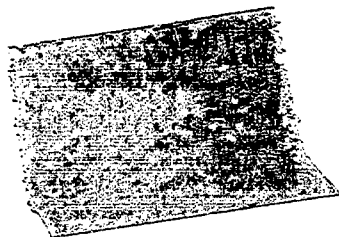


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**DETERMINATION OF THE MECHANISM
OF THE INCREASE OF VISCOSITY
OF ORGANOSILICON COMPOUNDS
AT HIGH TEMPERATURES**

O. F. SENN

STANFORD RESEARCH INSTITUTE

FEBRUARY 1955

WRIGHT AIR DEVELOPMENT CENTER

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O. F. SENN

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FEBRUARY 1955

MATERIALS LABORATORY
CONTRACT No. AF 33(616)-168
PROJECT No. 7340

WRIGHT AIR DEVELOPMENT CENTER
AIR RESEARCH AND DEVELOPMENT COMMAND
UNITED STATES AIR FORCE
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

FOREWORD

This report was prepared by Stanford Research Institute under Contract No. AF 33(616)-168. The contract was initiated under Project No. 7340, "Rubber, Plastic and Composite Materials", Task No. 73404, "Synthesis and Evaluation of New Polymers", formerly RDO No. 613-15, "Hydraulic Fluids and Lubricants", and was administered under the direction of the Materials Laboratory, Directorate of Research, Wright Air Development Center, with Capt J. F. O'Brien acting as project engineer.

The help of Mrs. A. Stafford, Miss C. Willard, and Dr. H. J. Eding of Stanford Research Institute in the procurement of data is gratefully acknowledged.

ABSTRACT

Oxidation of alkoxy- or aryloxysilanes is inevitably accompanied by hydrolysis. Oxidation rates were determined for tetraphenoxysilane, tetra(2-ethylhexoxy)silane, hexa(2-butoxy)disiloxane, and a series of isomeric tetrapentoxysilanes. The presence of 1020 steel, titanium, and copper during oxidation did not produce large changes in rate as compared to the rate for the test material alone.

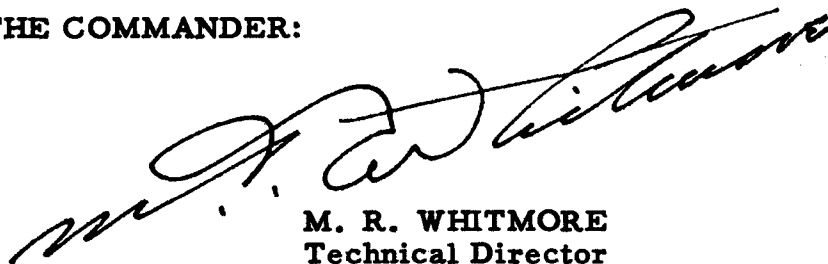
The hydrolysis of tetraaryloxy- and alkoxysilanes apparently proceeds through a stepwise degradation. The rate of hydrolysis is affected largely by structure, being very rapid for tetraphenoxysilane, less rapid for tetra(2-ethylhexoxy)silane, and slow for branched tetrapentoxysilanes.

Pyrolysis is probably the least important factor in the degradation of the tetraaryloxy or alkoxysilanes. No significant degradation was observed with tetraphenoxysilane while tetra(2-ethylhexoxy)silane was degraded only slightly by thermal cracking of the 2-ethylhexyl group.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:



M. R. WHITMORE
Technical Director
Materials Laboratory
Directorate of Research

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SECTION I. INTRODUCTION

The United States Air Force is engaged in a comprehensive study of synthetic hydraulic fluids capable of operating over a broad range of temperature. The present goal is a fluid operable from -54°C (-65°F) to $+204^{\circ}\text{C}$ (400°F), and it is anticipated that this range will be extended in the future. Several organosilicon compounds have shown promise in meeting these severe temperature requirements, but have one undesirable characteristic: a tendency to increase in viscosity irreversibly, sometimes even to gelation, when held for long periods at high temperature. The purpose of the project undertaken at Stanford Research Institute is to study the factors involved, and the mechanism of the processes, which lead to the increase in viscosity. The ultimate objective is to avoid this undesirable effect either through proper choice of the organosilicon compound or through the addition of an effective inhibitor.

SECTION II. PRELIMINARY LITERATURE SURVEY

In the initial part of this project a literature survey was undertaken. The pertinent findings are summarized in the following paragraphs.

The organosilicon compounds of greatest interest for hydraulic fluids at present are the so-called organosilicates, which may be monomeric derivatives of the hypothetical orthosilicic acid (or low polymers of it, such as hexalkoxydisiloxane) or highly polymerized polyalkylsiloxanes, as exemplified by the methyl silicone oils. It is, therefore, convenient for purposes of discussion to divide the compounds of interest into two classes: the so-called silicates, which are actually tetraalkoxysilanes or tetraaryloxysilanes with silicon bonded to carbon through oxygen; and the silicones, which are generally long-chain compounds with silicon bonded direct to carbon. This distinction is arbitrary since it is possible to synthesize alkylalkoxysiloxanes which would fall into either classification. The alkoxy-silanes have been used in England for technical and industrial purposes,^{1/} whereas until recently in the United States more attention has been given to the silicones. The silicones have, in the present connection, the advantage of good viscosity-temperature relationships and stability toward hydrolysis. They have, however, the disadvantages of poor wear characteristics and very high cost. Both the alkoxy-silanes and the silicones undergo an increase in viscosity when maintained at high temperature. Except for the case where a lower-boiling compound is being removed from a mixture, the viscosity increases which occur

^{1/} For superscript numbers see References.

are irreversible. There is no indication in the literature of the formation of physical aggregates such as are found in ordinary greases. Some of the reactions which may occur are considered in the following discussion:

Rearrangement Reactions. In the case of mixtures of alkoxy- and aryloxysilanes at high temperatures a continuous exchange of oxygen radicals could occur between the different molecules. The equilibrium mixture could have different properties from the original substance and be either more or less viscous than the starting mixture. However, thickening can occur with pure silicates, and in any case this mechanism could hardly lead to the gelation sometimes observed. Similarly, straight-chain silicones could cyclize without change in molecular weight. The resulting compound would be expected to be more viscous than the original linear one, but again the effect could not be so large as to lead to gelation.

Condensation of Residual Reactive Groups. If any hydroxyl groups remain unreacted from the silanol intermediates from which the silicones are derived, the residual radicals can react, thus increasing the molecular weight and viscosity. This tendency was so pronounced in some of the earlier silicones that they would gel in a few weeks at room temperature. The present commercial preparations are reportedly stabilized by "chain stoppers." In the case of alkoxy- or aryloxysilanes, properly prepared samples should contain too few residual hydroxy groups to lead to high polymers. There remains, of course, the possibility of reaction directly through the alkoxy- or aryloxy groups.

Hydrolysis. The alkoxy- or aryloxysilanes are much more susceptible to hydrolysis than are the silicones. Attack by a water molecule leads to the formation of an alcohol and to substitution of a hydroxyl group for an alkoxy group attached to the silicon. Subsequently two Si-OH groups from different molecules can condense to split off water and form a siloxane link. Theoretically one molecule of water per molecule of silicon can lead to an infinite linear polymer. Konrad, Bachle, and Signer^{2/} had some success in predicting the molecular weights of the polymers from this simple picture. Another author^{3/} has pointed out that the hydrolysis may be considerably more complex, with complicated cyclic structures resulting. If two molecules of water per molecule of silicate are available, three-dimensional silica can, and in some cases does, result. It should be noted that thickening can be caused by hydrated silica as well as by the formation of polymeric siloxanes.

Two further points should be mentioned in connection with the hydrolysis of the alkoxy- or aryloxysilanes. First, highly branched organic radicals promote hydrolytic stability. This is generally ascribed to steric hindrance, since the hydrolysis of the silicates is commonly considered to proceed through an intermediate involving a pentavalent silicon atom. Second, the hydrolysis is strongly catalyzed by acids.

Oxidation. It is well known that silanes and siloxanes thicken much faster when heated in the presence of oxygen than in an inert atmosphere. Polymerization again appears to take place through the formation of Si-O-Si bonds between molecules. There is little quantitative information on the oxidation of alkoxy- or aryloxysilanes. It has, however, been noted that the oxidation is inhibited by phenyl- α -naphthylamine, which suggests a free radical mechanism. The oxidation of silicones has been investigated more extensively, although more from a practical than a fundamental viewpoint. In the oxidation of methyl silicone, Atkins, Murphy and Saunders^{4/} identified formaldehyde, paraformaldehyde, and formic acid in the products. They could find no evidence of Si-Si linkages in the oxidized material and considered this to be evidence that the condensation products are linked through oxygen. They also found no evidence of branched or cyclic structures and suggested that the methyl groups ruptured or oxidized were principally on the terminal silicon atoms. However, as these authors pointed out, the method of detection (infrared) was not sufficiently sensitive to show up small concentrations of branches. An interesting result was that the silicone known to contain branched structures showed a much greater increase of viscosity than linear material of the same initial viscosity, even though the same quantity of oxidation products was produced. It was also noted that the mixed phenyl-methyl silicone showed much greater oxidation stability and that the attack was almost exclusively on the methyl groups.

Pyrolysis. When organosilicon compounds are subjected to high temperatures under vacuum or under inert atmospheres they ordinarily show a remarkable thermal stability as compared with carbon compounds. For example, the tetraphenoxysilane prepared here was stable at 255-275°C (491-527°F) over a period of 3-1/2 days in an atmosphere of dry nitrogen. This compound was successfully distilled at atmospheric pressure at 422°C (792°F); however, this compound was quite unstable to hydrolysis.

Hunter, Hyde, Warrick, and Fletcher,^{5/} Patnode and Wilcock,^{6/} and Atkins, Murphy, and Saunders,^{4/} showed that the viscosity of methyl silicones actually decreases when they are held for long periods at 250°C (482°F) to 400°C (752°F) in the absence of air. The polysiloxane chain appears to rupture and rearrange to form cyclic siloxanes of low molecular weight. If any polymerization has taken place at the same time, the decrease of viscosity indicates that the polymerization is slower than the competing cracking and cyclization reaction.

SECTION III. EXPERIMENTAL

In the initial stages of the experimental work it was decided to confine the research to an example of a tetraaryloxysilane, tetraphenoxysilane, and an example of a practical tetraalkoxysilane, tetra(2-ethylhexoxy)silane. These materials were prepared by methods discussed in Appendix I. As the research progressed, it was decided to prepare and test members of the isomeric tetrapentoxysilanes in order to explore the effects of structure upon the stability of the material. In addition, a sample of hexa(2-ethylbutoxy)disiloxane was supplied by California Research Corporation, and tetra(2-ethylhexyl)silane was prepared. Properties of the test materials are given in Table I.

In the early work it soon became apparent that the effects of oxidation, hydrolysis, and pyrolysis were paramount; consequently, experimental work is divided under these headings in the following discussion.

SECTION IV. OXIDATION

In the early stages of the project an attempt was made to use a recirculating system, shown schematically in Figure 1, in order to determine rates of oxidation. The test material employed in these initial studies, tetraphenoxysilane, proved to be remarkably stable to oxidation at temperatures up to 350°C (662°F) for extended periods (Table II). It was found that the experimental difficulties of maintaining a recirculating system gas-tight, at the high temperatures and extended test periods employed, vitiated much of the early work. Accordingly, the recirculating system was converted to a flow system in which dried oxygen was metered at constant rate through the test cell shown in Figure 1, then through a specially designed trap* immersed in a dry ice-acetone bath, a drying tube, an Ascarite tube, and a wet-test meter. The oxidation products were distilled out of the reaction zone and collected in the cold trap. The test runs usually extended for more than 100 hours and were under constant observation. At the conclusion of a run the oxidized residue in the test cell was examined by refractive index, viscosity measurements, and infrared spectroscopy. The material collected in the trap was distilled through a spinning-band microfractionating column and the fractions identified. The rate of the oxidation was followed by weighing the trap periodically during the run.

In practice, the early oxidation rate studies were confined almost entirely to tetra(2-ethylhexoxy)silane, since tetraphenoxysilane proved quite resistant to oxidation over extended periods at high temperatures (Table II).

* See Cadle, Ralston, and Magill, *Analytical Chemistry* 23, 475 (1951). The trap described in this article was modified by the addition of a calibrated sump. Stainless steel helices were used as a packing.

TABLE I
PROPERTIES OF TEST MATERIALS

COMPOUND	REFRACTIVE INDEX	VISCOSITY (CENTISTOKES)	SPECIFIC GRAVITY	MELTING POINT	CHARACTERISTIC INFRARED ABSORPTION BANDS (MICRONS)	ANALYSES			
						% C		% H	
						Calc.	Found	Calc.	Found
Tetraphenoxysilane	1.5583 (54.7°C)	6.6 (55°C)	1.1653 $\frac{5}{15}$	53.5°C	6.25; 8.1; 4.8; 4.9; 10.3; 13.2	71.2	71.98	5.1	5.03
Tetra(2-ethylhexoxy)silane	1.4373 (25°C)	9.5 (25°C)	0.8791 $\frac{2}{3}$	liquid	3.4; 9.2; 11.4	70.6	70.54	12.6	12.58
Tetra(2-butoxy)silane	1.4056 (25°C)			liquid	12.0	60.0	60.25	11.2	11.2
Tetra(1-pentoxy)silane	1.4212 (25°C)	3.5 (25°C)		liquid		63.78	64.0	11.78	11.9
Tetra(3-methyl-1-butoxy)silane	1.4165 (25°C)					63.78	63.3	11.78	11.7
Tetra(2-pentoxy)silane	1.4145 (25°C)					63.78	63.75	11.78	11.55
Tetra(2-methyl-1-butoxy)silane	1.4188 (25°C)								
Tetra(3-methyl-2-butoxy)silane	1.4182 (25°C)					63.78	64.0	11.78	11.7
Tetra(3-pentoxy)silane	1.4212 (25°C)					63.78	63.8	11.78	11.8
Hexa(2-ethyl-1-butoxy)disiloxane	1.4310 (25°C)					63.66	64.0	11.57	11.45

TABLE II
SUMMARY OF OXIDATION EFFECTS

	COMPOUND	TIME (HOURS)	TEMPERATURE °C	O ₂ PRESSURE (ATMS.)	REFRACTIVE INDEX		VISCOSITY (Cs)		MELTING POINT	
					Initial	Final	Initial	Final	Initial	Final
recirculating system	Tetraphenoxy- silane (cumula- tive treatment)	18	150	1						
		22	175	1						
		51	200	1						
		33	225	1						
		37	250	1	1.5583 (54.7°C)	1.5583 (54.8°C)	No change		52.5-53	46-52°C
static- bomb	Tetraphenoxy- silane (cumula- tive treatment)	33½	225	1						
		6	300	1						
		15½	350	1	1.5583 (54.7°C)	1.5723 (54.7°C)	6.6 (54.7°C)	34.2 (54.7°C)	52.5-53	Liquid
		6½	260 (500°F)	15	1.5583 (54.1°C)	1.5585 (54.1°C)	6.6	7.3	53.5	52.5 (plus liquid phase)
		9½	260	11.8	1.4373 (25°C)	gel	9.5	gel		
flow system	Tetra(2-ethyl- hexoxy)silane	54½	205 (400°F)	1	1.4373 (25°C)	1.4377 (25°C)	9.5	13.1		
	Tetra(2-ethyl- hexoxy)silane	132	205 (400°F)	1	1.4373 (25°C)		9.5	37.9		

1/ Degradation was slight at temperatures up to 300°C. Above this temperature phenol was evolved, and the viscosity increased.

2/ Traces of phenol were formed. (In contact with stainless steel and bronze, a resin and considerable phenol were formed.) Gas bled from bomb (corrected for nitrogen): O₂ = 84.5%; CO = 11.9%; CO₂ = 2.3%; H₂ = 1.0%; unsaturated hydrocarbons = 0.3%.

3/ Gel amounted to 38% of original charge. A liquid phase was almost completely 2-ethylhexanol. Gas bled from bomb: O₂ = 10.2%; CO = 39.1%; CO₂ = 30.8%; H₂ = 13.2%; saturated hydrocarbons (ethane) = 6.6%; unsaturated hydrocarbons = 0.2%. The predominant reaction was apparently hydrolysis.

4/ Approximately 1 ml of water plus hydrocarbon collected in the cold trap.

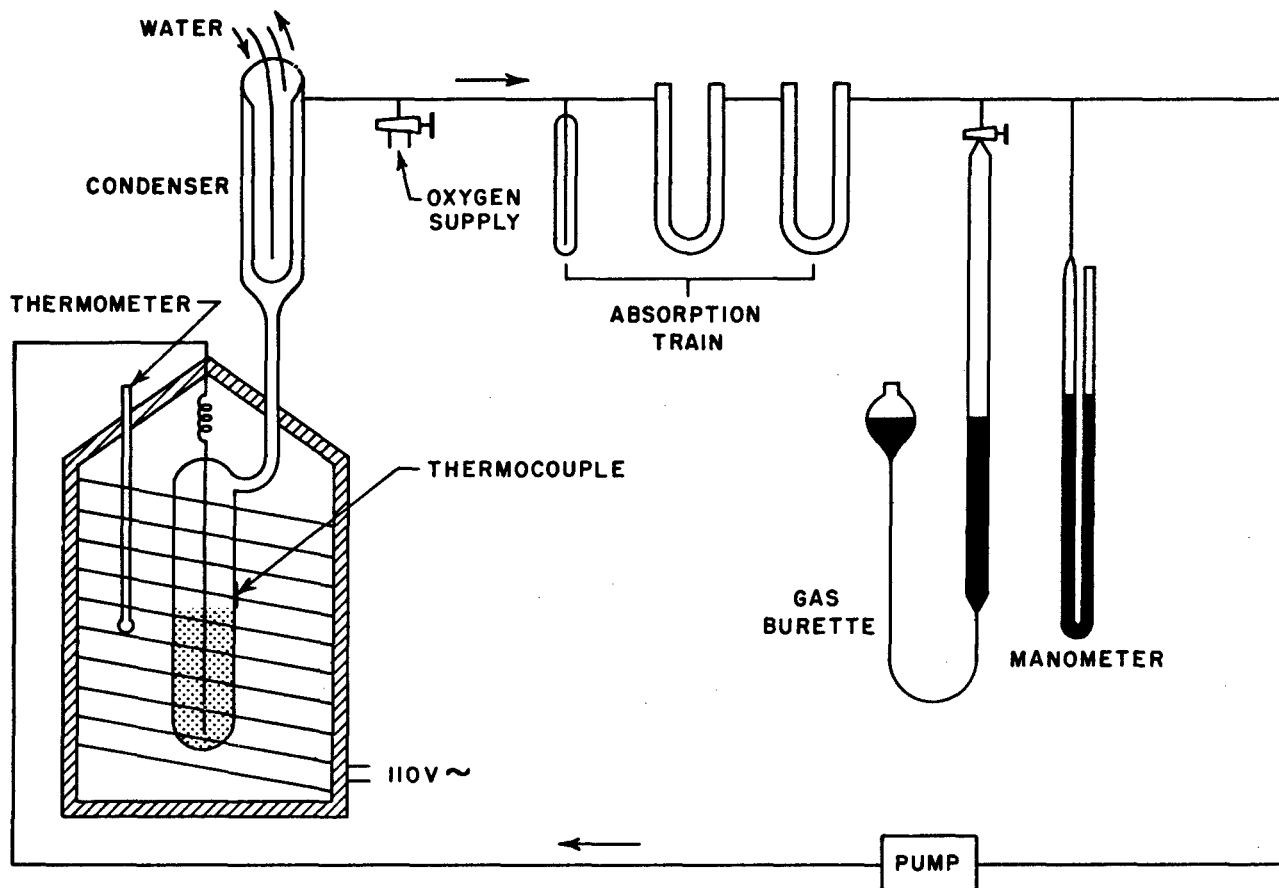
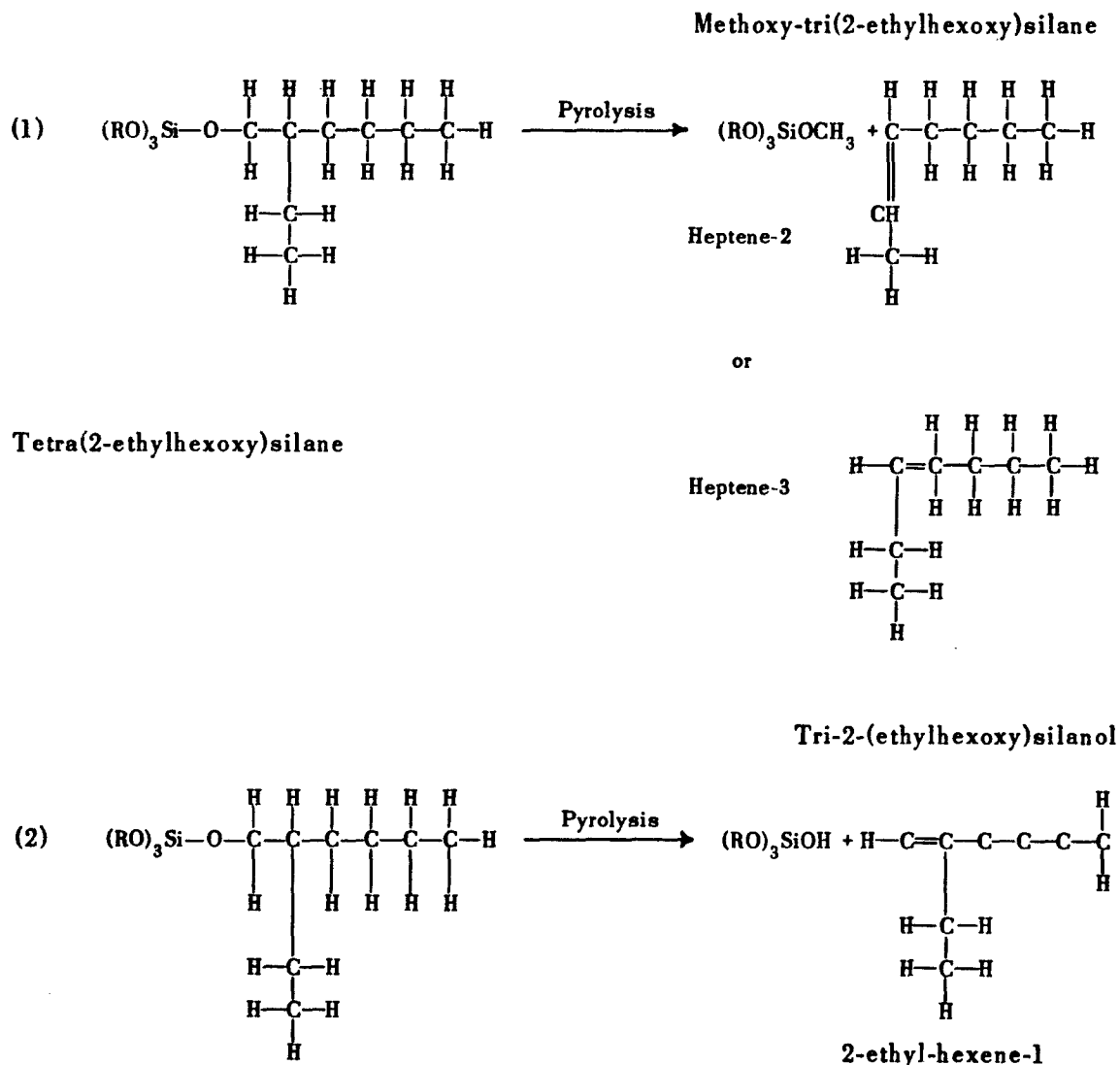


FIG. 1 - OXIDATION CELL - RECIRCULATING GAS SYSTEM

When tetra(2-ethylhexoxy)silane was oxidized at 205°C (400°F), a rate curve was obtained (Figure 2). Fractional distillation of the trap contents indicated the presence of 43% 2-ethylhexanol, 1.0% water, 1.5% heptene-2 (or 3), and 3% 2-ethylhexene-1. The balance was unreacted tetra(2-ethylhexoxy)silane which had been vaporized in the oxygen stream at 205°C (400°F). The oxidation temperature of 205°C (400°F) was selected after exploratory experiments indicated that at 260-270°C (500-518°F) an explosive mixture of organic vapors in oxygen was formed. Figure 2 shows the total rate of loss of material from the test cell, and therefore is representative of the effect obtained by oxidation plus entrainment at high temperature. To obtain the net oxidation rate, the weight percents should be divided by a factor of two, since approximately 50% of the distilled material was unreacted tetra(2-ethylhexoxy)silane.

