formed by splitting out alcohol from compounds of the type dibutyl tin diethylate. By virtue of their polymeric nature, they were, apparently, able to stay almost entirely in solution irrespective of the attack of water. Ethyl silicate showed only a very faint haze on the third day after a drop of water had been added.

(4) Westinghouse Copper-Corrosion Test

Westinghouse in 1949 turned down three very active scavengers which we suggested to them (Monsanto products known as Methasan, Sopanox and SA326) on the basis of the following test: A burnished strip of copper is heated at 100° in a solution of the proposed scavenger in Pyranol, for four days. It was required that there should be no darkening of the copper.

Compounds that were satisfactory under this test were:

Dibutyl diphenyl tin	Diphenyl tin diethylate
Phenoxypropene oxide	Paraplex G-60
Aluminum isopropylate	Di-α-thienyl tin

Ethyl silicate and also acridine did not tarnish the strip; but with ethyl silicate a haze developed in the solution, and with acridine the solution developed a yellowish color. With a solution of dimethyl glyoxime, the submerged portion of the strip remained bright, but the portion above the liquid was badly tarnished. Tetra-α-thienyl tin produced a new effect: a thin layer of a bright yellow or brassy color appeared on the copper. It was as if some tin had plated out. The strip was left in contact with the solution for about 18 months at 25°; when examined again, the brassy color had been replaced by a brown tarnish. (The strip in contact with di-thienyl tin remained bright.) Tri-α-thienyl stibine produced a dark film on the copper.

(5) Compatibility of Scavengers: Phenoxypropene oxide was found to be compatible with tetraphenyl tin in solution in Pyranol. (Information on this point was requested by Westinghouse.) As would be expected, no precipitation from solution was observed, nor was there interference in HCl scavenging action.

(6) Odor of Phenoxypropene Oxide in Pyranol: Solutions of 0.1% and 0.3% Phenoxy-propene oxide in Pyranol 1488 were tested by a sniffing panel of four chemists. It was observed that the odor at 0.3% is slight but perceptible when compared with straight Pyranol. No distinguishable difference was noted at 0.1%. On heating to 50°C, the trichlorobenzene odor practically completely masked the phenoxypropene oxide odor even at 0.3%.

It was concluded that it would be very difficult to detect the odor of phenoxy-propene oxide unless a comparative sample of straight Pyranol was also sniffed.

V. Discussion

A. Tentative criteria for a "good scavenger"

(1) A good scavenger must react rapidly with HCl in the Pyranol medium to give an innocuous product. T. L. Dakin of Westinghouse has expressed the opinion (see trip report no. 722) that tetraphenyl tin is not a sufficiently rapid-acting scavenger. Some time ago they arced several transformers in order to obtain an on-the-job test of tetraphenyl tin. Dakin said the results were quite equivocal, as to whether tetraphenyl tin gave any appreciable protection. Hence they were really the most interested in scavengers that gave more and quicker protection.

Unfortunately, this positive criterion, that the scavenger be active and rapid, tends to be incompatible (in terms of chemical structure) with most of the other (negative) criteria listed below. For example, the amines react very rapidly with HCl, and can be had with very low equivalent weight. But they are generally harmful to the electrical properties of Pyranol, and are far from being sufficiently stable.

(2) The electrical properties of Pyranol (resistivity, power factor and dielectric strength) cannot be seriously affected. This eliminates materials that ionize strongly or that cannot be freed from ionizing contaminants.

(3) The scavenger must be stable indefinitely at elevated temperatures. No definite temperature limits can be set, but we can guess that temperatures above 130° are quite unlikely. The temperature 100° for 96 hours is specified by G. E. for an accelerated test. (See Appendix D)

(4) The scavenger must be unreactive towards all materials normally found in transformers and in the equipment used in handling Pyranol. This is the reason for the copper-corrosion test (see p. 13). Water is included under this heading, because it is ordinarily difficult to exclude water totally from the systems for handling Pyranol, and it is absorbed from the atmosphere when Pyranol is exposed to moist air.

(5) The scavenger must not have a high vapor pressure from solution in Pyranol at elevated temperatures. As a rough guess, we may exclude any substance with a normal boiling point below 100°; and boiling points above 150° should be satisfactory.

(6) The scavenger must be soluble in Pyranol. The solubility of tetraphenyl tin, about 0.5% at 25°, is considered to be too small, because the scavenger tends to come out of solution at low temperatures and because it prevents the use of higher concentrations for extra protection.

B. Discussion of Compounds Tested

(1) Active Scavengers of known composition

(a) Tetra-α-thienyl tin and di-α-thienyl tin. These compounds were found to be considerably more active than tetraphenyl tin. In the only electrical test made, they had no harmful effect on the dielectric strength. Tetra-α-thienyl tin was unsatisfactory according to the copper-corrosion test.

(b) Ethyl orthosilicate. This was a very rapid-acting scavenger. It failed to meet the thermal stability and hydrolysis tests, though it did not fall down extremely badly.

(c) Tetra-2-furyl tin was a very active scavenger. There was not sufficient sample left after the tensile strength screening test (and testing at St. Louis as a polyvinyl chloride stabilizer) to run any further test. The yield in the preparation had been very low.

(d) Dibutyl tin diethylate. Very rapid action as a scavenger. Very susceptible to hydrolysis.

