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WADC TECHNICAL REPORT 58-44

PART I

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SYNTHESIS OF TIN-CONTAINING POLYMERS

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PAUL E. KOENIG
JAMES H. HUTCHINSON

ETHYL CORPORATION

Best Available Copy

MAY 1958

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PART I

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SYNTHESIS OF TIN-CONTAINING POLYMERS

*PAUL E. KOENIG
JAMES H. HUTCHINSON*

ETHYL CORPORATION

MAY 1958

MATERIALS LABORATORY
CONTRACT NO. AF 33(616)-3848
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 Paul E. Koenig and J. H. Hutchinson of the Ethyl Corporation under USAF Contract No. AF 33(616)-3848. This contract was initiated under Project No. 7340, "Rubber, Plastic and Composite Materials, Task No. 73404, "Synthesis of Tin-Containing Polymers". The work was monitored under the direction of the Materials Laboratory, Directorate of Laboratories, Wright Air Development Center, with Capt. J. F. O'Brien and Lt. Paul Shaw as Project Engineers.

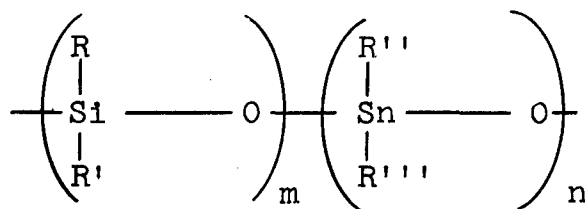
This report covers work conducted from April 1956 to December 1957.

Ethyl personnel who have contributed to this effort have been Dr. F. Conrad, Dr. R. P. Curry, Dr. A. J. Haefner, Dr. W. E. Foster, Dr. E. D. Hornbaker, Mr. J. H. Hutchinson, Dr. P. E. Koenig, Dr. M. B. Smith and Mrs. Ann Breaux.

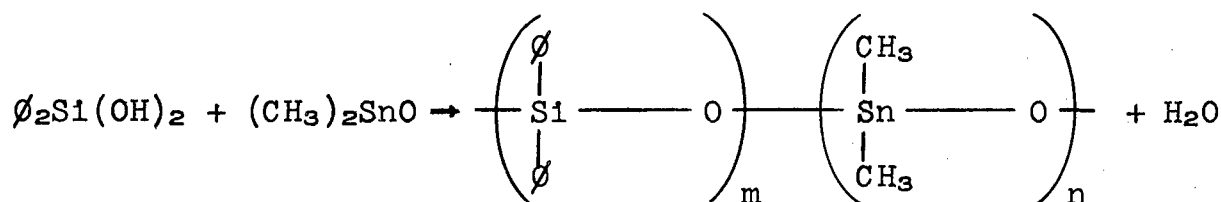
Work in the general area of organometallic polymers is continuing, and subsequent parts of this Report will appear in the future.

ABSTRACT

This investigation has been largely directed toward the preparation of stannosiloxane polymers, whose structure may be represented as follows:



These compounds have been prepared by various condensation polymerizations, including a novel reaction between silanediols and organotin oxides, typified by the following example:



A second excellent synthetic method involves cohydrolysis of mixtures of dichlorosilanes and organotin dihalides; this method is well-suited to the preparation of polymers containing alkyl groups bound to silicon.

An analogous cohydrolysis reaction employing different organotin dihalides but no silicon compounds leads to formation of copolymeric stannoxanes; these are interesting in that they represent the first thermoplastic metal-oxide type polymers other than the silicones.

The products obtained are viscous fluids or transparent glasses; their hydrolytic and thermal stability is good. Difficulty has been experienced in attempting to produce high polymers over the composition range examined; the molecular weights thus far observed have been of the order of 1,-5,000, and some properties of the products are therefore correspondingly deficient. Work is in progress to obtain higher molecular weight products, which may well be exceptionally stable and highly useful materials.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:

A handwritten signature in cursive script that reads "R. T. Schwartz".

R. T. SCHWARTZ
Chief, Organic Materials Branch
Materials Laboratory

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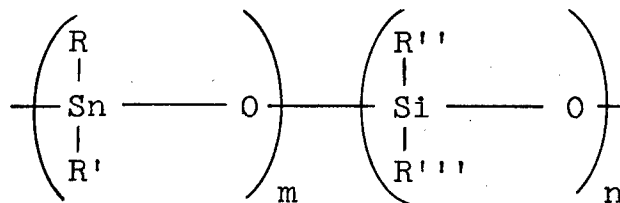
SECTION I

INTRODUCTION

There is a wide-spread and expanding need in both military and civilian circles for new materials possessing extraordinary resistance to chemical, thermal, electrical or radio-chemical degradation. Polymers which manifest such a high order of stability may well serve as lubricants, hydraulic fluids, rubbers, plastics or fibers under conditions destructive to materials presently used in these applications; therefore, the search for polymers which are unaffected by severe chemical or physical stress is of considerable importance.

The relative inertness of the siloxane resins and fluids is well known and well exploited in high-temperature service. However, the siloxanes leave much to be desired in several areas, including chemical resistance and lubricity, and there is room for improvement even in their thermal stability. The siloxane polymers are unique among useful polymeric materials in their possession of a metal oxide structure; they may be considered to be organo-substituted silica. To the extent that this oxide structure imparts thermal stability, it should be possible to prepare other oxygen-linked organometallic polymers which will more closely approach the required standards of stability.

The beneficial effects of organotin additives in lubricating oils are well documented⁷. It is known that the introduction of tin additives to silicone oils improves their lubricity¹⁶ and other characteristics¹⁴ without detriment to their thermal stability. The ultimate fate of the tin compounds is not known with certainty; whether they are strictly additives or become an integral part of the siloxane molecule is apparently a matter of conjecture. It is of interest therefore to study the copolymerization of suitable organotin and organosilicon compounds to produce stannosiloxanes, whose structure may be represented as follows,



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and to ascertain the effects of varying the organic groups, the tin:silicon atomic ratio, the molecular weight, etc.

This report describes the synthesis of these compounds and certain other tin-containing polymers and some preliminary evaluative studies of thermal and hydrolytic stability.

SECTION II

ORGANOMETALLIC OXIDE POLYMERS

A. THEORETICAL CONSIDERATIONS

Among the most stable useful polymeric materials presently known are the linear polysiloxanes; it is well known, however, that at high temperatures these materials undergo extensive rearrangement to form cyclic siloxanes of much lower molecular weight¹¹. It may be inferred that the resistance of silicone polymers to thermal degradation is largely limited by the stability of the siloxane bond (-Si-O-Si-), and that improved thermal stability might be obtained by modifying the electrical character of these bonds. The highly polar metallic oxides exhibit pronounced thermal stability; a "hybrid" structure, consisting of a siloxane chain in which some silicon atoms have been replaced by more electropositive metals, would be a more nearly ionic polymer and might well be highly resistant to thermal degradation.

Very little work has been reported on siloxane type polymers containing other metals in addition to (or instead of) silicon. Recently arsonosiloxanes have been described⁵, and some work has been reported on stannosiloxanes^{1,3} and titanosiloxanes¹.

Many of these compounds should be quite stable; the Si-O bond is 50% ionic¹² and its exceptional thermal stability is probably attributable to this highly polar nature. The Sn-O bond is even more nearly ionic (57%) and should produce an even more stable polymer than the siloxanes. However, the advantage offered by greater polarity might well be offset - at least in part - by other factors - e.g., the lower stability of Sn-C bonds (associated with the relatively large size of the tin atom⁶) or the basic character of the Sn-O bond (which could initiate rearrangements and depolymerization of the polymeric products⁴).

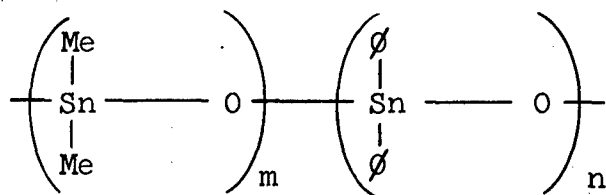
On the other hand any detrimental effect resulting from the introduction of Sn-O bonds into siloxane polymers might well be negated by fortuitous selection of the organic substituents on tin. It is known that di-*t*-butylsilanediol is an unusually stable compound¹⁷, which unfortunately cannot be induced to polymerize; we might speculate that a *t*-butylsiloxane polymer would be a particularly stable material. It seems reasonable to suppose then that a stannosiloxane polymer bearing *t*-butyl groups on tin and methyl groups on silicon might exhibit unusual stability by virtue of the same steric factors which render di-*t*-butylsilanediol so inert.

It may readily be seen that several factors operate in determining the stability of stannosiloxane polymers. Since these factors do not in general lend themselves to objective scrutiny at this time, it is necessary empirically to ascertain the effects of introduction of various groups by preparation and examination of a number of representative polymers.

Additional polymers which we have studied are the tin analogues of the polysiloxanes - the "stannoxane" polymers - of which the organotin oxides represent a well-known example. These compounds for somewhat obscure reasons assume an amorphous infusible state⁸. Structurally they should resemble the siloxanes; physically, however, they do not do so. Repeated efforts to prepare the organotin oxides in a state more closely resembling siloxanes have been unsuccessful¹⁸, although some low molecular weight soluble polystannoxanes have been reported⁹. It is difficult to explain the differences in properties of the two types of polymers, but we have speculated that the organotin oxides may be subject to extensive intramolecular bonding, so that some three-dimensional lattice formation takes place. Any disruption of symmetry should decrease this lattice formation with corresponding decrease of melting point, increase in solubility and increase in plasticity. This hypothesis received support when it was observed that copolymeric stannoxanes possessed appreciable solubility in organic solvents; thus the polymer obtained on cohydrolysis of dimethyltin dichloride and diphenyltin dichloride formed a clear very viscous toluene solution, implying high molecular weight.

The possibility of obtaining plastics or liquids containing the stannoxane structure is very intriguing. The ordinary organotin oxides possess excellent thermal stability, which should be retained in somewhat the same degree in a copolymer. Furthermore, these polymeric oxides show no tendency to hydrolyze under neutral conditions; they should be readily attacked by acids and bases, but this may be remedied by suitable selection of organic substituents.