The presence of the materials mentioned in the preceding paragraph may be explained by the following series of equations in which R is equivalent to the 2-ethylhexyl radical.



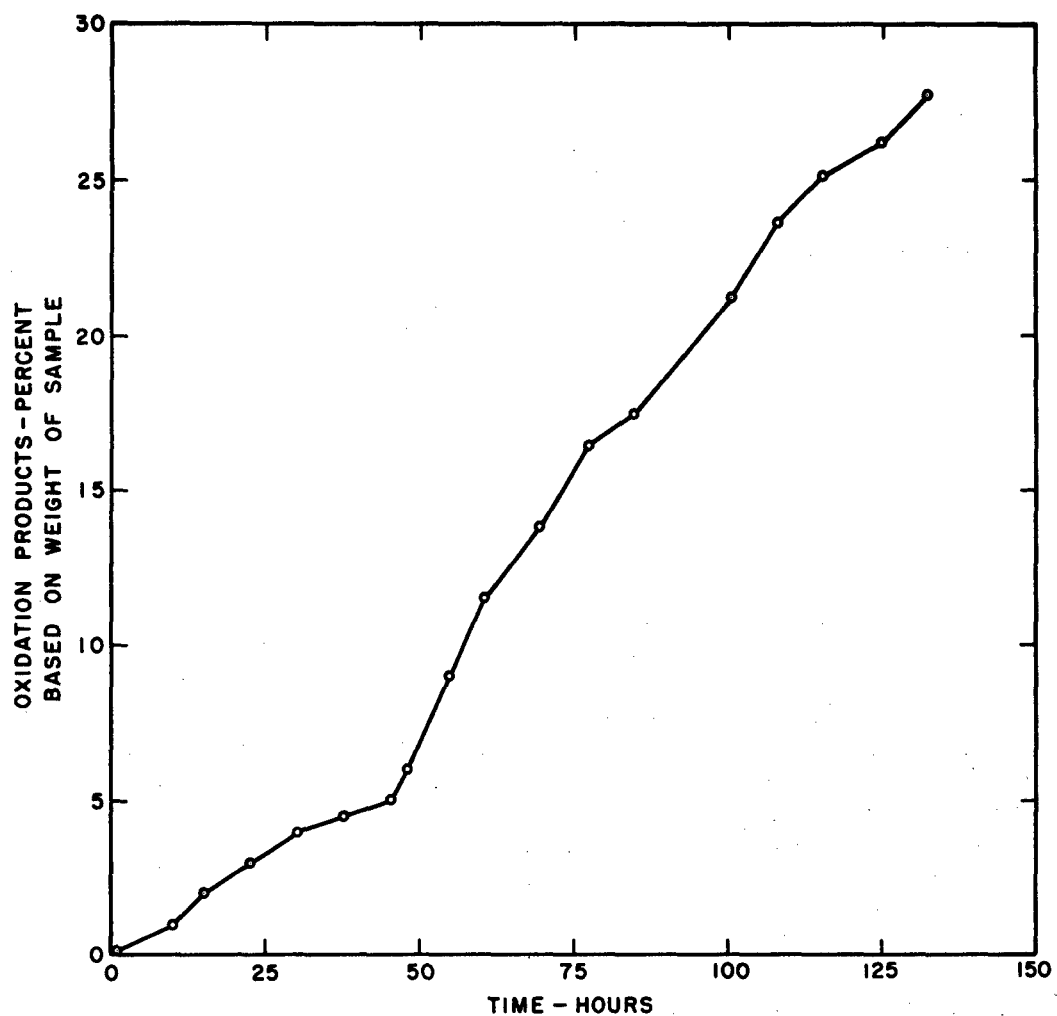
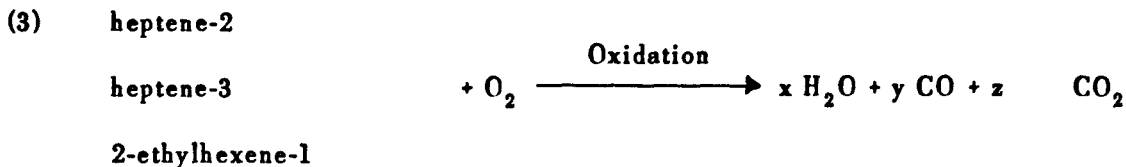


FIG. 2 - TETRA(2-ETHYLHEXOXY)SILANE
OXIDATION RATE AT 400°F (205°C)



It may be seen from the above series of equations that the observed reaction products may be explained on the basis that pyrolysis, oxidation, and hydrolysis are concurrent processes. It will be noted that the presence of heptene-2 or -3 can be explained by a mechanism which involves rupture of a carbon bond rather than a carbon-oxygen bond. Since this would involve the formation of a CH_3OSi group, as shown in Equation 1 above, methoxyl group determinations were made on the oxidized residues; these determinations demonstrated the presence of 0.5% to 1.5% methoxyl. Consequently, it is believed that it is valid to assume thermal rupture of the carbon bond adjacent to the C-O bond.

From Equation 2 above, the presence of 2-ethyl-hexene-1 may be readily explained on the basis of thermal rupture of the C-O bond, leaving the SiOH residue. It may be said, therefore, that the principal effect of pyrolysis is the production of unsaturated hydrocarbon chains which may then be readily and rapidly oxidized by either air or oxygen.

From the known properties of hydrocarbons it is believed proper to assume that oxidation of heptene-2 or -3 and 2-ethyl-hexene-1 may occur rapidly under both experimental and use conditions. This process is confirmed by the detection of the presence of water, carbon monoxide, and carbon dioxide as postulated in Equation 3. If water is available, either in the liquid or vapor state, then hydrolysis may proceed according to Equation 4 with the production of hydrated silica and 2-ethylhexanol. As discussed in Section VI, "Pyrolysis," it may be stated that pyrolytic reactions with the alkoxysilanes are relatively

slow; however, the hydrocarbon byproducts react rapidly with oxygen to form water, carbon monoxide, and carbon dioxide. Consequently, hydrolysis becomes an important consideration in the study of any oxidation mechanism with these materials. As discussed in Section V, "Hydrolysis," and as demonstrated by the presence of 43% 2-ethylhexanol in the trap contents, as described above, it is apparent that the principal degradative reaction under the experimental conditions was hydrolysis. The importance of this hydrolytic reaction is further demonstrated in the bomb runs described below.

Tetraphenoxysilane was more resistant to oxidation than tetra(2-ethylhexoxy)silane although tetraphenoxysilane is demonstrably much more susceptible to hydrolysis. It appears, therefore, that it is necessary for oxidation to liberate water vapor in order to produce degradation of either tetraaryloxy- or tetraalkoxysilanes. The relative stability of tetraphenoxysilane to oxidation could, therefore, be attributed to resistance of the benzene ring to either thermal cracking or oxidative removal of hydrogen attached to the ring. It should also be noted, in regard to the oxidation of tetraphenoxysilane, that, although this material was quite resistant to oxidation, small quantities of phenol of high purity were recovered from the cold trap. This observation confirms the previous conclusion that the most profound changes during oxidation are caused by hydrolysis induced by water released by oxidation of a portion of the alkyl or aryl groups.

Although previous studies in the oxidation of tetraphenoxysilane showed that this compound was quite stable up to 350°C (662°F), it was decided for reasons of safety to conduct further studies in steel equipment. An Aminco stainless steel rocking bomb of 100 ml capacity was used in this work. A glass liner protected the material from metallic contamination, except when the liner broke on one run. Tetraphenoxysilane showed only slight degradative changes, as is shown in Table II, but CO, CO₂, and H₂ were detected in the residual oxygen bled from the bomb, indicating some attack on the phenoxy group.

Accidental metallic contamination in a run in which the glass liner was broken resulted in the formation of a resin, and a dark liquid which was principally phenol.

When tetra(2-ethylhexoxy)silane was similarly treated in the oxygen bomb, attack was rapid and extensive. Of the starting material, 38% was converted to a gel, and the remainder to a thin liquid which was principally 2-ethylhexanol. In addition, the residual gas bled off from the bomb contained CO, CO₂, H₂, and hydrocarbons, principally ethane. Retention of the water formed in contact with the alkoxysilane apparently led to rapid hydrolysis.

It was decided to reconsider a recirculating type of apparatus for use during the second year of research since rate determinations could readily be made in such equipment if the operating difficulties could be overcome. Such equipment would be especially desirable for oxidation studies in the presence of metals. Therefore, an all-glass, sealed, recirculating oxidation apparatus was constructed and placed in operation (Appendix II). A photograph of this equipment is reproduced in Figure 35. The previous difficulties caused by the development of minute leaks over long periods of time were eliminated by the design of the apparatus.

After placing the recirculating all-glass oxidation apparatus in operation, several exploratory tests were made employing tetra(1-pentoxy)silane at 150°C (302°F), and tetra(2-ethylhexoxy)silane at 200°C (392°F). The oxidation rates are shown in Figure 3. In these experiments the oxygen was circulated at the rate of 193 ml per minute measured at standard conditions. At the end of each experiment approximately 1 to 3 ml of a mixture of the corresponding alcohol, water, and unsaturated hydrocarbon had accumulated in the cold trap. These results were in agreement with similar experiments made during the first year of the test program, when a non-recirculating type of apparatus was employed.

Toward the end of one of the runs using tetra(1-pentoxy)silane, the formation of a fog in the reflux condenser and cold trap was noted. Approximately ten minutes later there was a sharp detonation which destroyed the de-entrainment column. It should be noted that this portion of the apparatus was at room temperature and that the explosion did not take place in the reaction cell which was within the insulated hot zone of the apparatus. It is believed that peroxides resulting from the interaction of the unsaturated hydrocarbon and oxygen had accumulated in the column. Experiments conducted during the first year of the research program indicated that, for example, heptene-2 readily formed peroxides. This material or its isomer, heptene-3, has been detected among the oxidation products of tetra(2-ethylhexoxy)silane. Safety shielding adequately protected personnel working on the apparatus at the time of the explosion. This safety shielding is not shown in Figure 35, having been removed for purposes of photography. It consists of 3/8 inch methyl methacrylate sheet plastic firmly attached to the front edge of the laboratory bench.

During an exploratory experiment in the oxidation of tetra(2-ethylhexoxy)silane at 200°C (392°F) in the presence of a sample of 1020 steel, it was found that the reaction product ignited spontaneously within the apparatus. There was no damage to the apparatus since the supply of oxygen in the system was rapidly consumed and the flames were smothered within a minute. As a result, however, subsequent runs were made at a lower temperature.

Oxidation rates have been measured for several tetraalkoxy-silanes with and without the presence of 1020 steel, titanium, and

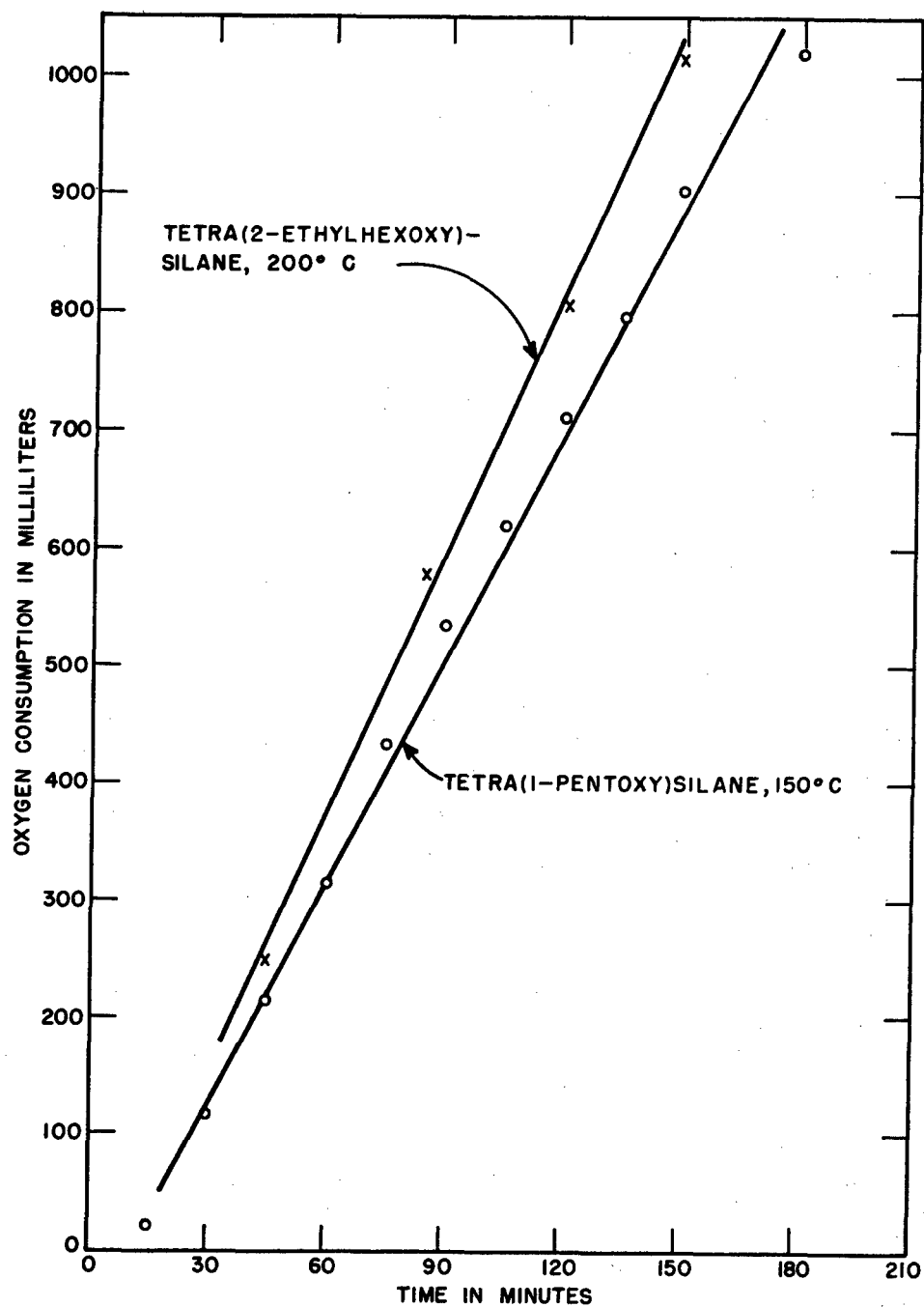


FIG. 3-OXYGEN CONSUMPTION OF TWO ALKOXY SILANES
IN A CLOSED RECIRCULATING SYSTEM

copper. The effects of these metals upon the rates of oxidation are summarized in Table III. Representative runs of the tetraalkoxysilanes showing the oxygen consumption are shown in Figures 4 to 28, inclusive. It may be concluded that there are no significant increases in the rates of oxidation in the presence of the test metals, since there was no statistically significant difference between the slopes of the rate curves for the blanks (containing no metal) and for the test runs. For a discussion of the statistical methods employed, see Appendix III. A "blank" run consisted of the determination of the oxidation rate for the tetraalkoxysilane with no metal present. For determinations in the presence of metal a sample of tetraalkoxysilane from the same fraction as the blank run was used. The metal test strips consisted of copper or titanium squares supplied by Wright Air Development Center and 1020 steel strips supplied by the Metallurgical Laboratory of Stanford Research Institute.

A question arose in the early stages of this work regarding the reproducibility of the surface of the test strips. Steel samples were cut from the same sheet and certain of them polished in the Metallurgical Laboratory. A surface or "skin" effect was observed that seemed to lower the initial oxidation rate. Continued heating or heating at a higher temperature appears to overcome the effect. In Figure 5, for example, this so-called "skin" effect is demonstrated by the determination of oxidation rates successively at 125°, 150°, and again at 125°C (257°, 302°, 257°F) and on the same sample of tetra(2-ethylhexoxy)silane in the presence of polished and unpolished steel. The same effect is shown in Figure 7 for titanium. Consequently, all titanium and steel samples were polished prior to oxidation test runs. In this connection it should be noted that this so-called "skin" effect is relatively minor and did not cause an important change in the oxidation rate. This effect was not noted for copper test strips. At the completion of a typical run with copper (Figure 8) the tetra(2-ethylhexoxy)silane was colored a characteristic bright green, indicating attack on the copper test strip. In view of this attack it is indeed surprising that there was no significant increase in the rate of oxidative attack upon tetraalkoxysilanes in the presence of copper.

In all of this work it should be noted that small but significant rates of oxidative attack by pure oxygen occurred at temperatures as low as 150°C (302°F). This fact is probably of importance to designers of systems employing tetraalkoxysilane materials.

While the comparative studies of the isomeric tetrapentoxysilanes are as yet incomplete, preliminary results indicate that branching increases the rate of oxidation. With reference to Table III it will be seen that tetra(1-pentoxo)silane showed the lowest rate of oxidation, while the tetra(2-pentoxo)silane showed the highest rate of oxidative attack. Tetra(3-pentoxo)silane and tetra(3-methyl-2-butoxy)silane had oxidation rates intermediate between the values for the first compounds. It is intended to pursue this subject further during the forthcoming research year.

ANALYSIS OF OXIDATION RATE DATA FOR ISOMERIC TETRAPENTOXYSILANES AT 120°C
IN THE PRESENCE OF STEEL, TITANIUM, AND COPPER

- 1 Rates determined from the slopes of the statistically determined regression lines. All regressions were highly significant at a confidence level of 95% or higher.
- 2 The symbol "t" indicates the calculated statistical "t" function for the significance of difference of slopes of the regression lines.
- 3 The symbol "n" indicates the statistical degrees of freedom used in calculating the "t" function.
- 4 The symbol "T" indicates the limiting value of the "t" function, when the "t" function table is used at a confidence level of 90%. The data indicate that there are no statistically significant differences in the rates of oxidation for these materials when the test metals were present, as compared to the blanks.

