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SILICON ORGANIC RESINS

A dissertation submitted to the
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in partial fulfillment of the
requirements for the degree of

DOCTOR OF PHILOSOPHY

1944

by

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I. INTRODUCTION

Although the use of paints for decorative or protective purposes goes back to prehistoric times, no generally suitable fire-resistant paint has ever been developed. The combustible part of the available paints is the organic vehicle. One of the obvious curatives is to use a fire-resistant vehicle. It is the object of this research to develop organo silicon fire-resistant vehicles. The reason for the choice of organo silicon resins is fivefold: 1). silicon is the second most abundant element in the world, 2). the fire resistance of some of the silicon compounds is great, 3). research with organo silicon compounds is small, 4). the availability of the initial raw material, sand, is great, 5). resins developed whether fire-resistant or not should have other interesting properties.

The fire-resistant requirement limits very definitely the types of silicon organo compounds that can be considered. It is obvious that it is necessary to keep the carbon content of the final resin to as low a value as possible. However, the ethyl orthoester and ethyl silicon halides are most frequently employed as starting materials because of the ease of preparing and working with these compounds justifies their use.

The experimental part of this thesis can be divided into three main divisions: formation of resins possessing silicon-oxygen-carbon bonds; formation of resins possessing silicon-oxygen-phosphorous bonds; and the formation of silicon-carbon bond compounds. Although some new silicon resins were obtained none suitable for paint vehicles were produced.

II. HISTORICAL

A brief review of the chemistry of the various compounds of silicon with different elements is indicated since there is no adequate modern review of the chemistry of these compounds. This will include compounds containing the following bonds: Si-H, Si-OC, Si-X, Si-C, Si-N, Si-S, and Si-O-Si. Two recently published specialized reviews will be referred to when the bonds, Si-X and Si-OC, are discussed. Stock (1), (2), and Kipping (3) who have done the greatest amount of the work with the silicon compounds have both written general reviews on this subject, but they tended to place emphasis on their own work. Bygden (4) has written a 200 page dissertation covering the chemistry of many of the silicon compounds but placed emphasis on their physical properties.

The greatest similarity in the chemistry of silicon and carbon is the exhibition of quaternary valence by both of the atoms. The greatest difference between the two atoms is the instability of the silicon-silicon bond and the apparent failure of silicon to form any type of double bond compound, with itself or any other atom. The silicon analogues of $C=C$, $C=O$, $C=N$, $C\equiv N$, $C\equiv S$, etc. have never been shown conclusively to exist. In cases where analyses have indicated a type of double bond, further substantiating physical and chemical properties (compare silica and carbon dioxide) were not encountered. The compounds can generally be shown to be polymeric. The lack of these silicon analogues is not an indication of scanty investigation along these lines, but rather the non-formation of these types of compounds.

The similarity of carbon and silicon compounds is noted mostly in physical properties and not in the chemical behavior of analogous compounds. The boiling and the melting point of many of the analogues are surprisingly close to one another, and the same can be said for some of the other physical properties.

In this review the silicon compounds are to be considered according to the stability of the silicon bond with respect to hydrolysis. The increasing resistance to hydrolysis can be arranged approximately according to the scheme: Si-X, Si-N, Si-S, Si-H, Si-OC, Si-C, and Si-O-Si. This arrangement is only approximate. It is not based on thermochemical data, but on the conclusions drawn from the chemical behavior of these compounds as recorded in literature. The preparation and chemistry of each bond shall be discussed with most emphasis on those bonds that were formed in this research.

Because of the brevity of this review the bibliography and examples of compounds given are not complete. An attempt has been made to pick out those works that are most important. Reviews mentioned at the beginning of some of the sections will give a much broader scope of that particular bond.

The nomenclature used in this paper is as follows:

Silane applies to SiH_4 or any compound possessing a silicon-hydrogen bond as R_3SiH , named trialkyl silane. Silicane applies to compounds not containing a silicon-hydrogen bond, and the term can sometimes be replaced by silicon such as R_2SiCl_2 , dialkylsilicane dichloride, or dialkylsilicon dichloride. The radicle $-\text{SiH}_3$ is termed silicyl, and cor-

responds to $-\text{CH}_3$ e.g. Ph_3SiCl , triphenyl-silicyl chloride. Silicanol and silicanediol are used for hydroxy derivatives:

H_3SiOH	Ph_3SiOH	$\text{H}_2\text{Si}(\text{OH})_2$	$(\text{Ph})_2\text{Si}(\text{OH})_2$
Silicanol	Triphenylsilicanol	Silicanediol	Diphenylsilicanediol

Silicone denotes analogues of ketones, Et_2SiO , diethylsilicone. The term siliconic acid or siliconate means the acid or ester of the silicon compound such as RSiO_2H . The grouping Si-O-Si is referred to as siloxane usually when this occurs in condensation products, but a compound as $\text{R}_3\text{SiOSiR}_3$ is termed trialkylsilicyloxi to emphasize the dissimilarity of the carbon analogues, the ethers. Other instances of terminology used in this thesis should be self-explanatory.

A. Silicon-halogen Bond:- A specialized review covering these bonds was published in Chemical Reviews in 1942 (5). However, this review is devoted to the recent research in this field, and makes no effort to include the general methods of formation and chemistry of the silicon-halide bond.

The methods of preparation and behavior of Si-I , Si-Br , and Si-Cl compounds are quite similar, and since the silicon tetrachloride is the starting halide used in the majority of the syntheses reported, the halo bond is to be studied largely through the Si-Cl compounds.

A commercial method of preparing silicon tetrachloride is the heating of a mixture of silicon dioxide and carbon in the presence of chlorine. A laboratory preparation that is successful is the passage of chlorine over elemental silicon heated to red heat. All of the silicon tetrahalides can be prepared by passing vapors of the halogen over hot silicon. The method that appears most suitable for small scale production involves

the use of calcium silicide or ferrosilicon and chlorine (6). With these alloys lower temperatures can be used, and significantly greater quantities of higher homologues are obtained. At higher temperatures the tetrachloride is almost exclusively formed, indicating that the initial compounds produced on chlorination are the more complex, with chains of Si-Si linkages, such as were present in the element itself. In presence of excess chlorine and higher temperatures, these linkages are broken down, finally yielding the tetrachloride.

In addition to the straight silicon halogen compounds, there exist compounds in which two or three different halogens are linked to silicon. The complete series of silicon chlorobromides, chloriodides, bromiodides, fluorochlorides, fluorobromides, and two fluorochlorobromides are known. There is no recorded instance in which four different halides have been attached to the same silicon atom.

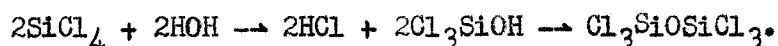
The mixed halides can be made in a variety of ways: 1). Swarts reaction (7) of antimony trihalide with a silicon halide (8); b). the explosion of hexahalodisilicane, Si_2X_6 , in presence of a gaseous halogen (9); c). passing a mixture of halides over hot silicon (9); d). displacement of one halide by an elemental halogen (9); e). double displacement involving silicon tetrachloride and hydrohalogen acid at red heat or silicon tetrahalide and a mixture of hydrogen and halogen under the influence of an electric discharge (10); and f). the substitution of a hydrogen atom of a halosilane by a halogen.

Another group of silicon halides consists of those containing more than one silicon atom. In most preparations of the tetrahalides, there is usually formed varying amounts of the higher molecular weight homo-

logues, especially when alloys are the source of silicon. From commercial "calcium silicon" (11) (containing 60-65 percent silicon) up to 25 per cent yields of disilicon hexachloride, Si_2Cl_6 , were obtained. Rapidly diminishing proportions of Si_3Cl_8 and higher halides were also formed. To form larger homologues than $\text{Si}_4\text{Cl}_{10}$ methods other than the interaction of elemental silicon or silicon alloys with chlorine must be used. Schwarz and co-workers (12), have obtained $\text{Si}_{10}\text{Cl}_{22}$ by the reaction of the tetrachloride and its decomposition products with hydrogen in a "hot-cold" tube. Some so-called unsaturated polymeric silicon chlorides, $(\text{SiCl}_2)_2$, and $(\text{SiCl})_x$ have also been prepared (13), by more complicated procedures.

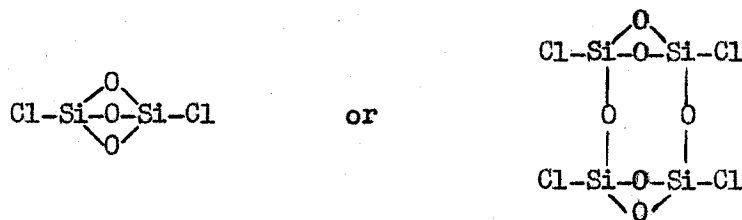
Most of the silicon halides are stable in dry air. Silicon tetrachloride liberates iodine when exposed to air or light, while silicohaloforms have been known to form explosive mixtures with air at room temperature. Silicobromoform when poured through the air burns brilliantly(5).

There has been an appreciable amount of work done on the hydrolysis of the silicon halides, and from this knowledge, it can be inferred that hydrolysis proceeds stepwise. Silicon tetrachloride would give initially a silicanol which could condense to chlorosilicyloxiide:



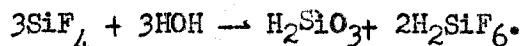
Schumb (5) states in his review that uncompleted experiments on the hydrolysis of silicon tetrachloride in anhydrous ether with a moist ether has produced appreciable quantities of oxychlorides. However, silicon oxyhalides can be made directly by passing a mixture of halogen and oxygen over heated silicon. The silicon oxyhalides are worthy of attention as this is one way of decreasing the functionallity of silicon without increasing combustibility.

The further hydrolysis of silicon tetrahalides cannot be controlled and the polymeric products formed have not been well verified experimentally. Some of the structures that have been offered for the empirical formula $(\text{Si}_2\text{O}_3\text{Cl}_2)_x$

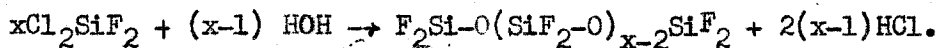


violate the structural requirements known to hold among silicates i.e. there is never a bridging of two or three oxygen atoms between two silicon atoms.

The hydrolysis of silicon fluorides is significantly different from that of the other halides. With water partial hydrolysis results in the formation of fluosilicic acid:

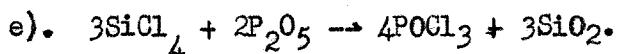


These facts lead to the question of what would happen in the hydrolysis of difluorosilicon dichloride. A water stable inorganic polymer might be formed according to the equation:



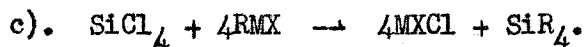
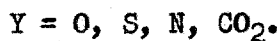
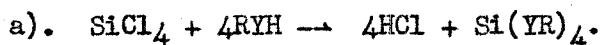
The interaction of silicon halides with other inorganic compounds will be listed in equation form to give an idea of what might be expected. The products are self-explanatory.

- a). $2\text{SiCl}_4 + 2\text{SO}_3 \rightarrow \text{Si}_2\text{O}_5\text{Cl}_2 + \text{Si}_2\text{OCl}_6.$
- b). $\text{SiCl}_4 + \text{H}_2\text{SO}_4 \rightarrow \text{HCl}, \text{SO}_2, \text{SiO}_2.$
- c). $\text{SiCl}_4 + 4\text{HNO}_2 \rightarrow 4\text{NOCl} + \text{Si}(\text{OH})_4.$
- d). $\text{SiCl}_4 + \text{Ag}(\text{CNO}) \rightarrow \text{AgCl} + \text{Si}(\text{OCN})_4 + \text{Si}(\text{NCO})_4 \text{ (trace).}$



There are other reactions involving silicon tetrachloride and inorganic compounds that can be found in the literature. An excellent review of these reactions can be found in the references given in Friend, Mellor, and Gmelin-Kraut.

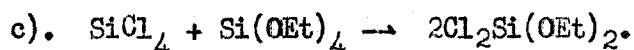
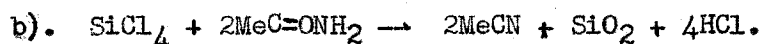
Silicon tetrachloride is used as the starting compound in the formation of most of the silico organic compounds. The reactions used in forming these compounds are similar to those used in carbon chemistry, i.e. Williamson synthesis, Grignard reaction, Wurtz reaction, double displacements, etc. Since most of these reactions are to be considered further in other sections, equations only will be given here.



With the first three reactions it is possible to control the number of organic radicals attached to the silicon by limiting the amount of organic compound added. With reaction (d) the tetraalkyl compound is favored almost exclusively.