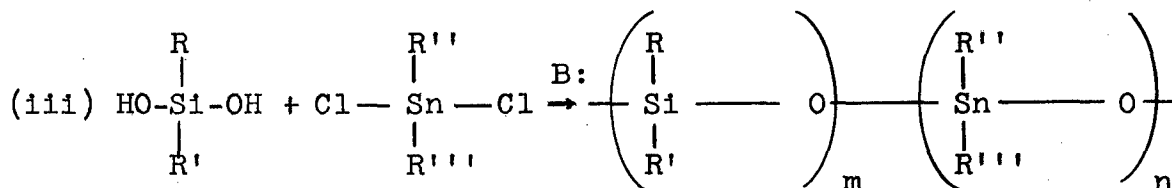
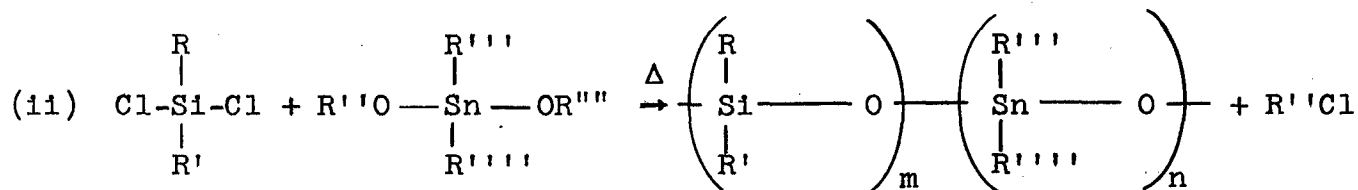
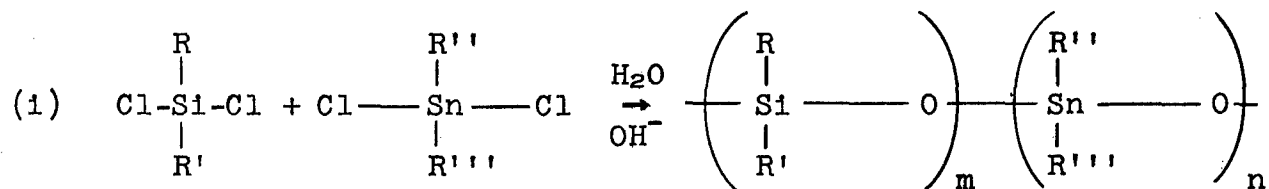
We have prepared the methyl-phenyl polystannoxane represented as follows:

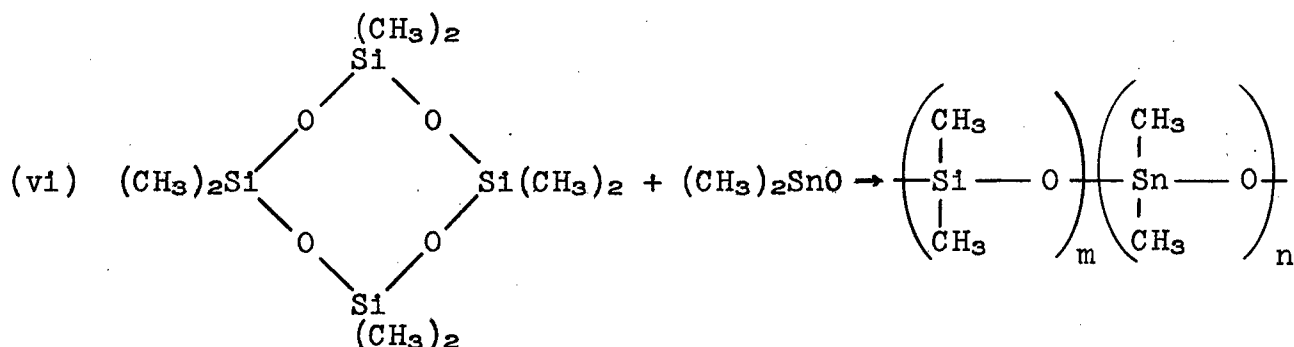
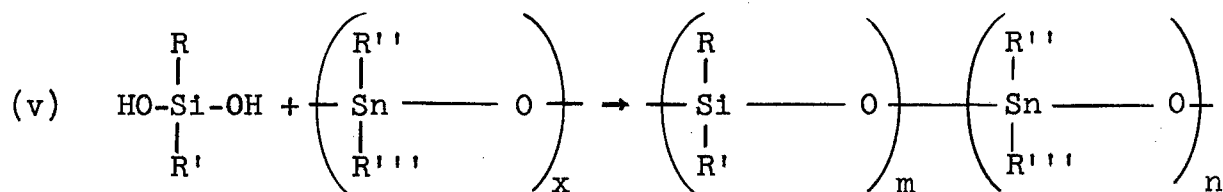
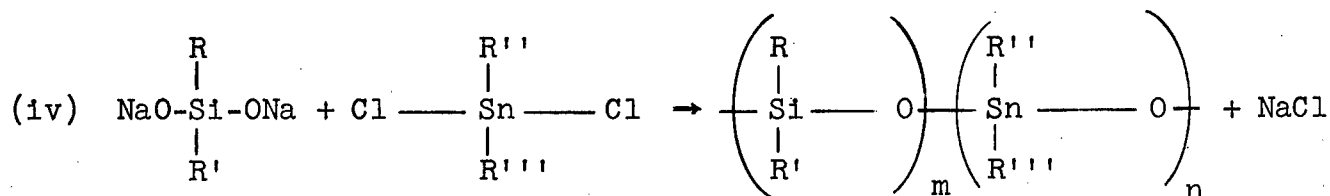


Evaporation of a toluene solution of this polymer forms a transparent film which is quite brittle (though it is plasticized by residual toluene solvent). The material softens at a high temperature (ca. 250°C) but is rapidly converted to a powdery amorphous material at such temperatures, possibly by oxidative cross-linking at methyl positions. We hope, by varying the organic substituents, to produce a polymer less subject to this undesirable transformation. Further work in this area is in progress.

B. SYNTHETIC METHODS

Stannosiloxanes. There are several types of reactions which might be expected to produce stannosiloxane polymers by condensation polymerization. Some of these are listed below:



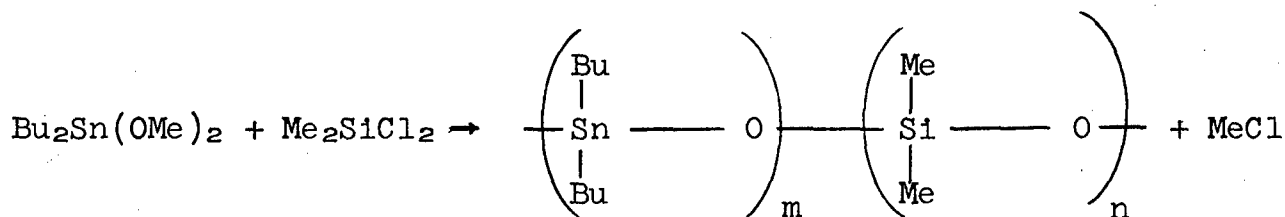
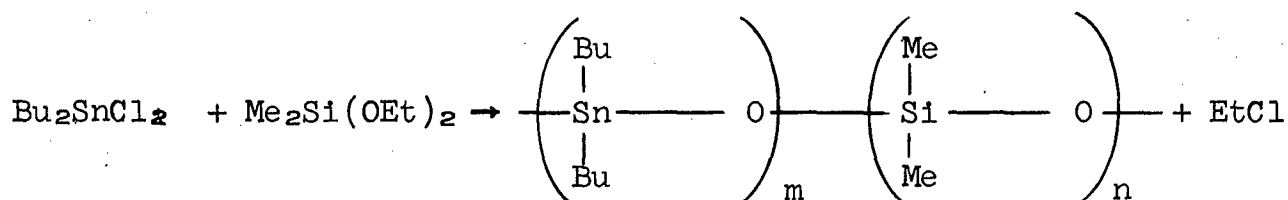


Many reactions involving polymerization by loss of some small molecule could be written³. They will not be listed, however, for the sake of brevity.

Reactions of Type (i) involve cohydrolysis of a dichlorosilane and a tin dichloride, generally in the presence of an organic solvent (e.g., toluene) which will remove the hydrolysis products from aqueous solution as they are formed. This is a general method, widely applicable to the preparation of metallosiloxane polymers. From dimethyldichlorosilane and dimethyltin dichloride, liquids or gums were prepared, depending on Sn:Si ratios. Somewhat similar results have been described by Andrianov¹.

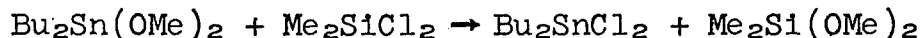
Reactions of Type (ii), involving loss of an alkyl halide (e.g. methyl chloride), would appear at first consideration very feasible. The analogous reaction between two organosilicon compounds is well known¹⁵. The polymeric product could be obtained by two alternative methods; either a tin alkoxide could be caused to react with a chlorosilane, as indicated above, or an alkoxysilane might react with a tin dichloride.

The following reactions of this type have been studied:

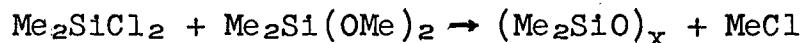


These reactions were observed to proceed partially to completion, with some elimination of the alkyl chloride. The corresponding reaction in organosilicon chemistry is catalyzed by Lewis acids - particularly FeCl_3 . No marked catalysis was observed in these reactions, though addition of FeCl_3 did appear slightly to increase the rate of elimination of alkyl chloride; nevertheless the reactions did not proceed satisfactorily to completion and therefore did not produce high polymers.

When the second reaction above was attempted, an exchange reaction was observed:



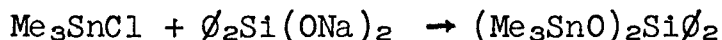
Since this exchange takes place, it is possible to account for the observed methyl chloride as having been eliminated from the two silane derivatives.



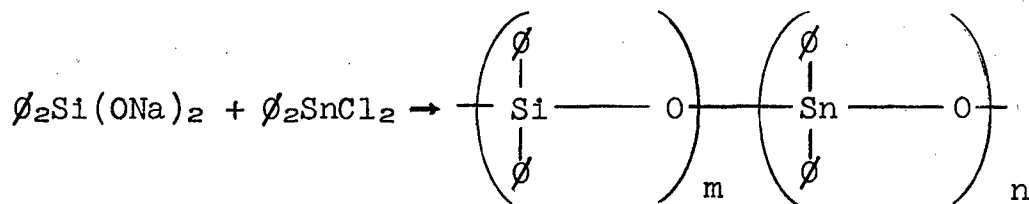
Thus the mere appearance of methyl chloride does not necessarily indicate the formation of stannosiloxanes.

Reactions of Type (iii) depend upon a base-catalyzed elimination of HCl from a silanediol and an organotin dihalide. The reaction was attempted without success using diphenylsilanediol, dibutyltin dichloride, and pyridine; the reactants were recovered unchanged. The use of different reaction conditions may render this reaction practicable for the preparation of polymers.

Reactions of Type (iv) involve metathetical formation of a polymeric organotin "salt" of a silanol. Such a reaction was first reported by Tatlock and Rochow¹⁹, who, however, were not seeking polymeric materials and therefore employed a mono-functional tin compound in their reaction:

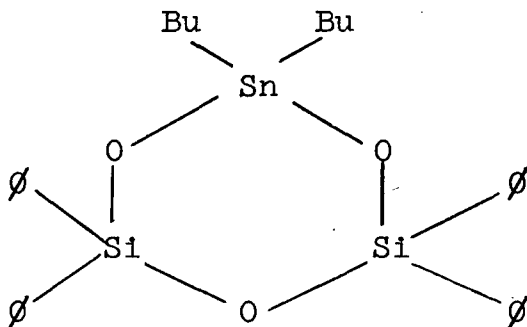


We have studied the corresponding reaction of diphenylsilanediol disodium salt with diphenyltin dichloride and obtained polymeric products:



This reaction also deserves further investigation; we have been unable to study it further because of interest in the following method.