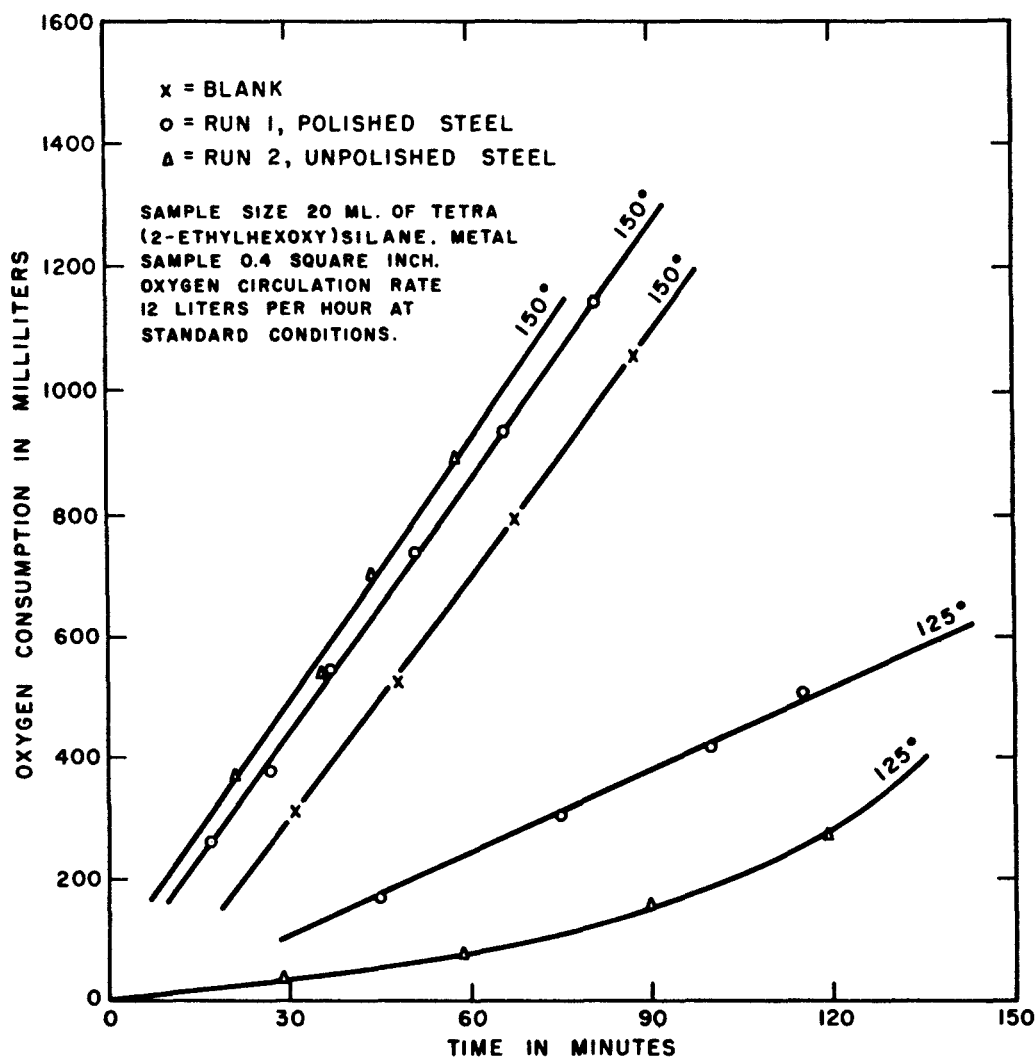


FIG. 4—OXYGEN CONSUMPTION OF TETRA(2-ETHYLHEXOXY)SILANE IN THE PRESENCE OF STEEL

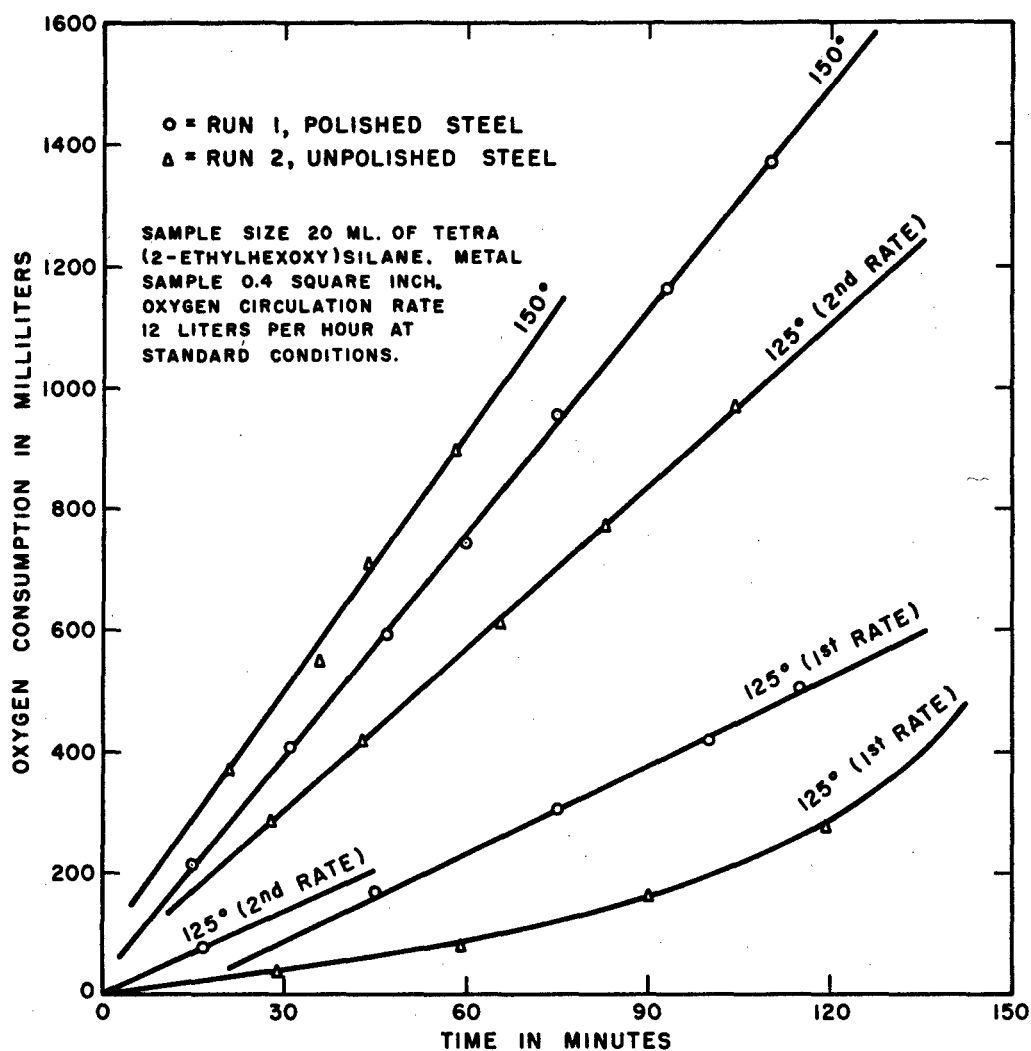
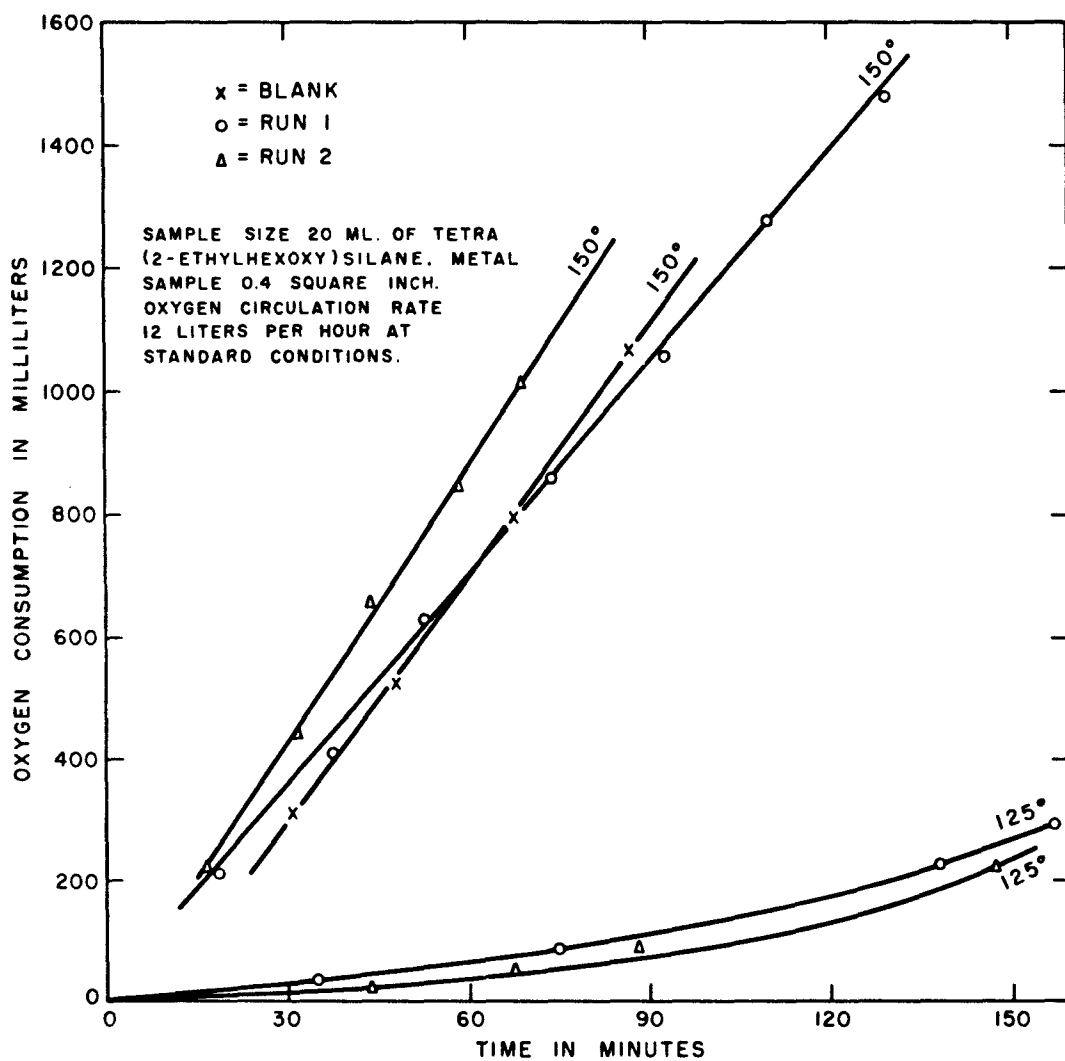


FIG. 5—OXYGEN CONSUMPTION OF TETRA(2-ETHYLHEXOXY)SILANE
 IN THE PRESENCE OF STEEL. SUCCESSIVE RATE
 DETERMINATIONS AT 125°, 150° AND 125° C



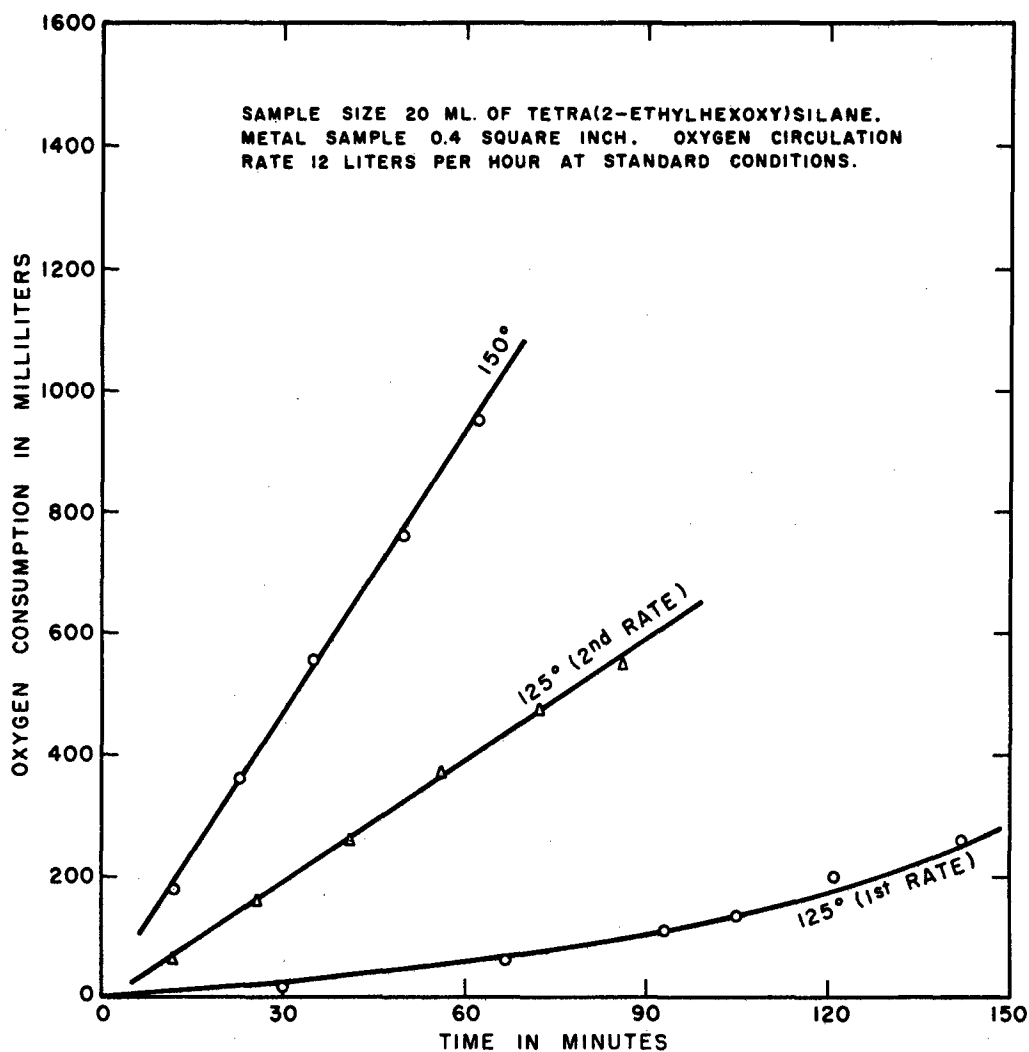


FIG. 7—OXYGEN CONSUMPTION OF TETRA(2-ETHYLHEXOXY)SILANE
IN THE PRESENCE OF TITANIUM (UNPOLISHED). SUCCESSIVE
RATE DETERMINATIONS AT 125°, 150° AND 125° C