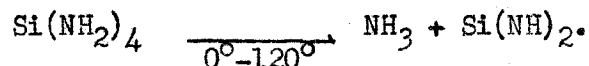
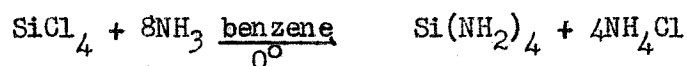
Silicon halides have been reacted with most of the other common organic reagents such as those listed below, but the silicon products are of no importance:



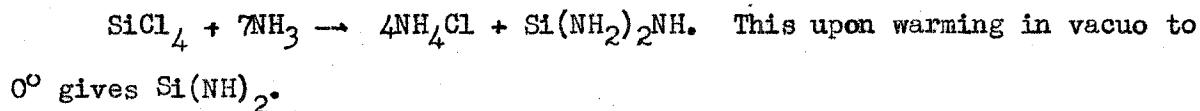


B. Silicon-nitrogen Bond:- There are not many compounds that contain silicon and nitrogen atoms directly united. Those compounds that do exist are easily decomposed by cold water and sometimes alcohol.

The compounds are usually formed by a direct combination of the silicon halide and the nitrogen containing compounds. These simple compounds can frequently be changed into more complex polymers by heating. Silicon tetramide can be prepared by passing ammonia into a benzene solution of silicon tetrachloride at 0°C (14). This forms a tetramide that is unstable at a little above 0°C losing ammonia. This decomposition is accomplished rapidly at 120°C to form silicon di-imide (15):

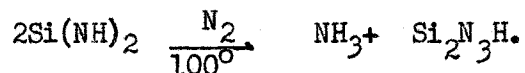


Stock and Zeidler (16) claim that the tetramide is not formed by the action of NH_3 on SiCl_4 , but diaminoiminomonosilane. according to the empirical equation:



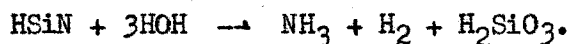
The di-imide is also claimed to be a by-product during the formation of the tetramide (15) Silicon disulfide or silicon thiochloride with liquid ammonia can also be used as reactants for the di-imide formation (16). This compound is a white infusible, amorphous solid which is stable to heat in the absence of air and like the tetramide is decomposed by water to silicic acid and ammonia. The di-imide is basic forming salts such as $\text{Si}(\text{NH})_2:2\text{HCl}$.

When the di-imide is heated to 200°C in a nitrogen atmosphere, silicon nitrimide is formed (18):

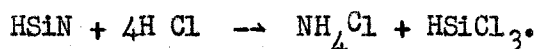


This product is of unknown structure and is of interest in that it is stable to hydrolysis. More complex compounds are formed by heating the nitrimide to 1,200-1,300°C. However, these compounds are not clearly characterized.

A gaseous mixture of trichlorosilane and ammonia with hydrogen as a diluent react to form ammonium chloride and a solid compound that analyzes for HSiN. It is doubtful whether the molecular formula given is the simple structure indicated (16), because by analogy to HCN, a solid compound that sublimates at 300°C would not be expected. The polymer is a good reducing agent resembling silicoformic anhydride in this respect:



It also possesses the property of decomposing as do some other silicon-nitrogen compounds, in reacting with hydrogen halides:



The reaction with excess siliclyl chloride and gaseous ammonia behaves as one would expect forming trisilicylamine, $(\text{H}_3\text{Si})_3\text{N}$ (19). This nonbasic compound boils at 52°C, is spontaneously combustible in air, and is decomposed by water to silica, ammonia, and hydrogen. The reaction between excess ammonia and siliclyl chloride is complex. Some of the products formed are $(\text{SiH}_3)_2\text{NH}$, $\text{SiH}_3(\text{NH}_2)$, $(\text{SiH}_3)_3\text{N}$, $(\text{SiH}_2(\text{NH}))_x$.

Complex silicon halides form compounds with ammonia that are even more unstable than those given above. Hexachlorodisilane forms bisaminoimino-disilane in liquid ammonia (20):

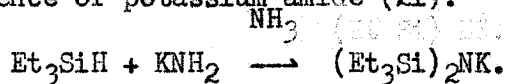


At -10°C ammonia is split off and a polymeric substance is produced. Both substances are decomposed by air and moisture with production of ammonia.

These inorganic compounds just considered show the behavior and instability of the Si-N bond and also the dissimilarity to their carbon analogues. Although there are more papers concerned with these inorganic type of silicon-nitrogen compounds, these will not be taken up in this review.

Work with organic amines is not as great as was expected. This is probably due to the instability of the compounds formed. In general the reactions are straight forward double decompositions.

A reaction that could also be mentioned under the behavior of silicon-hydrogen bond is the reaction of triethyl-silane in liquid ammonia in presence of potassium amide (21):

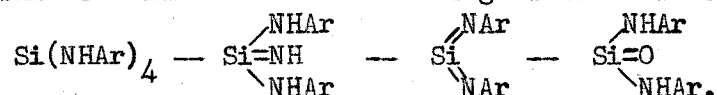


When ammonium bromide was substituted for potassium amide, bis(triethylsilyl) amine, $(\text{Et}_3\text{Si})_3\text{N}$, was produced. A compound, Et_3SiNHet , of camphor-like odor was formed when triethylsilane or triethylsilicon bromide reacted with ethyl amine in presence of lithium. Upon hydrolysis the bis(triethylsilyl) amine formed an oxide while the monosilico amines formed triethylsilicanols.

Silicylchloride, H_3SiCl , reacts spontaneously and quantitatively with methyl amine to yield $\text{MeN}(\text{SiH}_3)_2$. This amine is stable in air but is completely hydrolyzed by cold water. Hydrochloric acid decomposes it into its starting compounds. Ethyl amine behaves as does methyl amine throughout. Tertiary amines only form addition compounds with silicon halides. With trimethyl amine a solid compound precipitated, $\text{Me}_3\text{NSiH}_3\text{Cl}$, which was decom-

posed by water to trimethyl amine hydrochloride and silicyl oxide.

Silicon tetrachloride reacts with aniline to produce a tetranilide, $\text{Si}(\text{NHAr})_4$ (22). Reynolds drew attention to the following reactions of orthosilico anilide which are analogous to those of the carbon compounds:



A suspension of potassium pyrrole in petroleum ether was reacted with trichlorosilane (22). From this mixture a dark green liquid analyzing for tripyrrolesilane, $\text{HSi}(\text{NC}_4\text{H}_4)_3$, was obtained besides less pyrrole substituted silicon compounds. There were decomposed by acid, alkali, alcohol, and water.

The examples of organic amine compounds given serve as a guide to the method of formation of these compounds. These can be summarized:

1. $-\text{SiCl} + \text{RNH}_2 \rightarrow -\text{Si}(\text{NHR})$.
2. $-\text{SiCl} + \text{R}_2\text{NHL} \xrightarrow[\text{Liq. NH}_3]{\text{M}} \text{SiNHR}$.
3. $-\text{SiCl} + \text{KNR}_2 \rightarrow -\text{SiNR}_2$.
4. $-\text{SiCl} + \text{NR}_3 \rightarrow -\text{SiClNR}_3$.

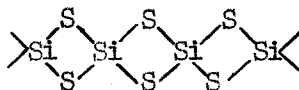
The compounds produced are without exception decomposed by water and frequently by hydrohalide acid and alcohol.

C. Silicon-sulfur Bond:- The number of compounds possessing the silicon-sulfur bond that are reported in literature is the smallest of any of the groups. The sulfur inorganic series is well represented, but the sulfur organic compounds number less than twenty. The scarcity of the latter group is probably due to the difficulty of preparation. This is rather surprising in view of the ease of preparation of the silicoorthoesters.

The silicon-sulfur inorganics that were found reported in the literature were: SiS_2 , SiS , SiOS , SiSCL_2 , SiSBr_2 , SiCl_3SH , $\text{SiS}(\text{NH}_2)_2$, and SiH_3SH .

None of these compounds had physical or chemical properties resembling those of their carbon analogues.

Of the several methods of obtaining silicon disulfide, SiS_2 , the best (23) is to heat a mixture of aluminum sulfide with powdered quartz in a stream of nitrogen at $1,200^\circ\text{C}$. The sublimation product, SiS_2 , is a white silky needle-like solid. This product, as borne out by x-ray investigation, seems to consist of a series of closed chains each of which contains silicon and two sulfur atoms:



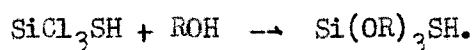
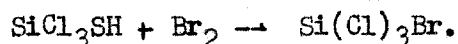
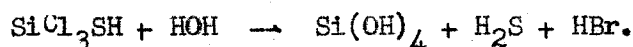
However this polymeric structure does not prevent it from being readily reactive with oxygen, water, chlorine, and sodium sulfide forming respectively $\text{SiO}_2 + \text{SO}_2$; $\text{H}_2\text{S} + \text{SiO}_2$; $\text{SOCl}_2 + \text{SiCl}_4$; and Na_2SiS_3 (sodium thiosilicate) (24).

The compound that analyzes for SiS seems to exist in two modifications, yellow and black. The silicon monosulfide can be prepared by heating ferrosilicon with sulfur in an electric furnace (25); by heating carbon disulfide with excess silicon (28); or by passing sulfur vapor over silicon heated in a porcelain tube. In the latter reaction SiOS is also a product. Cambi in his paper (25) showed that the dark modification of silicon monosulfide was really a mixture of silicon di- and monosulfide, and intermediate derivatives. The hydrolysis product of yellow silicon monosulfide has the composition $\text{H}_2\text{Si}_2\text{O}_3$, silicoformic anhydride.

Silicon thiochloride, SiSCl_2 , is formed together with silicon disulfide and silicon tetrachloride when the vapor of sulfur chloride reacts with crystalline silicon at red heat (27). A better method of preparation is to pass a mixture of silicon tetrachloride and hydrogen sulfide

through a tube at dull red heat. Silicon chlorohydrosulfide, SiCl_3SH , is formed as an intermediate which on prolonged contact with the heated tube partially decomposes into hydrochloric acid and silicon thiochloride (19). Silicon thiochloride is a crystalline solid m.p. 75°C ; b.p. $92^\circ\text{C}/23\text{ mm.}$, and is soluble in carbon disulfide. It is decomposed completely by water into silicic acid, hydrochloric acid, and hydrogen sulfide. It disproportionates upon being heated into silicon tetrachloride and silicon disulfide, and its halogens are readily replaced by ammonia to form silicothiourea. However, silicourea does not exist because SiOX_2 has never been prepared.

During the preparation of silicon thiochloride it was noticed that silicon chlorohydrosulfide was an intermediate. Workers took advantage of this observation to prepare good yields of the hydrosulfide by heating silicon tetrachloride and hydrogen sulfide at a lower temperature than that used for the thiochloride (28). The hydrosulfide is a liquid of b.p. 96°C which undergoes the reactions:



Silicon thiourea is made by passing dry gaseous ammonia into a solution of silicon thiobromide in dry benzene. The white product, silicon thiourea, left behind is unstable, decomposing at room temperature and giving off hydrogen sulfide and ammonia. Water decomposes it, but it is sufficiently basic and stable to form salts with hydrogen halides.

Because of the apparent failure to prepare Si-SR compounds from silicon tetrachloride and mercaptans, it has not been possible to say that

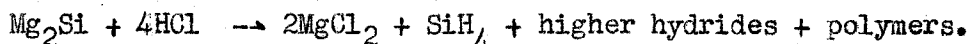
silicon tetrachloride readily reacts with compounds possessing active hydrogens. Gilman (29) arranged several of the organic compounds containing reactive hydrogen with respect to organic metallic compounds according to the descending order: RSH , ROH , RNH_2 , R_2NH , $\text{RC}\equiv\text{CH}$, RH . Except for the position of RSH which should be before or after the acetylene, this order holds for reactions with silicon tetrachloride. Neither thiophenol nor ethyl mercaptan reacted with silicon tetrachloride under usual conditions. The reaction in the latter case was slow even at 200°C (30). Thiophenol gave a small quantity of thiophenoxysilicon (31). The examples of successful preparations of Si-SR compounds involved the use of sodium alkyl sulfides (32). Tertiarybutyl mercaptan heated in absolute ether with sodium gave Me_3CSNa which on treatment with silicon tetrachloride gave $(\text{Me}_3\text{CS})_3\text{SiCl}$. This chloride was replaced with reagents MeSNa and EtSNa giving respectively $(\text{Me}_3\text{CS})_3\text{SiMe}$ and $(\text{Me}_3\text{CS})_3\text{SiEt}$. In a similar manner $(\text{Me}_3\text{CS})_3\text{SiSCHMe}_2$ and $(\text{Me}_3\text{CS})_4\text{Si}$ were obtained. However, the most interesting fact of this paper was that $(\text{Me}_3\text{CS})_3\text{SiCl}$ dissolved in absolute alcohol in presence of sodium hydroxide to give $(\text{Me}_3\text{CS})_3\text{SiOH}$. The stability of the silicon sulfur bond in this instance might be attributed to steric hinderance.