Reactions of Type (v) involve the loss of water between a silanol and an organotin oxide -- presumably a polymeric structure in itself⁸, as indicated in the above equation. The most convenient difunctional silanol for these studies is diphenylsilanediol, and its reaction with dibutyltin oxide was studied first. Clear viscous oils were obtained, whose structure apparently is as follows:



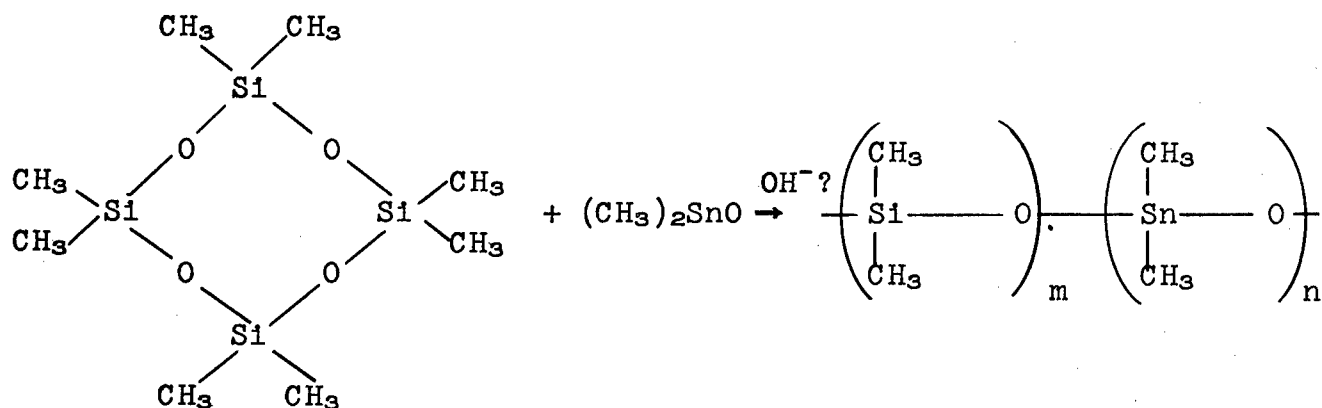
It was found that this reaction could be carried out with or without a solvent, and that other organotin oxides were equally useful. Linear polymers were easily obtained from diphenylsilanediol and diphenyltin oxide; the reactions were carried out either by heating in vacuo with no solvent or by refluxing a mixture of dioxan and the two reactants, during which operation the insoluble tin oxide gradually dissolved. Evaporation of the solvent then left the polymeric product as a viscous syrup which set to a hard brittle friable glass on cooling. None of these products exhibited any

tendency to crystallize. Their molecular weights ranged as high as 5000, as nearly as could be measured. Their thermal stability, however, was only fair, as apparently benzene was split out from the molecule at 300°C or so.

It is believed that a very desirable polymer of this sort would be that prepared from dimethylsilanediol and dimethyltin oxide. However, dimethylsilanediol polymerizes so rapidly with itself that it is deemed unlikely that any interaction with the tin oxide would be observed. A compromise can be effected by using diphenylsilanediol with dimethyltin oxide; many experiments using these reactants were performed. It was found that dioxan was not suitable solvent for this system, as only a small amount of dimethyltin oxide would react, so that the reaction product was substantially a polydiphenylsiloxane containing a small amount of tin. However, the use of toluene or xylene greatly ameliorated this difficulty, and Si:Sn ratios as low as 3 have been obtained. (In one non-reproducible experiment a 1:1 ratio was observed.) The reaction is rapid and quantitative. The products are transparent solid resins or extremely viscous oils, depending on the molecular weight and the tin-silicon atomic ratio.

It is probable that the molecular weights of these products are quite low (3,-5,000) because of the brittleness of the solid resins at room temperature and the low viscosity of the melt or of solutions of the materials. No method has been found to drive the reaction to produce higher polymers over the composition range examined. This is possibly a result of impurities in either the diol or the tin oxide or both. The silanediol used was Dow-Corning's "Purified Grade" or equivalent, which purports to be 99% pure. The dialkyltin oxides are difficult to purify because of their extremely low solubility; the only approach known to us to effect purification consists in recrystallizing the predecessor compound -- e.g. dimethyltin dichloride -- and then acting on the assumption that conversion to the oxide is not significantly detrimental to the purity of the product.

The reaction of silanediols with organotin oxides is the most promising yet discovered for the preparation of stannosiloxanes. However, it is unsuitable for preparation of polymers containing dimethylsilicon moieties. A closely related reaction (Type vi) which would serve for these compounds is that between a cyclic siloxane and an organotin oxide -- an equilibration reaction analogous to that employed in converting cyclic siloxanes to linear homopolymers. The reaction may be represented as follows on page 9.



The reaction as written above has not been realized; however, it was reported to us¹⁰ and subsequently confirmed in our own laboratory that dibutyltin oxide will indeed react with octamethylcyclotetrasiloxane to form an elastomeric gum of unknown structure. We are investigating these reactions further, as the method should be generally applicable in the preparation of organometallic polymers containing oxygen linkages.

Stannoxanes. The basic hydrolysis of organotin dihalides results in formation of amorphous infusible organotin oxides or polyorganostannoxanes. Similarly simultaneous hydrolysis of mixtures of different dialkyltin dihalides leads to copolymeric stannoxanes which are significantly more soluble and thermoplastic than their homopolymeric counterparts. The reaction is carried out in the presence of an immiscible organic solvent - e.g., toluene - and the copolymer is recovered from the organic layer; we have used ammonium hydroxide as the basic agent, but other bases can be used.

In theory any of the reactions indicated above for synthesis of stannosiloxanes can be applied also to the preparation of stannoxanes.

C. POLYMER EVALUATION

Sample polymers were run through a series of tests to include: Determination of Molecular Weight, Behavior on Reaching a Melting Point, Hydrolytic Stability, and Oxidation and Weight Loss.

Determination of Molecular Weight. A cryoscopic molecular weight apparatus with benzene as the solvent was used to determine the molecular weights. Not all of the polymers were soluble in benzene, presumably because of quite high molecular weight; therefore the molecular weights for these polymers will not be reported at this time. The following polymers and the molecular weights obtained are as follows:

1. (Si) diphenyl-(Sn) dimethylstannosiloxane,
Si:Sn = 3:1 - 1200
2. (Si) diphenyl-(Sn) diphenylstannosiloxane,
Si:Sn = 3:1 - 950
3. (Si) diphenyl-(Sn) diphenylstannosiloxane,
Si:Sn = 10:1 - 790

Behavior on Reaching a Melting Point. A Fisher-Johns Melting Point apparatus was used to determine the behavior of polymers upon reaching a melting point. The polymers tested and the results are as follows:

1. (Si) diphenyl-(Sn) diphenylstannosiloxane of a Si:Sn ratio (10:1). This sample became soft at 120°C with visible melting at 155°C, and was a liquid at 165°C. There was no further noticeable change or odor up to 300°C.
2. (Si) diphenyl-(Sn) dimethylstannosiloxane of a Si:Sn ratio (10:1). This sample became soft at 100°C, visible melting at 180°C. After melting, the polymer was a viscous milky colored liquid. There was no further noticeable change or odor up to 300°C.
3. (Si) diphenyl-(Sn) dimethylstannosiloxane of a Si:Sn ratio 3:1. This sample became soft at 70°C, visible melting at 135°C, a clear liquid at 170°C. There was no further noticeable change or odor up to 300°C.
4. (Si) dimethyl-(Sn) dimethylstannosiloxane of a Si:Sn ratio (3:1). This sample was soft at the beginning. A sharp odor was noticed at 90°C; bubbles formed at 120°C, began to get cloudy at 170°C, and began to get brittle at 200°C. This polymer was hard and brittle up to 300°C.
5. (Si) dimethyl-(Sn) dimethylstannosiloxane of a Si:Sn ratio (10:1). This sample was soft at the beginning. It began to spread at 190°C and an odor was noticed at 205°C. There was no further noticeable change up to 300°C.
6. (Si) diphenyl-(Sn) diphenylstannosiloxane of a Si:Sn ratio (3:1). This sample became soft at 45°C, with visible melting at 55°C; it was a liquid at 70°C, and a slight odor was noticed at 175°C. There was no further noticeable change up to 300°C.

7. (Sn) dimethyl-(Sn) diphenylstannoxane of a ratio of 1:1. This sample became soft at 55°C and developed a sharp odor at 90°C. This sample did not melt, but became brittle at 190°C and had a yellow tint at 280°C.

Hydrolytic Stability. Based on a procedure of the American Society for Testing Materials polymer samples up to 0.1 gram were conditioned in an oven at 55°C for 24 hours. After conditioning, the samples were weighed and put in a small beaker and covered with distilled water. After 24 hours the samples were removed, dried, and weighed. The results of this hydrolytic stability experiment are as follows:

<u>Polymers</u>	<u>Increase in Weight</u>
1. (Si) diphenyl-(Sn) dimethylstannosiloxane, Si:Sn = 10:1	0%
2. (Si) diphenyl-(Sn) diphenylstannosiloxane, Si:Sn = 3:1	0.25%
3. (Si) diphenyl-(Sn) diphenylstannosiloxane, Si:Sn = 10:1	0.36%
4. (Si) diphenyl-(Sn) dimethylstannosiloxane, Si:Sn = 3:1	0.65%
5. (Sn) dimethyl-(Sn) diphenylstannoxane of a ratio 1:1	1.95%

No results were obtained for (Sn) dimethyl-(Si) diphenylstannosiloxanes of ratios 10:1 and 3:1.

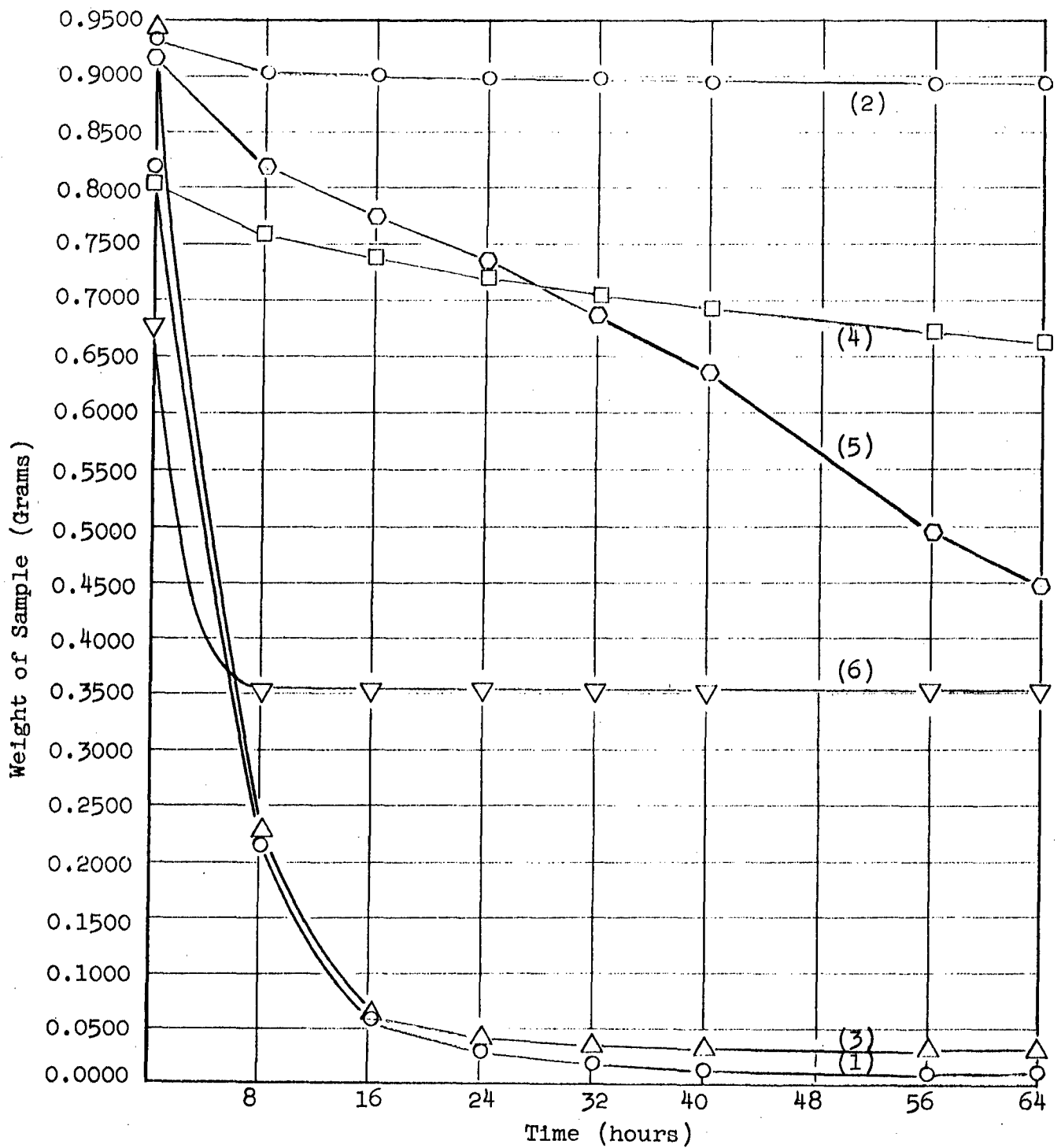
Oxidation and Weight Loss. Samples were weighed in weighing bottles and put into an oven with a constant temperature of 245°C. The samples were removed and weighed after every 8 hours for 72 hours. The oxidation and weight loss of these polymers is best shown by the attached graphs. Compounds represented on the graphs by numbers are as follows:

Figure 1

- No. 1 - Methylsiloxane
 No. 2 - Phenylsiloxane
 No. 3 - Vinylsiloxane
 No. 4 - (Si) diphenyl-(Sn) dimethylstannosiloxane Si:Sn = 3:1
 No. 5 - (Si) diphenyl-(Sn) diphenylstannosiloxane Si:Sn = 3:1
 No. 6 - (Sn) dimethyl-(Sn) diphenylstannoxane Si:Sn = 1:1

Figure 2

- No. 2 - Phenylsiloxane
 No. 3 - Vinylsiloxane
 No. 7 - (Si) diphenyl-(Sn) dimethylstannosiloxane Si:Sn = 10:1
 No. 8 - (Si) diphenyl-(Sn) diphenylstannosiloxane Si:Sn = 10:1
 No. 9 - (Si) dimethyl-(Sn) dimethylstannosiloxane Si:Sn = 10:1
 No. 10 - (Si) dimethyl-(Sn) dimethylstannosiloxane Si:Sn = 3:1
 No. 11 - (Si) diphenyl-(Sn) dimethylstannosiloxane Si:Sn = 3:1



Temperature Constant 245°C

Figure 1 - Effect of Heat on Polymer Samples

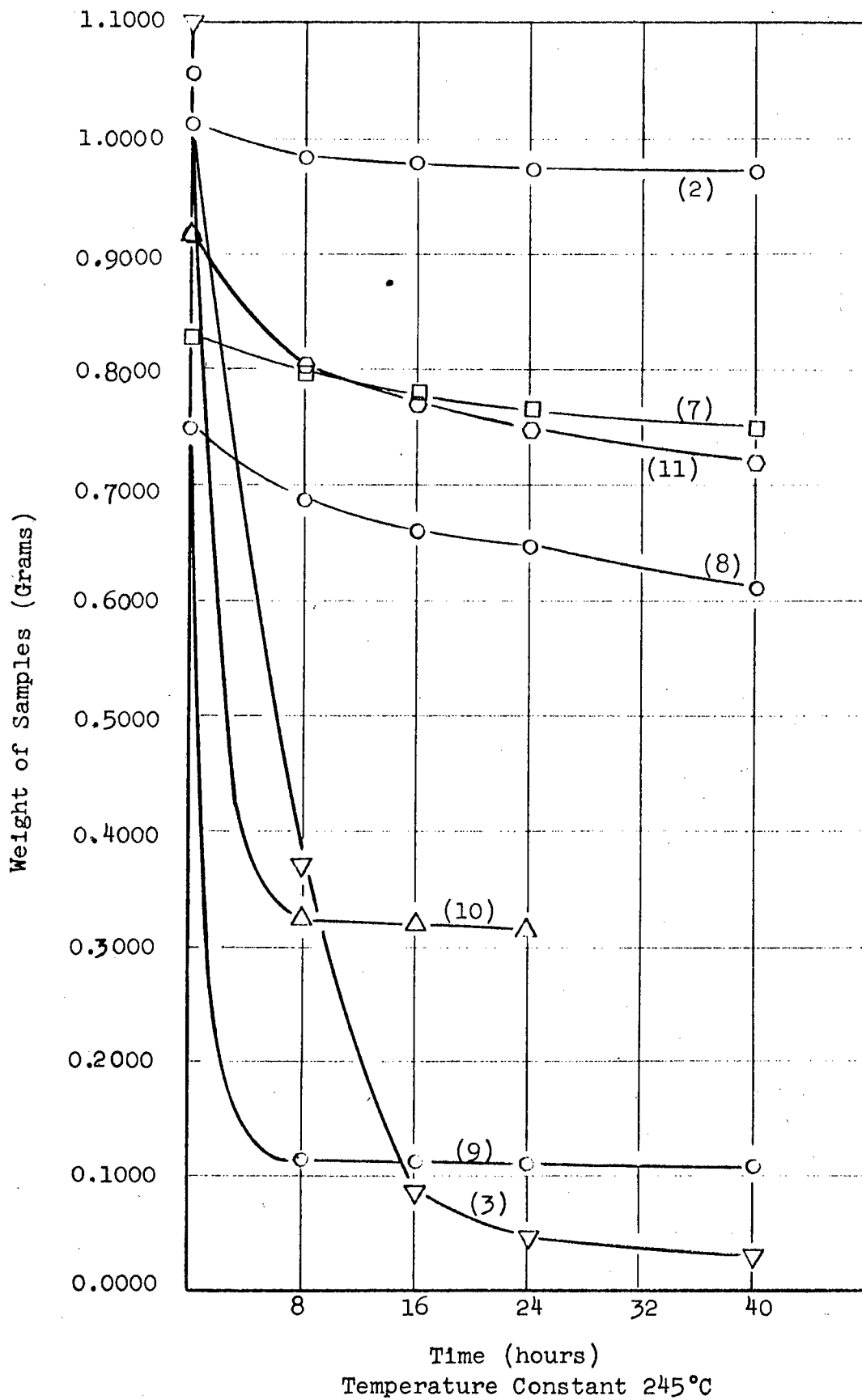


Figure 2 - Effect of Heat on Polymer Samples

From these graphs it is apparent that none of the compounds tested is as stable as poly(diphenylsiloxane); however, all the stannosiloxane polymers were less affected by prolonged heating than were poly(methylsiloxane) and poly(vinylsiloxane). Considering the stannosiloxane polymers as a group, those containing phenylsilicon moieties were more stable than their methylsilicon counterparts. The same conclusions may be drawn from consideration of behavior of the polymers on heating on a melting point block. It seems that future studies in stannosiloxanes might well be limited to those containing the phenylsilicon group - or another exceptionally stable group yet to be discovered.

It is also of interest that the polymers appear to be more stable the less the relative amount of tin. For practical purposes it will be necessary to determine the optimum Sn/Si ratio for a specific application - e.g., radiation resistance, lubricity, thermal stability, etc.

SECTION III

SUMMARY AND CONCLUSIONS

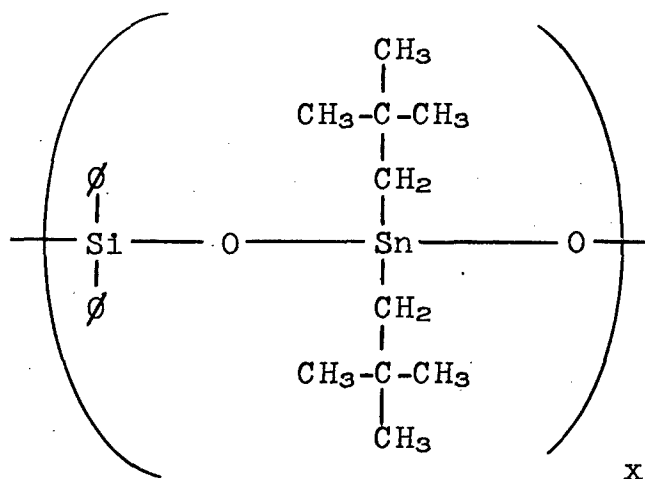
It is believed that stannosiloxane polymers are promising possibilities for fluids, resins and elastomers of extraordinary chemical and thermal stability.

An excellent method has been discovered for the preparation of stannosiloxanes; since the polymerization takes place by reaction of a silanediol with an organotin oxide, the method is of limited applicability in that only a few stable silanediols are known -- e.g., diphenylsilanediol and phenylmethylsilanediol. However, this limitation is not considered particularly significant, for the diphenyl - and methylphenylsilicon moieties are well known as components of useful siloxane polymers; indeed the (Si) diphenyl-(Sn) dimethylstannosiloxanes have been found to be more stable than certain other polymers bearing different organic substituents.

Another general method for preparation of stannosiloxane polymers involves simultaneous basic hydrolysis of mixed chlorosilanes and organotin halides. This approach permits preparation of polymers containing lower alkyl groups bound to silicon - e.g., (Si) dimethyl-(Sn) dimethylstannosiloxanes. These polymers to date, however, have not shown outstanding thermal stability.

Results thus far with stannoxane polymers are very interesting indeed; the copolymeric "organotin oxides" appear to be high polymers possessing good thermal and hydrolytic stability. Most interesting, however, is the fact that these represent a new class of soluble polymers; it may well be that a variety of soluble organometallic polymers containing metal-oxygen bonds can be prepared.

The identity of the organic substituents very significantly affects the thermal and chemical stability as well as other properties of these products; it is therefore desirable to discover organic groups which will impart maximum stability to the polymer. The neopentyl and neophyl groups, with quaternary β carbon atoms, are particularly stable; they are also sufficiently large as to afford good steric protection against chemical attack on the backbone of a polymer. Work is in progress to prepare hindered monomers, such as dineopentyltin oxide which may be polymerized with, for example, diphenylsilanediol, to produce a very stable product - (Si)diphenyl-(Sn)dineopentylstannosiloxane:



The corresponding stannoxane polymer should also be interesting.

The preparation of hindered monomers - specifically di-t-butyltin dihydroxide - has not proceeded smoothly. Yields of the corresponding dichloride have been very low, and no reliable samples of the dihydroxide have been obtained. It may be necessary to study a different monomer, such as the neopentyltin compound, or to use an entirely different approach to the synthesis of the t-butyl monomer.