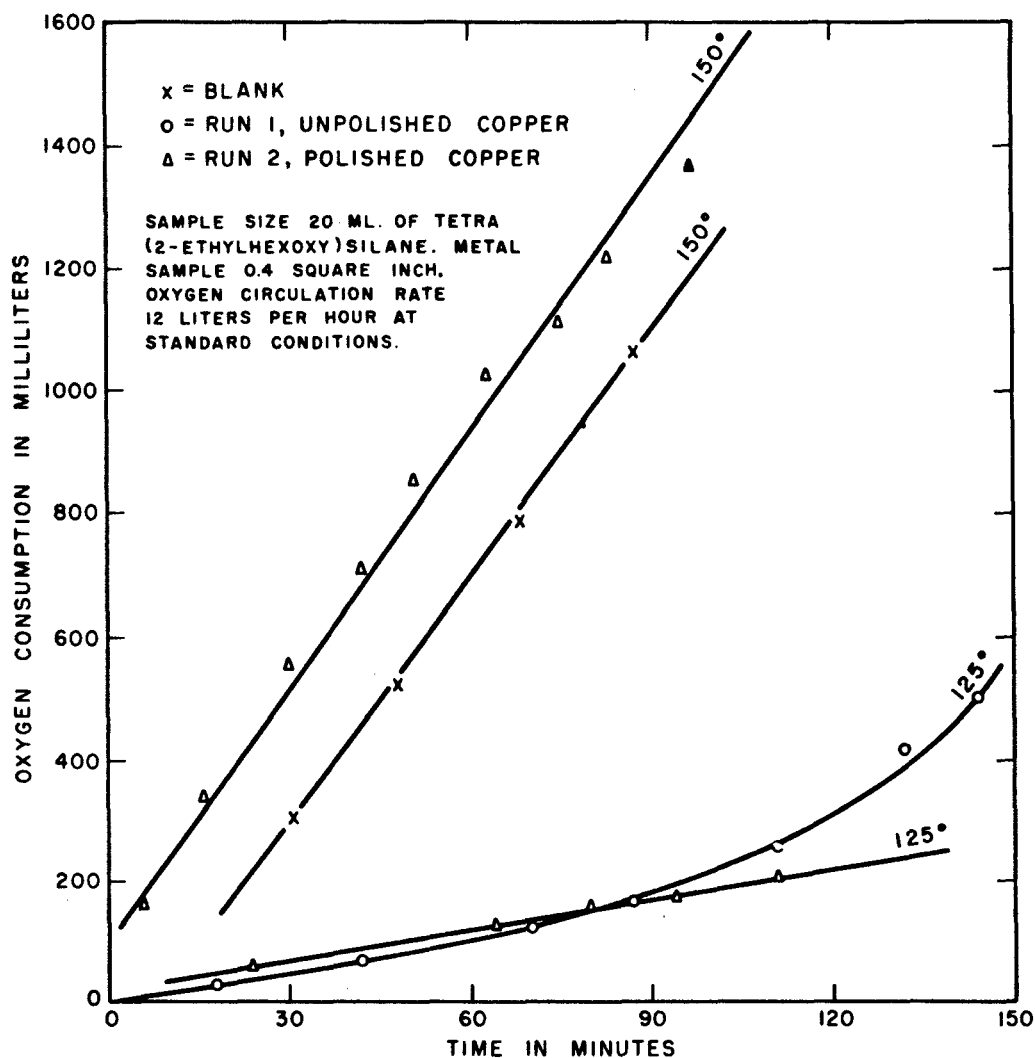


FIG. 8—OXYGEN CONSUMPTION OF TETRA(2-ETHYLHEXOXY)SILANE IN THE PRESENCE OF COPPER

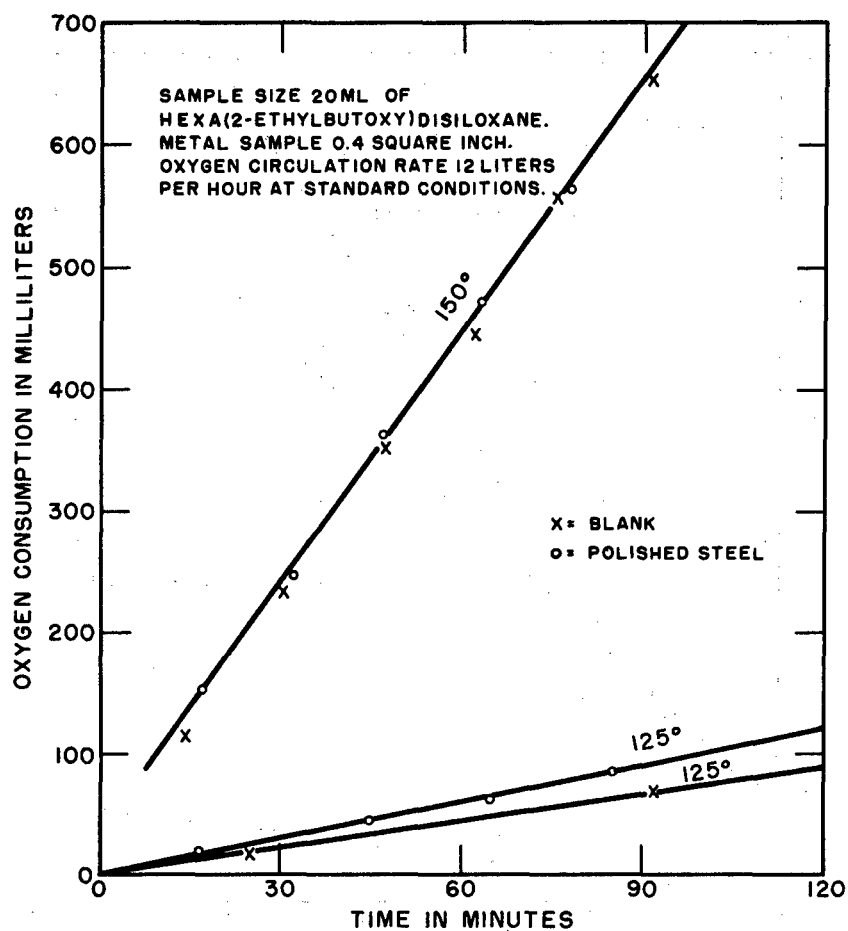


FIG. 9 - OXYGEN CONSUMPTION OF
HEXA(2-ETHYLBUTOXY)DISILOXANE
IN THE PRESENCE OF STEEL

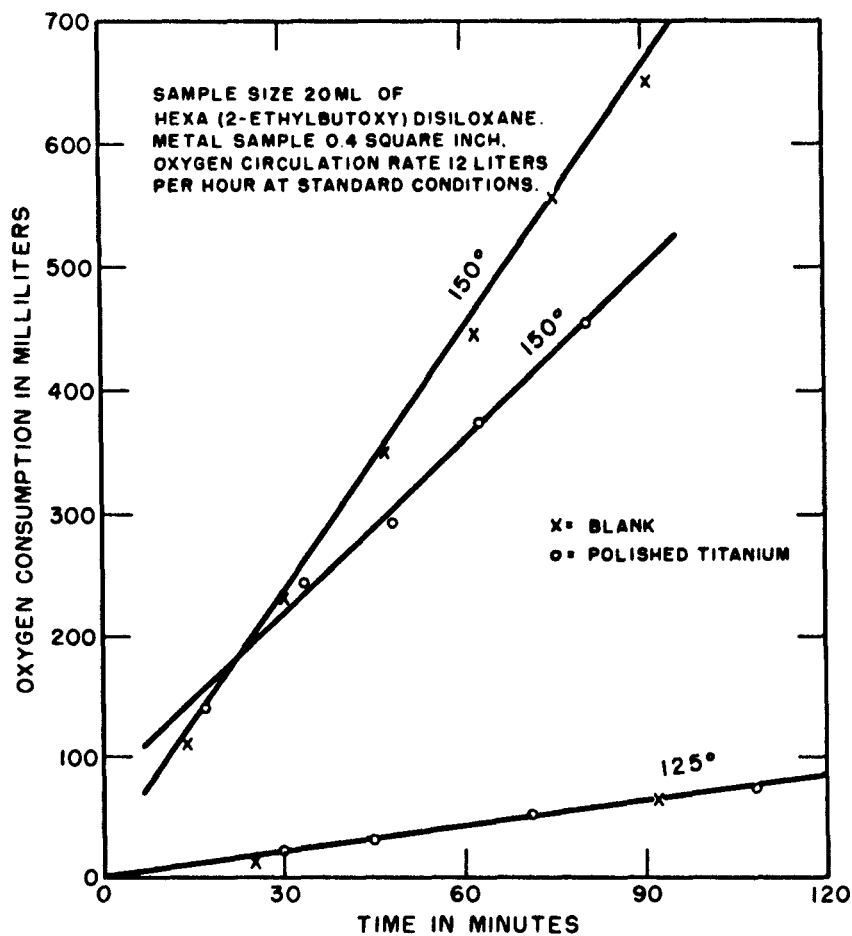


FIG.10-OXYGEN CONSUMPTION OF
HEXA(2-ETHYLBUTOXY)DISILOXANE
IN THE PRESENCE OF TITANIUM

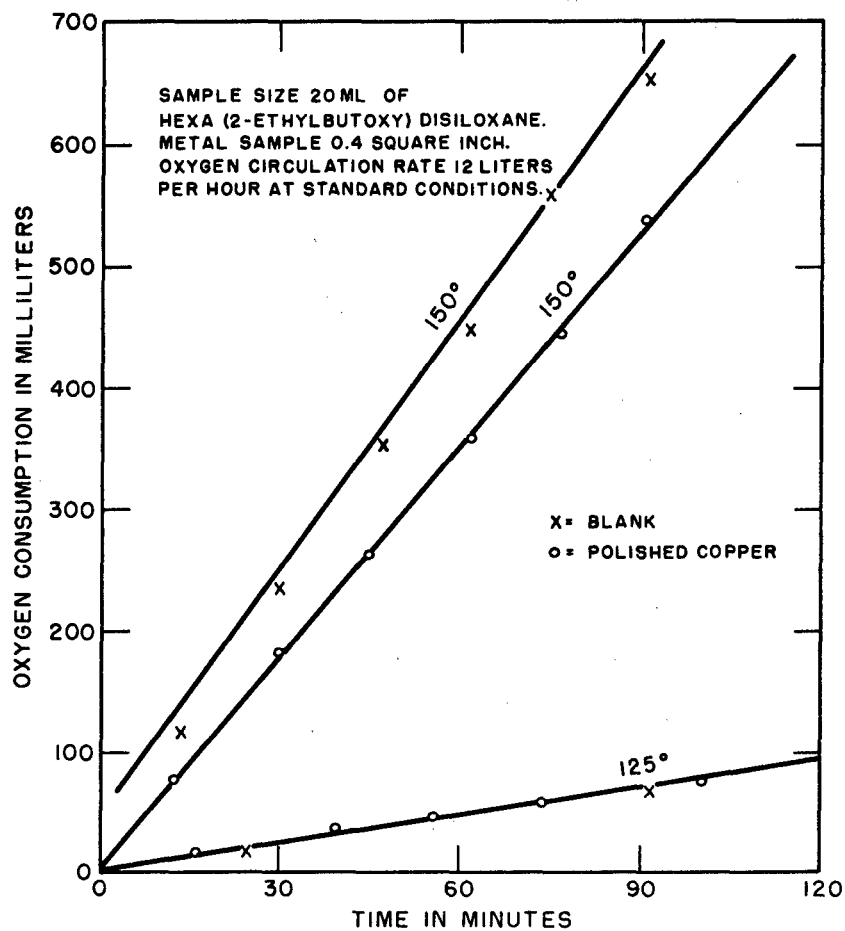


FIG. II—OXYGEN CONSUMPTION OF
HEXA(2-ETHYLBUTOXY)DISILOXANE
IN THE PRESENCE OF COPPER

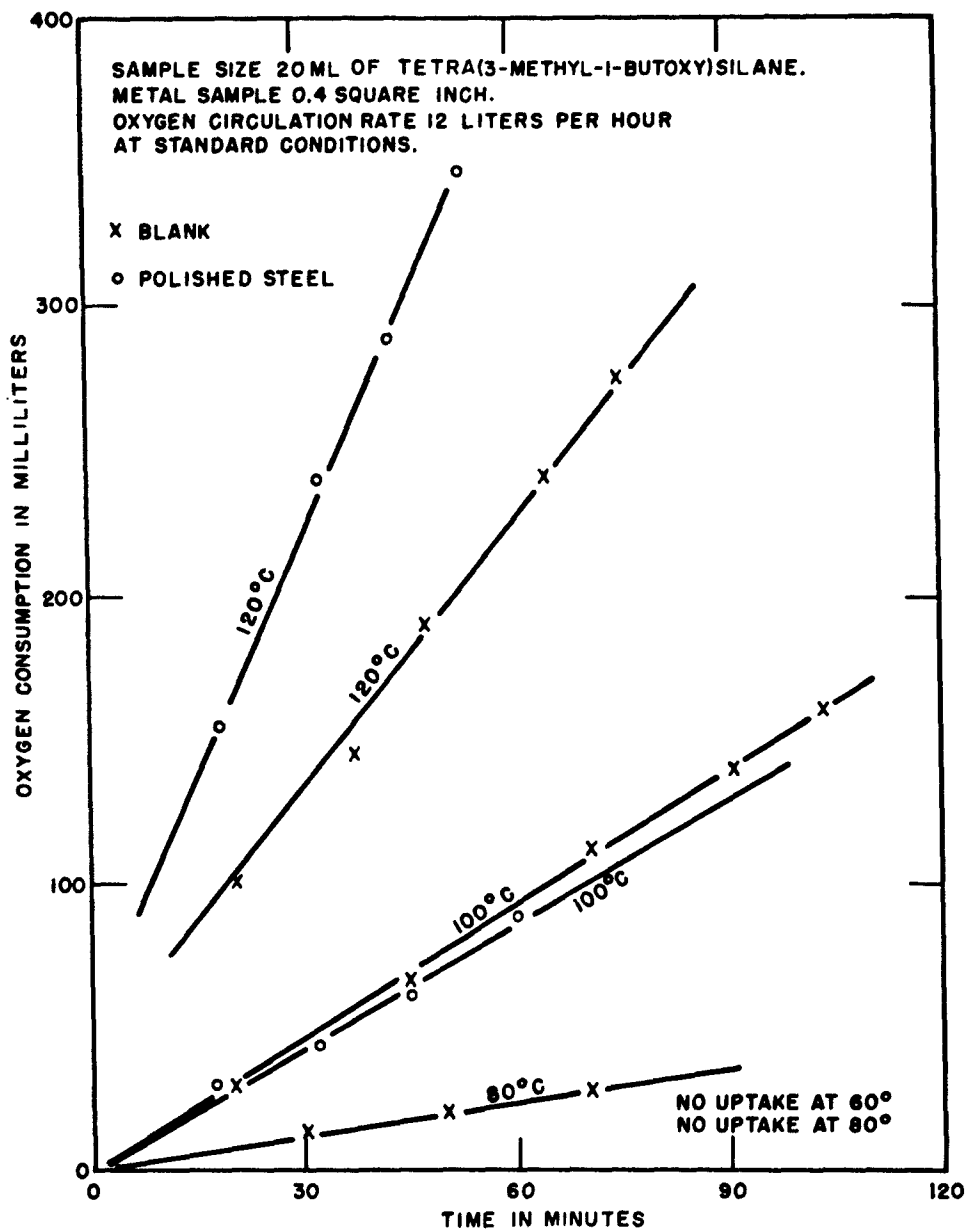


FIG. 12 - OXYGEN CONSUMPTION OF TETRA(3-METHYL-1-BUTOXY)SILANE
IN THE PRESENCE OF STEEL

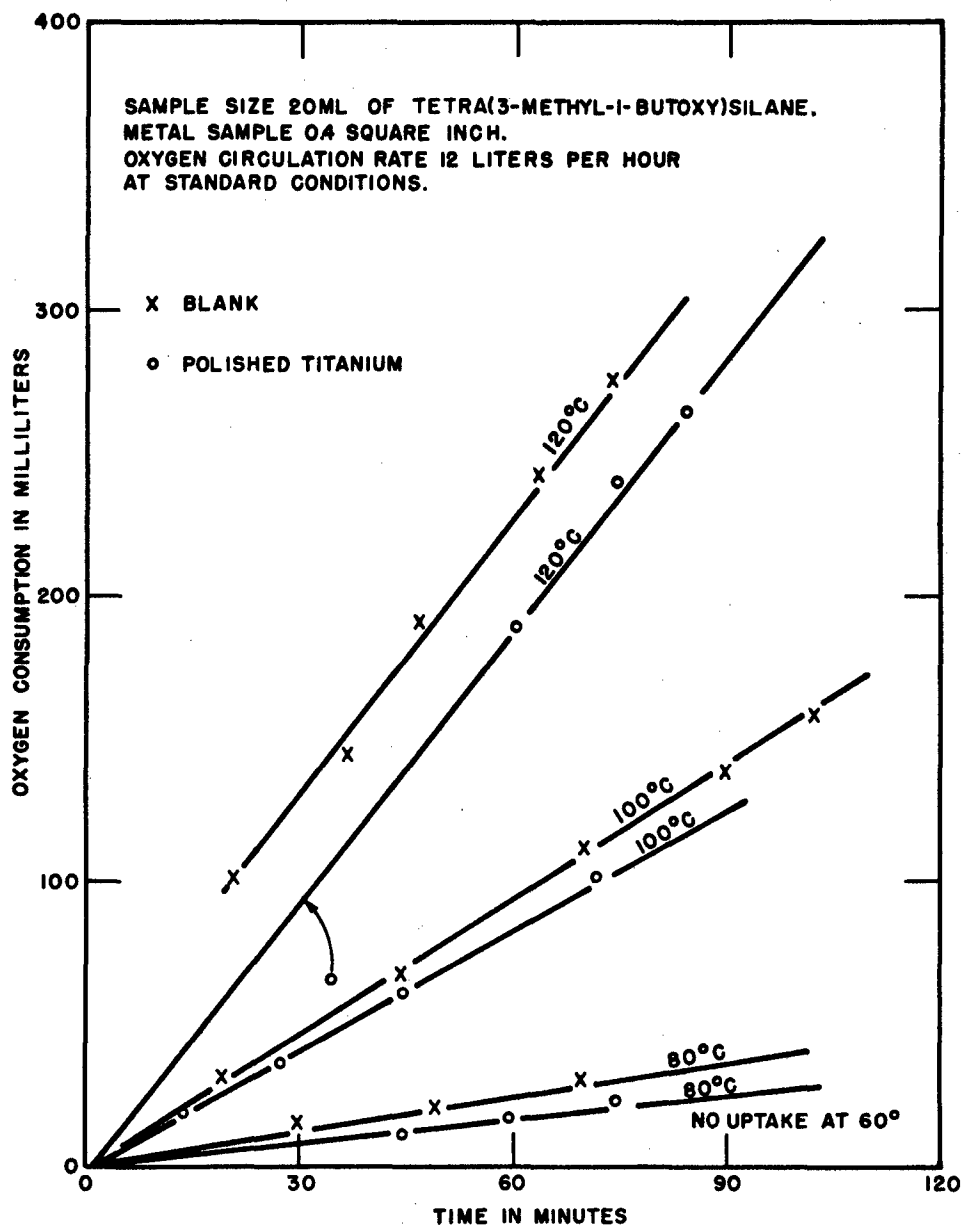


FIG. 13—OXYGEN CONSUMPTION OF TETRA(3-METHYL-1-BUTOXY)SILANE
IN THE PRESENCE OF TITANIUM

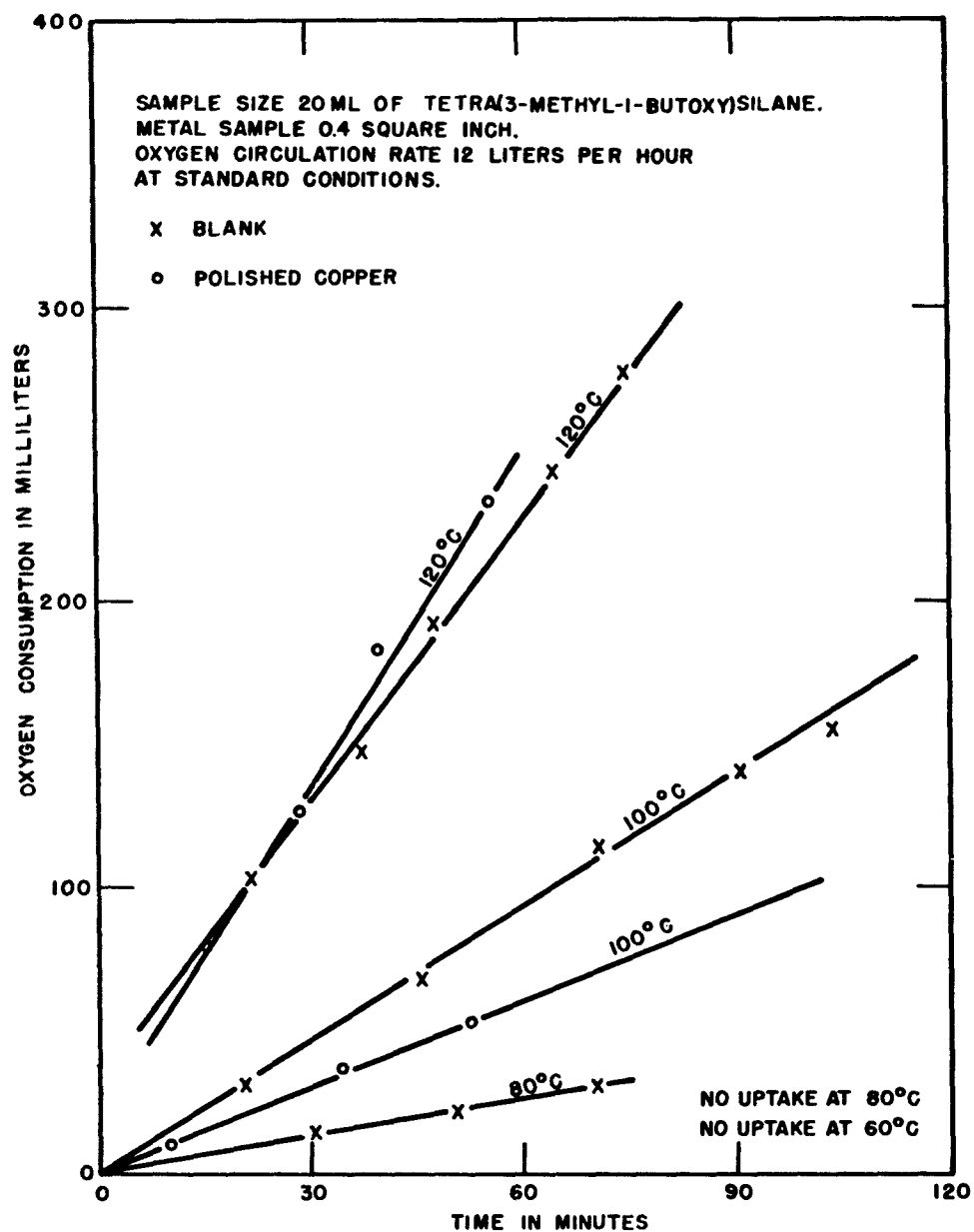


FIG. 14-OXYGEN CONSUMPTION OF TETRA(3-METHYL-1-BUTOXY)SILANE
IN THE PRESENCE OF COPPER

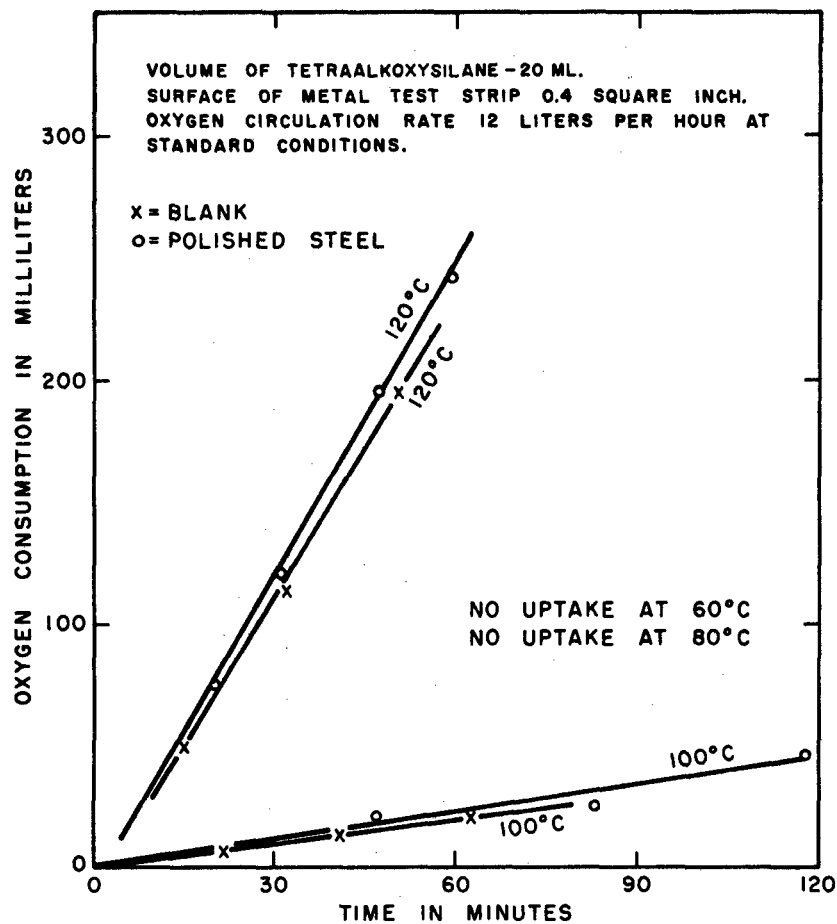


FIG. 15—OXYGEN CONSUMPTION OF TETRA(2-METHYL-1-BUTOXY)SILANE
IN THE PRESENCE OF STEEL

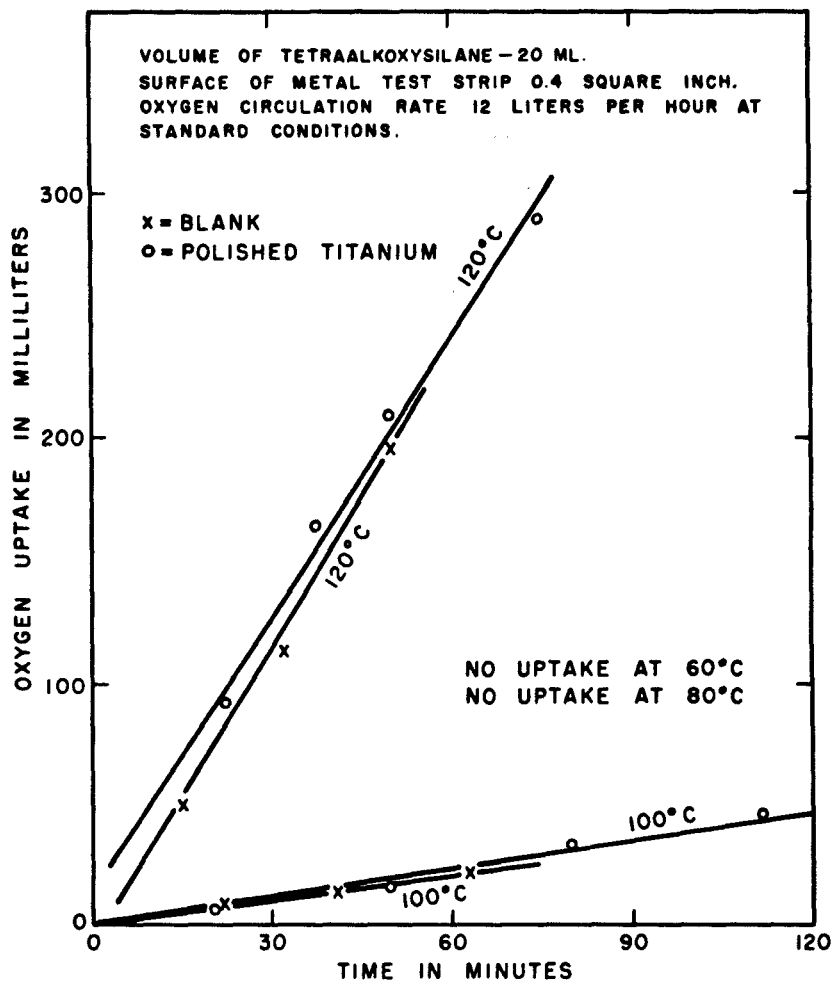


FIG. 16-OXYGEN CONSUMPTION OF TETRA(2-METHYL-1-BUTOXY)SILANE
IN THE PRESENCE OF TITANIUM

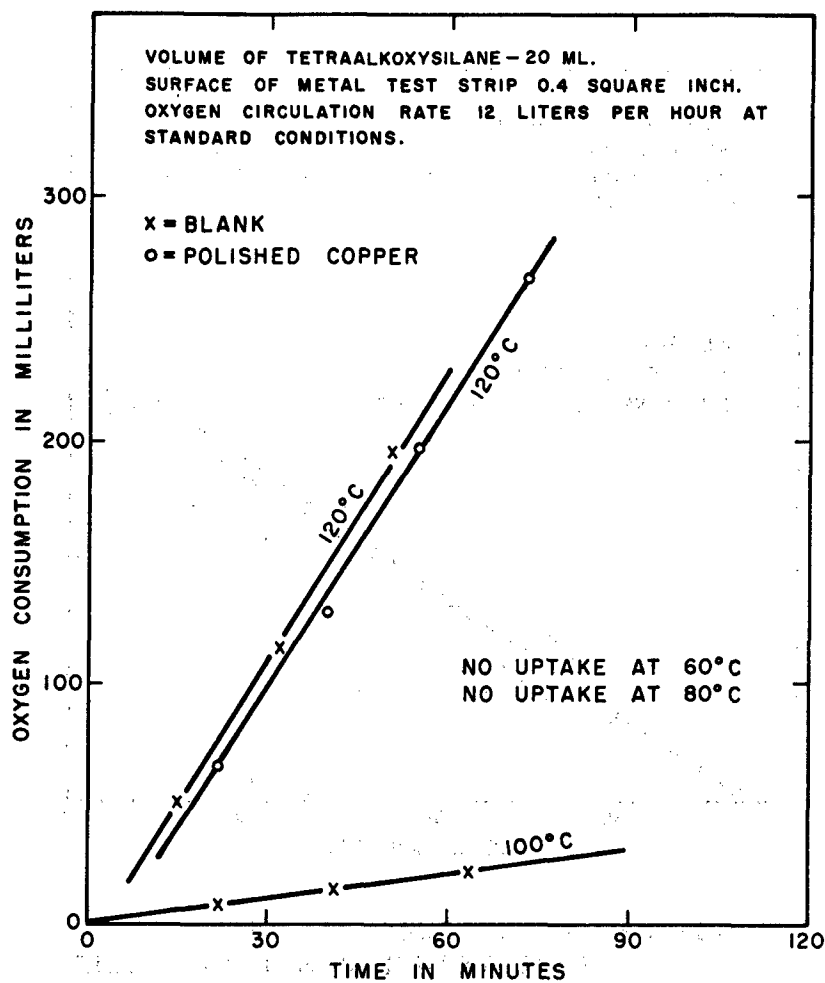


FIG. 17—OXYGEN CONSUMPTION OF TETRA(2-METHYL-1-BUTOXY)SILANE
IN THE PRESENCE OF COPPER

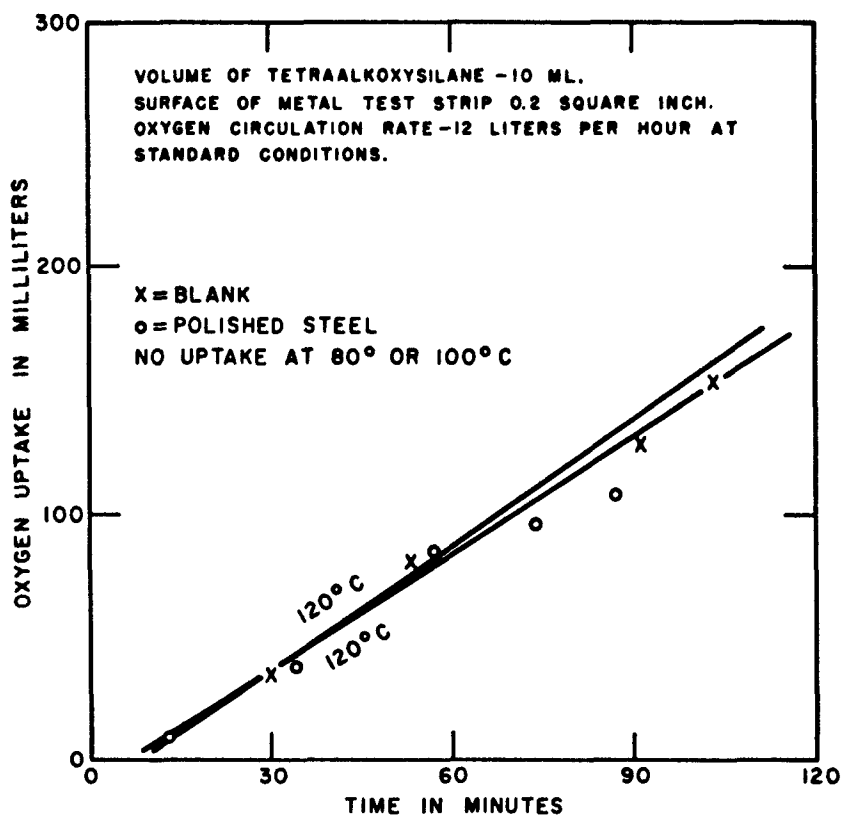


FIG. 18 - OXYGEN CONSUMPTION OF
 TETRA (3-METHYL-2-BUTOXY)SILANE
 IN THE PRESENCE OF STEEL

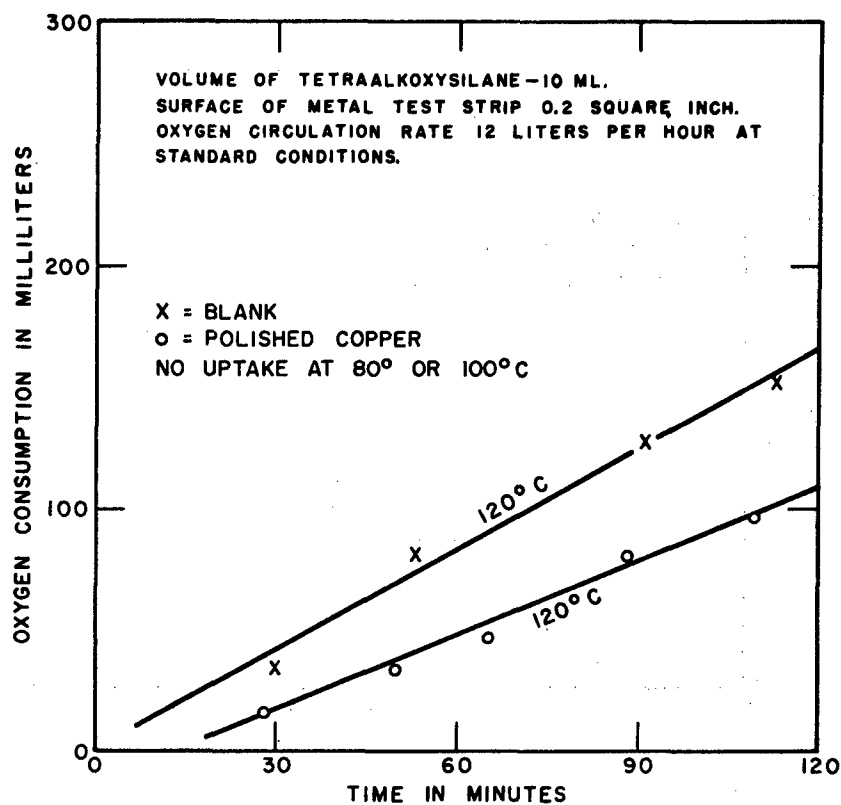


FIG. 19-OXYGEN CONSUMPTION OF TETRA(3-METHYL-2-BUTOXY)SILANE
IN THE PRESENCE OF COPPER

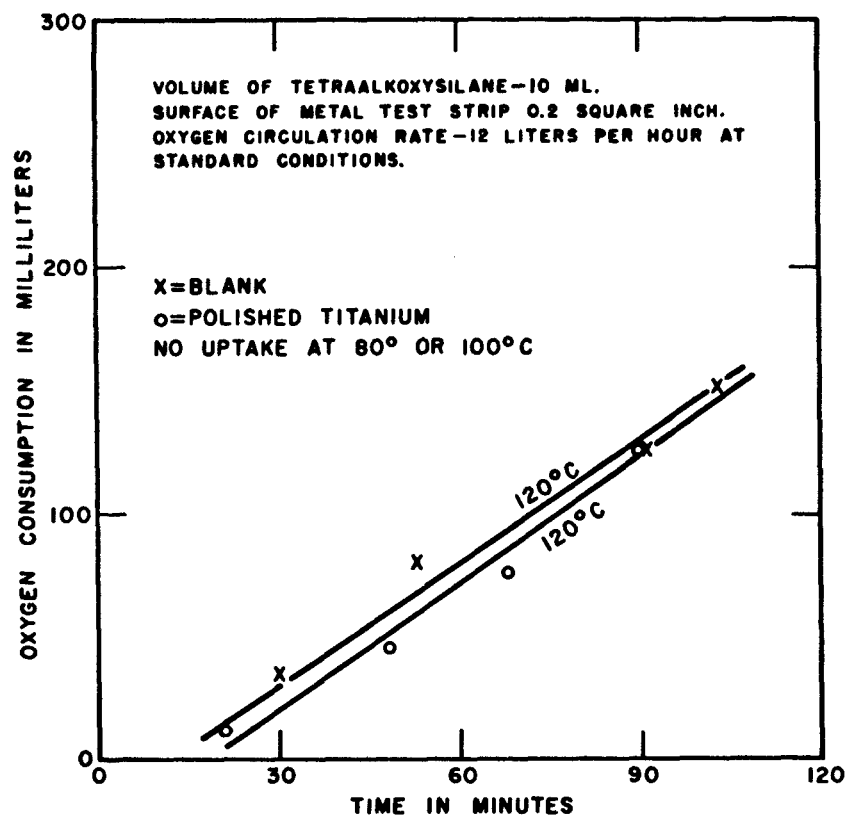


FIG. 20-OXYGEN CONSUMPTION OF
TETRA(3-METHYL-2-BUTOXY)SILANE
IN THE PRESENCE OF TITANIUM

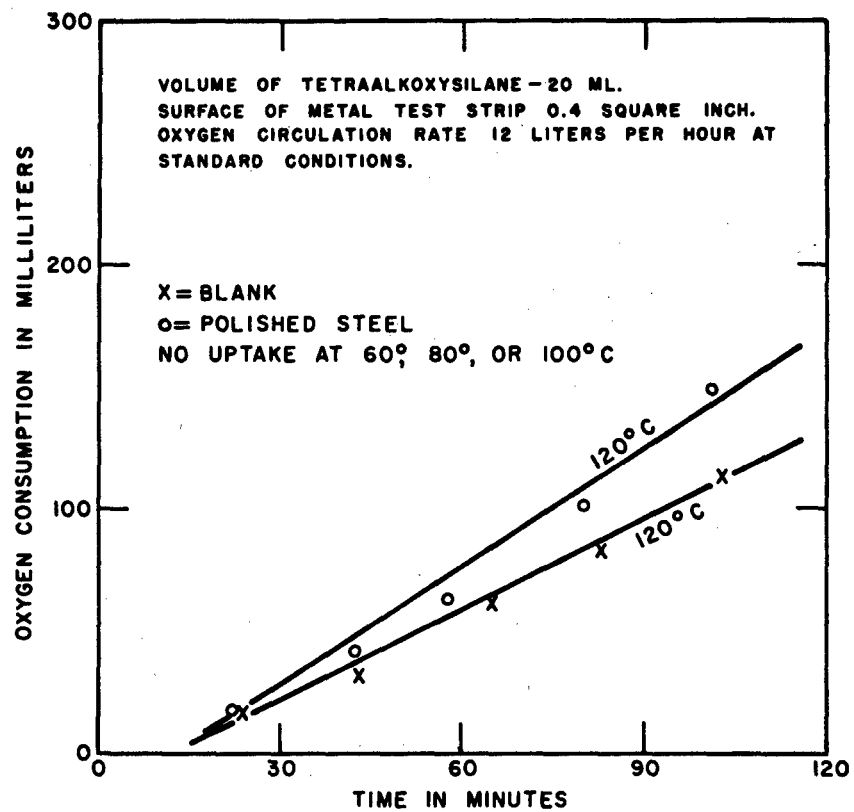


FIG. 21-OXYGEN CONSUMPTION OF TETRA(3-PENTOXY)SILANE
IN THE PRESENCE OF STEEL

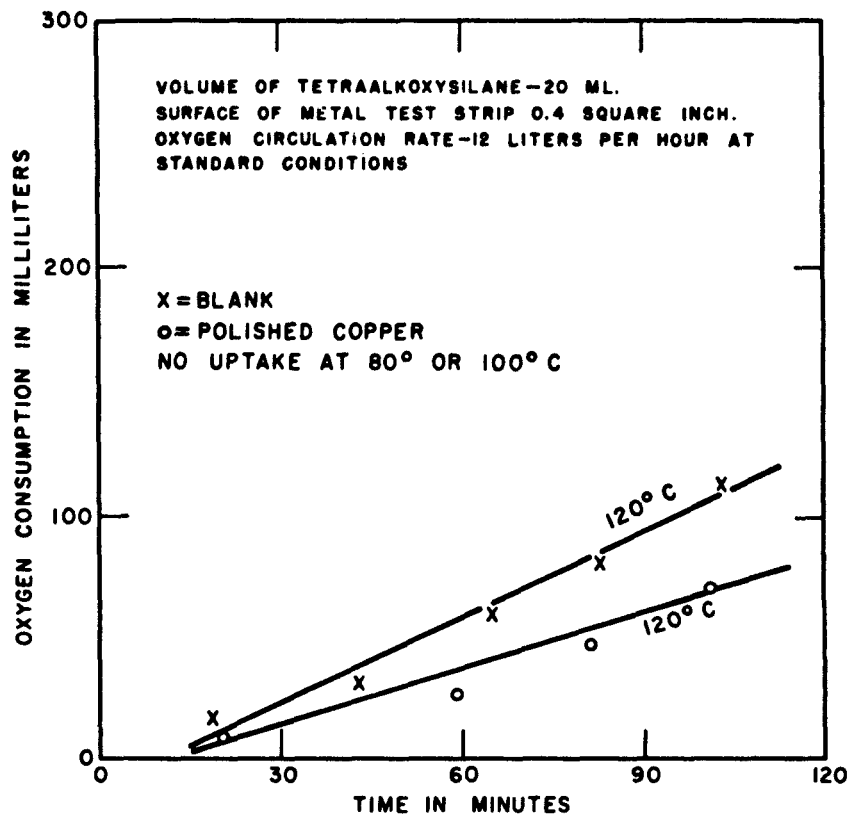


FIG. 22 - OXYGEN CONSUMPTION OF
TETRA(3-PENTHOXY)SILANE
IN THE PRESENCE OF COPPER

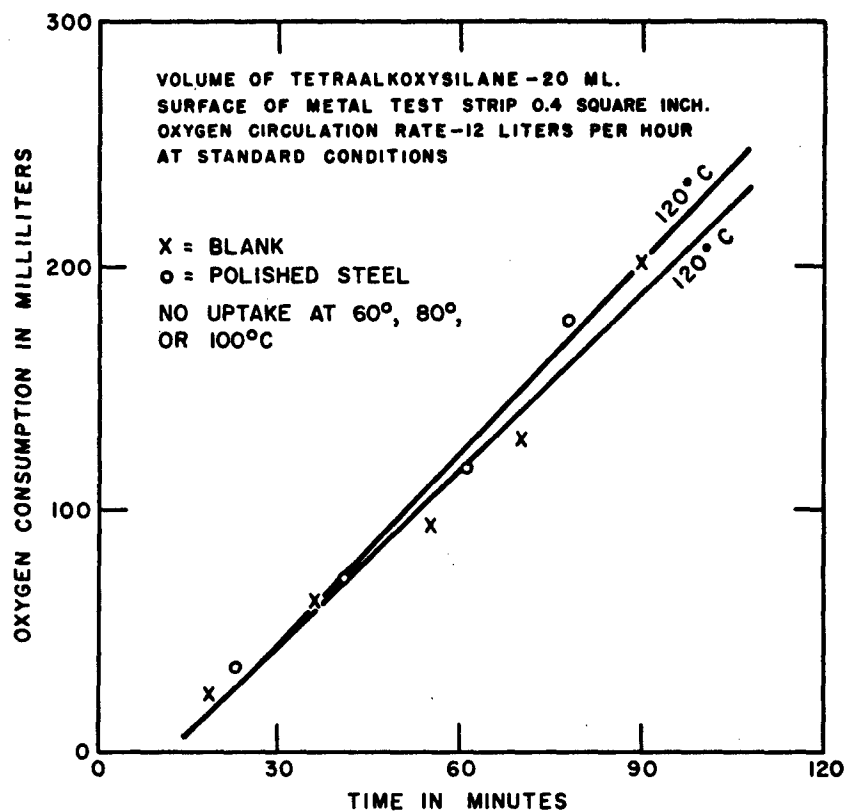


FIG. 23 - OXYGEN CONSUMPTION OF
TETRA(2-PENTOXY)SILANE
IN THE PRESENCE OF STEEL

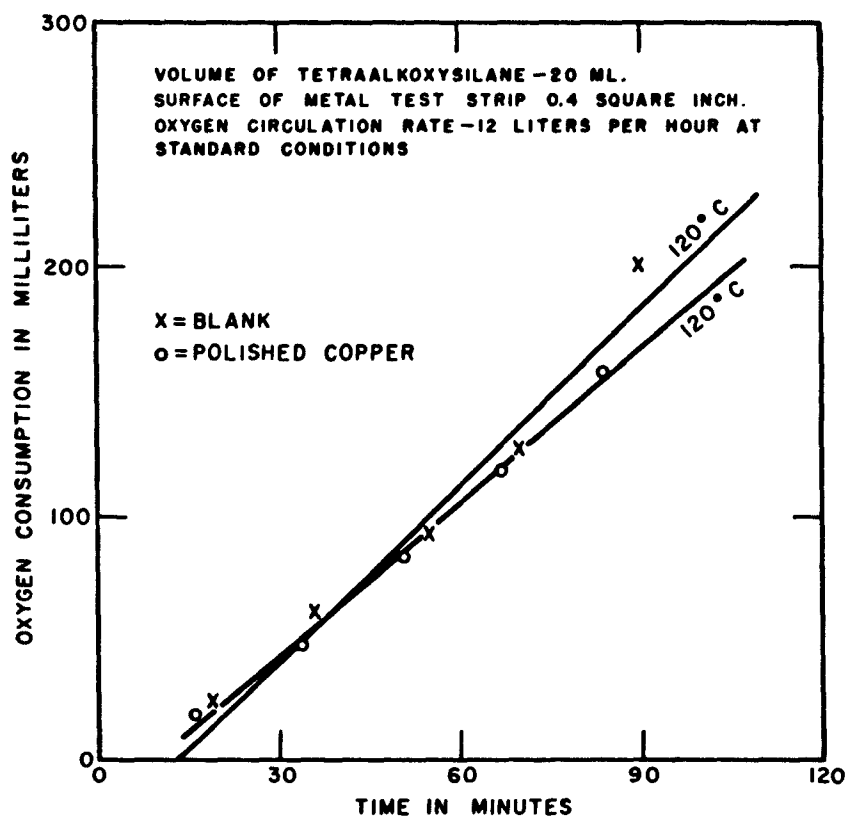


FIG. 24 - OXYGEN CONSUMPTION OF
TETRA(2-PENTHOXY)SILANE
IN THE PRESENCE OF COPPER

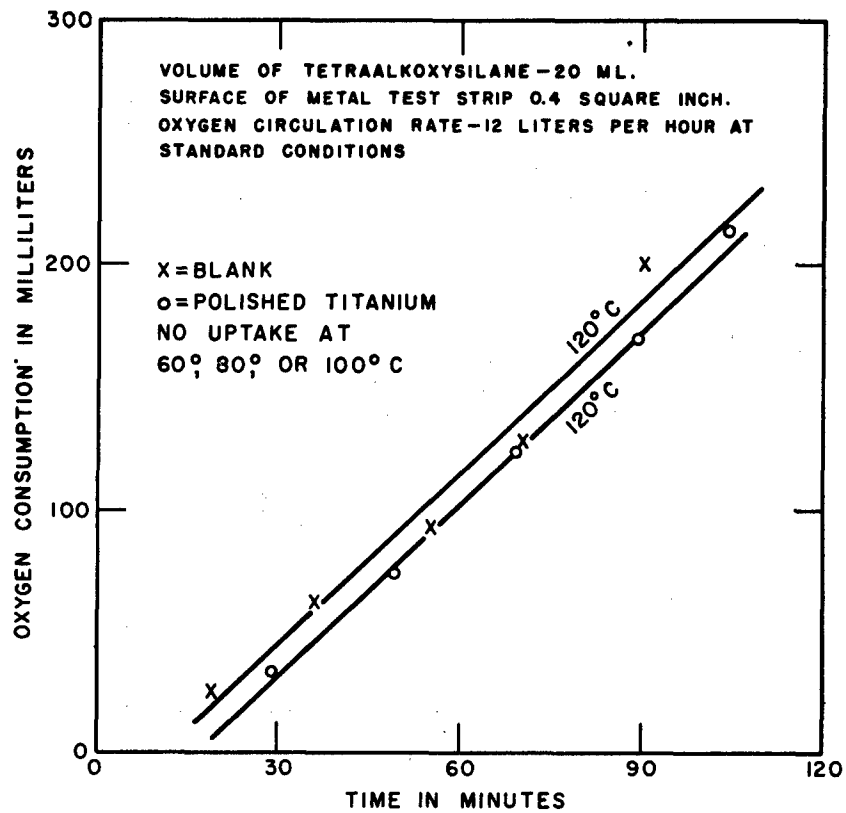


FIG. 25— OXYGEN CONSUMPTION OF
TETRA(2-PENTOXY)SILANE
IN THE PRESENCE OF TITANIUM

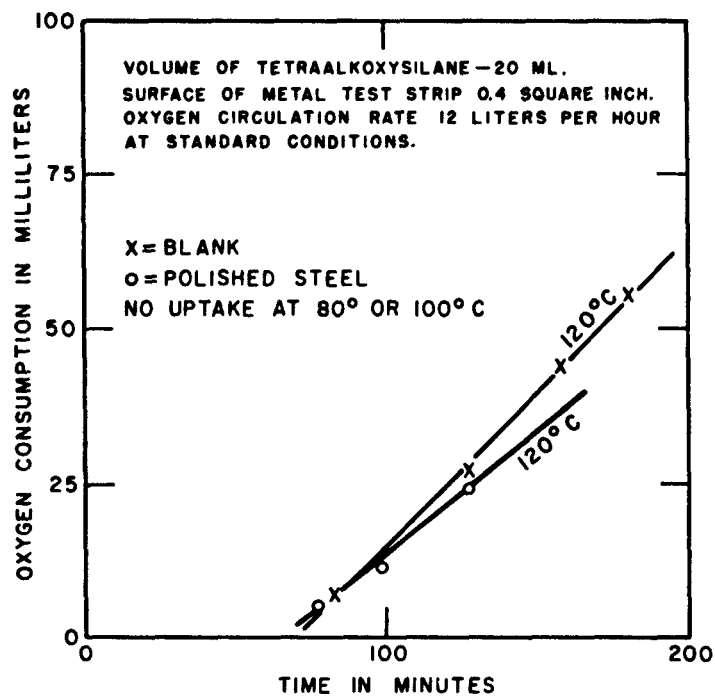


FIG. 26—OXYGEN CONSUMPTION OF TETRA(I-PENTOXY)SILANE
IN THE PRESENCE OF STEEL

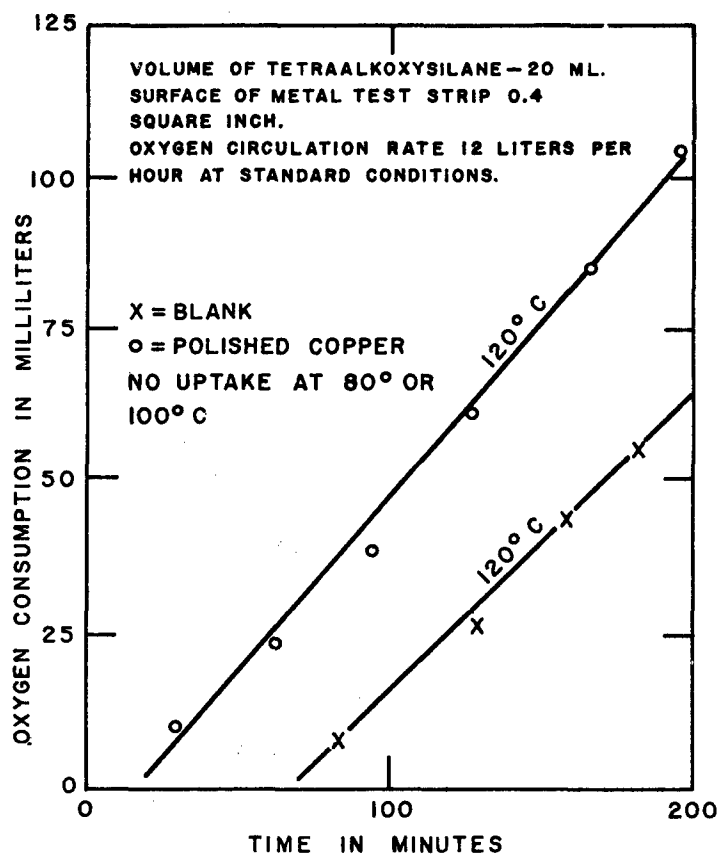


FIG. 27 - OXYGEN CONSUMPTION OF TETRA(I-PENTOXY)SILANE
IN THE PRESENCE OF COPPER

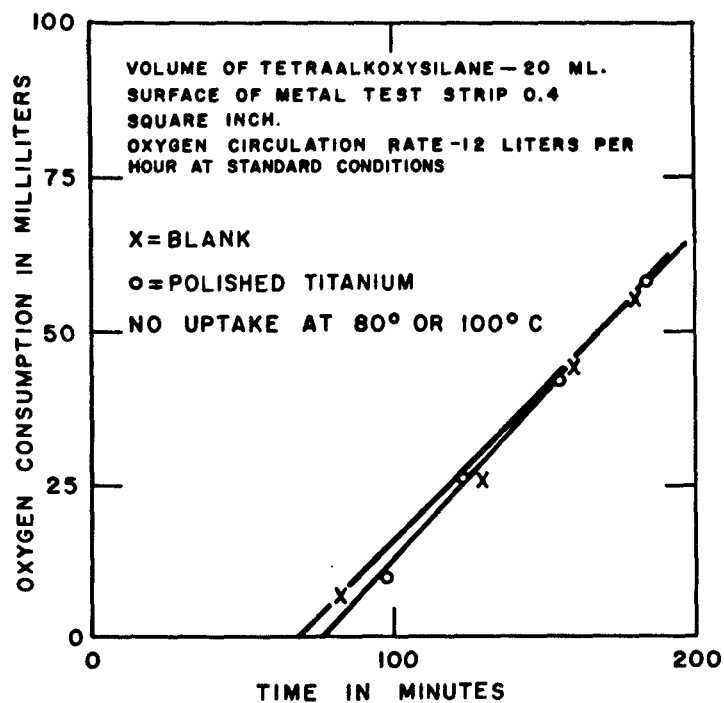


FIG. 28—OXYGEN CONSUMPTION OF
 TETRA(I-PENTOXY)SILANE
 IN THE PRESENCE OF TITANIUM

SECTION V. HYDROLYSIS