The chemical properties of the other silicon-sulfur carbon bonds would be expected to parallel those of the orthoesters.

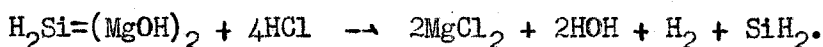
D. Silicon-hydrogen Bond:- Alfred Stock and co-workers after years of laborious experimentation developed a high-vacuum technique which enabled them to work with gases which came into contact only with glass and mercury. The specialized technique was necessary in order to exclude air, moisture, and lubricants while working with unstable, volatile substances

as some of the silicon hydrides. Stock gives a summary of his work with the hydrides of silicon and boron in a lectureship at Cornell University.

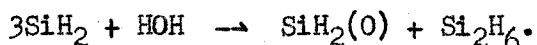
Silane, SiH_4 , is a simple preparation which can be represented by the equations:



With slight variation in yield, different experiments gave only a 23 per cent conversion of the magnesium silicide to hydrides. Of the total amount of hydrides 40 per cent was SiH_4 , 30 per cent was Si_2H_6 , 15 per cent was Si_3H_8 , 10 per cent was Si_4H_{10} , and 7 per cent was higher hydrides. A large amount of the magnesium silicide was converted into a white to brownish polymeric dioxo-disiloxane, $((\text{SiH}(\text{O}))_2\text{O})_x$. To account for these products, Schwarz and Hoefer (33) proposed the following mechanism based on an intermediate (34) $\text{H}_2\text{Si}=(\text{MgOH})_2$, (34) isolated during the decomposition of magnesium silicide using alcoholic instead of aqueous hydrochloric acid.



The radical SiH_2 is transitory:



and so forth.

For the monomer prosiloxane, SiH_2O , to exist a silicon double bond oxygen grouping, $\text{Si}=\text{O}$, would be postulated. As in all cases where a silicon double bond is postulated, the monomer was never obtained but instead the solid polymer was the end product.

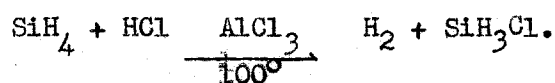
Higher yields, 65-80 per cent based on the silicon used in the preparation of magnesium silicide, of silicon containing gases can be obtained by the addition of magnesium silicide to a liquid ammonia-ammonium bromide solution (15). The Schwarz and Konrad (34) mechanism cannot be used to explain the formation of the silanes using the liquid ammonia medium, because this mechanism can only give a 50 per cent yield as a maximum and also a nitrogen complex analogous to (SiH_2O) should be formed. The mechanism of silane formation from magnesium silicide must take into account such factors as method of preparing the silicide, solvent, and temperature of reaction.

Besides the higher molecular weight saturated silicon hydrides which are unstable at room temperature above Si_4H_{10} there exists a group of polymeric, hydrogen poor hydrides. Some of the methods of producing these compounds are: a). the action of acids on CaSi (36) or CaSi_2 (37); b). silent electric discharge on SiH_4 (38); or c). by the action of Na on SiH_3Cl , SiH_2Cl , or SiHCl_3 (2). The composition of the solids varies between $(\text{SiH})_x$ to $(\text{SiH}_2)_x$ depending on the method of formation. These polymeric substances are amorphous, yellow to brown solids, unaffected by water, insoluble in organic solvents, but react with alkali to form silicates with simultaneous evolution of hydrogen. They take up bromine by both addition and substitution (39).

The behavior of the silicon hydrides gives an excellent insight into the difference between the chemistry of silicon and carbon compounds. Saturated silicon hydrides above Si_6H_{14} probably do not exist because they are too unstable. Silane and disilane are stable in sunlight for years. Trisilane, Si_3H_8 , will show signs of decomposition after several months, while during the same period Si_4H_{10} showed considerable dissociation form-

ing hydrogen, silane, disilane, and some trisilane. Pyrolysis or cracking of disilane behaved in a manner similar to that of hydrocarbons, but, of course, no unsaturated silicon hydrides were formed (40).

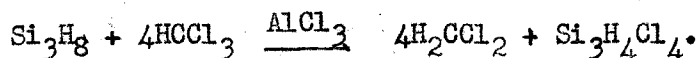
All the hydrides are sensitive to oxidation, and the lower members are spontaneous combustible upon contact with air. This necessitates the special techniques that were developed by Stock. Three other general reactions of hydrides with inorganic compounds are: a). their reductive action on inorganic salts; b). their formation of silicates with aqueous alkali which acts as a catalyst; and c). their formation of substitution products with halogens. The latter products can best be made by reacting hydrochloric gas with heated silicon or hydrochloric gas with gaseous silane using aluminum chloride as catalyst (41):



It is difficult to obtain these halo hydrides in pure form because of exchange reactions:



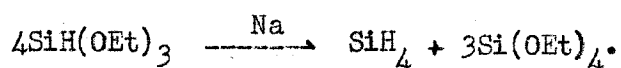
A similar type of exchange was performed by Stock and Stiebeler (42) using carbon tetrachloride or chloroform and aluminum chloride with the exclusion of oxygen:



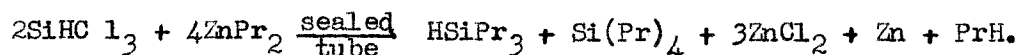
The halohydrides undergo the same reactions as do the silicon halides. Thus, for example, the action of alcohol or a Grignard reagent on a halosilane form an alkoxyl silane or alkyl silane respectively. The hydrogen of the alkyl silanes react in manner similar to hydrogen of the saturated silanes. However, there are several instances of steric hinderance where a trialkyl

silane is stable toward alkali hydrolysis (43). Ordinarily this lone hydrogen may be hydrolyzed or oxidized to a hydroxyl group or be replaced by bromine.

There are two reactions of silanes involving organic radicals that are interesting. The first is a transformation found by Friedel and Ladenburg (44) to take place quantitatively at room temperature in the presence of metallic sodium:



The second reaction is the reported action of zincpropyl on trichloro silane (2):



The amount of the tetrapropylsilicane was equal to that of tripropyl silane.

Boron hydrides react with acetylene (45). For example, acetylene and excess B_2H_6 yielded at 50°C a non volatile substance with an aromatic odor containing about three molecules of C_2H_2 per molecule of B_2H_6 . A reaction of this type with silane would prove valuable.

From these facts some of the comparative points of the chemistry of silicon and carbon compounds may be summarized: a). Both atoms tend to form chain hydrides, but the silicon chain becomes rather unstable above Si_4H_{10} . b). Carbon has about equal affinity for both positive and negative elements. Silicon shows greater affinity for negative elements such as oxygen and halogens than for positive elements such as hydrogen. This is what one expects from its position in the periodic chart. Going down in any series increases the metallic character of the elements of the series. c). Silicon has a tendency to form polymeric compounds, especially with oxygen and when unsaturated linkages are formed.

E. Silicon-oxygen-carbon Bond:- A recent monograph (46) on the chemistry of the aliphatic orthoesters contains two chapters, or thirty-one pages, on the preparation and chemistry of silicon orthoesters. The chapter devoted to preparations gives the material in a chronological order, while the chapter devoted to the chemistry of the orthoesters is more orderly and logically arranged. In the review presented here, only the material that is related to the present research problem shall be considered.

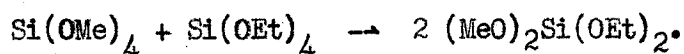
The silicon-oxygen-carbon compounds can be classified into three groups: simple or mixed orthoesters, orthoesters containing functional groups, and so-called silico acid anhydrides. Since von Ebelmann in 1846 (47) prepared the first orthoester, $\text{Si}(\text{OEt})_4$, over two hundred different compounds containing a silicon-oxygen-carbon bond have been prepared and isolated. Besides these compounds there exists in literature descriptions of a number of high boiling polymeric materials that were found in the residue or mother liquors of the types of compounds listed above. In many cases the investigator merely stated that a high boiling dark residue remained but did not investigate the products further.

There are three general methods of preparing simple or mixed orthoesters: a). adding the silicon halide directly to an alcohol, or vice versa; b). reacting the halide and an alcohol in an inert medium; and c). substituting one alkoxyl group with another. The first method is obviously the easiest. The yield of the orthoester, however, is usually not over 80 per cent. The highest yield of an orthoester found to date (prepared by the dropwise addition of five mole excess of butyl alcohol to silicon tetrachloride) is the 84 per cent yield of tetrabutyl orthosilicate (48). Andrianov (49) reported similar yields of orthoesters with a

series of alcohols; however, Kalinin (50) and several patents seem to favor an inert diluent for the ester formation. The use of a medium such as benzene or benzine is claimed to be favorable because the dehydration of alcohols is not necessary when these diluents are used. There are several reasons for the low yields of orthoesters: a). the evolution of large volumes of gas carry over both alcohol and the silicon halide; b). the formation of partially substituted silicon halides; c). the formation of condensation products, probably caused by the presence of dissolved hydrohalides; and d). the reaction of the hydrohalide acid with the alcohol liberating water which reacts with the silicon halide. For best yields these difficulties must be overcome.

It is obvious that by limiting the quantity of alcohol added to the silicon tetrachloride the various intermediates can be produced. Size or nature of the alkyl group generally has no detrimental effect upon the results obtained. Long chain alcohols up to C_{14} (51), branch chain alcohols (52), cyclic alcohols, (53) and even phenols (54), react. In the case of secondary alcohols it has been reported that the alcohols are dehydrated by silicon tetrachloride.

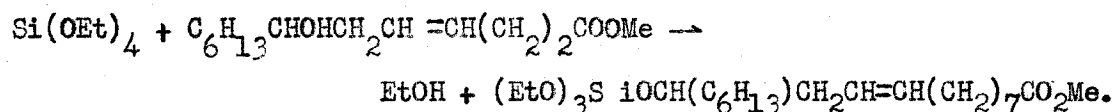
The substitution of an alkoxyl for one usually of lower molecular weight is a method of preparing mixed orthoesters and the preparation of orthoesters containing a functional group. The exchange of alkoxyl groups can take place between different orthoesters (55) or an orthoester and an alcohol:



Post and Hofrichter (48) in a recent investigation observed some limita-

tions to the latter reaction. They found that if the alkoxy group attached to the silicon was larger than ethoxy, the exchange was slight and high molecular weight products were formed. The reason given was the larger alkoxy groups attached to silicon interfered with coordination between the alcohol and the SiOR group. In their experiment they used ethyl orthosilicate and butyl alcohol to obtain a 22 per cent yield of triethylbutyl orthosilicate, 30 per cent of diethyldibutyl orthosilicate, and 25 per cent of impure ethyltributyl orthosilicate.

The preparation of functional orthosilicates is brought about by an exchange reaction especially if the functional group is one that has a possibility of reacting with a silicon halide. Tetra-(β -aminoethyl)-orthosilicate was prepared by heating together the orthoester with ethanolamine (56). There are a number of patents that are concerned with the exchange reaction of ethyl orthosilicate with hydroxy esters such as α -monostearin (57) or methyl ricinoleate (58):



Halohydrins have been reacted with silicon tetrachloride for the preparation of some bromo- and chloroalkyl orthoesters (59). Hydroxycarboxylic acids, their esters, or salts have been reacted with silicon tetrachloride (preferably in the presence of pyridine) to prepare esters of orthosilicate esters (60). There are undoubtedly other functional orthoesters that can be prepared from alcohols containing such groups as keto, aldehyde, nitro, etc.

Both silicon tetrachloride and silicon orthoesters have been used as addition products with some commercial resins containing hydroxy groups.

One patent (61) is concerned with a mixture of ethyl orthosilicate and partially or completely esterified cellulose. The amount of silico ester could be varied from 20-50 per cent of the total composition. In another patent (62), silico esters that were prepared from long chain alcohols were used as plasticizers in cellulose nitrate resins. It was claimed that these plasticizers reduced the tendency of the nitro cellulose to ignite. Silico esters containing functional groups (63) were also suggested as plasticizers. In another patent (64) the free hydroxy groups of resol or novalac resins were etherified with α - or β -monochlorotetraethylsilanes or more highly chlorinated derivatives. The silico esters in another patent (65) were not added to a preformed resin but were one of the reactants. An alkyl phenol, an alkyl orthosilicate, silicon tetrachloride, or alkyl substituted silicon halides, and a vegetable oil were heated to 175°C for twenty hours. The resin could be used for molding, films, etc.