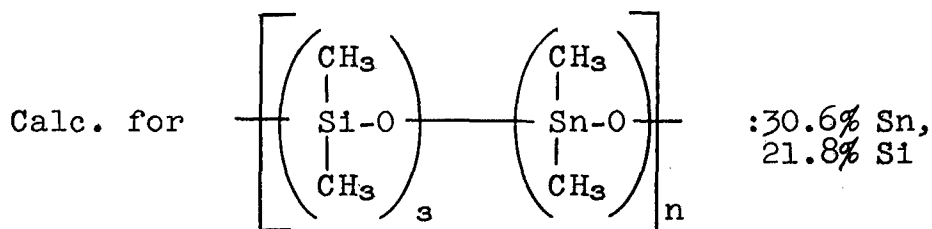
SECTION IV

EXPERIMENTAL PART*

A. COHYDROLYSIS OF CHLOROSILANES AND TIN HALIDES

Cohydrolysis of dimethyldichlorosilane and dimethyltin dichloride. A 1-liter 3-necked creased flask was set up with a high-speed stirrer, a reflux condenser and an addition funnel. In the flask were placed 12.5 ml concentrated ammonium hydroxide (ca. 3.4 g, 0.2 mole, NH_3) and 50 ml toluene. A solution of 6.4 g (0.05 mole) dimethyldichlorosilane and 10.9 g (0.05 mole) dimethyltin dichloride in 300 ml toluene was added via the addition funnel over a period of about 45 minutes. The mixture was warmed to 45-50°C at the start of the reaction. A white precipitate appeared as the addition of reagents progressed. Toward the end of the addition, it was necessary to add 5-10 ml concentrated ammonium hydroxide to restore alkaline conditions. Stirring was continued for 15 minutes after all reagents had been added; 100 ml water was then added and the mixture filtered. A gelatinous white solid remained on the filter, which on drying became a white friable powder -- presumably dimethyltin oxide; it weighed 5 g. The filtrate consisted of two layers; the aqueous layer was discarded and the toluene layer concentrated to leave a gum. Final removal of solvent in a vacuum left a rubbery plastic "bouncing putty" (62104B) which was submitted for analysis. Andrianov¹ has described the preparation of "glassy polyorganostannosiloxanes" by a similar technique.

Anal: Found 33.13% Sn, 19.9% Si



Cohydrolysis of dimethyldichlorosilane, diphenyldichlorosilane, and dimethyltin dichloride. This experiment was carried out as described above except that the reagents used were 65.3 g (0.5 mole) dimethyldichlorosilane, 25 g (0.1 mole) diphenyldichlorosilane, and 10.9 g (0.05 mole) dimethyltin dichloride; 70 ml concentrated ammonium hydroxide was used. The heterogeneous reaction mixture was filtered to remove traces of solids. The toluene layer, which was water-white, was concentrated on the hot-plate; it became extremely thick and viscous. The viscous mass could be diluted with 2B ethanol, petroleum ether (40-70°C) and other solvents. A portion of this viscous material, which contained considerable toluene, was heated at 130°C at about 5 mm pressure for 16 hours. It was then less viscous

*Temperatures are given in °C; melting points are uncorrected.

and was opaque (white) (62106A).

Anal: Found 22.66% Si, 9.51% Sn

A sample of this material was heated on the hot-plate at 350°C for 15-20 minutes. Considerable steam and smoke was evolved and a yellow rubbery gum retained (62109D).

Anal: Found 25.25% Si, 8.25% Sn

Calc. for $\begin{matrix} \text{(Si-O)} & \text{(S-O)} & \text{(Sn-O)} \\ | & | & | \\ \text{Me}_2 & \text{O}_2 & \text{M}_2 \end{matrix}$ 25.8% Si, 9.1% Sn

A larger run was made using twice the quantities of reagent described above; the product from this reaction was heated on a stainless steel plate to 340°C and converted to a very viscous fluid which could be milled to a rubber. A sample of this material was submitted to Wright Air Development Command laboratories for their examination:

Anal: Found 26.98% Si, 5.74% Sn

B. REACTION OF ALKOXIDES WITH HALIDES

Preparation of dimethoxydimethylsilane. In a one-liter 3-necked creased flask fitted with a high-speed stirrer, a solid CO₂ condenser, and an addition funnel was placed 92 g of a 25% sodium dispersion in xylene. This was diluted with more xylene (ca. 300 ml) and the mixture heated to 105-110°C on an oil bath. Methanol (31.5 g, 0.98 mole) was added dropwise through the addition funnel over about 30 minutes. The hot mixture was stirred for about an hour, until no further refluxing of methanol took place. The mixture was then cooled to 20-25°C, and 64.5 g (0.5 mole) dimethyldichlorosilane added in small portions. The mixture was cooled externally during this addition, then allowed to warm to room temperature and finally heated to 150° or so on an oil bath. About 150 ml of distillate was collected and fractionated through a small packed column. Dimethoxydimethylsilane was collected at 82-84°C; the yield was 30 g (50%).

Reaction of dimethoxydimethylsilane with dibutyltin-dichloride. In a 200 ml flask were placed 35 g (0.115 mole) dibutyltin dichloride and 12 g (0.10 mole) dimethoxydimethylsilane. Upon being warmed the mixture formed a homogeneous solution. The solution was refluxed, a solid CO₂ condenser and drying tube having been placed at the upper end of the condenser. After 2 hours' refluxing no methyl chloride was evident in the trap.

The mixture was allowed to stand several days at room temperature, then refluxed further after addition of a small amount (100 mg) of anhydrous FeCl_3 . After a total of about 20 hours' refluxing about 3-3.5 g of methyl chloride had been produced.

The reaction mixture was distilled to give a small amount (about 10 ml) of distillate boiling over the range 88-140°. The residue was relatively non-volatile and is probably unreacted dibutyltin dichloride.

The distillate described above has not been examined further. It is probable that some condensation took place, to form a trimer, perhaps; that this reaction is far from complete is indicated by the small amount of methyl chloride produced.

Preparation of dibutyltin dimethoxide. In a one-liter 2-necked flask was placed 23 g (1 g atom) of sodium dissolved in 500 ml methanol and a solution of 151.5 g (0.5 mole) Bu_2SnCl_2 was added with vigorous stirring. The resulting precipitate of sodium chloride was removed by filtration, and the filtrate concentrated under reduced pressure to leave 116.5 g of a tan oil which could not be induced to crystallize; however, when the oil was spread in a thin film (as in routine transfers) it showed a tendency to crystallize. This may be due to a hydration or oxidation effect, however. A sample of the liquid was submitted for analysis.

Calc. for $\text{C}_{10}\text{H}_{24}\text{SnO}_2$: Sn, 40.2%
Found: Sn, 39.9%, 40.4%

Reaction of dimethyldichlorosilane with dibutyltin dimethoxide. In a 100 ml flask were placed 29.4 g (0.1 mole) dibutyltin dimethoxide, 14 g (0.108 mole) dimethyldichlorosilane and about 100 mg anhydrous ferric chloride. A vigorous reaction took place on mixing, with evolution of considerable heat so that the silane refluxed vigorously. The mixture was heated and allowed to reflux for 4-5 hours, after which time a small amount (3-4 g) methyl chloride had collected in the trap. The mixture was allowed to stand overnight, during which time it crystallized. The crystalline material was identified as dibutyltin dichloride, indicating that an exchange reaction had taken place. Further heating did not increase the yield of methyl chloride; the experiment was abandoned.

Another preparation of dibutyltin dimethoxide was carried out (Expt. 48348), in which 151.5 g (0.5 mole) dibutyltin dichloride was added to a solution of 23 g (1 g atom) of sodium in methanol. The resulting product was liquid. It was heated in vacuo to remove final traces of methanol, and inadvertently heated too hot; as a result some polymerization took place (presumably) with loss of methyl ether, so that some gelatinous white solids appeared in the reaction flask.

No separation of the components was attempted; instead the entire yield of tin methoxides was treated with 65 g (0.504 mole) dimethyldichlorosilane (Expt. 48350). The chlorosilane was added in successive small portions to the methoxytin compound; a vigorous reaction took place at once and some methyl chloride was produced. The addition of each portion of chlorosilane was marked by the appearance of a white precipitate, which redissolved immediately; when most of the chlorosilane had been added, however, the precipitate remained in the mixture. The mixture was then heated to reflux, and maintained at that temperature for a total of about 20 hours. About 15 g (0.3 mole) of methyl chloride was produced, after which no reaction appeared to take place. During the first 8-10 hours of refluxing a waxy white solid appeared in the reaction mixture. Later this material disappeared, and two liquid layers formed. The upper layer was colorless and somewhat viscous. On attempted distillation in vacuo (1 mm) a small amount (1-2 g) of distillate was obtained at 105°; the contents of the pot, however, turned milky and viscous, and no further distillation took place. Both the distillate and the residue appeared, by their burning characteristics, to contain both tin and silicon. Analytical data, however, are not available.

The lower layer from the reaction mixture was also distilled, to recover about 6-8 ml of unreacted dimethyldichlorosilane, followed by higher-boiling material which was not characterized. Further reaction of the material in the pot took place during the distillation. This experiment was not worked up completely because of the low yield of methyl chloride obtained.

Reaction of diphenyldichlorosilane with dibutyltin dimethoxide. In a 100 ml flask were placed 30.4 g (0.1 mole) dibutyltin dimethoxide and 26.0 g (0.1 mole) diphenyldichlorosilane. The mixture was heated. No evolution of methyl chloride took place until the mixture reached reflux temperature (about 320°C in the pot). After prolonged heating about 3 g of methyl chloride was obtained; further heating was without effect. Considerable charring had occurred in the reaction flask, presumably because of the high temperature of the mixture.

This experiment follows the pattern observed in previous attempted polymerizations of chlorosilanes with methoxytin compounds; that is, the reaction apparently proceeds to a small extent, but stops far short of completion. This would necessarily produce only low molecular weight polymers.

C. REACTION OF SILANOLS WITH TIN CHLORIDES

Reaction of diphenylsilanediol with dibutyltin dichloride. In a 50 ml flask were placed 10 g (0.046 mole) diphenylsilanediol and 15.1 g (0.05 mole) dibutyltin dichloride; 25 ml dried pyridine was added and the mixture refluxed 4-5 hours and allowed to stand at room temperature 24 hours. Crystalline products were obtained,

including one melting at 185°C which was probably hexaphenylcyclotrisiloxane (for which melting points in the vicinity of 188-200° are reported¹³). No linear polymeric products were observed.

D. REACTION OF SILANOLATES WITH TIN CHLORIDES

Reaction of diphenylsilanediol disodium salt with diphenyltin dichloride. In a 500 ml 3-necked flask was placed 43.2 g (0.2 mole) diphenylsilanediol in 250 ml dry purified dioxan. Sodium metal (0.2 g, 0.4 g atom) was added portionwise from a flask connected to one neck of the reaction vessel. A stirring apparatus and reflux condenser were also connected to the reaction flask. Vigorous evolution of hydrogen was observed as the first portions of sodium were added; the reaction subsequently slowed down, and some small flecks of sodium remained even after several hours' refluxing. The mixture was transferred to a one-liter 3-necked creased flask, and 68.6 g (0.2 mole) diphenyltin dichloride in benzene was distilled from the reaction mixture, and the latter was refluxed with vigorous stirring for about an hour, then allowed to stand several days. The mixture was then filtered with suction; the dioxan filtrate yielded an oil on addition of water. The solid remaining on the filter was a gray plastic solid. It was boiled repeatedly with large quantities of water to remove sodium chloride. Finally the material (for which no good solvent could be found) was placed in a large Soxhlet thimble, and was extracted with acetone over a period of several days. Only a trace of material was extracted, however. The solid residue was considered too intractable to be of further interest.

The oil mentioned above was extracted with benzene and recovered as a heavy syrup (53187B).

<u>Anal.</u>	Found:	20.88% Sn
		7.16% Si
	Mol. wt.	830

Infrared analysis indicated linearity of the chain. The elemental analysis and mol. wt. do not correspond to any one molecular species, so presumably a mixture of polymers is present.