When the importance of hydrolytic effects became apparent, the various methods used for studying hydrolysis of similar materials were reviewed. Many of the screening methods suffer from the defects of heterogeneous systems in which surface effects and interface areas become overwhelmingly important.

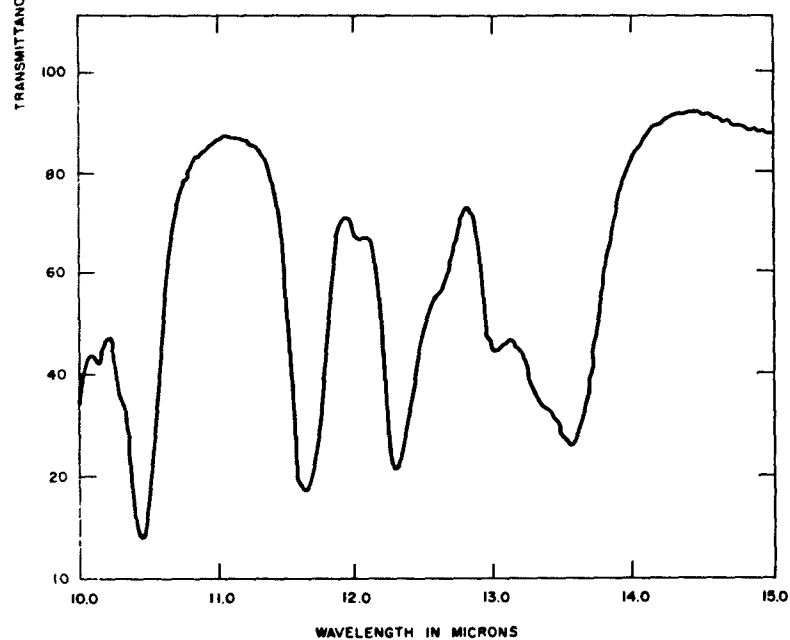
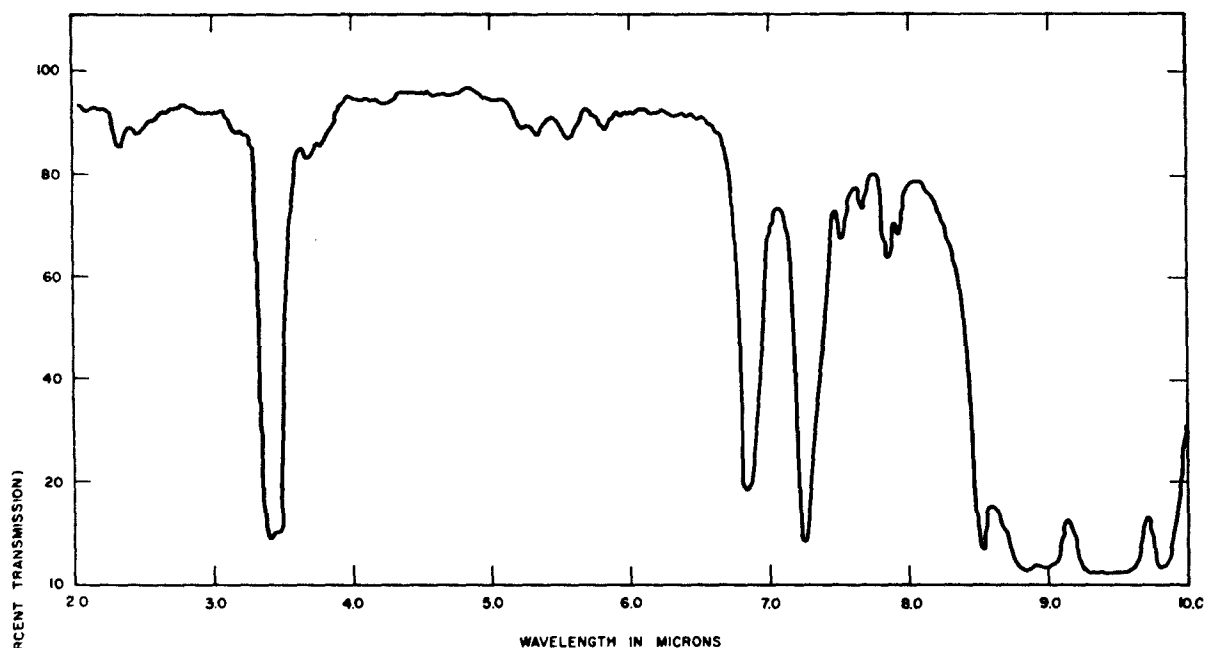
Consequently, after some preliminary experiments, dioxane was selected as a mutual solvent for water and for the organosilicon compound under test. This system was homogeneous, and rates could be studied by following the disappearance of water by titration with Karl Fischer reagent. The test method is described in Appendix IV.

The initial hydrolytic rate studies were carried out with tetraphenoxysilane and tetra(2-ethylhexoxy)silane (Figure 34). The former compound hydrolyzed very rapidly, while the latter hydrolyzed much more slowly. Since chemical structure apparently influenced the rate of hydrolysis, this aspect of the problem was studied in further detail.

As an aid toward determining the mechanism of the hydrolytic reaction, tetra(2-butoxy)silane and certain of its hydrolysis products were prepared. The 2-butoxy grouping was chosen because its silanol and silane-diol derivatives are moderately stable and can be isolated and characterized.

Tri(2-butoxy)silanol, hexa(2-butoxy)silane, and the hydrolysis product of di(2-butoxydichloro)silane were prepared and characterized by infrared spectrometry (see Appendix I for preparative methods). A solution of tetra(2-butoxy)silane in dioxane was treated with water in 1:1 molar ratio. The homogeneous reaction mixture was held in an oil bath at 94°C (200°F). At intervals samples were removed and examined by infrared spectrometry.

The infrared spectra readings made on tetra(2-butoxy)silane and its hydrolytic intermediates are represented in Figures 29 to 32. In the interpretation of the infrared data it was found that the presence of water interfered with the determination of the OH group in the hydrolytic intermediates. It was necessary, therefore, to strip each sample in a high vacuum to remove water vapor at low temperature, as well as to remove the alcohol resulting from hydrolysis of the tetra(2-butoxy)silane. The stripped material was then redissolved in appropriate solvents for infrared studies. While these data are of an exploratory nature, they indicate that the hydrolysis of tetra(2-butoxy)silane proceeds through the formation of a silanol, followed by successive hydrolysis of the butoxy groups, rather than through the intermediate formation of a disiloxane.



<u>Compounds</u>	
—	TETRA(2-BUTOXY)SILANE N.B. 1447524 AMT. 4
<u>Source and Purity</u>	