(e) t-butyl glycydyl thioether. The presence of sulfur in the compound is highly undesirable, as leading to unstability and reactivity toward copper. No further tests were made on this material.

(f) Advance Solvents Co. poly alkyl alkoxy tin stabilizers, Nos. P-1276, 3 and 52. Very active and rapid. Only very slightly susceptible to hydrolysis. They did poorly on the thermal stability test, and were harmful to the electrical properties. Treatment with attapulgus earth produced a satisfactory resistivity in the case of No. 3, but did much less good for No. 52.

No. P-1276 was a special sample prepared by advance Solvents Co., to specifications: approximately the tetramer of $BuO[SnBu_2O]_nBu$. It was not as soluble as Nos. 3 and 52. Since Nos. 3 and 52 were the only ones commercially available at present, the further tests beyond the tensile strength screening were made on them only. The composition of Nos. 3 and 52 is not known beyond general formula, $RO[SnR_2O]_nR$.

(g) Meta-toluene-bis-ethylene urea and p-aminoazobenze are of molecular types known to be relatively unstable and harmful to the electrical properties of Pyranol. No further tests were made on them.

(h) Carbide and Carbon G-18 (glycidyl oleate) and A-5 ("glycydyl ether of diphenylol propane"):

$$(C_3H_8)\ (\bigcirc\!\!-O-CH_2CHCH_2)_2$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\quad O$$

Although the stated composition of A-5 sounds like the mono-ether, that substance would probably have too high an equivalent weight to show much scavenger activity. Hence we write the di-ether. No further tests were made on these, beyond the dielectric strength of G-18, which was satisfactory.

Since A-5 was active, it is anomalous that Epon 1164-1 (see Appendix A) was found inactive. (It gave a 95% loss in tensile strength in a test by the early method.) Possibly this was because of the lower accuracy of the earlier tests.

(2) Active Scavengers of Unknown Composition

Two of the three materials listed here are believed to be wholly organic polymers. The manufacturers have not disclosed their composition, to our knowledge at this writing. Since the Patent Department advises that we will have difficulties obtaining legal protection when we cannot specify the compositions, these materials were not pursued as thoroughly as others.

(a) Paraplex G-60. This appears to be very rapid in its action. It does not affect the electrical properties seriously, and stands the thermal stability test satisfactorily.

(b) Advance Solvents E6B. A little more harmful to the resistivity than was Paraplex G-60. Stands thermal stability test well. E6B is believed to be an epoxy compound.

(c) Advance Solvents No. 21. This is described as the cadmium salt of No. E6B. It caused a serious drop in the resistivity and did poorly on the thermal stability test.

(3) Proof of Non-validity of the Broad Claim of the G. E. Tetraphenyl tin Patent

The broad claims of U. S. Patent 2,468,544 which might be considered to dominate our patent on dibutyldiphenyl tin are as follows:

> "2. A normally liquid dielectric and insulating composition consisting essentially of halogenated aryl hydrocarbon and containing in solution by weight about one-fourth to one per cent of organo-metallic compound having the formula MR_x in which M is a metal chosen from the group consisting of tin, lead, and mercury; R is an organic radical chosen from the group consisting of aliphatic and aromatic radicals; combinations of such radicals and radical containing substituentes; and x is an integer in the range of 2 to 4.

3. A normally liquid dielectric and insulating composition consisting essentially of halogenated aryl hydrocarbon and containing in solution by weight about one-fourth to one per cent of organo-metallic compound having the formula MR_xY in which M is a metal chosen from the group consisting of tin, lead, and mercury; R is a radical chosen from the group consisting of aliphatic and aromatic radicals, combinations of such radicals, and such radical containing substituents, x is an integer in the range of 2 to 4, and Y is an inorganic substituent chosen from the group consisting of halogen and hydroxyl attached directly to the metal.

10. A liquid dielectric and insulating composition including chlorinated diphenyl as an ingredient and containing in solution by weight about 0.05 to 1 per cent of an organo-metallic compound of a metal selected from the group consisting of tin, lead, and mercury, the metal being attached directly to a carbon atom of an aromatic radical."

Claims 2 and 3 clearly cover tetralauryl tin. The results of the tensile strength screening tests, table 1-c, show that in the range up to 1.0%, tetralauryl tin is ineffective as a scavenger. At 1.5%, it shows some activity, though this result has not been confirmed.

Kharasch's series (see literature reference 10) predicts that ease of cleavage by HCl decreases with increasing alkyl chain length in alkyl tin compounds. We can be confident that a yet higher homologue, say tetraoctadecyl tin, would be even less active, or would show activity only at concentrations considerably higher than 1.5%. The increase in equivalent weight per se would certainly reduce the scavenger activity, and the Kharasch effect makes an additional contribution in the same direction. Hence we can conclude that claims 2 and 3 of the G. E. patent are not valid.

The data on diphenyl tin dichloride and dibutyl tin dichloride prove the non-valididity of other of the broad claims, including No. 10 in particular. It may be seen from Table 1-c that their action is, if anything, distinctly harmful. In the absence of HCl, no harm was done. Since the pressure drop indicated by the manometer was greater than that when no scavenger was used, the two substances must have reacted with the HCl. A possible mechanism is the following reaction:

$$R_2SnCl_2 + 2HCl \xrightarrow[\text{rapid}]{} H_2(R_2SnCl_4) \xrightarrow[\text{slow}]{} 2RH + SnCl_4$$

The chloroalkyl stannic acid postulated should be strong enough to attack the paper. If a substance such as this is an intermediate in the reaction of tetraphenyl tin with HCl, it must decompose rapidly. In the present case, it must persist for at least two hours, all the while increasing the effective concentration of HCl in the solution.