E. REACTION OF SILANOLS WITH ORGANOTIN OXIDES

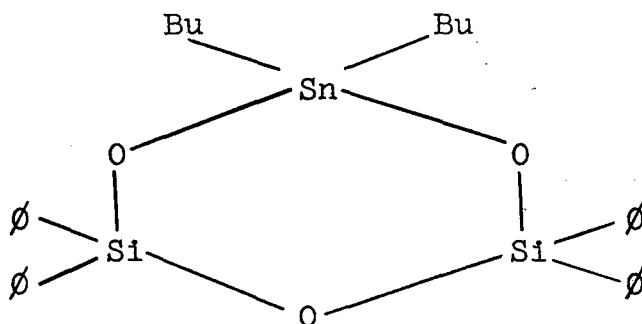
Reaction of dibutyltin oxide with diphenylsilanediol (Expt. 53151). In a 300 ml flask were placed 12.4 g (0.05 mole) dibutyltin oxide, 10.8 g (0.05 mole) diphenylsilanediol, and 100 ml purified dioxan (previously purified over KOH followed by sodium). The mixture was refluxed an additional 3-4 hours. After this time the reaction mixture had become essentially homogeneous; only a slight turbidity remained. The mixture was filtered and the clear filtrate allowed to stand overnight, during which time it deposited a white solid. This solid was removed by filtration and dried. It did not melt even at 300°, but burned (on heating in an open flame) with a flame

reminiscent of that shown by tin and silicon compounds. A sample was submitted for analysis and molecular weight determination.

The filtrate from the reaction mixture was concentrated in vacuo on a hot water bath to leave a thick syrup, which from its flame characteristics also contained both tin and silicon. A sample was submitted for analysis.

Found	% Sn:	18.6
	% Si:	8.1
	Mol wt.:	673 (cryoscopic in benzene)

Infrared studies indicated the presence of butyl and phenyl groups, and of an Si-O-R linkage where R is any element other than hydrogen. The spectrum indicated no Si-H or Si-OH bonds, and no -Si-O-Si- group as part of a linear molecule. The Si-O-Si group in a cyclic molecule is consistent with the observed spectrum. Therefore the following structure is proposed on the basis of all the analytical data at hand.



Calculated composition:	% Sn:	18.3
	% Si:	8.7
	Mol wt.:	644

Preparation of dimethyltin oxide. It was felt that the use of dibutyltin compounds in stannosiloxane polymers would not lead to maximum stability of the product; therefore dimethyltin oxide was prepared by hydrolysis of the dichloride, prepared in turn by the direct reaction of methyl chloride with tin metal as described by Rochow.¹⁸ Tin metal was placed in a stainless steel reactor as illustrated in the accompanying figure (Figure 3). Approximately 5% by weight of copper (wire) was added. The reactor was closed and heated to 400-450°C by means of an electrical heating coil (18' of 20-gage chromel wire). Methyl chloride was then passed through the molten metal at a slow rate (about 100 g/hr). Dimethyltin dichloride immediately began to condense in the glass tube connected to the reactor. The outlet assembly was warmed with an infrared lamp to melt the collected product. Some methyl tin trichloride is produced also. The product is dissolved in benzene and filtered to

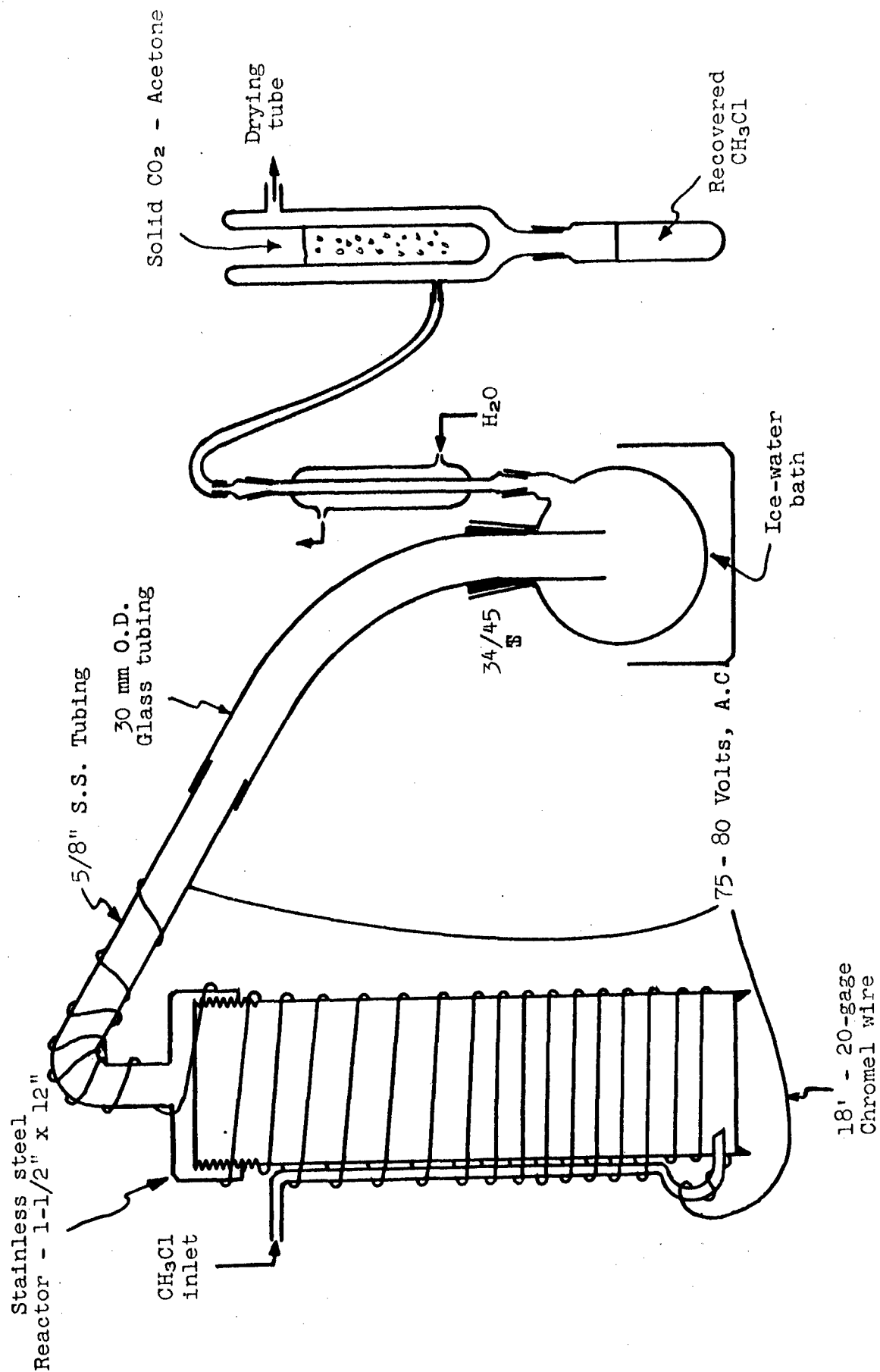


Figure 3 - Apparatus for Reaction of Methyl Chloride with Tin Metal

remove small amounts of insoluble material including some carbon. It crystallizes upon addition of petroleum ether or carbon tetrachloride to the filtrate. The product may then be dissolved in hot carbon tetrachloride and decanted from a small amount of insoluble oil; it is obtained as colorless crystals, m. 106°.

The dichloride was converted to dimethyltin oxide by solution in water and addition of a slight excess of ammonium hydroxide; the oxide is precipitated as a white gelatinous mass, best separated and washed by centrifugation.

Reaction of triphenylsilanol with dimethyltin oxide. This reaction was studied as a model, to obtain some basic information about the interaction of silanols with tin oxides. In a beaker containing xylene were placed 27.6 g (0.1 mole) triphenylsilanol and 8.2 g (0.5 mole) dimethyltin oxide. The mixture was boiled about 20 minutes, filtered to remove traces of solids, and concentrated to a heavy oil which crystallized on cooling. The product was recrystallized from benzene, then from chloroform and petroleum ether. The white crystalline material melts at 165-166°C.

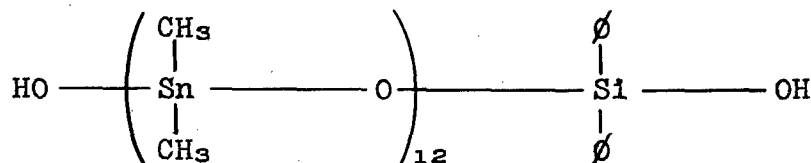
<u>Anal.</u>	Found	% Sn:	17.3
		% Si:	8.35

Calc'd. for $(\phi_3\text{Si-O})_2\text{Sn}(\text{CH}_3)_2$,	16.9 % Sn
	8.02% Si

Reaction of diphenylsilanediol with dimethyltin oxide in dioxan. Diphenylsilanediol (25.9 g, 0.12 mole) and dimethyltin oxide (19.8 g, 0.12 mole) were mixed with 125 ml purified dioxan and the mixture refluxed for 16-18 hours. The mixture was then filtered to remove 11.5 g of a white solid, which was washed with dioxan and dried in the vacuum oven.

<u>Anal.</u>	Found	% Sn:	63.63
		% Si:	1.01

The product is substantially polymeric dimethyltin oxide containing a few siloxane groups. The possible structure shown below contains 54% Sn and 1.3% Si:

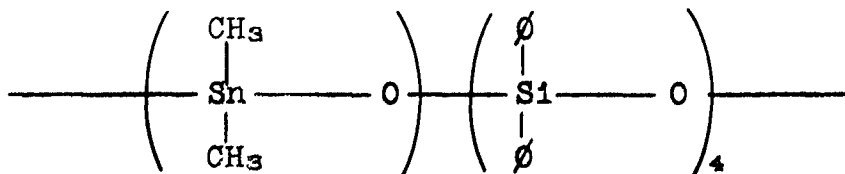


For practical purposes the material resembles dimethyltin oxide, which is to be expected.

By evaporation of the filtrate there was obtained a viscous syrup which cooled to a brittle transparent colorless glass (53195A).

<u>Anal.</u>	Found	% Sn:	12.82
		% Si:	11.27

The following structure contains 12.1% Sn and 11.5% Si:



This experiment was repeated, but the glassy product was heated in vacuo to 315°C. Some relatively volatile material was removed. The residue was dissolved in benzene and the solution treated with several volumes of petroleum ether. An oil precipitated (53199A) which on removal of solvent formed a hard clear glass.

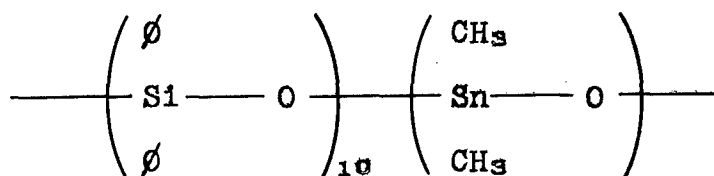
<u>Anal.</u>	Found	% Sn:	12.32
		% Si:	12.83

This is substantially the same composition as the glass described above (53195A).

Evaporation of solvent from the benzene-petroleum ether solution left a wax (53199B).

<u>Anal.</u>	Found	% Sn:	5.53
		% Si:	13.75

This corresponds roughly to a structure of the following type:



Calc'd:	% Sn	5.5
	% Si	12.9

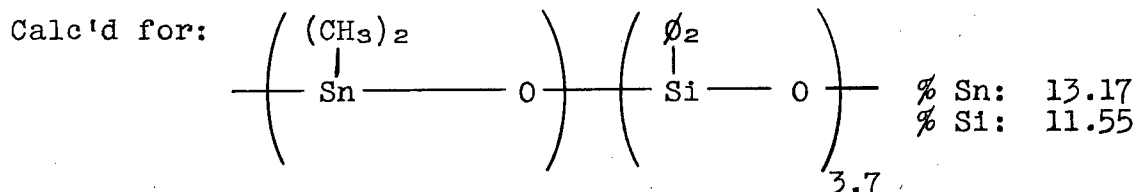
Unfortunately no molecular weight data are available on these compounds.