Before considering the resins that are prepared directly by the hydrolysis of silico orthoesters, it is well to discuss briefly the preparation of the third type of compounds containing the Si-OC bond, viz; the silico anhydrides. There are two obviously general methods of preparing the silico anhydrides. One involves the reaction of silicon tetrachloride with an acid or its salt; the other uses orthoesters for exchange reactions. An example of the first is to suspend potassium methacrylate in benzene and add silicon tetrachloride slowly (66). After the reaction is complete, the potassium chloride can be removed by filtration, and the silicon tetramethacrylate remains after the benzene is evaporated. This product and its polymers have been patented. Silicon tetra-acetate

can be obtained directly by reacting silicon tetrachloride with either acetic acid or acetic anhydride (67). However, with larger molecular weight acids or anhydrides there is a tendency to form acid chloride and silica as the end products. Esters such as ethyl acetate and phenyl acetate (68) give silicon tetraesters, but the yield is reduced by the formation of alkyl halides, acid chloride, and partially substituted silicon halides.

As previously mentioned, the second general method of obtaining silico anhydrides is to react the orthoesters with an acid anhydride (69). When monoalkyl ethyl siliconates were used, all the ethoxyl groups could be replaced by acetate groups as determined by the quantity of ethyl acetate recovered. $\text{EtSi}(\text{OEt})_2(\text{O}_2\text{CMe})$, $\text{EtCO}_2\text{Si}(\text{OEt})_3$, and $(\text{EtCO}_2)_2\text{Si}(\text{OEt})_2$ were obtained in about 40 per cent yield when the respective esters were used. High molecular weight products were also formed.

Esterification of silicols is useful for the preparation of monoacetates whenever the silicol can be obtained. The esterification has to be performed by means of the acid anhydride (70) since the acid chloride gives silicon chlorides (71).

Both the chlorides $\text{Cl}_3\text{SiSiCl}_3$ (72) and $\text{Cl}_3\text{SiOSiCl}_3$ (73) have been reacted with alcohols to replace all the chlorine by ethoxy groups.

The chemical property of orthosilicates previously discussed involves the exchange of an alkoxyl group with either an orthosilicate, alcohol, ester, acid or anhydride. The hydrolysis products of esters will be considered next.

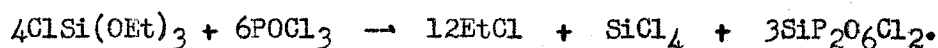
Variable quantities of water will naturally give different products. Treatment of one mole of methyl orthosilicate with one-half mole of water

leads almost exclusively to the formation of the disilicyl ester, $(\text{MeO})_3\text{SiOSi}(\text{OMe})_3$. The use of one mole of water per mole of ester gives practically a quantitative yield of a polymeric ester having a molecular weight of approximately 10,000 (74). Ellis suggested that the structure is a linear continuation of the dimer obtained when the small water ratio was used (75). When even more water is added a complex thermoset resin is obtained, and this property is the basis of the commercial orthosilicate paints (76). The initial setting of these paints, depending upon the solvent and atmospheric moisture, takes place in approximately one hour; final setting, which is the completion of the hydrolysis, requires a longer period, up to six months. The end product of this hydrolysis is silica. Ethyl orthosilicate has limited use as a protective medium for stone and plaster, for metals exposed to high temperature, for stiffening and fire-proofing textiles, and as a binding agent for sands and fireproof brick.

Andrianov (77) studied the mechanism and obtained a patent (78) on the hydrolysis of alkyl orthosiliconates, $\text{RSi}(\text{OEt})_3$. If these compounds were heated with water for two hours at 93°C , 93 per cent of the ethoxyl groups were removed. When insufficient water was used a polymer, $-\text{RSi}(\text{OEt})-\text{O}-\text{RSi}(\text{OEt})-\text{O}-$, was predicted. In presence of more water, the remaining ethoxy groups would be removed with the formation of more siloxane bonds. Andrianov was not able to get any type of compound analogous to silicic acid, RSiO_2H , as claimed by others.

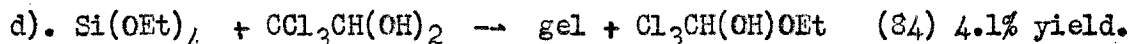
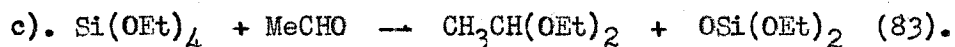
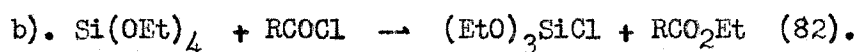
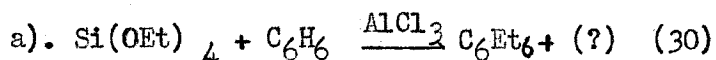
There are several reactions with inorganic compounds that are interesting. Boric acid reacts with ethyl orthosilicate to form ethyl borate (79), and boric anhydride reacts with phenyl orthosilicate to form various

phenyl borates (80). Stokes carried out some reactions with phosphorous oxychloride (81). When ethyl orthosilicate was heated with excess POCl_3 for two hours at $180-200^\circ\text{C}$ a solid compound containing silicon and phosphorous was obtained along with much ethyl chloride. Triethoxysilicon chloride reacted in a similar manner. The reactions are expressed as follows:



These products will be further considered in the experimental part of this thesis which deals with the silicon-oxygen-phosphorus bond.

Aside from the reaction between orthoesters and Grignard reagent which comes under the formation of a silicon-carbon bond, only exploratory work has been done with other organic compounds. Some of these reactions shall be indicated here by equations:



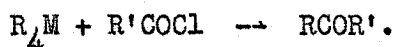
It may be well to point out here that the method of preparation and chemistry of the higher molecular weight esters such as $(\text{RO})_3\text{SiSi}(\text{OR})_3$ or $(\text{RO})_3\text{SiOSi}(\text{OR})_3$ is predictable for the behavior of the orthosilicates.

There is considerable similarity between the chemistry, method of preparation, and physical properties of the silicon orthoesters and carbon orthoesters. Again a pronounced difference between the two esters is the tendency of the former compounds to form polymers with a silicon-oxygen-silicon bonding.

F. Silicon-carbon Bond:- There is no one general review devoted to the preparation and chemistry of silicon-carbon bonds, but the reviews by Kipping (3), Bygden (4), and in Friend (85) which is the best, give excellent views of this bonding.

A polymerization or condensation to be useful for the preparation of commercial synthetic resins must be controllable. There are few instances where a monomer with more than three functional groups has been successfully used in the preparation of resins. Thus, it appears that at least one or two of the valencies of silicon must be rendered non-functional. Of the groupings considered, it appears that they are either too active to be non-functional or, in other words, they would be too unstable to appear in the final film. However, the silicon-carbon bond is sufficiently stable to act as a blocking group.

It would be useful to know which silicon-carbon bonds are the most stable and whether this bonding is stronger than the carbon-carbon bond. Without a table of the bonding energies possessed by various silicon-carbon compounds, it is necessary to resort to some qualitative information considering the stability of silicon compounds. Gilman (29) lists five properties that the compounds of group IV-B from carbon to lead possess in a definite gradation: a). the tendency to form mixed hydrides like RMH_3 , R_3MH_2 , and R_3MH is lowest with the organolead compounds; b). thermal stability decreases so that organolead compounds are the least stable; c). the tendency to form polymetallic compounds decreases in the same order; d). the rate of cleavage by halogen or acids is greatest with organolead compounds; e). organolead compounds are the most reactive toward acid halide and some reactive alkyl halides:

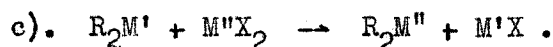
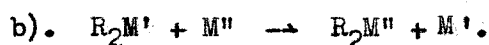
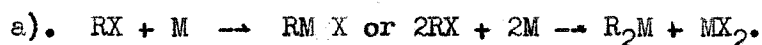


This list indicates that the carbon-carbon bond is the most stable physically and chemically. However, Stock (1) maintains that the silicon-carbon bond is more stable than the carbon-carbon bond. He bases his belief on the ease of formation of siliconium compounds in comparison to the carbonium compounds and the greater stability of hexasubstituted disilanes in comparison to hexasubstituted ethane. Furthermore neopentyl rearrangements that are encountered in carbon chemistry have no counterpart in silicon compounds.

There are several theories for the dissociation of hexaphenyl ethane and formation of triphenyl methane free radicals. At the present time it is generally considered that the dissociation of the hexaaryl ethanes is more or less adequately explained on the basis of resonance and steric hinderance. Thus the odd electron on triphenyl methane is pictured resonating among nine other positions. In these resonating structures the central carbon of necessity forms a double bond with the quinoid ring possessing the odd electron. These resonating forms lower the energy content of the resultant hybrid structure and stabilize the free radical. The silicon compound, however, in not forming any types of double bonds cannot form a free radical which would be stabilized by resonance. Therefore tetraarylsilicane or hexaaryldisilicane are in their stablest form and would not dissociate. Furthermore, from a consideration of ionic radii, it can be seen that silicon of 0.41×10^{-8} cm. ionic radius has more room for radicals than carbon with 0.15×10^{-8} cm. In general it may be said that the silicon-

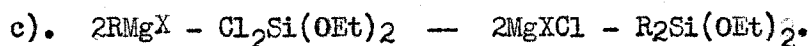
carbon bond is probably less stable than carbon-carbon bond, but the difference in case of the two bonds is not very great.

There are three syntheses of wide application for the formation of organometallic compounds:



Method (b) generally takes place when M'' is above M' in the electromotive series and R_2M'' is more reactive than R_2M' ; while in (c) the reverse is true. Of these three methods only (c) can be used for the preparation of organo silicon compounds. In this procedure $M''X_2$ can be either SiX_4 or $Si(OEt)_4$ while R_2M' may be R_2MgX , ZnR_2 , HgR_2 , or NaR . It is evident from these synthetic methods that the cost of forming a silicon-carbon bond is out of proportion commercially to the cost of silica as one of the starting materials.

There are two well established ways of forming the silicon-carbon bond by method (c): a Grignard reagent may be reacted with either the silicon halide, or silicon ester, or the Wurtz and Fittig types of reaction may be used. The latter reaction is most suitable for the preparation of tetraalkyl or aryl silicon compounds. The Grignard procedure is very versatile and with it almost any of the other alkyl or aryl silicon-element bonds can be prepared such as:



Reaction b). can be run stepwise so that four different alkyl or aryl

groups are attached to the same silicon, thereby making an optically active compound.

There are three general procedures that can be followed in the preparation of silicon-carbon compounds by use of the Grignard and silicon halide or orthoester: a). the preformed Grignard reagent and silicon compound are reacted together in the presence of a solvent until the reaction is completed; b). the reactants are brought together and partially reacted in the presence of a solvent, usually ether, which is then distilled off and the remaining mixture is heated at a higher temperature until the reaction is completed; c). the Grignard reagent is formed in the presence of the silicon halide and a solvent. This latter reaction is the simplest and deserves the most consideration (86).

Besides the simple compounds already mentioned, there are several more complicated ones that have been prepared by use of the Grignard reagent. A cyclic compound in which silicon is one of the atoms was obtained from silicon tetrachloride and dimagnesium dibromopentamethylene. The cyclopentamethylenesilicon dichloride was further reacted with methyl magnesium iodide to give the dimethyl compound (87). A compound that gave the theoretical silicon percentage and molecular weight for tetraacetylenesilicane and decolorized bromine water, was obtained from silicon tetrachloride and magnesium acetylene (88). When chlorosilicic oxide was used in place of silicon tetrachloride only 4 per cent of the hexaacetylene product was obtained. Other compounds containing a functional group have been also made by means of the Grignard reagent: $(\text{ClC}_6\text{H}_4)_4\text{Si}$ (89), tetrathiophene, $(\text{C}_4\text{H}_3\text{S})_4\text{Si}$ (90), $(\text{C}_6\text{H}_5\text{OC}_6\text{H}_4)_2\text{SiCl}_2$ (91), etc.