(4) Verification and Extension of Previous Results

Table 1-d shows, first, that dibutyldiphenyl tin is very slightly less effective as a scavenger than is tetraphenyl tin. The difference, is to small, however, to be considered significant.

Phenoxypropene oxide is definitely more active than tetraphenyl tin. The difference is certainly meaningful in this case.

Aluminum isopropylate is considerably more active than tin tetraphenyl. It was also a notably rapid scavenger. Westinghouse raised the objection that the final reaction product of this compound with excess HCl would be $AlCl_3$, and $AlCl_3$ is known to catalyze the decomposition of Pyranol with the evolution of yet more HCl. The single experiment at 0.05% was undertaken in order to test this objection. The result was negative, i.e., aluminum isopropylate was still beneficial at the lower concentration, although HCl was evidently present in excess.

These experiments were not pursued, because of the other drawbacks to aluminum isopropylate: its low solubility and appreciable susceptibility to hydrolysis. Besides, it was felt that a very extensive series of experiments would be necessary to convince Westinghouse, and the prospects of obtaining good enough proof were by no means certain.

Acridine was found to be a rapid-acting scavenger; but, surprisingly, at low concentrations it was found to be harmful. There is no obvious mechanism for this effect. In addition, acridine gave poor results in the thermal stability test by producing a decrease in the resistivity, and the solution became colored.

(5) Results Reported by Westinghouse

Westinghouse has reported that, as scavengers, dibutyldiphenyl tin and phenoxypropene oxide are satisfactory. Negotiations are being carried on at present through the sales department. Westinghouse is carrying out a study of the kinetics of the reaction of these and presumably other compounds with HCl. This is partly with the object of verifying our report to them that tetralauryl tin is a non-scavenger, and that the broad claim of the G. E. tetraphenyl tin patent is invalid.

They have stated that they are still interested in new rapid scavengers. We have sent them samples of Advance Solvents Stabilizers Nos. 3 and 52, as well as tetralauryl tin.

As mentioned on p. 3, Westinghouse purchased 55 gallons of Pyranol with dibutyldiphenyl tin scavenger in January, 1950, and a tank car of Pyranol with phenoxypropene oxide scavenger in January, 1952.

VI. Conclusions

Phenoxypropene oxide and dibutyldiphenyl tin are the materials that have shown up best, according to the criteria listed under V-A. As might be expected, we must compromise and sacrifice extremely rapid scavenging action in order to satisfy the other criteria. Particularly in view of Westinghouse's acceptance, we may conclude that these compounds constitute a satisfactory end for our search.

Next best, after the above two scavengers, rank the organic polymers (see V-B(2)). Paraplex G-60 was the most extensively tested, and would very possibly be satisfactory to Westinghouse. Advance Solvents E6B and Carbide and Carbon G-18 and A-5 might very possible be found satisfactory on more extensive tests. These have not been pursued because the Patent Department advises us that we will probably be unable to obtain legal control of the materials in the absence of knowledge of their structures.

There are various drawbacks to the other materials discussed above — in some cases absolutely prohibitive, in others only "possibly" or "probably" fatal. It is not profitable at present to attempt to rank these materials in order of merit.

VII. Recommendations

In view of the favorable reports from Westinghouse on phenoxypropene oxide and dibutyldiphenyl tin, it is recommended first that we devote no more time to the search for new scavengers.

Second, if for any reason it should be decided to reopen the project, it is recommended that we concentrate first on the polymeric type scavengers. Either we should offer said scavengers to Westinghouse after a minimum of further tests of electrical properties, etc.; or else we should attempt to duplicate these materials ourselves. The latter suggestion is made because it is believed that Paraplex G-60 is not specifically protected by patents. Rohm and Haas (its manufacturer) are reported to have declined to reveal its composition, and to have intimated that the proprietary formula and "know how" are their only protection. (The Paraplex resins are believed to be of the polyester type.)

It is reported that some epoxidized polyester resins are being prepared at Dayton. These should be investigated if the scavenger job is reopened.

VIII. Description of Recommended Process

Does not apply.

IX. Patent Status

The Patent Department has expressed the opinion that, in view of the inactivity of tetralauryl tin and diphenyl tin dichloride as scavengers, the broad claims Nos. 2, 3 and 10 of the G. E. tetraphenyl tin patent are invalid. Hence we are free to sell Pyranol protected by dibutyldiphenyl tin.

They have also expressed the opinion that the U. S. application of G. E., corresponding to British Patent 601,359, covering phenoxypropene oxide as an HCl scavenger, will never issue. Hence we are free to sell Pyranol protected by phenoxypropene oxide.

The following patent applications have been filed, and those that have been issued at the date of this writing are noted.

1. Case A-36 Russell L. Jenkins - Ser. No. 691,652 - Filed Aug. 19, 1946
STABILIZATION OF HALOGENATED ORGANIC COMPOUNDS WITH DIBUTYL DIPHENYL TIN

This application covers the use of dibutyl diphenyl tin as a scavenger for Pyranol.