STANFORD RESEARCH INSTITUTE PROJECT CU-663	
State:	LIQUID
Temperature:	ROOM
Cell Length:	0.0127 mm
MODEL 21 PERKIN ELMER SPECTROMETER	

FIG. 29 - INFRARED SPECTRA OF BUTOXYSIANE

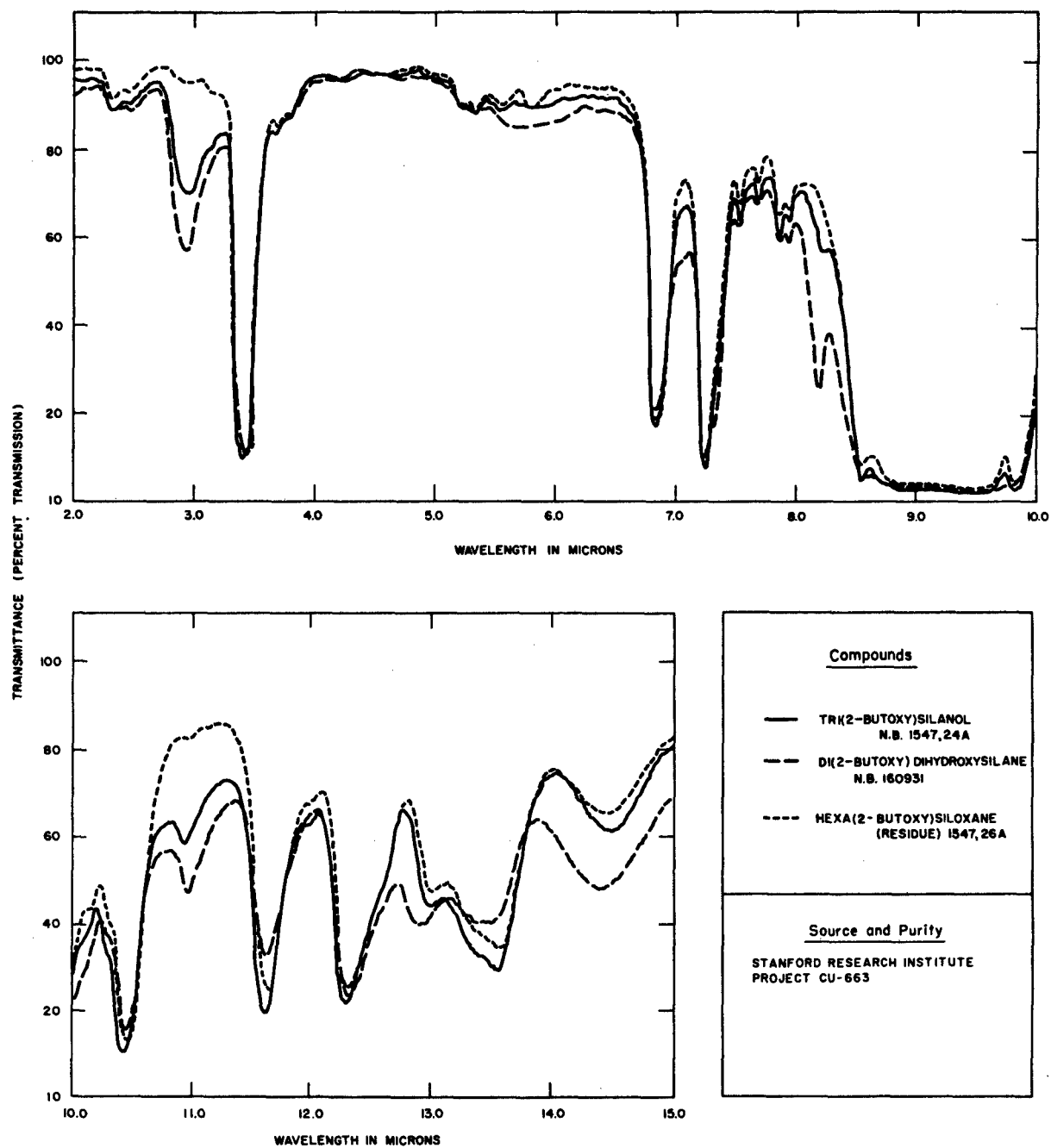


FIG. 30 - INFRARED SPECTRA OF HYDROLYTIC INTERMEDIATES OF BUTOXSILANE

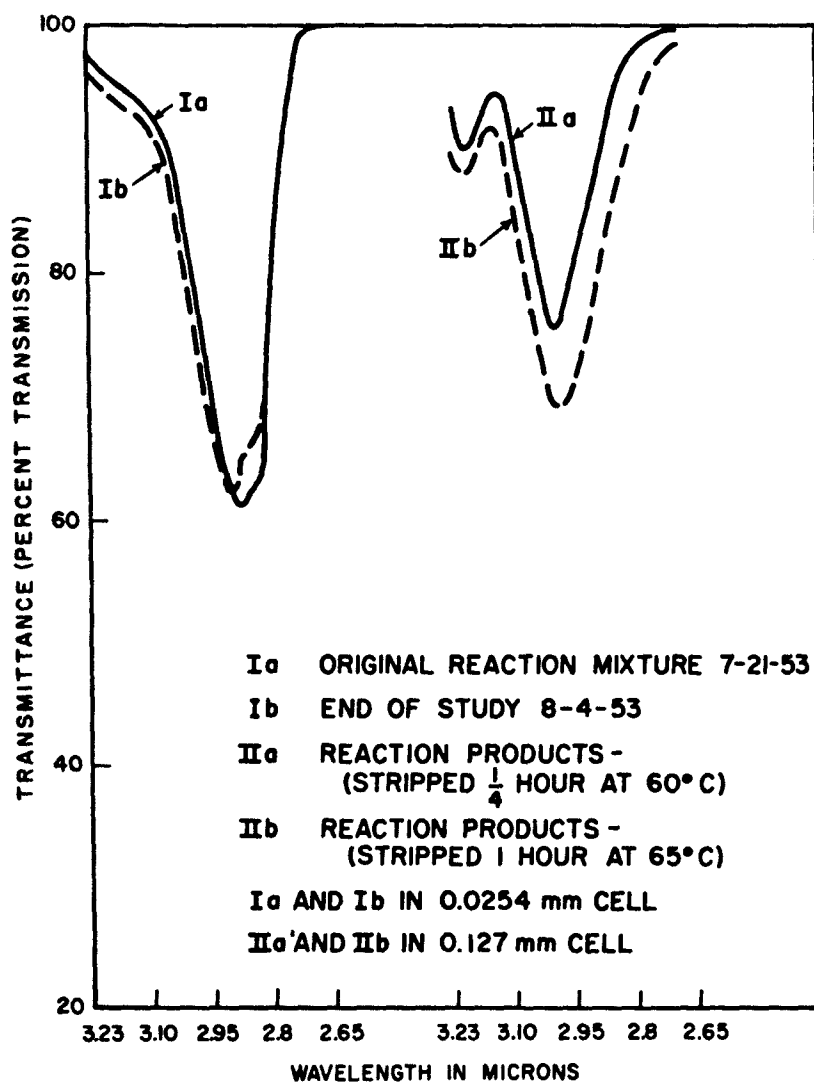
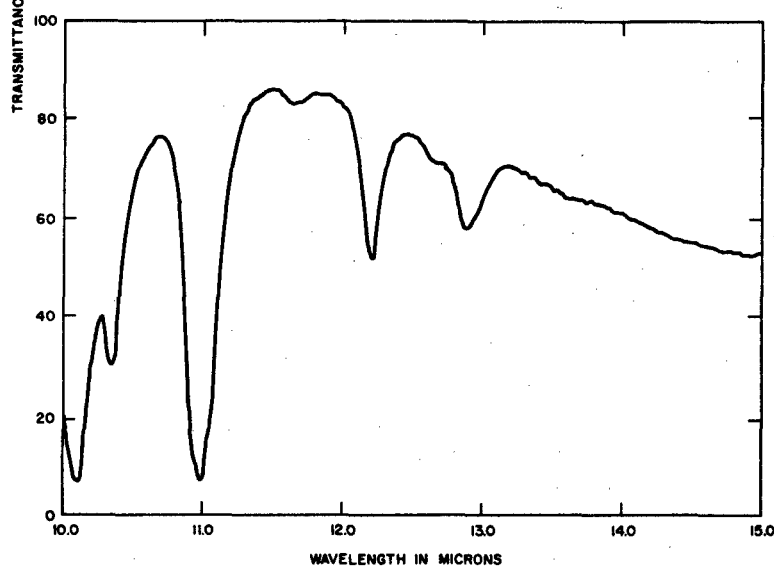
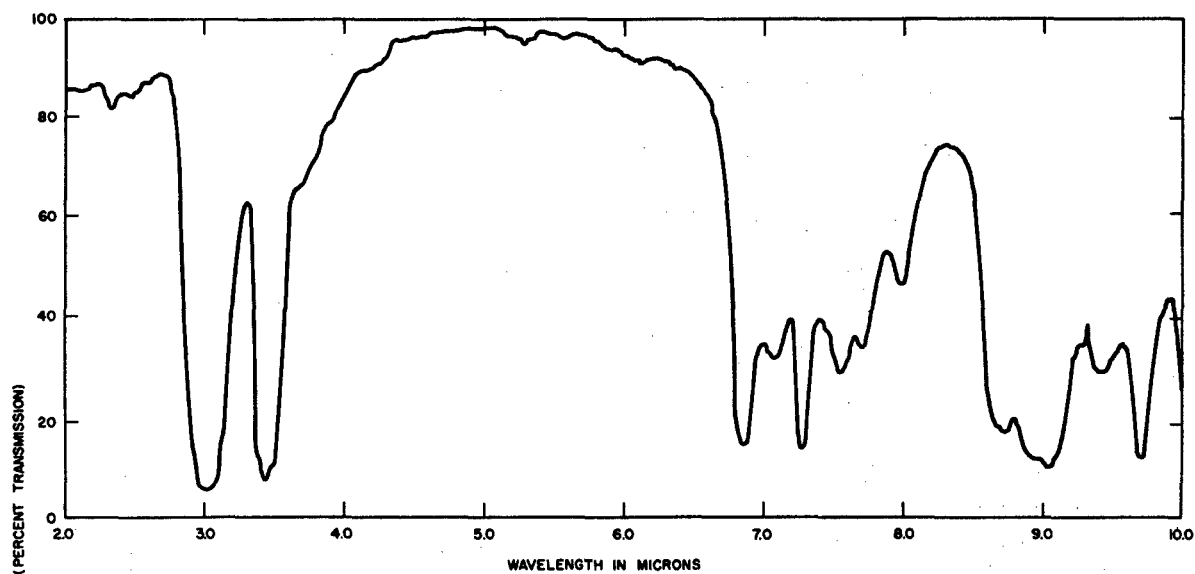


FIG. 31-INFRARED SPECTRA OF HYDROLYTIC STUDY
OF TETRA(2-BUTOXY)SILANE



<u>Compounds</u>	
BUTANOL-2	
<u>Source and Purity</u>	
STANFORD RESEARCH INSTITUTE PROJECT CU-663	
State:	LIQUID
Temperature:	ROOM
Cell Length:	0.0127 mm
MODEL 21 PERKIN ELMER SPECTROMETER	

FIG. 32 - INFRARED SPECTRA OF BUTANOL-2

Hydrolysis rate studies were then carried out on the following compounds:

Tetra(3-methyl-1-butoxy)silane

Tetra(2-methyl-1-butoxy)silane

Tetra(2-pentoxo)silane

Tetra(3-pentoxo)silane

Tetra(1-pentoxo)silane

Tetra(3-methyl-2-butoxy)silane

The conditions employed were those described in Appendix IV except that the temperature was raised. The compounds tested were heated with a five-fold molar ratio of water in dioxane solution in sealed tubes at 131°C (270°F). Over a period of ten days, of the compounds tested, only tetra(3-methyl-1-butoxy)silane, Figure 33, and tetra(1-pentoxo)silane showed any significant consumption of water. Eight to ten samples of each compound were analyzed over the same period. The stability of the medium was tested by heating dioxane and water alone in a sealed tube. After ten days the contents of the tube had the same analysis as the original sample. No differences were noted when the tubes were filled with nitrogen instead of air prior to sealing. In view of the failure of these compounds to hydrolyze as expected, further tests were made. Dioxane-water solution was added to aliquots of the turbid and partially gelled residual material from the oxidation of tetra(3-pentoxo)silane. However, no consumption of water occurred after five days in a sealed tube at 131°C (270°F). This would seem to indicate polymerization rather than hydrolysis to be the cause of gelation and turbidity. To test the effect of the acidic products of partial oxidation on the rate of hydrolysis, material collected in the cold trap from the oxidation of tetra(3-pentoxo)silane was diluted with dioxane. One-milliliter portions, each equivalent to one milliliter of 0.1N base, were added to another series of samples of tetra(3-pentoxo)silane. No consumption of water was noted after heating for five days in sealed tubes at 131°C (270°F). It should be noted that tetra(1-pentoxo)silane showed a measurable hydrolysis rate at 94°C (200°F), as shown in Figure 34.