Reaction of diphenylsilanediol with dimethyltin oxide in toluene. The preceding experiment was carried out in dioxan; a large part of the dimethyltin oxide was recovered substantially unchanged. The following experiments were therefore performed using toluene as a solvent.

In a reaction flask fitted with a reflux condenser and a Dean-Stark trap were placed 43.2 g (0.2 mole) diphenylsilanediol, 8.1 g (0.05 mole) dimethyltin oxide, and 250 ml toluene. The mixture was refluxed; water began to separate at once, and within about 30 minutes essentially all the solids present in the mixture had dissolved. The mixture was filtered to remove traces of solids and the filtrate distilled to remove toluene. A clear viscous liquid remained, which solidified to a glass on cooling. A similar experiment using dioxan as solvent never resulted in solution of all the tin oxide, even after several days' refluxing.

The successful utilization of the dimethyltin oxide in the above case prompted a similar run containing a 1:1 mole ratio of tin oxide to diol. Considerable oxide remained unreacted after several hours, so additional silanediol was added until eventually the mixture contained 32.8 g (0.2 mole) dimethyltin oxide and 103.2 g (0.48 mole) diphenylsilanediol. When the mixture was filtered, 12 g of insoluble white solid, presumed to be unreacted dimethyltin oxide, was recovered. Removal of solvent gave a polymeric product derived, presumably, from 21 g (0.128 mole) of dimethyltin oxide and 103 g (0.48 mole) diphenylsilanediol, representing an atomic ratio of tin to silicon of 1 to 3.75. (Sample 62079 A)

<u>Anal.</u>	Found	% Sn:	13.15
		% Si:	11.55



This material is a flexible transparent plastic solid at room temperature, becoming quite fluid at relatively low temperature (60-70°). Fractionation by addition of petroleum ether to a benzene solution produced a hard brittle resin and a soft transparent putty-like material.

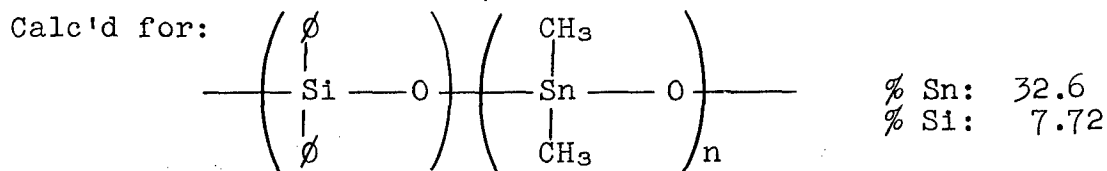
The reaction of equimolar amounts of diphenylsilanediol with dimethyltin oxide was also studied in refluxing toluene with a Dean-Stark trap in the system. The reaction mixture contained solid material at all times, but the theoretical amount of water

was eliminated within an hour or so. The bulk of solid material present had increased. The white solid product was insoluble for practical purposes in all solvents (except concentrated hot mineral acids, which decomposed the material). Some of the material was washed thoroughly with acetone and dried in the vacuum oven (53196 A).

<u>Anal.</u>	Found	% Sn:	38.65
		% Si:	5.90

Another sample was boiled with 10% sodium hydroxide solution containing some isopropyl alcohol, filtered, washed, and dried (53196 B).

<u>Anal.</u>	Found	% Sn:	34.81
		% Si:	7.65



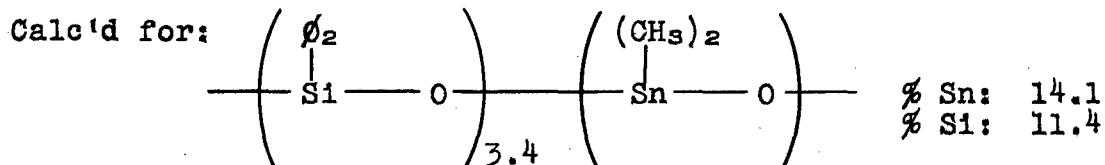
No molecular weight measurements have been made because of the practical insolubility of the product. However, behavior of the material in a press indicated a fairly high molecular weight. At 400 °F, application of several thousand pounds/sq. in. pressure formed a hard glossy coating which, however, was quite brittle.

Reaction of dimethyltin oxide with diphenylsilanediol in xylene. The polymerization described above in toluene apparently will not produce a soluble polymer containing a ratio of tin to silicon significantly higher than 1:3.7. It was thought that the use of a higher-boiling solvent might promote further utilization of the tin oxide starting material. Consequently, 6.48 g (0.03 mole) diphenylsilanediol and 1.64 g (0.01 mole) dimethyltin oxide were placed in an open beaker with 200 ml xylene. The mixture was boiled on a hot plate; within a few minutes substantially all the solids had dissolved. The mixture was filtered and concentrated to a heavy viscous syrup -- more viscous at high temperature than preceding polymers. The product was fractionated by solution in benzene and precipitation with petroleum ether; to produce a hard brittle resin (62081 A) and a soft transparent plastic material (62081 B). Analyses are not available.

The above experiment involves a tin-silicon ratio of 1:3. The reaction proceeded smoothly, so it was decided to investigate a 1:2 ratio. The reaction was carried out as described above, but using 6.2 g (0.038 mole) dimethyltin oxide and 16.4 g (0.076 mole) diphenylsilanediol. When all the solvent had been boiled off, some undissolved dimethyltin oxide still remained. However, when this mixture was heated to 250°C, the alkyl tin oxide was gradually

dissolved by the polymer. The mixture was cooled, dissolved in benzene, and filtered to remove traces of solids. The filtrate was concentrated to a syrup which was heated at 250°C in a current of air to remove residual solvent. The remaining liquid solidified to a transparent resin which exhibited some cold flow but easily retained a given shape (62082 A).

<u>Anal.</u>	Found	% Sn:	14.66
		% Si:	11.80



It is apparent that some of the tin introduced into the reaction mixture was lost, presumably as a soluble organotin derivative; a Si/Sn ratio of 2:1 would contain about 21% Sn, 10% Si.

The effect of varying proportions of reactants in a run like the above was studied as follows. Four parallel experiments were carried out using dimethyltin oxide prepared from carefully purified dimethyltin dichloride and Dow-Corning's "Purified Grade" diphenylsilanediol. The experimental procedure was that described above. The quantities of reactants were 10.8 g (0.05 mole) diphenylsilanediol and dimethyltin oxide in the following amounts:

- | | | |
|----|--------|-------------|
| a) | 1.64 g | (0.01 mole) |
| b) | 3.28 g | (0.02 mole) |
| c) | 4.92 g | (0.03 mole) |
| d) | 6.56 g | (0.04 mole) |

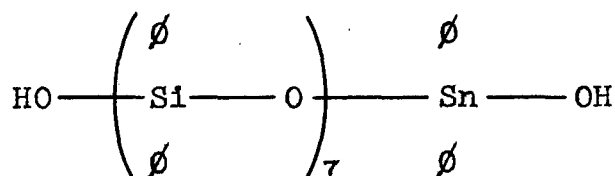
The reaction time and temperature required to form a clear solution increased in the order listed, but all the mixtures formed clear resins varying only slightly in viscosity at a given temperature. Analytical data are not available but it is no doubt correct to assume that molecular weights were substantially the same in all four cases. It is believed that these molecular weights are quite low (3,-5,000); it may well be that varying tin-silicon ratios at higher molecular weights would produce extensive changes in properties. This remains to be seen.

Reaction of diphenylsilanediol with diphenyltin oxide.

Diphenyltin oxide was prepared by hydrolysis of an ethanolic solution of diphenyltin dichloride. The dichloride was prepared by a disproportionation reaction between tetraphenyltin and stannic chloride. Hydrolysis was effected by addition of concentrated ammonium hydroxide, and the precipitated diphenyltin oxide filtered with suction and washed thoroughly with water.

Approximately equimolar quantities* of diphenyltin oxide and diphenylsilanediol were intimately mixed by grinding in a mortar, and placed in a 100 ml flask. The flask was evacuated and heated in a molten metal bath. At about 200° the solids melted to a yellow liquid which effervesced as water was lost. After about a half hour the flask was arranged for distillation (1 plate) using special large-diameter apparatus. At a bath temperature of 280-300° a small amount of liquid distilled and set to a mushy solid on cooling. The bath temperature was raised to 400°, whereupon some material distilled from the pot and immediately condensed on the walls of the side arm. This waxy solid was recrystallized from a mixture of benzene and petroleum ether (30-60°). It was found to possess a melting point of 186-189°, and a molecular weight of 572. This strongly suggests hexaphenylcyclotrisiloxane, for which the reported melting point is 188-189° and the molecular weight 594.

The residue in the pot set to a hard brittle yellow glass on cooling. It was dissolved from the flask with benzene; addition of petroleum ether precipitated an oil, which on removal of solvent became glassy and hard as before. Three small fractions were precipitated in this manner, with the result that essentially all the color was lost from the benzene solution. The benzene was evaporated to leave a colorless glass, which was powdered in a mortar and dried in an Abderhalden pistol over P₂O₅ and paraffin. The product was soluble in organic solvents except petroleum ether. Infrared analysis indicated the presence of ϕ -Sn and ϕ -Si bonds, of the Si-O-R group, and of a linear molecule. Cryoscopic molecular weight was 1640. Analysis showed 7.32% Sn and 12.50% Si. These data correspond most closely to a structure of the following type:



Mol wt: 169.4
 % Si : 11.6
 % Sn : 7.0

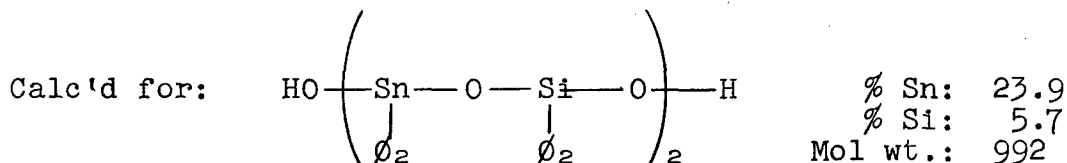
Reaction of diphenyltin oxide with diphenylsilanediol in refluxing dioxan. This experiment is summarized on the accompanying diagram; numbers over the arrows are keyed to the following text.

*It is now believed that the diphenyltin oxide used was partly hydrated, so that some excess of silanediol was present in this reaction.

(1) In a 500 ml flask were placed 14.4 g (0.05 mole) diphenyltin oxide and 10.8 g (0.05 mole) diphenylsilanediol; about 250 ml purified dioxan was added and the mixture refluxed for 16 hours. During the refluxing the white diphenyltin oxide dissolved; only a small amount of white ppt was evident in the reaction flask. This was removed by filtration and discarded. The dioxan solution was concentrated to leave a pale yellow viscous syrup (53188 A).

Anal. Found % Sn: 23.33
% Si: 6.36
Mol wt.: 1030

I.R., Linear molecule, contains OH groups.



(2) A portion of this material was heated in an open beaker with a pellet of KOH; the viscosity of the hot (ca 250°C) syrup increased somewhat, and on cooling a hard brittle resin (53189 A) was formed.

Anal. Found % Sn: 26.87
% Si: 7.41
Mol wt.: 1290

It is apparent that the percentages of tin and silicon are too high for a structure of the type indicated above. Apparently some disproportionation takes place.

(3) A portion of this brown resin was dissolved in benzene; petroleum ether was added to the solution to precipitate a white solid (53189 B).