Patent No. 2,578,359. Issued Dec. 11, 1951.

2. Case A-54 Edgar E. Hardy - Ser. No. 38733 - Filed July 14, 1948
COMPOSITIONS OF MATTER COMPRISING HALOGENATED ORGANIC COMPOUNDS.

This application covers the use of biguanide and its substituted derivatives as scavengers for Pyranol.

3. Case A-56 Elwood F. Jackson - Ser. No. 49986 - Filed Sept. 18, 1948
DIELECTRIC WITH N,N'-1-3 DIMORPHOLINO ISOPROPANOL AS SCAVENGER

This application covers the use of morpholine and its substituted derivatives as scavengers for Pyranol.

Patent No. 2,572,808. Issued Oct. 23, 1951.

4. Case A-58 Edgar E. Hardy - Ser. No. 53695 - Filed Oct. 9, 1948
COMPOSITIONS OF MATTER COMPRISING HALOGENATED ORGANIC COMPOUNDS.

Patent No. 2,532,616. Issued Dec. 5, 1950

This application covers the use of zinc dithiocarbamate and derivatives thereof as scavengers for Pyranol.

5. Case A-59 Edgar E. Hardy and Robert J. Slocombe - Ser. No. 53696 - Filed Oct. 9, 1948
DIELECTRIC COMPOSITION OF HALOGENATED AROMATIC COMPOUND AND ALUMINUM ISOPROPYLATE AS A CORROSION INHIBITOR.

Patent 2,566,195. Issued Aug. 28, 1951.

This application covers the use of aluminum isopropylate as a scavenger for Pyranol.

6. Case A-60 Russell L. Jenkins - Ser. No. 54258 - Filed Oct. 13, 1948
DIELECTRIC COMPOSITION OF HALOGENATED AROMATIC HYDROCARBON AND ORGANIC ANTIMONY COMPOUND AS A CORROSION INHIBITOR.

Patent 2,566,208. Issued Aug. 28, 1951.

This application covers the use of stibines as scavengers for Pyranol.

7. Case A-61 Edgar E. Hardy - Ser. No. 57968 - Filed November 2, 1948
COMPOSITIONS OF MATTER COMPRISING HALOGENATED ORGANIC COMPOUNDS.

This application covers phenoxy propene oxide, butadiene monoxide and styrene oxide as scavengers for Pyranol.

8. Case A-62 Edgar E. Hardy - Ser. No. 67662 - Filed Dec. 28, 1948
CHLORINATED AROMATIC DIELECTRIC WITH SCAVENGER

Patent No. 2,566,196. Issued Aug. 28, 1951

This application covers the use of aminated-N-phosphoryl-o-amino biphenyl as a scavenger for Pyranol.

9. Case A-63 Edgar E. Hardy - Ser. No. 67663 - Filed Dec. 28, 1948
COMPOSITIONS OF MATTER COMPRISING HALOGENATED ORGANIC COMPOUNDS.

This application covers the use of diphenyl guanidine as a scavenger for Pyranol.

10. Case A-64 Edgar E. Hardy, Elwood F. Jackson and Robert J. Slocombe
Ser. No. 67664 - Filed Dec. 28, 1948
COMPOSITIONS OF MATTER COMPRISING HALOGENATED ORGANIC COMPOUNDS

This application covers the use of pyridine and its substituted derivatives as scavengers for Pyranol.

11. Case A-65 Edgar E. Hardy and Elwood F. Jackson - Ser. No. 67665 Filed Dec. 28, 1948
COMPOSITIONS OF MATTER COMPRISING HALOGENATED ORGANIC COMPOUNDS.

This application covers the use of dimethyl glyoxime as a scavenger for Pyranol.

12. Case A-66 Edgar E. Hardy and Elwood F. Jackson - Ser. No. 67666 Filed Dec. 28, 1948
COMPOSITIONS OF MATTER COMPRISING HALOGENATED ORGANIC COMPOUNDS

This application covers the use of o-anisidine, p-anisidine, p-nitro aniline and 2,4-diamino diphenylamine as scavengers for Pyranol.

13. Case A-67 Russell L. Jenkins - Ser. No. 67388 - Filed Dec. 27, 1948
COMPOSITIONS OF MATTER COMPRISING HALOGENATED ORGANIC COMPOUNDS.

This application covers the use of diphenyl tin diethylate as a scavenger for Pyranol.

14. Case A-82 Buford H. Hartzog - Ser. No. 110,518 - Filed Aug 16, 1949
COMPOSITIONS OF MATTER COMPRISING HALOGENATED ORGANIC COMPOUNDS

Patent No. 2,582,200. Issued Jan. 8, 1952

This application covers the use of ethyl silicate as a scavenger for Pyranol.

15. Case A-83 Arthur M. Ellenburg - Ser. No. 109,576 - Filed Aug. 10, 1949
COMPOSITIONS OF MATTER COMPRISING HALOGENATED ORGANIC COMPOUNDS.

Patent No. 2,573,894. Issued Nov. 11, 1951

This application covers the use of thienyl tin as a scavenger for Pyranol.

16. A-106 Arthur M. Ellenburg and Robert J. Good - Ser. No. 260,156 - Filed Dec. 6, 1951
COMPOSITIONS OF MATTER COMPRISING HALOGENATED AROMATIC COMPOUNDS.