While the above results are by no means conclusive, there is some indication that the more highly branched materials are somewhat less susceptible to hydrolysis than the straight chain or slightly branched materials. A very recent article 7 indicates that certain substituted silanols may react with Karl Fischer reagent. In view of this recent finding it is probable that some or all of the data obtained to date should be recalculated.

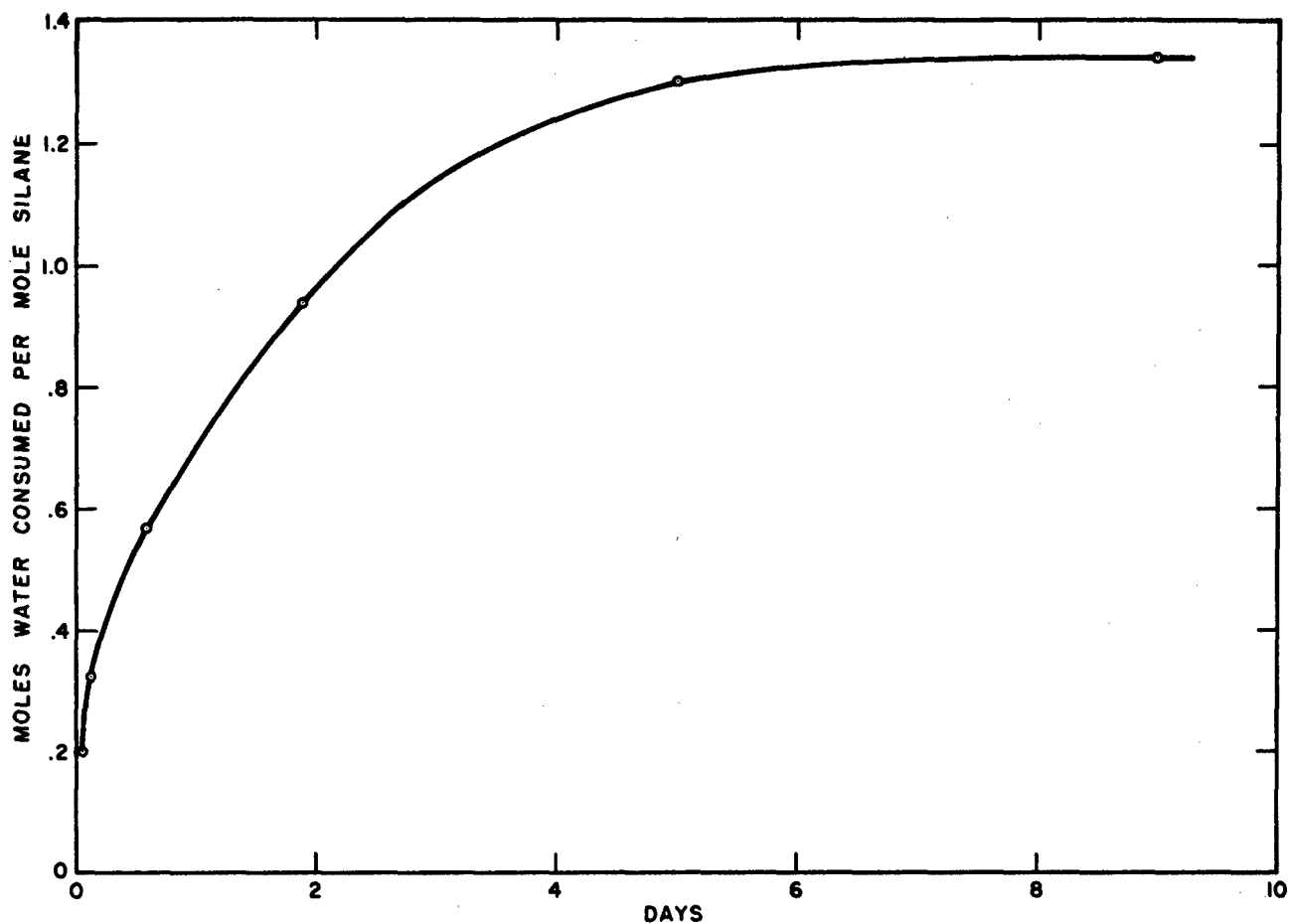


FIG. 33 - HYDROLYSIS OF TETRA(3-METHYL-1-BUTOXY)SILANE
AT 131°C (270°F)

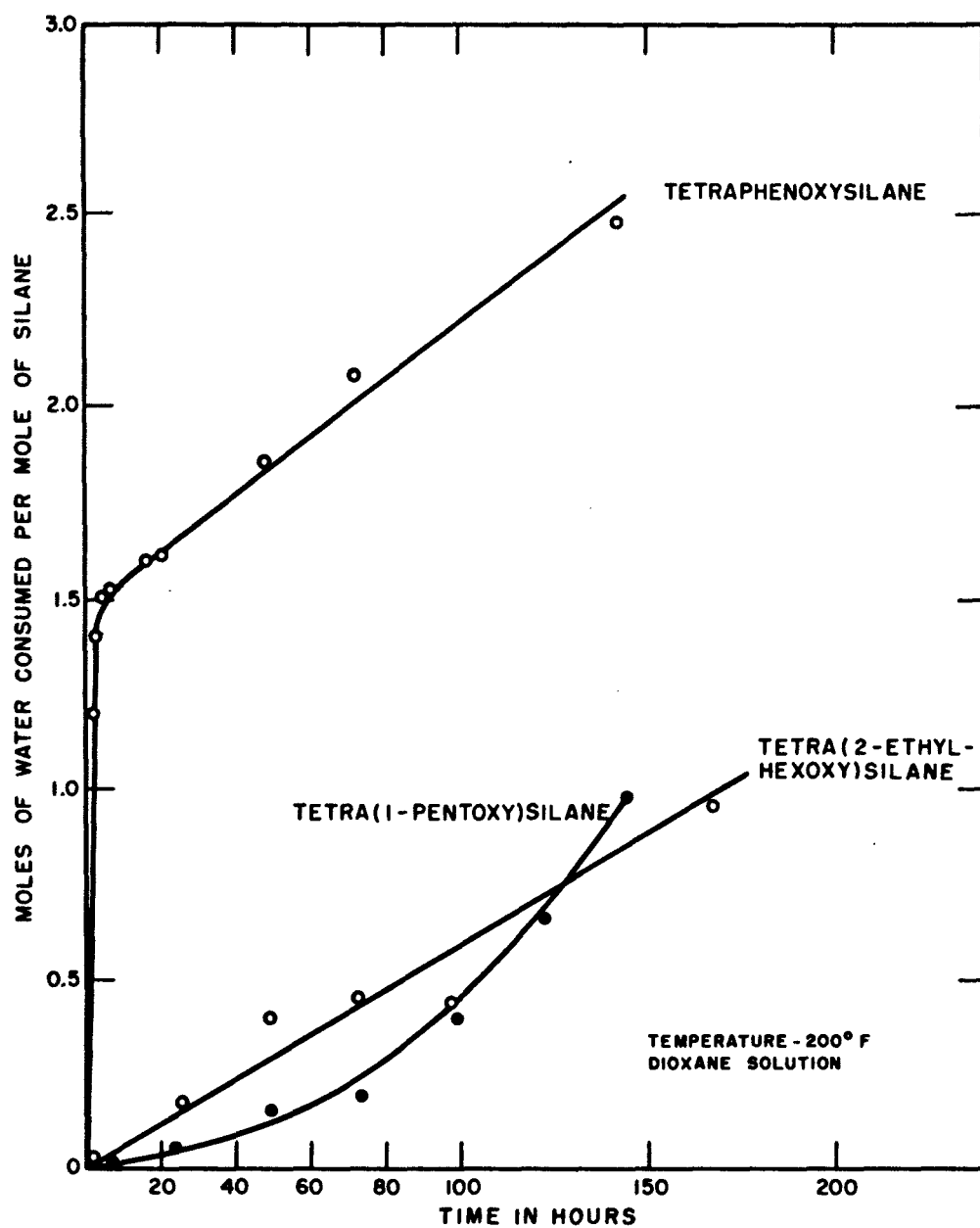


FIG. 34-HYDROLYTIC RATE CURVES

SECTION VI. PYROLYSIS

The oxidation system previously described (Figure 1) was employed in the pyrolytic studies. However, the recirculating system was not used; nitrogen from a cylinder was led through a flowmeter, a drying train, and the reaction cell, then successively through a cold trap immersed in a dry ice-acetone mixture, a drying tube, an Ascarite tube, and a mercury trap. Since there was always a slight pressure on the system, any leakage would have been outward, and the difficulties encountered with the recirculating system were minimized. Because of the high temperatures used, the condenser was cooled with an air stream. Considerable trouble was caused by the freezing of standard taper joints; after some of the runs the equipment could be dismantled for cleaning only by cutting the joints.

Tetraphenoxysilane was heated at reflux 422°C (792°F) for 114 hours. This material was remarkably stable, and only slight changes occurred (Table IV). Apparently the benzene nucleus confers considerable resistance to pyrolysis and oxidation; unfortunately this compound was the most susceptible to hydrolysis of those tested. The mechanisms for pyrolysis and oxidation were compared in Section IV, Oxidation.

Tetra(2-ethylhexoxy)silane was treated in a similar fashion except that its reflux temperature varied from 340 to 350°C (674° to 692°F) as pyrolysis proceeded. After 18 hours, approximately 2 ml of a clear, colorless, mobile liquid collected in the cold trap. This material was identified as heptene-2 (or -3). The mechanism of formation of this substance has been discussed in the section on oxidation. In view of the fact that approximately 50 grams of tetra(2-ethylhexoxy)silane was used in the test sample, the proportion of heptene-2 or -3 formed was relatively small.

Apparently pyrolysis contributes the least to degradative changes in the aryloxy- or alkoxysilanes. It is probable that the thermal cracking effects can be minimized by choice of a suitable structure.

SECTION VII. SUMMARY AND CONCLUSIONS

Oxidation

It may be concluded that while measurable rates of oxidation occur with the tetraalkoxysilanes at temperatures as low as 150°C (302°F), the mechanism of viscosity increase is complicated by the fact that water is produced in the oxidation and ultimately leads to hydrolysis,

TABLE IV
SUMMARY OF PYROLYTIC EFFECTS
(Atmospheric Pressure in Nitrogen)

COMPOUND	TIME (HOURS)	TEMPERATURE, °C	REFRACTIVE INDEX		VISCOSITY (Cs)		MELTING POINT	
			Initial	Final	Initial	Final	Initial	Final
Tetraphenoxy- silane	114 ^{1/}	442 (792°F)	1.5583	1.5593 (54.8°C)	6.6	7.8	53.5°C	42- 49°C
Tetra(2-ethylhex- oxy)silane	18 ^{2/}	340-350 (644- 662°F)	1.4373	1.4398 (25°C)	9.5	13.3	Liquid	

^{1/}The material darkened; infrared spectroscopy confirmed the presence of phenol in material crystallized in the reflux condenser.

^{2/}A liquid condensed in the cold trap and was identified as either heptene-2 or heptene-3 with approximately 20% 2-ethylhexene-1. Methoxyl groups were identified in the residue

at least in part. In cases where the products of combustion were confined, hydrolysis was rapid and extensive. These observations lead to the conclusion that mechanical systems employing these fluids should either be protected from air or oxygen or be equipped with provision for rapid removal of water, vapor, or both. This conclusion is strengthened by experiments which indicated that heating of either tetraphenoxysilane or the tetraalkoxysilanes in an inert atmosphere did not lead to large changes in viscosity. The presence of steel, titanium, and copper did not produce large changes in the rate of oxidation of the test materials.

Hydrolysis

Hydrolytic rate studies in a heterogeneous system indicated that a typical tetraaryloxysilane was very susceptible to hydrolysis. Tetra(2-ethylhexoxy)silane hydrolyzed at a much lower rate although this rate was measurable (Figure 34). Of the isomeric tetrapentoxysilanes studied only tetra(1-pentoxy)silane and tetra(3-methyl-1-butoxy)silane showed measurable rates of hydrolysis even in sealed tubes at 131°C (270°F). These experiments lead to the conclusion that structure of the test material may have a profound effect upon the resistance to hydrolysis. It is planned to explore the effects of structure on hydrolytic susceptibility during the forthcoming year. It may also be possible to obviate hydrolytic effects in otherwise acceptable materials by inclusion of suitable inhibitors or water scavengers.

Pyrolysis

Of the factors involving the viscosity increase of the tetraaryloxy- and alkoxysilanes, pyrolysis is probably the least important. Tetraphenoxysilane and tetra(2-ethylhexoxy)silane were both remarkably stable when heated for long periods of time in a nitrogen atmosphere. Only the tetra(2-ethylhexoxy)silane showed a measurable change in properties which was accompanied by evidence of thermal cracking. This degradation apparently resulted from the breaking of the carbon-carbon bond adjacent to the carbon-hydrogen-silicon bond. This conclusion was confirmed by the presence of methoxyl groups in the pyrolysis residue.

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APPENDIX I

METHODS OF SYNTHESIS

Preparation of Tetraphenoxysilane (TPS)

Pilot Synthesis



Fifty-eight g of silicon tetrachloride were added to 194 g of fused CP phenol which had previously been dried by distillation. The addition of the SiCl_4 occupied about ten minutes. The apparatus was protected from water with Drierite (anhydrous CaSO_4). A smooth, steady reaction began immediately, as evidenced by the evolution of HCl gas, and continued for two hours. When the reaction began to slow down, the mixture was heated up to reflux temperature and continued for 19 more hours. The excess phenol was distilled out of the reaction mixture at atmospheric pressure, employing a 2-foot Vigreux column. As soon as the phenol had been distilled off, a vacuum distillation with a nitrogen bubbler was begun at 2 mm. A small amount of residual phenol distilled over at 55°C (131°F), followed by the TPS at 237°C (459°F). The TPS distillate was a water-white liquid which became hazy after three days at room temperature. When the liquid was cooled down to 5°C (37°F), it solidified and did not remelt at room temperature. Supercooling appears to be a characteristic of this material particularly when not quite pure.

Large Preparation

The pilot synthesis went so smoothly that a large preparation was made in the same way, except that a much smaller excess of phenol was used. SiCl_4 (533 g) was added over a period of 30 minutes to 1200 g of molten phenol, which had been carefully dried and redistilled. The reaction proceeded spontaneously for four hours and the mixture was then heated for 17 hours at about 250°C (482°F). It did not reflux at this temperature. The reaction vessel was protected by Drierite.

The reaction mixture was vacuum fractionated in a 5-foot heated column packed with jack chain. The small quantity of excess phenol was distilled off at a reflux ratio of 10:1 and a pressure of 5 mm Hg. After the TPS began to distill over, the reflux ratio was increased to 30:1. The TPS was distilled over at 210°C (410°F) and 1.3 mm. A very small stream of nitrogen was bubbled into the boiler to facilitate smooth boiling.

A total of six cuts were taken, all but the first of which spontaneously solidified. The distillate was clear and water-white and remained so.

All of the reaction mixture which was distilled went over without any change in the distillation temperature. The distillation was finally stopped when the residual volume was reduced to about 50 ml.

There appear to have been no appreciable amounts of chlorosilanes or of polymers formed during this preparation.

The physical properties are reported in Table I.

Preparation of Tetra(2-ethylhexoxy)silane (TEHS)

One hundred and eighty g of silicon tetrachloride were added slowly to 600 g of 2-ethylhexanol-1 (Eastman Practical Grade). After three hours at room temperature the mixture was slowly heated to 110°C (230°F) and held at this temperature for 24 hours. The temperature was then raised to 145°C (293°F) and held for an additional 36 hours. During this period dry nitrogen was slowly bubbled through the reaction mass to remove HCl. The mixture remained clear but darkened. The reaction mass was then vacuum-distilled at 0.3 mm pressure. The heart-cut distilled at 170°C (338°F) at 0.3 mm pressure. Properties of this material are reported in Table I.

Preparation of Tetra(1-pentoxo)silane

In a 2-liter 3-necked flask fitted with a condenser and drying tube, a pressure-balanced dropping funnel, and a stirrer, were placed 682 g of normal amyl alcohol (pentanol-1). The alcohol was of analytical reagent grade, fractionated at 5:1 reflux in 30-plate column. The forerun was discarded and only the heart-cut of this material was used. The flask was immersed in crushed ice and 313 g of silicon tetrachloride were added slowly over a period of 1-1/2 hours. Agitation was continued for an additional half hour after addition was complete. The ice bath was then removed and the reaction mass allowed to warm up to room temperature. Hydrogen chloride was steadily evolved during the addition of the silicon tetrachloride and during the subsequent warm-up period. The reaction mass was then permitted to stand overnight at room temperature. Dry nitrogen was then bubbled through the mass while it was heated to 143°C (289°F), at which point the hydrogen chloride evolution was complete. This mixture was distilled and the heart-cut collected at 165°C (329°F) at 45 mm pressure. The properties of this material are reported in Table I.

Preparation of Tetra(2-butoxy)silane

The same procedure was followed as for tetra(1-pentoxo)silane except that 312 g of butanol-2 were reacted with 170 g of silicon tetrachloride. Initially two liquid layers were formed. The ice bath was removed and the reaction was allowed to warm up to room temperature with agitation. The reaction mass became homogeneous after warming and the balance of the silicon tetrachloride was then added. The

solution was heated at reflux temperature for one hour during which dry nitrogen was continuously bubbled through the reaction mass. At the end of this time the reaction was complete. The reaction mass was distilled under vacuum and the heart-cut collected at 86°C (187°F) at 0.7 mm pressure. The heart-cut was then redistilled.

Preparation of Di- and Tri(2-butoxy)chlorosilanes

A method of preparation of the di- and tri(2-butoxy)chlorosilanes and their hydrolytic products was supplied by Dr. J. N. Wright of the California Research Corporation. Butanol-2 (741 g) was placed in the apparatus described for the preparation of tetra(1-pentoxy)silane. Silicon tetrachloride (680 g) was added slowly with agitation while the temperature was maintained between -10° and 0°C (14° 32°F). The reaction was endothermic. It was noted that the ice-salt bath froze to the sides of the flask after all of the silicon tetrachloride had been added. Stirring was continued while the surrounding bath was replenished with ice. The stirrer was then turned off and the mixture allowed to stand overnight and come to room temperature. The following morning the stirrer was turned on. Dry nitrogen was bubbled through the reaction mixture to remove excess hydrogen chloride. This latter operation covered a period of four hours. The mixture was then fractionally distilled under vacuum through an all-glass column packed with single-turn helices. Two main cuts were taken, one at 50°C (122°F) at 0.7 mm pressure and the other at 72°C (162°F) at 0.4 mm pressure. After redistillation of the heart-cuts, these cuts were used for the preparation of the corresponding silanols and silanes.

Preparation of Tri(2-butoxy)silanol

A 56.4 g sample of tri(2-butoxy)chlorosilane was weighed into a dry, 250 ml, stoppered Erlenmeyer flask. This material was chilled by immersing in an ice bath. Water (7.2 g) was mixed with 31.6 g of pyridine in another dry, glass-stoppered flask which was similarly chilled in an ice bath. The water and pyridine mixture was then carefully poured into the tri(2-butoxy)chlorosilane with shaking. The mixture was kept submerged in an ice bath during this operation. At the completion of the reaction the contents of the flask were carefully poured into a dry separatory funnel and the lower layer separated in a dry, glass-stoppered flask. Both layers were stored over anhydrous sodium sulfate. The material was vacuum-distilled, and, after removal of the pyridine, a fraction was collected at 125°C (257°F) at a pressure of 0.6 mm. This material was submitted for analysis and infrared spectroscopy.