The most convenient laboratory method of forming a silicon-carbon

bond is through the use of the silicon ester. This reaction can be accomplished by the reaction of a preformed Grignard with an ester or by forming the reagent in presence of the ester. However, from the literature it is evident that conditions for best yields have not been worked out completely. The originators (92) of the method claimed that only one alkoxyl group could be replaced from ethyl orthosilicate but more recent work (48) indicates that tetrabutylsilicane is obtained in 56 per cent yield from butyl magnesium bromide and ethyl orthosilicate.

In all of these reactions involving the Grignard reagent for the preparation of silicon-carbon bonds, the yields are rather low because of the formation of the other alkyl derivative besides the desired one. Separation of some of these products is sometimes difficult because of the nearness of boiling points. The second reason for the low yields is the formation of a large amount of magnesium salt which always retains some of the silicon compound tenaciously.

The modified Wurtz and Fittig methods of forming a silicon carbon bond have not been used as frequently as the Grignard method. The methods are best suited for the preparation of tetrasubstituted silicon compounds, since the reaction is rather difficult to control or stop at an intermediate stage. Taurke (93) has used the method to prepare trialkyl silanes from trichlor silane and tetraisooamylsilicane from silicon tetrachloride, while Kipping and Lloyd (94) were able to obtain tetraethylsilicane in the same manner. Several patents have been obtained for the production of alkyl and aryl silicon compounds by this method: one (95) uses silicon tetrafluoride and another (96) requires the addition of the calculated amount of sodium in toluene to a mixture of silicon tetra-

chloride and an organic halide.

Hexasubstituted alkyl or aryl disilanes or hexasubstituted silicyl-oxides could not be prepared from the respective silicon halides by the Wurtz type of synthesis (97). The silicon-silicon linkage was invariably broken leading to the tetrasubstituted monosilicane. However this splitting was obviated by a two stage Wurtz reaction (98).

One attempt was made (99) to form a silicon-carbon bond through use of sodio acetoacetate. The final product was a polymer which could not be distilled or purified.

The chemistry of silicon-carbon compounds can be divided into three classes: a). the reactivity of any functional group still attached to silicon; b). the stability of the silicon-carbon bond; and c). the reactions of the attached carbon radical.

The reactions of the functional groups still attached to the silicon are with few exceptions similar to those possessed by that type of grouping. Most of these reactions have already been considered in their respective section.

There are instances in which the silicon-carbon bonds are broken, sometimes very easily. In organometallic compounds it is possible to arrange the attached organic radicals in a series of relative stabilities to one another with respect to some cleavage. Once such a series is established other correlations based on the arrangement can be made. Predictions that can be based on some cleavage series are: a). preferential cleavage in an unsymmetrical molecule; b). thermal stability; and c). relative reactivities toward some functional group. So far there has been found no suitable reagent for the study of ease of cleavage of silicon

organic compounds, and the few studies and cleavages that have been made do not permit definite conclusions to be drawn.

When unsymmetrical organometallic compounds of mercury, lead, tin, etc. are cleaved by halogens and halogen acids, there is a preferential replacement of some of the radicals. By a comparison of the amounts of products obtained by the reaction of hydrochloric acid with various unsymmetrical mercury compounds this abbreviated series arranged according to the decreasing electronegativity (i.e. the affinity with which the organo radical holds its valence electrons) was given (29): p-methoxyphenyl, p-tolyl, phenyl, p-chlorophenyl, methyl, ethyl, propyl, n-butyl, benzyl, p-chlorobenzyl.

One series of cleavages that can be established with respect to a silicon-carbon bond is that obtained from the sulfonation of organosilicon compounds.

- 1). Dibenzylethylpropylsilicane - H_2SO_4 — $\text{C}_6\text{H}_5\text{CH}_2\text{Si.Et.Pr.CH}_2\text{C}_6\text{H}_4\text{SO}_3\text{H}$.
- 2). Phenylmethylethylpropylsilicane - H_2SO_4 — $\text{C}_6\text{H}_6\text{-HOSiMe.Et.Pr.}$
- 3). Phenylbenzylethylpropylsilicane - H_2SO_4 — $\text{C}_6\text{H}_6\text{-HOSiEt.Pr.CH}_2\text{C}_6\text{H}_4\text{SO}_3\text{H}$.
- 4). Benzylmethylethylpropylsilicane - H_2SO_4 — $\text{CH}_4\text{-HOSiEt.Pr.CH}_2\text{C}_6\text{H}_4\text{SO}_3\text{H}$ -
 $\text{MeSiEtPrCH}_2\text{C}_6\text{H}_4\text{SO}_3\text{H}$.

Thus the ease of splitting the radicals from silicon by sulfuric acid is approximately: phenyl, methyl, ethyl, propyl, benzyl. The sulfonation work was done by Kipping for purpose of isolating optically active compounds some of which were resolvable. This work is best reviewed in Friend (85). It has been shown that ethyl groups are split from silicon easier than phenyl groups by hydrogen under pressure and at higher temperatures (100). Unexpectedly triethylphenylsilicane gave benzene and hexaethyl disilicane

while triphenylethylsilicane decomposed into ethane and hexaphenyldisilicane (101). The conclusion from these last two results is that where there are three substituents of one kind and one of another, the latter is loosely bound and is easily displaced.

There are other examples of fissions that have been accomplished, but unfortunately there are not enough examples to make comparisons. Ladenburg (70) found that bromine reacted with tetraphenylsilicane to give triphenylsilicon bromide and brombenzene. Some recent patents (102), however, obtained chlorophenylsilicanes by direct chlorination. In the examples given, chlorine was added to the arylsilicon chlorides in presence of a catalyst until the ratio of chlorine per aryl group was three to one. Tetranitro derivatives obtained from interaction of tetraphenylsilicane gave nitrobenzene and bromnitrobenzene when treated with aqueous solutions of sodium hydroxide or bromine (103). When simpler nitro compounds as p- or m-nitrophenyltriethylsilicane were used, it was possible to show that both p- and m- isomers were stable to acids, but much less so towards alkali. On the other hand the amine phenyl-silicon bond undergoes fission by acids, but the m-amino phenyl-silicon bond is stable not only toward acids but also toward boiling alkali (104).

Redistribution of alkyl groups was evident during fission of silicon-carbon bonds with hydrogen (105). Kipping believed that an interchange of hydrocarbon radicals occurred to a slight extent between a Grignard reagent and a substituent attached to silicon (106). In an actual study of alkyl silicons, redistribution was found to occur in a random fashion (107). Tetraethylsilicane and tetrapropylsilicane when heated together gave 5 per cent Et_4Si , 21 Et_3PrSi , 40 Et_2SiPr_2 , 24 EtSiPr_3 and 10 Pr_4Si .

In the discussion of the fission of the silicon-carbon bond certain of the chemical reactions that the radicals could undergo were mentioned. These were sulfonation, chlorination, nitration, reduction, and rearrangements. Most of these reactions were carried out on the aryl radicals attached to silicon. An idea of the conditions required to perform these reactions will be found in references given. In general, care must be exercised in performing these reactions or fissions are apt to take place.

Some chlorinations of alkyl silicon compounds gave valuable information on the effect of the silicon atom on attached organic radicals. The liquid phase, photochemical chlorination of tetramethylsilane at 0°C gave a 35 per cent yield of silicon neopentyl chloride, $\text{Me}_3\text{SiCH}_2\text{Cl}$ (108). This chloride reacted with magnesium easily to give a Grignard reagent which was successfully reacted with mercury chloride, and phenyl isocyanate. By means of the mercury compound it was possible to determine that the siliconeopentyl group is more electronegative than any aliphatic group and less electronegative than phenyl.

When ethyltrichlorosilane, EtSiCl_3 , was chlorinated (109) with sulfuryl chloride in presence of peroxide there was two and one half times as much β -chloroethylsilane trichloride formed as there was α -chloroethylsilane trichloride. Moreover, methylsilane trichloride could not be chlorinated by this manner indicating that the $-\text{SiCl}_3$ group deactivates the alpha carbon. Hydrolysis of either the α -chloro or β -chloroethylsilane trimethyl proved that the β -chlorine was much more active than the α -derivative. This further demonstrates the influence of silicon on the alkyl radicals.

Conclusions to be drawn are: 1). Although the silicon carbon bond

is easily formed, the formation reactions are several steps removed from sand. The best laboratory method of forming this bond is by use of the Grignard reagent on ethyl orthosilicate. 2). The silicon-carbon bond is less stable than the carbon-carbon bond, but the difference in stability is not very great. 3). Silicon exerts considerable influence on the alpha carbon atom.

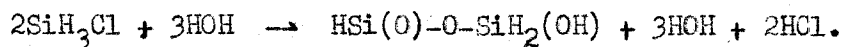
G. Silicon-oxygen-silicon Bond:- There are no reviews covering the silicon-oxygen-silicon bond.

For commercial resins this is probably the most important linkage. Sand will not burn because it is already completely oxidized. The nearer any resin can approach this state of oxidation the more desirable it should be for vehicles in which fire-resistance is most important.

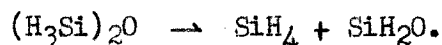
From a study of the vast array of inorganic silicates by means of x-ray, only two types of oxygen linkages have been found: a). the oxygen atom belongs to two silicon atoms; b). the oxygen atom is linked on one side only to silicon and the other negative charge of the oxygen can be neutralized by a positive cation. In no instance was there any evidence of a silicon-double bond oxygen, or two oxygen atoms linked between two silicon atoms such as: $-\text{Si}=\text{O}$ or $-\text{Si}-\underset{\text{O}}{\text{O}}-\text{Si}-$.

With this in mind the chemistry, physical properties, and structure of some of the compounds containing the Si-O-Si bond will be considered.

The simplest kind of silicon-hydrogen containing compound of this type is $\text{H}_3\text{SiOSiH}_3$ (110) which is a stable gas boiling at -15°C . This is formed instantaneously in water from silicyl chloride, H_3SiCl , but upon standing longer in contact with water hydrolysis is effected:

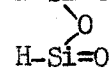


When $(\text{H}_3\text{Si})_2\text{O}$ is treated with a limited amount of water a curious reaction takes place:



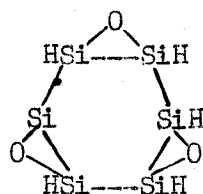
The compound SiH_2O polymerizes, and has given a benzene-soluble polymer containing six SiH_2O molecules by hydrolyzing a benzene solution of SiH_2Cl_2 . It has already been mentioned that the monomer, SiH_2O , analogue of formaldehyde, was predicted as a by-product during the decomposition of magnesium silicide. This silicoformaldehyde monomer could be reasonably expected to form polymers containing units analogous to the methylene oxide units present in formaldehyde polymers. These polymers are hydrolyzed by alkali to silicic acid.

Other silicon compounds of oxygen and hydrogen for which a siloxane bonding has been postulated are silicoformic anhydride, $\text{H}_2\text{Si}_2\text{O}_3$, and siloxene polymers of empirical formula, $\text{Si}_2\text{H}_2\text{O}$. The former compound which is the analogue of formic anhydride is a nonvolatile solid polymer. In none of the hydrolysis products of the di- or trihalosilanes is there any conclusive evidence of a $-\text{Si}=\text{O}$ formation. Experimental evidence seems to show that there is no intramolecular loss of water, but instead a progressive intermolecular condensation forming closed and open chain polymers (3). Thus a structure such as (111) $\text{H}-\text{Si}=\text{O}$ is not probable.



The structure of this compound is such that it probably cannot be elucidated by chemical reactions.

The siloxene polymer was obtained when calcium silicide, CaSi_2 , was treated with a mixture of hydrochloric acid and alcohol. Kautsky and Herzberg (112) attributed to siloxene the cyclic structure:



The chemical evidence pointing to this arrangement was mainly its reaction with halogens. Siloxene reacts with halogens, the hydrogen atoms being partially or completely replaced by halogen with the formation of hydrohalide gas. Iodine gave a compound, $\text{Si}_6\text{O}_3\text{H}_5\text{I}$, which established six silicon atoms in the molecule. Bromination gave either a partially brominated compound, $\text{Si}_6\text{O}_3\text{H}_3\text{Br}_3$, or caused a degradation to the bromosilicyloxide, $(\text{Br}_3\text{Si})_2\text{O}$. Other properties indicating this structure are its ease of ignition and powerful reducing ability.

Mention was made of the formation of silicon oxyhalides when discussing the silicon-halide bond. These compounds should prove useful for the preparation of fire-resistant resins. Besides the silicyloxide already mentioned several times, molecules possessing several siloxane groups are formed during the reaction of oxygen and halogens on hot silicon. Most of the products fit the formula, $\text{Si}_n\text{O}_{n-1}\text{Br}_{2n-2}$ (113), but an exception was found in a crystalline cyclic tetramer, $(\text{SiOBr}_2)_4$. The straight chain products are oily liquids which are stable and can be fractionated. The reactions they undergo are similar to those of any other silicon-halides such as ease of hydrolysis, reaction with alcohols, Grignard reagents, etc.