This application covers the use of a polyalkyl alkoxy tin compound as a scavenger for Pyranol.

An application is in preparation on tetra-2-furyl tin as a "new composition of matter", having utility as an HCl scavenger.

X. Cost Estimates

Not applicable

XI. Material Specifications, Analytical Procedures

See Appendix D for specifications for various Pyranols.
See Apendices E and F for the manufactures' specifications on dibutyldiphenyl tin and phenoxypropene oxide. See literature reference 12 for method of analysis for epoxides.

The electrical tests were made according to the following methods (see the Dielectrics file):
(a) "Procedure for Testing Dielectric Media for Dielectric Constant and Power Factor", 9-14-50, by R. J. Good.
(b) "Procedure for Dielectric Strength Testing", 10-4-48, by R. R. Knight. (This has since been revised, mainly by the addition of more detail in the instructions, by R. J. Good, 12-27-50.)

XII. Toxicity and Hazards

Does not apply

XIII. Acknowledgement

The author wishes to express his thanks to those who carried out the earlier phases of this study (see references 1 to 7); to Dr. R. L. Jenkins and Dr. E. E. Hardy for their active interest and encouragement throughout the project; and to Central Research at Dayton for their helpful suggestions and for the synthesis of compounds that would otherwise have been unavailable.

APPENDIX A

Compounds found to be less active scavengers than tetraphenyl tin, by tensile strength screening test.

	Source
Lead monomethyl triisobutenyl succinate	MD
Carbazole	B
Anethole	F
Isosafrol	EK
Eugenol	EK
Santovar O	M
Hydroquinone	EK
Benzil	EK
Stabilizer JCX	A
" XB12	A
" MD50B	A
" XB14	A
Plastoflex VS	A
Dioctyl dioctoxy silane	MD
Tetrabutyl titanate	AL
Tributyl borate	AL
Tetra-2-ethylhexyl silicate	MD
Dimethyldiethoxy silane	AL
Methyl triethoxy silane	AL
Amyl " "	AL
Phenyl " "	AL
Tetrabutyl silicate	AL
p-nonylphenoxypropene oxide	MD
Tri-p-chlorophenyl stibine	MD
Methyl-9,10-epoxystearate	MD
Dimethylphenylglycidate	MD
Sintol T (condensation product of toluene and sulfur by Friedel-Crafts reaction)	MD
Epon 1164-1 (x,x'-bis-glycydyl biphenyl)	S
2-chlorothiophene	SV
2,5 dichlorothiophene	SV
2,3,4,5, tetrachlorothiophene	SV
4,4' diphenylmethane-bis-ethyleneurea	ME
Melamine	M or EK
Triphenyl phosphine	EK
2,7 dihydroxynaphthalene	EK
Stannic octyl phosphate	MA
Oleic acid	F
Dibenzyl	EK
Tin oleate	F
Camphene	EK
Antimony salt of t-dodecyl mercaptan	M
Antimony Trioxide	H and also B

APPENDIX B

Compounds covered by the broad claims of the G. E. tetraphenyl tin patent, found to be active scavengers.

	Source
Diphenyl mercury	EK
Dibutyl "	EK
Tetrabutyl tin	MT
Triphenyl tin chloride	MT
Tetra - (p-biphenyl) tin	MD
Tetramethyl tin	MD
Tetrabenzyl tin	MD

APPENDIX C

Code of manufacturers.

A	Advance Solvents Co.
AL	Anderson Laboratories, Adrian, Michigan
B	J. T. Baker
CC	Carbide and Carbon
EK	Eastman Kodak
F	Fischer Scientific Co.
H	Harshaw
M	Monsanto
MA	Monsanto, Anniston
MD	Monsanto, Dayton
ME	Monsanto, Everett
MT	Metal and Thermit Co.
R	Reilly Tar and Chemical Co.
RH	Rohm and Haas
S	Shell Chemical Co.
SV	Socany-Vacuum
TEC	Tennessee Eastman Corp.

APPENDIX D

No. 1488 Pyranol Specifications

Composition	- 60% No. 1482 Pyranol (Aroclor 1260) by weight - 40% No. 1478 Pyranol (trichlorobenzene) by weight
Viscosity at 37.8°C.	- 54" ± 2" Saybolt Universal
Gravity at 15.5/15/5°C.	-1.560 - 1.568
Color (APH)	- 150 maximum
Acidity	- Less than 0.01 mg NaOH/gram
Free chlorides (H-6845480)	- .10 ppm max.
Fixed chlorine	- 59.1% minimum
Burn Point	- None up to the boiling point
Pour Point	- Lower than -32°C.
Distilling Range 1st Drop Below 270°C. 90% point	 - 200°C. minimum - 40% maximum - 385 - 400°C.
Corrosion (H-3954201)	- After heating with aluminum for six hours at 200-220°C., the aluminum must not be corroded either on visual or weight inspection and the Pyranol should meet the following specifications:- Color..... 200 APH Acidity..... .01 Free Chlorides. .10 ppm max. Condition..... Clear
Chemical Stability	- (1) No generation of free chlorides when refluxed with distilled water in presence of air for 6 hours. (2) No free chloride generation when heated with distilled water in sealed glass bomb at 150°C. for 6 hours.
Arc-formed Gases (oxygen-free liquid at 25°C.)	- (1) Less than 1.0% total combustible gases including carbon monoxide, hydrogen and volatile hydrocarbons.