Preparation of Hexa(2-butoxy)siloxane

A 1.6 ml sample of pyridine was mixed with 2.6 g of tri(2-butoxy)silanol in a dry, glass-stoppered flask and chilled in an ice bath. Tri(2-butoxy)chlorosilane (2.8 g) was weighed into a dry, glass-stoppered flask and similarly chilled in an ice bath. The pyridine-silanol mixture was then poured slowly into the chlorosilane with agitation. A white precipitate of pyridine hydrochloride was formed. The mixture was centrifuged and a clear liquid decanted. This clear liquid was vacuum-distilled at 0.6 mm pressure. A small quantity of volatile material was removed. The clear residue and distillate were separated and submitted for infrared spectroscopy.

Hydrolysis of Di(2-butoxydichloro)silane

A 25.6 g sample of di(2-butoxydichloro)silane was weighed into a dry, glass-stoppered flask. Into another flask were weighed 3.6 g of water and 24 g of pyridine. Both flasks were chilled in an ice bath. The water-pyridine mixture was shaken into the chlorosilane. A white precipitate formed. Shaking was continued until the white precipitate coagulated; then the clear liquid was decanted and vacuum-distilled at a pot temperature of 40°C (104°F) and a pressure of 0.6 mm. The excess pyridine was stripped off and the residue submitted for infrared spectroscopy.

Preparation of Tetra(2-ethylhexyl)silane

To 4.6 g of metallic sodium "sand" (0.2 mol) suspended in 200 ml of anhydrous ether was added a mixture of 15 g of 2-ethylhexyl chloride (0.1 mol), 4.25 g of SiCl_4 (0.025 mol), and 10 drops of ethyl acetate (catalyst). The reaction proceeded smoothly and yielded 10.7 g of crude material. After washing with sulfuric acid in water, drying, and fractional distillation, there was obtained 3.4 g of pure material.

Larger runs in which the sodium sand was added to the mixture of 2-ethylhexyl chloride and silicon tetrachloride gave 27% yields of quite pure material; however, this procedure involved somewhat larger losses of silicon tetrachloride.

APPENDIX II

RECIRCULATING ALL-GLASS OXIDATION APPARATUS

The following paragraphs describe the design and operation of the all-glass recirculating oxidation system developed at Stanford Research Institute for this project. Reference to Figure 35 will show that oxygen is transferred by the Toepler pump at the lower right-hand corner of the photograph, through a one-liter glass flask which serves as a surge tank, to the reaction cell inside the insulated reaction chamber. This cell is not visible in the photograph but is shown in Figure 36. The reaction cell is encased in an aluminum heating block which contains cartridge-type electric heaters controlled by an automatic temperature regulator. The temperature in the reaction cell is recorded on a continuous strip recorder. The glass spiral visible in the photograph immediately above the reaction chamber serves as an air condenser. Attached to the top of the spiral air condenser is a column packed with stainless steel, single-turn helices. This column effectively eliminates entrainment of material from the reaction cell. The oxygen stream from the deentrainment column is led through a dry ice trap and then through a catalytic combustion pipette which serves to convert carbon monoxide formed during the oxidation to carbon dioxide. An absorption train following the catalytic combustion pipette removes water vapor and carbon dioxide from the gas stream. From the absorption train the oxygen is led back to the intake side of the Toepler pump. In Figure 35 a mercury-filled glass burette is visible at the right-hand end of the absorption train. This glass burette contains the only stopcock in the entire system. Since this joint is at room temperature and is spring loaded, no difficulty from leaks was experienced. In all parts of the system the oxygen stream is exposed only to the sample, and to glass, mercury, or stainless steel.

In performing oxidation studies a 20-ml sample is placed in the reaction cell. If the effect of the presence of metal is being studied a sample of the test metal measuring 0.4 square inches in area is also placed in the cell. In some experiments, it was necessary to reduce the size of the sample, but the area of the metal test strip was decreased correspondingly. The cell is then sealed into the oxidation train and the entire apparatus evacuated and tested for leaks with a light frequency vacuum tester. The sample is then heated to the desired temperature. Pure, dry oxygen is introduced into the system at atmospheric pressure, completely filling the system and the glass burette. The glass burette stopcock is then closed and the Toepler pump started. Since the pump is of the positive displacement type with a uniform pumping rate it is possible to measure the oxygen circulation rate quite accurately. In addition, an automatic counter is incorporated into the electrically controlled system for the Toepler pump so that the total number of pumping cycles is recorded. At intervals during the run the Toepler pump is momentarily shut down, the pressure in the system rapidly adjusted to atmospheric pressure, the stopcock opened to the glass burette, and a reading made of the amount of oxygen absorbed during the previous time interval.

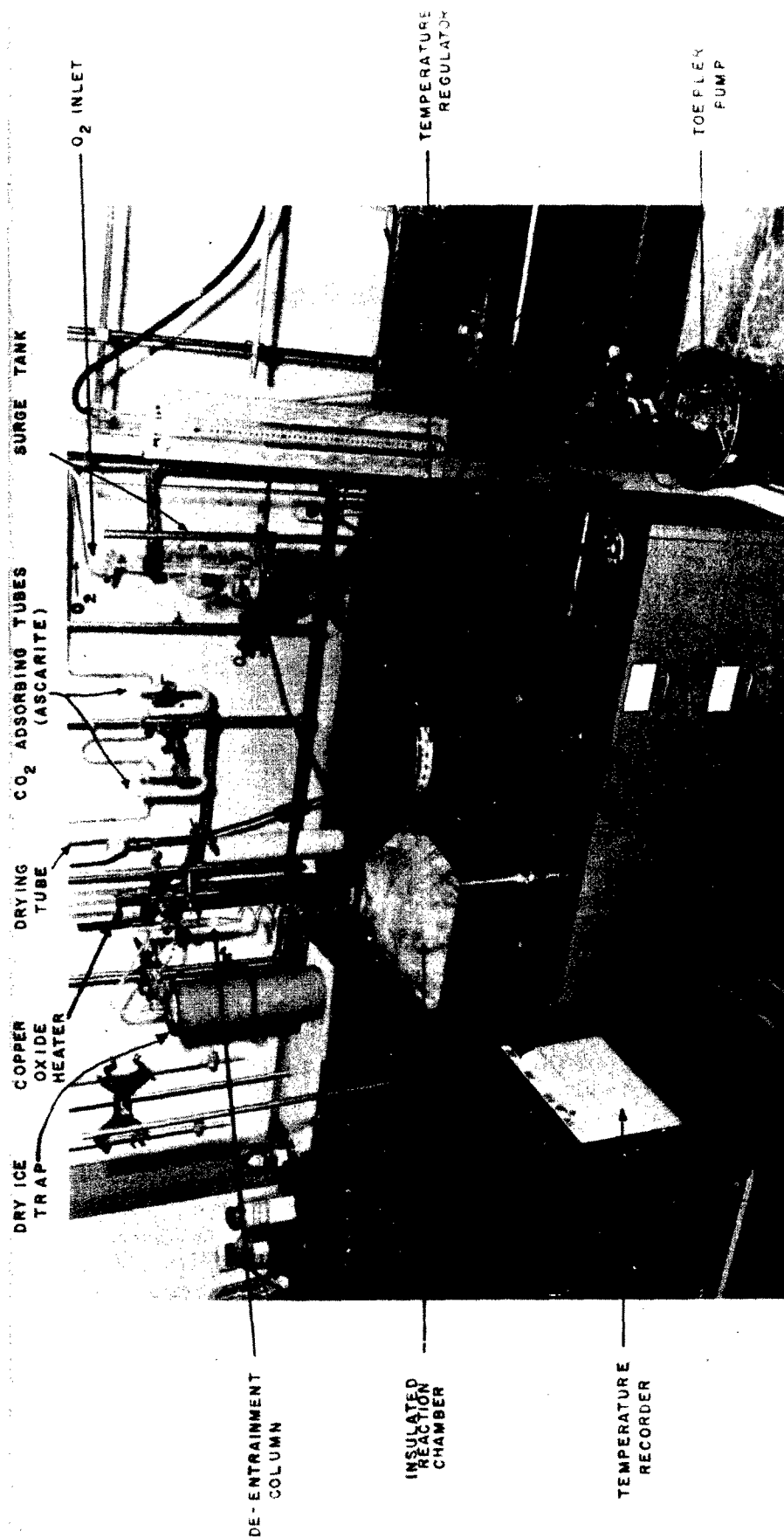


FIG 35 - RECIRCULATING OXIDATION APPARATUS

FIG 35 RECIRCULATING OXIDATION APPARATUS

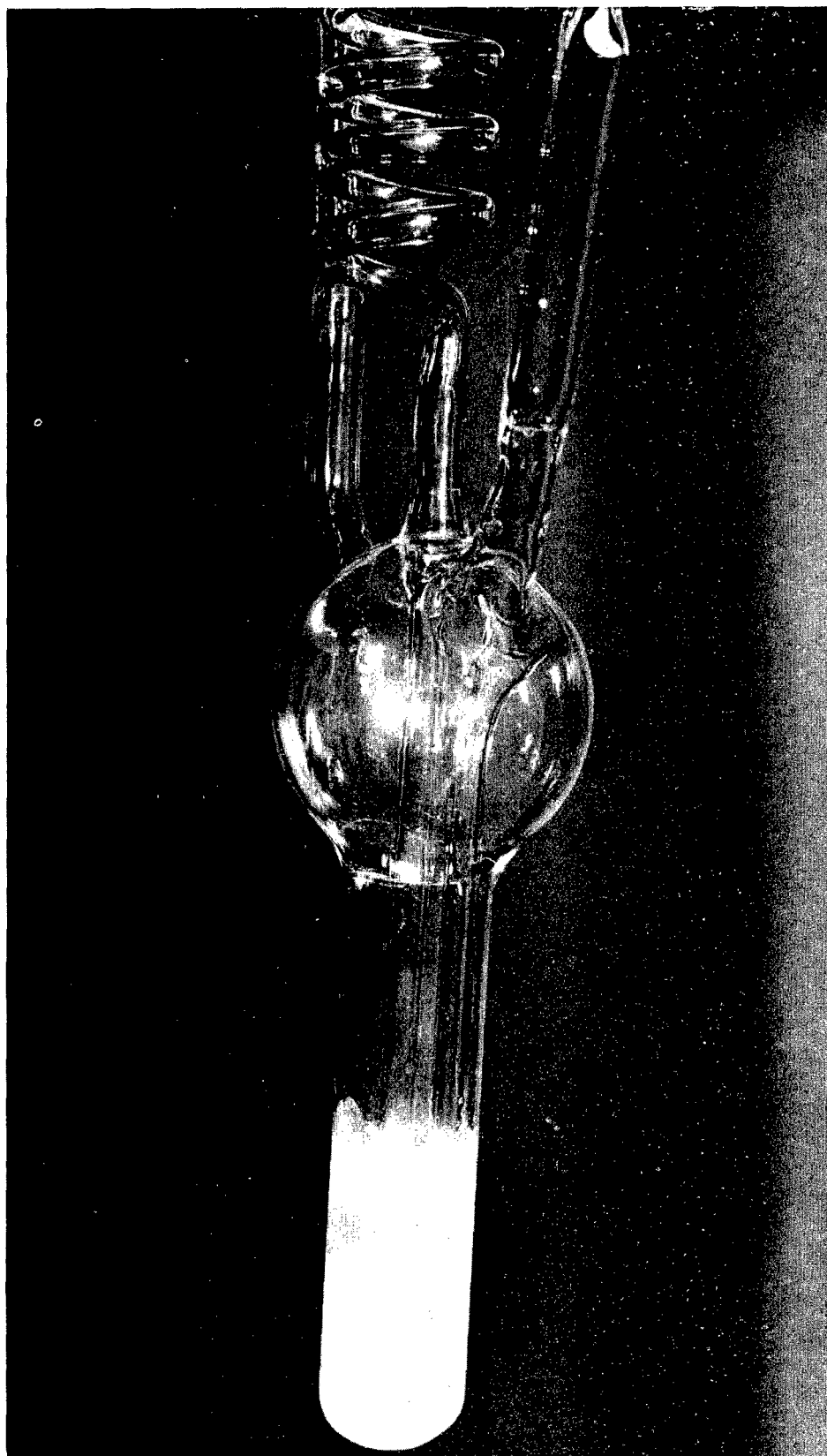


FIG. 36-REACTION CELL SHOWING GELATION OF
TETRA(3-METHYL-2-BUTOXY)SILANE
AFTER HEATING IN THE PRESENCE OF OXYGEN

P-663-ML28-25

In deciding upon the best temperature for blank runs it was found that the method of cleaning the apparatus between runs was important if major variations in the amount of oxygen apparently consumed at low temperatures were to be prevented. After some experimentation with tetra(2-ethylhexoxy)silane it was found that negligible oxidation blanks could be obtained at 100°C (212°F) if the reaction vessel was soaked in an alcoholic potassium hydroxide solution, rinsed repeatedly with distilled water, rinsed with dilute nitric acid to neutralize the residual potassium hydroxide, and finally rinsed 20 times with a total of 2 liters of distilled water.

The experimental results obtained in the blank study are summarized in Table V. A blank below 500 in the "relative oxygen consumption" scale of this table is considered negligible, since this represents a "consumption" of 0.25% by volume of the oxygen circulated per cycle, or less than 0.03% of the oxygen in the system. Such a blank may be accounted for by the solubility of oxygen in the test solution and by temperature changes in the laboratory (the apparatus is not in a constant-temperature room). No corrections were made for the temperature of the apparatus as a whole, since there is obviously a large temperature difference between the reaction cell and the glass measuring burette which is at room temperature. Such corrections would amount to only hundredths of a percent at a maximum, since all successive measurements are made by difference. It may be noted that at temperatures greater than 100°C, where oxidation begins at a significant rate, the absorption of oxygen is so great that the side effects discussed above are negligible. It should be pointed out that temperature measurements are made at the glass burette during readings and that all readings are corrected to standard conditions.

The washing procedure outlined above was adopted as standard procedure and the apparatus is cleaned by this method between each oxidation rate determination.

Table V

SUMMARY OF EQUIPMENT TEST RUNS

TEST MATERIAL	TREATMENT OF APPARATUS	TEMPERATURE, °C	RELATIVE OXYGEN CONSUMPTION ^{1/}
20 ml TEHS ^{2/}	Ordinary washing	100	948
20 ml TEHS	Ordinary washing	100	1,857
Dry run	Ordinary washing	Room (24-29)	0 ^{3/}
Dry run	Ordinary washing	100	0 ^{3/}
20 ml TEHS	NaOH wash with HNO ₃ and H ₂ O rinse	0	134 ^{3/}
20 ml TEHS	NaOH wash with HNO ₃ and H ₂ O rinse	100	212 ^{3/}
20 ml TEHS	NaOH wash with HNO ₃ and H ₂ O rinse	125	3,211 ^{4/}
20 ml TEHS	NaOH wash with HNO ₃ and H ₂ O rinse	150	12,252 ^{4/}
20 ml TEHS	NaOH wash with HNO ₃ and H ₂ O rinse	Room (24-29)	430 ^{3/}
20 ml TEHS	NaOH wash with HNO ₃ and H ₂ O rinse	100	133 ^{3/}
20 ml TEHS	Base washed only, 20 water rinses	Room (24-29)	60 ^{3/}
20 ml TEHS	Base washed only, 20 water rinses	100	711
20 ml TEHS	Base washed only, 20 water rinses	125	2,095 ^{4/}
20 ml TEHS	Base washed only, 20 water rinses	150	13,513 ^{4/}

^{1/} Expressed as milliliters oxygen per cycle of oxygen circulation x 1000.

^{2/} Tetra(2-ethylhexoxy)silane.

^{3/} These runs are considered to be satisfactory blank runs.

^{4/} At these temperatures the oxidation reaction becomes appreciable, which accounts for the large oxygen consumption.

APPENDIX III

STATISTICAL METHODS

It is not possible in a few pages to give the theories behind the statistical procedures used in these studies. However, the following formulas are the ones that have been worked out for these types of data. For additional details "Industrial Experimentation" by K. A. Brownlee (Chemical Publishing Company, N. Y.) should be consulted.

Statistical methods of analysis were applied to data represented in Figures 12 through 28. The experimental data were set up in a tabular form in which the Y coordinates represented the oxygen consumptions in milliliters and the X coordinates represented the elapsed time in minutes. Since most of the data, by inspection, could be represented by a straight line, it then became necessary to develop a regression line, which is the equation of a line representing the most probable fit to the data. The generalized equation is

$$Y = a + b (X - \bar{x}).$$

In this equation the coefficient b represents the slope of the line and consequently the rate constant for the data in question. The constants of this equation may be determined from the following two equations:

$$a = \bar{y} = \frac{\sum Y}{N} = \text{mean of the Y values}$$

$$b = \frac{\sum XY - \frac{(\sum X)(\sum Y)}{N}}{\sum X^2 - \frac{(\sum X)^2}{N}}$$

X = individual value

$\bar{x}$ = mean of values of X

Y = individual value

$\bar{y}$ = mean of values of Y

N = number of observations

S = summation of

degrees of freedom numerically equal 1 less than the number of observations

Once the equation of the regression line has been determined it is possible to draw the line best fitting the data.

From equations of the regression lines, it was a simple matter to test the significance of the individual regression lines. In effect this permitted a check of the reliability of the data obtained during the individual experiments. A table of analysis for variance was constructed as follows:

<u>Source of Variance</u>	<u>Degrees of Freedom</u>	<u>Sums of Squares</u>	<u>Mean Squares (Variance)</u>
Regression	1		
Residual	N-2		
Total	N-1		

The total sum of squares of y values is given by

$$S(Y-\bar{y})^2$$

The sum of the squares accounted for by the regression line is

$$\frac{[S(Y-\bar{y})(X-\bar{x})]^2}{S(X-\bar{x})^2}$$

Consequently, the residual variance is determined by the difference between the total sum of the squares and the variance accounted for by the regression lines. The degrees of freedom are one for the regression line, one less than the total number of pairs of observation for the total, and the residual number of degrees of freedom is the difference between the two. Consequently, under the mean squares column, the regression value will be the same as that under the sum of squares column, and the mean square for the residual will be equal to the sum of the squares for the residual divided by the number of degrees of freedom for the residual. The ratio of the regression mean square to the residual mean square is called the variance ratio. If a table of variance ratios, as found in any standard text on statistical analysis, is consulted, the significance level of the regression line in question can be determined immediately. All of the regression lines were highly significant at a confidence level of 95% or greater. In fact, the majority of the lines possessed a significance level of 99% or greater. This indicates a probability of at least nineteen to one and in most cases ninety-one to one that the relationship did not develop by chance.

Once the reliability of the individual regression lines, or rate curves, was established, it was then possible to test the significance of the differences in slope between the curves for the same material tested with and without the presence of iron, copper, and titanium. It is possible to make this test by using the fact that the variance σ^2 of a regression coefficient is given by the formula

$$\sigma^2 = \frac{\text{residual variance } y}{S(X-\bar{x})^2}$$

The residual variance of y is the same value as the residual mean square shown in the above analysis of variance. In comparing two regression coefficients, b_1 and b_2 , which have residual variances, about the regression lines of σ_1^2 and σ_2^2 with degrees of freedom n_1 and n_2 we form the weighted average residual variance

$$\sigma^2 = \frac{(n_1 \sigma_1^2 + n_2 \sigma_2^2)}{n_1 + n_2}$$

where $n_1 = (N_1 - 1)$ $n_2 = (N_2 - 1)$. The variance of b_1 is then

$$\sigma^2 / S_1(x-\bar{x})^2$$

The variance for b_2 is determined similarly and the variance of the difference is then given by

$$\sigma_{12}^2 = \frac{\sigma^2}{S_1(X-\bar{x})^2} + \frac{\sigma^2}{S_2(X-\bar{x})^2}$$

The Student "t" function is then calculated from the following equation:

$$t = \frac{b_1 - b_2}{\sqrt{\sigma_{12}^2}}$$

The degrees of freedom for this function are given by $n_1 + n_2$. If a table of the "t" function is then consulted a decision may be made immediately as to whether the regression coefficients, in this case the oxidation rates, are significantly different. In no case was there found a significant difference in the rate of oxidation for the materials tested when the test metals were present as compared to the blanks which were run upon the tetraalkoxysilanes alone.

APPENDIX IV

HYDROLYTIC RATE DETERMINATION METHODS

In the hydrolysis studies, 10-ml aliquots of a dioxane solution containing 2 millimoles of the aryloxy- or alkoxysilane were transferred to dry, glass-stoppered 100-ml volumetric flasks. Then 10-ml aliquots of a dioxane-water solution containing 10 millimoles of water were added to each flask, which was then stoppered and transferred to a thermostatically controlled oil bath at 94°C (200°F). The 5:1 mol ratio of water to silane represents 25 to 150% excess over theory, depending upon whether the reaction product is fully hydrated silicic acid or SiO_2 . At intervals, flasks were removed from the bath, their contents transferred to dry, glass-stoppered 250-ml Erlenmeyer flasks with the aid of 50 ml of dry methanol, and titrated with Karl Fischer reagent, using a deadstop electrometric end point. Comparison of the titration results with a blank permitted estimation of the water consumed by the hydrolysis. The results obtained are shown graphically in Figure 34. It was noted that with all three compounds tested a flocculent precipitate appeared in small amounts after about 100 hours. The dioxane used in these studies was purified by two treatments with potassium hydroxide, followed by distillation over sodium metal.