Siloxane compounds possessing the oxygen-carbon bonding are obtained either by the controlled hydrolysis of an orthoester or by the reaction of alcohols on the oxyhalide. It was stated in the discussion

of the alkoxy linkage, that an appreciable residue always remained after distilling a freshly prepared orthoester. In all investigations of these residues, compounds possessing the siloxane linkage were found. These could arise either from the use of wet alcohol, air oxidation, or fission of the oxygen-carbon bond by the acid liberated.

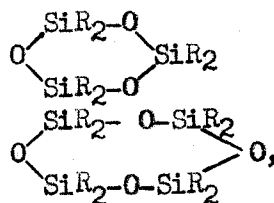
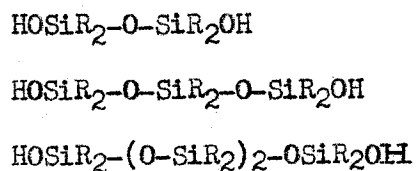
Schumb and Hollaway (73) prepared the ethyl ester of oxyhalides up to $\text{Si}_6\text{O}_5(\text{OEt})_{14}$ by adding anhydrous alcohol to the corresponding halides. The esters of the bromide compound had to be prepared using sodium ethoxide, because the hydrobromic acid, as did the hydrochloric acid, reacted with the alcohol forming water which hydrolyzed the halide. Water had little if any effect upon the esters even after prolonged contact with water at 100°C .

The siloxane group containing alkyl or aryl groups is probably the linkage of the organo silicon resins being prepared by The Dow Chemical Company for war work. To my knowledge no information in journals or patents concerning the manufacture of the Dow resins exists at this time. However from some of the patents and articles published on this linkage, there is reason to suspect that this type of resin would be successful.

The alkyl or aryl siloxanes are obtained by the condensation of the appropriate silicol. It is generally possible to obtain a silicanol, R_3SiOH , in pure form but the silicanediol, $\text{R}_2\text{Si}(\text{OH})_2$ frequently has too great a tendency to split out water intermolecularly to make the isolation of the pure compound possible.

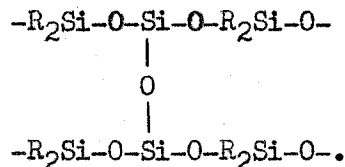
Silicanols have been made by the hydrolysis or oxidation of a trialkylsilane, the oxidation of a tetraalkylsilane, or by the hydrolysis of an alkyl- or arylsilicon halide or ester, and the action of Grignard reagents on silicones, R_2SiO .

The first two methods of preparation have already been considered. The Grignard reaction with the silicones is interesting in that it seems to belie the nonexistence of a silicon double bond. However the predicted physical properties and other expected ketone reactions with the silicones are not encountered. Diethylsilicone, obtained by the hydrolysis of diethylsilicon dichloride, is a liquid polymerized to a high molecular product of about 575 (114). It cannot be reduced nor does it react with hydroxylamine or phenyl hydrazine (115). However when the phenylethylsilicone was heated with methyl magnesium iodide at 190°C in the absence of any solvent for one hour and then treated with water, an oily liquid could be obtained by distilling under reduced pressure. The compound analyzed for phenylethylmethy silicanol. This product on standing for one day self-condensed to form the siloxane compound. Although it is assumed that the silicanediol, $\text{Et}_2\text{Si}(\text{OH})_2$, was an intermediate of diethyl silicone, it was not possible to isolate the diol. However some of the silicon dihalides having at least one phenyl group attached to the silicon atom form sufficiently stable diols to permit their isolation. These are sparingly soluble in water, but dissolve freely in solutions of alkali from which they may be reprecipitated by acidifying. These diols undergo condensation very readily, sometimes spontaneously, and especially when they are heated or in the presence of acids or alkali. The types of condensation products of the diols that have been reported (3) as isolated and identified are:



and mixtures of more complex products formed from twenty or more molecules of diols, but these have not been obtained pure. The conditions under which the various condensation products were obtained are very exacting. Hyde and DeLong (116) question Kipping's work because they were not able to duplicate the results and furthermore found that the straight chain condensation products reported in literature were not sufficiently characterized. They found that the hydrolysis of phenylethyl-, diethyl-, phenylmethyl-, and dimethylsilicon dichloride gave relatively low molecular weight products. A cyclic trimer appeared definitely to be formed upon hydrolysis of phenylethylsilicon dichloride under the conditions described and cyclic trimeric condensation products also seemed to be present in the hydrolysis products of diethyl and dimethyl compounds. This tendency to cyclize is of importance because removal of an organic radical by oxidation or some other chemical reaction such as ring opening will be necessary for further condensation. Actually it was found that the organic radicals could be removed by either hydrolysis or oxidation which resulted in the formation of siloxane linkages giving in both cases higher polymers that were identical in physical properties. In the resinification of cyclic dimethyltrisiloxane by running air through it while heating, a gel was obtained when approximately one-fifth of the disubstituted silicon atoms were converted to monosubstituted atoms as determined by the increase in silicon content of the set resin. Gellation attained by means of hydrolyzing in presence of hydrochloric acid requires a lower loss of organic radicals to reach the same condensation stage. These facts seem to indicate that the condensation of diols is not as simple a process as that given by Rochow and

Gilliam (117) who picture an intermolecular condensation giving polymers of structure:



These workers did not work with a pure diol, but a mixture of methyl silicane diols and triols. They obtained approximately the same results by the hydrolysis of either a mixture of pure methylsilicon trichloride and dimethylsilicon dichloride or from the alkylsilicon chloride mixture obtained from silicon tetrachloride and a calculated amount of methyl magnesium bromide. They found that with a methyl to silicon ratio of 1 to 1.3 in the polymer by analysis, the hydrolysis product of the chloride went from a sticky sirupy stage to a hard transparent resin. Heating made this a brittle glassy mass. A ratio of 1.3 to 1.5 of methyl to silicon gave a hydrolysis product of oily consistency at room temperature. Heating to 100°C caused the viscosity to rise and volatility to decrease. At 150-200°C gelation occurred in a few hours giving a clear, hard, horny resin. A ratio of 1.5 to 1.9 of methyl to silicon gave a hydrolysis product which was volatile at the condensation temperature. It required continued heating at 200° C for several weeks to obtain a hard brittle gel. These brittle transparent resins could withstand a temperature of 200°C for an indefinite time, at 300° C in air disintegration of surface methyl groups took place, while at 400°C oxidation was rapid. There are series of patents obtained on these types of resins. (118).

III. COMPOUNDS CONTAINING SILICON-OXYGEN-CARBON BONDS

A. Discussion of Preparation of Monomers: - From the number of organic alcohols and acids that exist together with the different silicon bonds that have already been made, it is evident that the list of Si-O-C type of compounds that could be made would run well into the thousands. From the preliminary work and literature search of silicoorthoester it was not evident that many of these compounds would be worth investigating from the standpoint of forming fire-resistant films. However, the three silicon orthoesters whose preparations from the methyl, ethyl, and chlorohydrin alcohols are described in the experimental part were prepared for definite purposes.

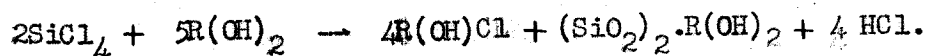
Ethyl orthosilicate, $\text{Si}(\text{OEt})_4$, was prepared in highest yield by Dearing and Reid (30) who obtained 70 per cent of the theoretical amount of the ester by dropping silicon tetrachloride into a 10 per cent excess of absolute alcohol, cooled by an ice mixture, and fractionating under reduced pressure after drawing through air to rid the ester of hydrochloric acid and excess alcohol. The main difficulty in the preparation of orthoesters is that four molecules of hydrochloric gas are eliminated for each mole of silicon tetrachloride. The large gas evolution causes considerable loss of the volatile reactants. In the hope of improving this yield and to test the film forming properties of the orthoesters as well as their residues, the ethyl ester with its residue was prepared as described below. The yield obtained was 68 per cent and the weight of residue was 25 g. for one mole of silicon tetrachloride used. The films from both the ester and its residue were the typically inferior films obtained from all orthoesters.

As stated previously, orthoesters undergo exchange reactions when refluxed with other alcohols to form mixed orthoesters. It was with this in mind that ethyl orthosilicate was reacted with dimethylol urea to form silico-urea-formaldehyde resins. The films from these resins although uniform, clear, and hard were combustible. Since the methyl orthoester contains the lowest percentage of carbon, this ester was prepared for the purpose of lowering the carbon content and thereby lowering the combustibility of any urea resins prepared.

In attempting to prepare the methyl orthoester, the same difficulty of self-condensation was encountered as recorded by Ebelmann (47), Friedel and Crafts (79) and others when absolute methyl alcohol was not used. Ordinary commercial alcohol containing 2-3 per cent water yielded less than 5 per cent of the methyl silicate. The main product was a non-constant, high boiling condensation product. A satisfactory yield of methyl silicate was obtained when 99.5 per cent pure methyl alcohol was used with cooling as described in the experimental part.

The methyl orthosilicate-urea-formaldehyde films resembled those of the ethyl ester in appearance and combustibility.

Taurke (93) reported the formation of three products when reacting glycol and silicon tetrachloride, viz; chlorohydrin, silicon ester of chlorohydrin, and a white mass consisting of two molecules of silica and one molecule of glycol. He interpreted the reaction according to the equations:



To confirm these reactions, Taurke added silicon tetrachloride to pure dry, cold glycol in about the amount demanded by the first equation. After the ethylene chlorohydrin was distilled from the reaction mixture, silicon tetrachloride was slowly added to it. The resulting β -chloroethyl orthosilicate was obtained in an unstated yield boiling at 177-180°C. per mm. Dearing and Reid (30) reacted ethylene chlorohydrin with silicon tetrachloride but were unable to distill their product and the analysis showed it to be only 94 per cent pure.

β -Chloroethyl orthosilicate was obtained in 73 per cent yield by dropping anhydrous ethylene chlorohydrin into ice-cooled silicon tetrachloride. The only explanation for the failure of Dearing and Reid to obtain this ester is that their chlorohydrin was not anhydrous. It is essential to realize that in the preparation of orthoesters one-half mole of water is sufficient to condense one mole of ester. If 98 per cent ethyl alcohol was used for preparing ethyl orthosilicate, the theoretical yield would not be over 75 per cent while the actual laboratory yield would probably be about 50 per cent.

The main object of making the β -chloroethyl orthosilicate was to ascertain whether or not a resin could be obtained by reacting the silicate with sodium polysulfide. Anhydrous sodium polysulfide was prepared in absolute alcohol and added to some β -chloroethyl silicate. A precipitate was formed soon after mixing these compounds. Since ethyl orthosilicate behaved in a similar manner, the attempt to form an Thiokol type resin from chloroethyl orthosilicate was not further investigated.

Since the ethyl orthosilicate-urea-formaldehyde resins burned, it was thought that this type of resin from β -chloroethyl silicate

might prove incombustible. However a film of this type also burned when held in an open flame.

The possibility for the formation of β -chloroethyl silicate by the addition of ethylene oxide to silicon tetrachloride exists:



There was little evidence of reaction when these compounds were mixed at $0^\circ\text{C}.$, but after standing at room temperature for one year and distilling the mixture, none of the starting reagents were recovered. Instead a clear liquid of steadily increasing boiling point was obtained. Both the residue and the highest boiling cut $250\text{--}55^\circ\text{C}.$, reacted vigorously with either alcohol or water. The liquids were hydrolyzed by atmospheric moisture to a gel which when heated at $140^\circ\text{C}.$ left a sand-like residue. Analysis of a fraction boiling between $150\text{--}60^\circ\text{C}.$ checked for β -chloroethoxysilicon trichloride, $\text{Cl}_3\text{SiOCH}_2\text{CH}_2\text{Cl}$. The identity of this compound was verified by synthesizing it from ethylene chlorohydrin and silicon tetrachloride. The reaction between silicon tetrachloride and ethylene oxide is thus a new method of making this particular type of compound. The higher boiling fractions are undoubtedly β -chloroethoxy esters, and the use of a pressure bomb should enable one to form the orthoester. It would also be interesting to investigate the reaction between ethers and silicon tetrachloride in a pressure bomb, and to investigate the rapidity of the reaction between ethylene oxide and silicon tetrachloride.