Dielectric Constant at 1000 cycles	
at 100°C.	- 3.5 - 3.8
at 25°C.	- 4.0 - 4.3
Analysis of Products of Fractional Distillation	- When fractionally distilled, the distillate shall be separated into 10-cc boiling fractions. No fraction on analysis shall show less than one chlorine atom for each hydrogen present in the mixture. This shall be determined by chemical analysis. No fraction of the distillate so collected shall give more than 1.5% total combustible gases on arcing (Including carbon monoxide, hydrogen and volatile hydrocarbons).
Refractive Index at 25°C.	- 1.6137 - 1.6147

No. 1467 Pyranol Specifications

Composition	59.5% O. B. 1482 (1260) 40.5% O. B. 1478 (TCB) plus 0.125% Tin tetraphenyl by wt.
Tin Tetraphenyl content	0.125% ± 0.01%
Viscosity at 37.8°C	52-56 Saybolt Universal Seconds
Sp. Gr. at 15.5/15.5°C	1.560-1.568
Color APHA	150 max.
Acidity, mgm. NaOH/gm	0.01 max.
Free chlorides	0.1 ppm max.
Fixed chlorine	59.1% min.
Condition	Clear
Burn point	None to boiling pt.
Pour Point	Lower than - 32°C
Distilling Range	
1st dup	200°C min.
40%	270 or higher
90%	385-400°C
Resistivity at 100°C	100×10^9 ohm cm minimum
Diel. Constant at 1000 cycles 100°C	3.5-3.8
" " 25°C	4.0-4.3
Refractive Index at 25°C	1.6137-1.6147
Water ppm	<30
Corrosion (H-3954201)	after heating with aluminum foil for 6 hours at 200-220°C, the aluminum must not be corroded either on visual or weight inspection and the Pyranol should meet the following specifications.

MONS 088523

Color	200 A.P.H.
Acidity	.01 Max.
Free chloride	5 ppm Max
Condition	Clear

Arc-formed gases (oxygen-free liquid at 25°C)	Less than 1.0% total combustible gases including carbon monoxide, hydrogen and volatile hydrocarbons.
Dielectric Strength at 25°C	Greater than 35 KV.
" at 100°C	" 35 KV.
Electrical Stability	after heating 1467 Pyranol for 96 hours at 100°C in a closed container, the resistivity shall not be less than 25 x 10^9 ohm cms at 100°C or have a decrease in resistivity over the original greater than 10%.
	The container shall contain 85% of its volume as 1467 Pyranol and 15% of its volume as air.
Analysis of Products of Fractional Distillation	When fractionally distilled, the distillate shall be separated into 10 cc. boiling fractions. No fraction on analysis shall show less than one chlorine atom for each hydrogen present in the mixture. This shall be determined by chemical analysis. No fraction of the distillate so collected shall give more 1.5% total combustible gases on arcing (including carbon monoxide, hydrogen and volatile hydrocarbons).

No. 1478 Pyranol Specifications (Trichlorobenzene)

Composition	a technical mixture of TCB
Viscosity at 37.8°C.	28 to 32 Sabolt Universal Seconds
Gravity at 15.5/15.5°C	1.460-1.477
Refractive Index at 25°C	1.5680-1.5715
Color	15 APH Max.
Free Acidity	less than 0.01 mg. NaOH/gm.
Free Chloride	0.10 ppm max.
Fixed Chlorine	58.5% minimum
Burn point	None to boiling point
Four Point (Freezing Point)	Lower than 10°C
Condition	Clear
Distilling Range (Corrected)	
1st drop	205°C. min.
5% point	210°C. min.
50% point	213°C. min.
90% point	215°C. min.
Water	75 ppm
Dielectric Strength	Greater than 30 KV

Corrosion	after heating with aluminum foil for 6 hours at 210°C. ± 10°C, the aluminum must not be corroded either on visual or weight inspection, and the Pyranol should meet the following specifications: Color 200 APH max. Acidity (mg NaOH/gm) 0.01 max. Free Chloride (ppm) 0.10 max. Condition Clear
Arc-Formed Gases	Total combustible gases (including carbon monoxide, hydrogen and voltatile hydrocarbons) —less than 1.5%.
Chemical Stability	(1) No change in color or acidity, no formation of free chlorides when refluxed with water in the presence of air for 6 hours. (2) No free chloride generation when heated 6 hours in a glass sealed bomb with distilled water at 150°C. (3) No free chloride generation on exposure to direct sunlight for a minimum of 30 days at normal temperature. No color or acidity increase from original value.

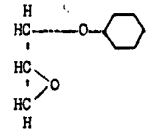
No. 1482 Pyranol Specifications (Aroclor 1260)

Burn Point (ASTM D-92)	Greater than 350°C.
Viscosity at 98.7°C. (ASTM D-88)	73-78 S.U.S.
Specific Gravity at 90°C/15.5°C. (ASTM D-287)	1.550-1.560
Pour Point (ASTM D-97	30°C + 4°C.
Color	150 APH max.
Acidity mg. NaOH/g	less than .01
Chlorides	0.10 ppm max.
Sulfates (ASTM D-117)	None
Evaporation at 100°C for 6 hrs.	less than 0.2%
Distillation Range (ASTM D-20)	10% Point 370-377°C. 50% Point 377-385°C. 90% Point 385-400°C.
Refractive Index, 25°C.	1.6460 ± .0005
Stability	There shall be no liberation of chlorine or chlorides when the material is heated to 100°C. in a glass vessel in contact with air for periods of at least one month.
Fixed Chlorine Content (Carius)	60% ± 1/2%
Resistivity 100°C	500 x 10^6 ohm cm. min.