Anal. Found % Sn: 39.26
% Si: 5.6
Mol wt.: 1960

Evaporation of the solvent left a small amount of viscous liquid which was not characterized.

(4) This fractionation by solution in benzene and addition of petroleum ether was repeated with a second sample of the resin 53189 A, but two fractional precipitations were made. Molecular weight data are not available, but polymeric materials were obtained high in tin content and near in composition to 53189 B, above.

(5) Another sample of the initial polymeric product (53188 A) was placed in an Abderhalden pistol and heated at 280° and 1 mm pressure for 16 hours. Small amounts of water and benzene were removed. At the end of the heating period the sample was a brittle resin. This material was dissolved in benzene and petroleum ether was added to precipitate a white solid (53193 A). This product was dried for 1-1/2 hours at 120°C.

<u>Anal.</u>	Found	% Sn:	32.76
		% Si:	7.34

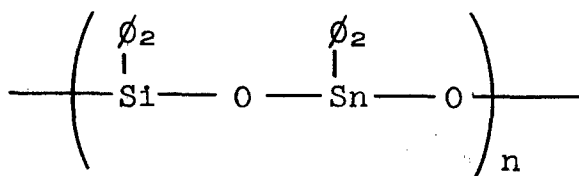
The molecular weight of this material was found to be 4300. This is too high for accurate determination by the cryoscopic method employed, however; therefore the molecular weight can only be estimated as being 3,-5,000.

Reaction of diphenylsilanediol with diphenyltin oxide.

These compounds have been observed to react in dioxan to form linear polymers capable of further polymerization at the end groups. It was therefore thought that a longer reaction time might increase the molecular weight of the product initially separated. Diphenylsilanediol (22.5 g, 0.104 mole), diphenyltin oxide (30 g, 0.104 mole) and 150 ml purified dioxan were heated at reflux for 60 hours; a clear solution was formed. Dioxan was removed to leave a pasty residue -- not a brittle glass. The product was heated in refluxing toluene in an attempt to remove water azeotropically and thus increase the molecular weight further; however, only a drop or so of water was removed. The polymeric product slowly (2-3 hours) dissolved in the toluene; the solution was then allowed to cool and stand overnight, whereupon a gelatinous precipitate appeared. This material was removed and washed by centrifugation, and dried by heating at 140°C. This material was somewhat soft at 140°, but at room temperature consisted of a friable resin, easily ground to a free-flowing powder.

<u>Anal.</u>	Found	% Sn:	43.32
		% Si:	5.37

This analysis is not consistent with the expected structure. A polymer of this type



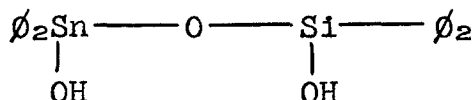
contains 5.76% Si and 24.3% Sn. To increase the tin content to 43% some of the phenyl substituents must be removed; this is possibly what happened.

Evaporation of the toluene solution left a yellow wax which was freed of solvent in the vacuum oven.

<u>Anal.</u>	Found	% Sn:	22.65
		% Si:	8.25

This polymer contains somewhat more Si than Sn on an atomic basis.

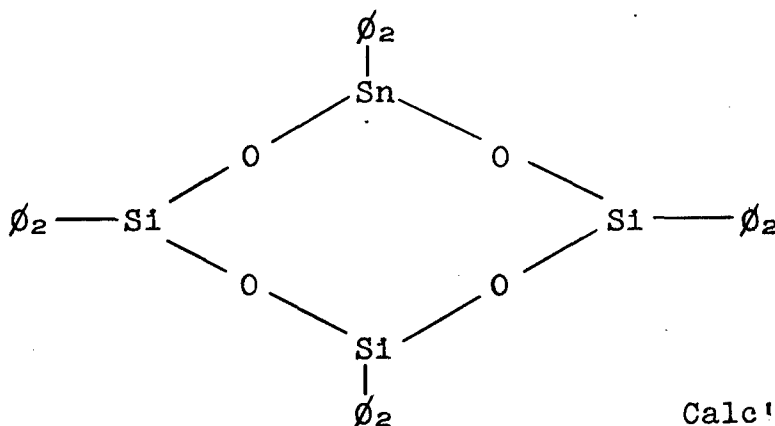
The reaction of diphenyltin oxide with diphenylsilanediol in ether. This reaction was carried out at lower temperatures than previously used, in an attempt to prepare a simple monomeric condensation product:



In a one-liter flask were placed 22.4 g (0.104 mole) diphenylsilanediol, 29.2 g (0.101 mole) diphenyltin oxide, 400 ml ether, and a magnetic stirring bar. The mixture was refluxed for several hours, then filtered. The white solid recovered has not been analyzed to date. The clear ether solution (filtrate) was concentrated to a partly crystalline oil; treatment with ether left a white crystalline solid, which was dried and submitted for analysis.

Found	% Sn:	13.59,	13.15
	% Si:	9.29,	9.32
	Mol wt.:	≤ 1070	

These data can be correlated fairly well with the following structure:



Calc'd:	% Sn:	13.4
	% Si:	9.5
	Mol wt.:	882

The infrared spectrum showed traces of -OH, which is probably present as end groups of small open chains, or as H₂O.

F. REACTION OF CYCLIC SILOXANES WITH TIN OXIDES

Reaction of octamethylcyclotetrasiloxane with diphenyltin oxide. The best reaction discovered to date for preparation of tin-silicon polymers involves the reaction of disilanol with organotin oxides. This, however, is impossible with methylsilicon compounds since the dimethyl silanediol is not a stable monomer. It was therefore thought that it might be possible to equilibrate a mixture of a cyclic siloxane with an organotin oxide in such a manner that a linear tin-oxygen-silicon polymer would be produced.

In a 200 ml reaction flask were placed 28.8 g (0.1 mole) of diphenyltin oxide, 7.4 g (0.25 mole) of octamethylcyclotetrasiloxane, and 150 ml of dioxan. The mixture was heated to reflux and maintained at that temperature for several days. Some solid material remained in the reaction mixture throughout. The solids were removed by centrifugation and extracted with boiling benzene. The insoluble material weighed 7.9 g. Analysis indicated that this material contained 63.06 wt % tin and no silicon. The diphenyltin oxide starting material contains only 41% tin.

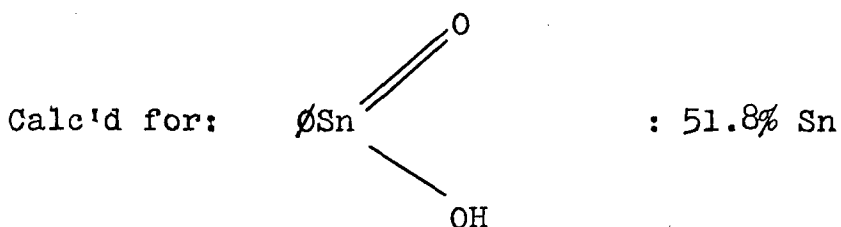
Evaporation of the benzene and of the dioxan solutions gave a highly crystalline colorless solid with a sharp melting point of 100°. This compound was found to contain 31.36 wt % tin and no silicon. To date no organotin compound of this composition and melting point has come to mind.

This experiment was repeated substantially as described above except that one drop of concentrated sulfuric acid was added to the reaction mixture in the hope of catalyzing the desired equilibration (Run 53209). The mixture was refluxed for several days, then filtered to remove a white solid (53211 A) which weighed 3.6 g. Evaporation of the dioxan filtrate left a waxy mass; this was boiled with benzene and the solution filtered. A white solid remained on the filter paper (53211 B); this weighed 8.2 g. The benzene filtrate was heated to remove the solvent; a yellow liquid remained which crystallized on cooling (53211 C). This material weighed 9.6 g, and had a melting point of 92°C.

Analysis of the above three compounds was as follows:

53211 A - Found	% Sn:	52.7
	% Si:	0.91
53211 B - Found	% Sn:	51.2
	% Si:	0.25
53211 C - Found	% Sn:	32.8
	% Si:	0.25

It is tempting to speculate that a disproportionation has taken place to produce phenylstannonic acid and triphenyltin hydroxide.



Calc'd for $\text{C}_6\text{H}_5\text{SnOH}$: 32.2% Sn

However, no likely mechanism for this transformation has come to mind. The matter will be investigated further.

A similar reaction was carried out as follows using dimethyltin oxide. In 100 ml of dioxan were placed 16.4 g (0.1 mole) of dimethyltin oxide and 7.4 g (0.025 mole) of octamethylcyclotetrasiloxane; again one drop of concentrated sulfuric acid was added as a catalyst. The mixture was refluxed 24 hours and was then filtered to separate a white solid present in the reaction mixture. This material was dried in the vacuum oven and found to weigh 14.8 g (5313 A).

<u>Anal.</u>	Found	% Sn:	64.7
		% Si:	1.2

This material is substantially dimethyltin oxide. If an actual polymeric species were present it would contain about 10 atoms of tin to 1 of silicon.

Evaporation of the filtrate left 2.6 g of a crystalline solid, contaminated so as to be somewhat pasty. This material was not examined.

A somewhat similar experiment was performed using a pellet of solid potassium hydroxide as catalyst. However, in this run (53215) a considerable molar excess of the cyclic siloxane was utilized in the hope of obtaining a polymer containing a relatively low mole-percent tin. The reaction was run by placing 14.8 g (0.05 mole) of octamethylcyclotetrasiloxane and 4.1 g (0.025 mole) of dimethyltin oxide in about 100 ml of purified dioxan. The pellet of KOH was added and the mixture refluxed about 72 hours. The mixture was filtered to remove a small amount of white solid which was dried in a vacuum oven and found to weigh 2.4 g. The dioxan filtrate was concentrated on the hot plate to leave a colorless syrup which became quite viscous on cooling and smelled strongly of methyltin compounds.

However, no tin was found in the material on analysis. It was concluded that the product was merely a polymethylsiloxane gum.

G. COHYDROLYSIS OF MIXED ORGANOTIN HALIDES

Cohydrolysis of dimethyltin dichloride and diphenyltin dichloride. In a 2-liter 3-necked creased flask were placed 750 ml toluene, 22 ml concentrated ammonium hydroxide (ca 6 g., 0.35 mole, NH_3) and 200 ml water. The flask was equipped with a stirrer (high speed), a condenser and an addition funnel containing a solution of 17.2 g (0.05 mole) diphenyltin dichloride and 11.0 g (0.05 mole) dimethyltin dichloride and 11.0 g (0.05 mole) dimethyltin dichloride in 500 ml toluene; this solution was added to the contents of the flask over about an hour with very vigorous stirring. Stirring was continued for about an hour after addition of reagents was complete. The reaction mixture consisted of a white emulsion which tended very slowly to separate into layers; all of the material passed through a "coarse" fritted-glass filter. The mixture was poured onto a fluted filter paper which permitted a slow filtration of a clear colorless very viscous toluene solution; as the filtration continued (it was allowed to stand overnight) evaporation of toluene at the surface resulted in formation of films of polymeric material. Evaporation of solvent from 11.62 g of solution left 0.22 g of a transparent slightly brittle material, indicating that the solvent contained about 2 g of polymer per 100 g of solvent. When the filtration was completed about 5 g of a white solid material remained on the paper. This was partly soluble in hot toluene; it was apparently a polymer similar to that dissolved in the filtrate but of higher molecular weight.

Additional runs corroborated the above results. The transparent stannoxane polymers can be redissolved in benzene or toluene. Heating to 300°C or so on a hot plate produces a brittle solid. Further work is in progress.

SECTION V

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