Ebelmann (47) reported that dry chlorine reacted with ethyl orthosilicate energetically. Although the chloro compounds were formed, investigation of them was not completed; but Ebelmann stated that these would be further investigated. However no further mention of this

reaction was found in the literature. Thus it seemed worth while to investigate the action of halogens on an alkyl orthosilicate. When liquid bromine was added to the ethyl ester an exothermic reaction took place with a simultaneous gradual disappearance of the bromine color. This solution could be refluxed to eventually produce a solution with a yellowish color. If more than equal molar equivalents of the reagents were used, the mixture gelled if heated. When the heating was accomplished with the aid of a controlled temperature oil bath, a low boiling liquid which proved to be ethyl bromide was obtained. Slightly more than one equivalent of ethyl bromide was collected besides a small amount of bromine and a product coming over between 70-80° C. The remaining residue could not be distilled without gellation at atmospheric pressure. This clear liquid analyzed for 15.25 per cent silicon and 21.5 per cent bromine. These figures require an empirical ratio of two atoms of silicon to one atom of bromide giving a molecular weight of about 370. A compound that would fit these figures is pentaethoxy disilicon bromide, $(\text{EtO})_3\text{SiSi}(\text{OEt})_2\text{Br}$, molecular weight 361; Si, 15.5; Br, 22.2.

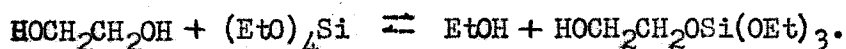
B. Discussion of Formation of Silicon-oxygen-carbon Bond Resins: -

Taurke (93) from the reaction of glycol with silicon tetrachloride obtained a white mass, an analysis of which gave an indication of an empirical molecule consisting of two molecules of SiO_2 and one molecule of glycol, $2\text{SiO}_2 \cdot \text{C}_2\text{H}_4(\text{OH})_2$. Several attempts were made to prepare films from the glycol-silicon tetrachloride reaction. If glycol is added dropwise to cold silicon tetrachloride, the vapor of the latter immediately reacts with each drop of glycol forming a gel-like film around each drop.

This complicates the addition of glycol making it an unsatisfactory procedure. If the reverse addition is used, the mixture gels after about one-fourth of the calculated amount of silicon tetrachloride is added. This gel can be put into solution by the addition of a mono-functional alcohol. The alcohol, of course, reacts with the unreacted silicon halide group thus forming an ester grouping, stopping cross condensation, and aiding in solublizing the gel. However if this solution of glycol, alcohol, silicon tetrachloride is heated, gellation sets in again, and it is not possible to break the gel by addition of alcohols. A sample of this gel was dried and analyzed for silicon which amounted to 28.7 per cent, while the silicon content of Taurke's white mass, $(\text{SiO})_2 \cdot \text{C}_2\text{H}_4(\text{OH})_2$ is 30.8 per cent. The hypothetical possibilities such as

$$\begin{array}{c} \text{OMe} \quad \text{or} \\ | \\ -\text{Si}-\text{OCH}_2\text{CH}_2\text{O}- \\ | \\ \text{OMe} \end{array}$$

$$\begin{array}{c} \text{O} \\ | \\ -\text{Si}-\text{OCH}_2\text{CH}_2\text{O}- \end{array}$$
 contain lower amounts of silicon i. e. 18.7 and 20.8 per cent respectively. It can be concluded, therefore, that although mono-functional alcohols solublize the first gel, through ester formation, the alkoxy groups are readily displaced by glycol groups which then by cross condensation cause gellation. This may be demonstrated by refluxing together excess glycol with a performed orthosilicate. Gellation does not set in, however, until about half of the theoretical amount of displaced alcohol is removed by distillation which is good evidence of the displacement equilibrium:

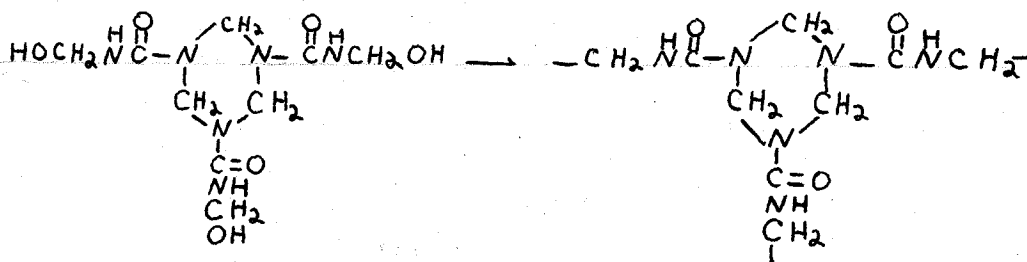


The films formed from the glycol-orthosilicate mixtures, although greatly ~~crazed~~, were the best films of this type. Diethylene glycol gave a better result than glycol itself, which might have been due to the lower

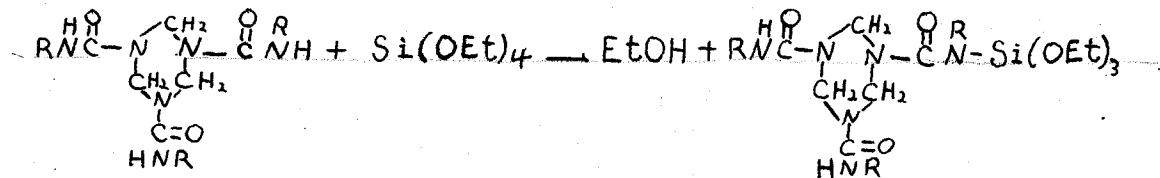
volatility of the former compound. This is further borne out by the slight deliquescent nature of the hardened film when diethylene glycol was used as the polyfunctional alcohol.

Glycol reacts with bifunctional acids to give the thermoplastic alkyds. If the gel from the silicon tetrachloride glycol reaction contained an appreciable number of free hydroxy groups, necessitating the formation of compounds of the type $\text{Si}(\text{OCH}_2\text{CH}_2\text{OH})_4$, it might be possible to obtain a thermoset resin by reaction with any bifunctional acid. The gel from the glycolsilicon tetrachloride reaction with phthalic anhydride gave a heterogenous powder layer instead of a film, while the mixture of glycerol, ethyl orthosilicate, and maleic anhydride produced an alcohol insoluble gel.

C. Discussion of Formation of Urea-formaldehyde-orthosilicate Resins: - The use of methyl, ethyl, and β -chloroethyl orthosilicates with urea-formaldehyde resins has already been briefly mentioned. In conjunction with these resins, several of the obvious experiments were also performed. From the analysis of the silicon content of the intermediate and the film from a dimethylol urea, ethyl orthosilicate and alcohol mixture, it could be concluded that there was present at least one silicon atom per urea unit of the film. Since the thermosetting of urea resins has been explained as resulting from the cross condensation of methylol groups (119):



it appears feasible that a thermosetting resin might be prepared from monosubstituted ureas by reacting with silicon orthoesters.



Since there are still hydrogens present to displace alkoxy groups of silicon esters, sufficiently large molecules might be prepared to give higher softening temperatures if not a thermosetting film. An organic solvent soluble butylureaformaldehyde resin was prepared and part of this was mixed with some ethyl orthosilicate. This film was harder and less sticky at 150°C than was the standard butylurea-formaldehyde film, but the silicon containing film was not thermoset. More work along this line was indicated, but was not carried out as the films were combustible.

It was not possible to form a urea-formaldehyde-ethyl orthosilicate resin by starting with urea, paraformaldehyde and ethyl orthosilicate. Neither was it possible to obtain a resin of high silicon content from the methyl ether of dimethylol and the silicon esters. Attempts to prepare organic soluble resins by reacting together dimethylol urea and alkoxy-silicon halides failed. In these instances the dimethylol urea clumped together forming an insoluble unreactive ball in the liquid ethoxy silicon chloride. This would be expected as any hydrochloric acid liberated should catalyze the methylene urea formation.

D. Experimental: - The same apparatus was used for the preparation of all the silicon esters described in this section. A 500-cc. three-necked flask was provided with a mercury-sealed stirrer and a 22-cm. condenser. To prevent the loss of the most volatile component, silicon

tetrachloride, by the large volume of hydrochloric acid that was evolved, the condenser was filled with glass beads which were held up by several indentations made at the bottom of the inner tube, and the alcohol was allowed to drop onto the glass beads countercurrent to the gas evolved. The top of the condenser was provided with a three-hole stopper which held a dropping funnel, a tube for pressure equalizing, and a gas outlet tube. A large calcium chloride drying tube could be attached to the outlet which would stop most of the alcohol thereby providing a means for a check of alcohol lost and also protecting the apparatus against moisture. In all the preparations of orthosilicates or their derivatives, the alcohols were anhydrous, and the silicon tetrachloride (Stauffer Co. product) used was the fraction that boiled constant at 57°C . in a 22-cm. glass-bead filled Claisen column described by Post and Hofrichter (120). Recorded b.p. $59-60^{\circ}\text{C}$. (121) The tetraethyl orthosilicate (Carbide and Carbon Co. product) used in most of the resin preparations was the distilled fraction b.p. $164-66^{\circ}\text{C}$; recorded b.p. 166 (121).

1. Tetra-(β -Chloroethyl)-orthosilicate: - Two hundred grams (2.22 moles) of anhydrous ethylene chlorohydrin (Carbide and Carbon product) was dropped slowly (about 2.5 hours) through the glass-bead filled condenser into 84 g.(0.5 moles) of constantly stirred silicon tetrachloride in a 500-cc. three-necked flask. Although not necessary, it was well to cool the flask with ice as the decreased temperature permitted a more rapid addition of the alcohol. After all the alcohol had been added, the ice bath was removed and the mixture stood at room temperature until the evolution of hydrochloric gas lessened appreciably. Then a hot plate was placed beneath the flask and its temperature was regulated so

as to maintain a steady evolution of hydrochloric gas. About four hours time was required to drive off most of the gas. After standing overnight, dry air was drawn thru the mixture for three hours. The product was then placed in a 500-cc. Claisen flask and the following fractions were collected under reduced pressure:

Temperature	Pressure	Weight	20 n _D	20 d ₂₀
60° C	50-51 mm.	34.4 g.	1.4407	1.216
140-44	2	35.5	1.4635	1.345
147-154	2	90.1	1.4640	1.346
154-174	2	-----	1.4645	-----
Residue	-	-----	-----	-----

The first fraction was unreacted ethylene chlorohydrin as its boiling point determined on a micro scale (8) was 127.0° C, while the recorded boiling point and density are respectively 128.8° C and 1.213 ²⁰/₄ (122). The total weight of fractions 2 and 3 gave a 72.6 per cent yield of β -chloroethyl orthosilicate. The only physical data in literature for this compound is that given as the boiling poiling point of 177-80° C/8 mm. by Taurke (93). At about 170° C/2 mm. decomposition set in as was evident by the slight discoloration of the distillate collected.

2. Tetraethyl orthosilicate: - The same apparatus and procedure was used for this ester as was used for the previous compound and the absolute ethanol was prepared as recommended in Organic Syntheses (123). One hundred two grams (2.2 moles) of alcohol was added to 84 g. (0.5 moles) of silicon tetrachloride in about three hours. The more rapid evolution of hydrochloride gas necessitated a slower addition of the alcohol. In-order to lessen the loss of ester during the removal of hydrochloric gas, air was drawn through the product for only one hour. All of the hydrochloric was not removed as there was an appreciable evolution of hydrochloric at

the start of the distillation. The ester was distilled from a 250-cc. distilling flask. The receiver was a filtering flask attached to the condenser by means of an adapter. The side arm of the filtering flask was connected to a calcium chloride drying tube to protect the system from atmospheric moisture. Seventy-one grams of product boiling from 160-166° C/747 mm. pressure which amounted to a 68 per cent yield. The recorded boiling point is 165-167° C (121). The weight of the brownish residue was 18 g.

3. Tetramethyl orthosilicate: - Using the same apparatus as in the two previous runs, 150 g. of 99.5 per cent methyl alcohol (4.7 moles) were dropped over a period of three hours into 170 g. of silicon tetrachloride (1.0 mole). The procedure followed was that for the ethyl orthosilicate preparation. When the commercial methanol (97-98 per cent pure) was used, there was no definite fraction obtained as the boiling point steadily increased until 220° C was reached when gellation set in stopping further treatment of the ester. The product boiling between 118-24° C.; recorded b. p. 120-22° C. (124), weighed 70 g. which amounted to a 46 per cent yield. The rather large amount of residue weighing about 50 g. had a boiling point over 200° C.