Corrosion	after heating with aluminum for six hours at 210°C ± 10°C., the aluminum must not be corroded either on visual or weight inspection and the Pyranol should meet the following specifications:
	Color APH 150 max.
	Free chlorides 0.1 ppm. max.
	Acidity mg NaOH/gm .01 max.
	Condition Clear
Dielectric Strength 50°C.	30 K.V. min.
" " 100°C.	30 K.V. min.
Water content ppm.	35 max.

APPENDIX E

GLYCIDYL PHENYL ETHER (Phenoxypropene Oxide)



Molecular Formula	$C_9H_{10}O_2$	Molecular Weight 150.17
Boiling Point	245°C at 760 mm.	
Melting Point	+3.5°C	
Flash Point (Tag Open Cup)	175°F = 79°C	
Specific Gravity (vac.)	$d\frac{0}{4}$	1.1273
	$d\frac{10}{4}$	1.1183
	$d\frac{20}{4}$	1.1092
	$d\frac{30}{4}$	1.1001
	$d\frac{40}{4}$	1.0913
	Coefficient of Expansion	(22.5°C) 0.00081 per °C. (27.5°C) 0.00081 per °C.
Refractive Index	$n\frac{20}{D}$	1.5314
	$n\frac{20}{C}$	1.5269
	$n\frac{20}{F}$	1.5428
	$n\frac{25}{D}$	1.5290
Refractive Dipersion	$(n_F - n_C) \times 10^4 = 159.2$	
Viscosity	t°C	Centipoise
	20	7.05
	30	4.88

Surface Tension

t°C	Dynes/Cm.
20	41.7

Solubility at 20°C, %:

0.24 compound in water

0.4 water in compound

12.9 compound in octane

10.0 octane in compound

Miscible with acetone and toluene

Vapor Pressure

t°C	P mm. of Hg.
120	11.41
130	18.25
140	28.30
150	42.67
160	62.69
170	89.99
180	126.47
190	174.3
200	235.9
245	760

$$\log p(\text{mm.}) = 6.97812 - \frac{1657.89}{t(°C) + 160.00}$$

Toxicity

Tests on animals show glycidyl phenyl ether to be a toxic material and to produce phenol type burns after exposure to the skin. The vapor hazard at normal temperatures is not serious due to its low vapor pressure.

Adequate precautions should be observed in handling this material to prevent spillage. If accidental spillage does occur, the affected area should immediately be washed with water and then alcohol.

Shell Development Company

Emeryville, California

Bulletin DS-47:19

APPENDIX F

Dibutyl Diphenyl Tin

Formula $(CH_3CH_2CH_2CH_2)_2Sn(C_6H_5)_2$

Formula Weight - 387

Contains - 30.7% Sn

A clear slightly greenish liquid

Insoluble in water. Soluble in most organic solvents.

Boiling Point - 175° at 2 mm.

Refractive Index - 1.563 at 17.50 C.

Density 1.19

Metal and Thermit Corp.

New York, N. Y.

Bulletin, 1949

APPENDIX G

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APPENDIX H

Monsanto Chemical Company
Research Department - Phosphate Division
Anniston, Alabama

HCL Scavenger Test Method

Scope: This is the method used here for screening suggested HCl scavengers for transformer Pyranols. It is intended to give a semi-quantitative comparison of scavenger activity, using tetraphenyl tin (an accepted scavenger) as a reference compound.

Equipment: (See sketch, p. 4 of main report)
1 Heating bath with thermostat attachments
1 1-l. 3-necked flask with 35/25 spherical joints
1 Flat ended test tubes, 2 1/2"i.d. x 10"
1 No. 13 rubber stopper
1 High-speed stirrer motor
1 Stirrer bearing with lubricated seal to impeller shaft
1 Hoesch-type impeller
1 Adapter for introducing gas
1 Adapter for bottom take-off of liquid from flask.
1 Glass rod support (see sketch)
1 Glass weight (see sketch)
10 Glass ring spacers
1 Gas-sampling bulb, approximately 275 ml capacity
1 Separatory funnel, to be used as mercury reservoir and levelling bulb
1 Water aspirator
1 U-tube mercury manometer
1 Beaker, 600 ml or larger
8 2-way stopcocks, 2 mm bore
2 3-way stopcocks, 2 mm bore
(Note: Stopcock lubricant should not be a silicone. "Celvacene Medium" is satisfactory.)
Glass tubing, 8 mm o.d., for T's, connections, etc., (see sketch)
Tygon tubing to connect glass tubing
1 Sulfuric acid drying train for HCl
6 Strips of 3 mil manila cable wrapping paper (manufactured by John A. Manning), cut in strips 7" x 1", with hole punched 1/2" from each end. (Tensile strength about 50 lb per inch under the tests described below.)

Chemicals:
Pyranol 1488 (60% Aroclor 1260, 40% trichlorobenzene, by weight)
HCl scavenger to be tested
Anhydrous HCl (cylinder)
Dry nitrogen (cylinder)
Mercury
Sulfuric acid, conc.
Methanol
Benzene

Procedure:

(1) A solution of the scavenger under test, in Pyranol 1488,is prepared. 1400 g of this solution are placed in the 1-l flask, and allowed to come to the temperature of the bath. The papers are suspended on the arm of glass rod support, separated by the spacer rings, and threaded on the glass weight (with spacers). The mercury is adjusted so that only the bulb and tubing down to stopcock 6 contain mercury. The bulb is supported on a ring-stand at such height that when the gas-sampling bulb is full of mercury, up to stopcock 3, the level in the bulb is above stopcock 3. The beaker is filled with water.

(2) HCl from the drying train is swept through the gas-sampling bulb, with the exit gas being passed into the beaker of water, until the lack of bubbles indicates that all air has been swept out. At the same time, the space above the Pyranol in the 1-l flask is evacuated several times and dry nitrogen is admitted after each evacuation. A slow sweep of dry nitrogen is passed through the test tube containing the papers. The rate and duration of this sweep must be reproduced as closely as possible. In the tests described in Report 2755, the time was 30 minutes and the rate was such as to give a back-pressure of 2.0 cm on the manometer.

(3) The HCl is diverted (at stopcock 1) from the sampling bulb, stopcock No. 5 is opened and No. 4 closed, and then the HCl may be turned off. The flask is evacuated, stopcock No. 9 is closed and No. 7 is turned, opening the bulb to the flask. Stopcock No. 6 is opened, and the mercury is allowed to displace the HCl from the bulb up to stopcock No. 3.

(4) Stopcock 7 is next closed, and the high-speed agitator started. The Hoesch-type impeller gives very rapid absorption of the HCl into the Pyranol, by projecting streams of liquid through the gas space. Nitrogen is admitted from time to time, to keep the pressure inside the flask up to atmospheric pressure.

(5) After 20 minutes agitation, the motor is turned off, and enough Pyranol is blown over (with nitrogen) into the test tube to cover the paper strips completely. The papers are allowed to soak in the Pyranol for 1.5 hours. They are then removed from the Pyranol, soaked for 15 minutes in benzene followed by 15 minutes in methanol, and placed on a paper towel to dry. When dry, 1/2 inch is cut from each end, leaving strips 1" x 6".

(6) The tensile strengths of the strips of paper are determined on a Scott IP2 Serigraph, having a jaw separation of 3 inches and a rate of travel of 34.5 seconds for a load of 40 lb. Those papers that do not break under a 40 lb. load are cut to a narrower width, and a suitable correction factor applied. Before testing, the papers are humidified at 65% RH and 70°F for a minimum of 48 hours. The tensile strength is reported as the average of six breaks.

Reporting Results:

With every series of scavengers tested, there should be run (1) at least two sets of papers treated with Pyranol containing neither HCl nor scavenger (let b = average tensile strenght from these tests). (2) at least three sets of papers treated with Pyranol containing no scavenger, but which had been treated with the HCl. (Let a = average tensile strength from these tests.)

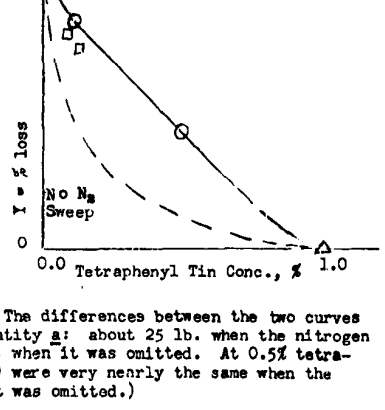
Then if x = average tensile strength of papers that had been exposed to Pyranol containing the scavenger under test, and which had been treated with HCl.

$$Y = \% \text{ loss in tensile strength} = 100\ \frac{(b-x)}{(b-a)}$$

Alternatively, the values of a, b and x may be reported.

Standardization:

The accompanying figure shows a series of tests using the method described above, with varied tetraphenyl tin concentration. The three circles were obtained in a closely-spaced series of tests, and the two squares in another closely-spaced series. The point represented by the triangle, at 1% tetraphenyl tin, was obtained a considerable time earlier than the rest of the points, and perhaps it should not be taken too seriously.



(When the nitrogen sweep was omitted, the dashed curve was obtained. The experimental points for this curve are not shown. The differences between the two curves was due to different values of the quantity a: about 25 lb. when the nitrogen sweep was employed, and less than 5 lb. when it was omitted. At 0.5% tetraphenyl tin, the tensile strengths (x's) were very nearly the same when the nitrogen sweep was employed and when it was omitted.)

Notes and Discussion

This is not intended as a "final" form of the scavenger screening test. It was actually a compromise between the method as it existed when the author started on the project, and a form toward which it was evolving. While it was held constant during the last two major series of tests, several experiments were made (e.g. the variation of the nitrogen sweep) which pointed to some further changes. Certain changes would, no doubt, have improved the quantitative nature of the method.

While only one each of the 3-necked flask, test tube, glass rod support, etc., are specified, it is found convenient to have at least two and preferably three, in order to carry on semi-simultaneous experiments. The 3-nscked flasks should be of matched volumes, to within 10 cc or closer if possible.

R. J. Good

adl
3/27/52