4. Dimethoxysilicon dichloride: - Using the same procedure as for tetramethyl orthosilicate and a three to one molar ratio of methyl alcohol to silicon tetrachloride, 107.3 g. of a product boiling between 97-108° C. was collected; recorded boiling point for dimethoxysilicon dichloride is 98-103° C. (79).

5. Mono-(β-chloroethyl)-silicon trichloride: - Seventeen grams (0.4 moles) of liquid ethylene oxide was directly added to 17 g. (0.1 moles) of ice-cold silicon tetrachloride in a 50-cc. ground glass-joint,

round-bottomed flask. The flask was immediately connected to a calcium chloride protected condenser and surrounded by about 1,000 g. of ice. After the ice was permitted to melt, the mixture stood at room temperature for two days. During this period 9 g. of reactants were lost. The mixture was then transferred to a 50-cc. bottle, stoppered by a rubber stopper, allowed to stand for one year, and then distilled. The following fractions were collected:

Temperature	Weight
60-90°C.	3.0 g.
150-60	6.6
205-250	7.5
250-255	1.1
Residue	<u>5.0</u>
	23.2

Anal: Fraction b.p. 150-60° C. calcd. for $C_2H_4OCl_4Si$: Si, 13.12.

Found: Si, 13.15, 13.04.

The same compound was prepared by adding 50 g. (0.625 moles) of ethylene chlorohydrin b. p. 125-126° C. to 85 g. (0.5 moles) of silicon tetrachloride. After proceeding according to the method described for dimethoxysilicon dichloride, the reaction mixture was fractionated through a 20-cm. Vigreux column, and the following fractions were collected:

Temperature	Weight
55 - 60° C	19.9 G.
152 - 153	27.0
234 - 238	18.8
Residue	<u>35.</u>
	100.7 g.

Anal. Fraction b. p. 152-53° C. calcd. for $C_2H_4OCl_4Si$: Si, 13.12;

Cl, 49.72. Found: Si, 13.40, 13.35; Cl, 49.05, 49.18.

6. Reaction between Ethyl orthosilicate and Bromine: - To 83.0 g. (0.4 moles) of ethyl orthosilicate in a 250-cc flask cooled by ice, 64 g. (0.4 moles) of bromine was added over a period of several minutes. A condenser was attached, the ice bath removed, and the mixture was allowed to stand at room temperature for about one hour during which time an exothermic reaction completed itself. The flask was then immersed in an oil bath that was slowly heated to 100° C. during a period of another hour. By this time the solution had changed from an opaque, dark red bromine color to that of a transparent reddish solution. Continued heating brought no further color change, indicating an equilibrium. The condenser was replaced by a 20-cm. Vigreux column, and the following fractions were collected:

Temperature	Weight	Color of fraction
36-37° C.	20.0 g.	Br ₂ color
37-40	33.5	Slight yellow color
70-77	8.7	Clear
Residue	<u>81.4</u>	Nitrobenzene yellow
	143.6	

Fractions (1) and (2) proved to be a mixture of bromine and slightly more than 0.4 moles of ethyl bromide. The residue could not be distilled at atmospheric pressure without gellation, it would gel rapidly in presence of water, but it was stable at room temperature for nine months.

Anal: Found Si, 15.1, 15.3; Br, 21.75, 21.13, 21.99, 21.83.

7. Attempted Film Formation from Tetraethyl orthosilicate: - For the purpose of describing the method of testing the orthosilicate solutions, the run with tetraethyl silicate is described. One drop of dilute hydrochloric acid was added to a mixture of equal volumes (10 cc.) of the silicon ester and 85 per cent ethyl alcohol. This mixture was

poured into a Petri dish in a layer sufficiently deep to completely cover the bottom. Then the dish was tilted to a 45 degree angle to allow the excess solution to drain off. The dish was placed in a constant temperature oven (about 110° C.) where it remained for at least fifteen minutes or longer whenever necessary to reach complete condensation. The result in the trials with ethyl, methyl, β -chloroethyl orthosilicate and their residues was the formation of a white powdery, almost pure silica layer which could be readily removed by rubbing. This white powdery layer could not be called a film and could not have any protective power for metals.

8. Attempted Resin Formation from β -chloroethyl orthosilicate and Sodium tetrasulfide: - The sodium tetrasulfide was prepared essentially as described in Friend (125). To a solution consisting of 40 g. of NaOH in 500 cc. of absolute alcohol saturated with hydrogen sulfide was added another solution of 40 g. of sodium hydroxide in 500 cc. more of absolute alcohol. Ninety-six grams of powdered rolled sulfur was added and stirring was continued overnight; the solution being out of contact with the atmosphere. Ninety grams of the resulting dark reddish solution contained 7 grams of a solid which was assumed to be sodium tetrasulfide. To a 50-g. portion of the alcoholic sodium tetrasulfide solution was added five hundredths of a mole of either β -chloroethyl orthosilicate or ethyl orthosilicate. With both esters a white powdery precipitate was obtained by either refluxing or allowing the mixture to stand overnight. The powder could not be analyzed for the silicon content accurately by simply igniting in a porcelain crucible as sublimation occurred when the glow temperature was reached. This high temperature sublimation is a property of silicon disulfide, SiS_2 . The

identity of the silicon sulfide could be confirmed qualitatively by the odor of hydrogen sulfide by boiling it with water (126). The failure of formation of any resinous product warranted the discontinuation of further investigation along this line.

9. Attempted Film Formation from Glycol and Silicon tetrachloride: -

A gel can be obtained by refluxing together the three components silicon tetrachloride, glycol, and a monofunctional alcohol irrespective of the order of addition of these compounds. Just as the films from these condensation products are identical, it would be expected that the silicon content in all of their films would be the same.

The process given here is the most convenient for the formation of the glycol-silicon tetrachloride-alcoholic solutions. It amounts to the initial formation of the dimethoxy silicon dichloride followed by the addition of glycol. Thirty-two grams (1.0 mole) of 99.5 per cent methyl alcohol was reacted with 85 g. (0.5 moles) of silicon tetrachloride as described for the preparation of dimethoxy silicon dichloride. After the removal of most of the hydrochloric gas, 31 g. (0.5 moles) of glycol was slowly added. Dry air was drawn through this product for two hours which weighed 79.8 g. indicating the loss of 71 g. of material. This condensation product upon heating for about fifteen minutes with a hot plate gelled. Some of this gelled product was placed over phosphorous pentoxide in a vacuum desiccator for twenty days. An analysis of this dried product showed a 28.7 per cent silicon content. Films from the condensation product before gellation, although very undesirable for a protective film, were different from the powdery layer given by heating ethyl orthosilicate. The material in the Petri dish consisted of flakes

that charred when held in a flame. These flakes were nonadherent, water clear, and brittle.

10. Attempted Film Formation from Glycol and Tetraethyl ortho-silicate: - Although the films from the condensation products of polyfunctional alcohols and ethyl orthosilicate were the best of the orthosilicate type, they were not satisfactory. Polyfunctional alcohols are not miscible with ethyl orthosilicate, but when they are refluxed together for a short while the mixtures become homogeneous. Glycerol, however, when heated with the silicon ester produces a white precipitate and never forms a homogeneous solution. In order to produce a gel from ethyl ortho silicate and a glycol, it is necessary to remove the ethyl alcohol as it is displaced, thereby forcing cross condensation. The directions given here were used with either ethylene glycol or diethylene glycol in ratios of either two or four moles of alcohol to one mole of ethyl orthoester. Twenty and six-tenths grams of ethyl orthosilicate (0.1 moles) and 24 g. of ethylene glycol (0.4 moles) were refluxed together until the temperature of the liquid in the flask became constant. This was 115° C. after two hours of refluxing. The mixture was transferred to a Claisen flask with a 20-cm Vigreux column attachment. The flask was heated by an oil bath to 175° C, and 14.6 g. of a liquid boiling between 78-81° C was collected before there was any sign of gellation. This liquid driven over was ethyl alcohol which amounted to 0.318 moles. Films of the condensation product burned and were slightly hygroscopic indicating a rather high carbon content. However it was not possible to tell without quantitative work whether the product was a homogeneous polymer with some free hydroxyl groups or a silica gel

containing free glycol. Probably both conditions prevailed. The films baked at 130-50° C to the nontacky stage were homogeneous while in the oven, but upon cooling they crazed and broke away from the bottom of the Petri dish.

11. Preparation of Resins from Dimethylol urea and Ethyl orthosilicate: - It was not possible to prepare a resin solution from dimethylol urea and any compound containing a silicon chloride bond. In presence of a compound with a silicon halide bond, dimethylol urea clumped together to form a solid, insoluble unreactive mass. Although it was not possible to obtain a resin solution from urea, paraformaldehyde, and ethyl orthosilicate, good results were obtained with dimethylol urea and the orthosilicate. With these resins it could be quantitatively shown that the silicon was chemically combined to a urea-formaldehyde unit. An intermediate could be obtained which contained approximately one silicon atom per urea unit, the final film contained a constant amount of silicon, and during the resin formation a reasonable amount of alcohol would be liberated. The experiments described here demonstrate these facts.

a. Intermediate from the Ethyl orthosilicate and Dimethylol urea

Reaction: - To 20.4 g. of ethyl orthosilicate (0.1 mole) in a 50-cc. Erlenmeyer flask was added 6.0 g. (0.05 moles) of dimethylol urea, and one drop of 6 N hydrochloric acid. The flask was placed in a water bath heated to 50° C., and the mixture was stirred by hand. As the reaction progressed, the powdery dimethylol urea was slowly converted to crumb-like white particles. These particles were collected on a filter and after drying in air weighed 11.2 g. This is only 0.4 g. less than the expected weight of 0.05 moles of dimethylol urea and ethyl orthosilicate splitting out 0.05 moles of ethyl alcohol forming the

possible compound:



Anal.: Calcd. for $\text{C}_9\text{H}_{22}\text{N}_2\text{O}_6\text{Si}$: Si, 9.94. Found: Si, 10.06, 10.10.

The only unexpected property of this product is that it did not melt as might be expected but decomposed at 239°C which is near the decomposition point of methylene urea.

b. Orthosilicate and Dimethylol urea Resins: - Twenty-four grams (0.2 moles) of dimethylol urea, 10 g. of 95 per cent ethanol and 1cc. of alcoholic hydrochloric acid made from 9cc. of 95 per cent ethanol and 1 cc. of 6 N hydrochloride (a total of 0.23 moles of ethanol for the reaction), and 49.5 g. (0.24 moles) of ethyl orthosilicate were placed in a three-necked 250-cc. round-bottomed flask. The flask was provided with a stirrer, condenser, and heated by means of an oil bath. The bath temperature was maintained at 65°C . for one hour at the end of which time the materials had formed a clear solution. By replacing the condenser with an angle tube connected to a condenser and increasing the oil bath temperature to 95°C . it was possible to collect 25 g. of a liquid boiling from $74\text{--}78.5^\circ\text{C}$. This liquid which possessed a slight ethyl orthosilicate odor, had a density of $0.7979 \frac{20}{20}$ and consisted almost entirely of ethanol. The films of this resin were analyzed in the following manner. About one gram of the resin solution was poured into a porcelain crucible and then baked at 120°C . until a reasonable constant weight was obtained which took from one to two hours depending on the thickness of the film. Then the film was slowly ignited until the full flame of the Meker burner was reached. The residue was ignited at white heat until constant

weight was attained. Four analyses of this resin gave the following silicon percentages: 15.2, 16.2, 15.1, 16.3.

Considering that there is only one silicon atom per methylol molecule in the intermediate, it is reasonable to assume not more than one silicon atom per urea residue in the baked film. This would give a unit weight of 181 which is reasonable since the unit, $\text{CH}_2\text{-}\overset{\text{O}}{\underset{\text{||}}{\text{N}}}\text{-}\overset{\text{O}}{\underset{\text{||}}{\text{C}}}\text{-}\overset{\text{O}}{\underset{\text{||}}{\text{N}}}\text{-}\text{CH}_2\text{-Si-}$, has a molecular weight of 112 leaving the difference to be made up by ethoxyl groups.

To show that the silicon is not present only as a solvent, two other resin solutions were made. The first was prepared from the dimethyl ether of dimethylol, ethyl orthosilicate, and butyl alcohol in the same ratios as used above, and the second was prepared from the standard Ault and Wiborg urea resin of 50 per cent solids content, silicon orthosilicate, and butyl alcohol to give approximately the same urea to silicon content as in the resin solution above. The film from the dimethyl ether of dimethylol urea had a silicon content of 1.33, 1.43 per cent, while the latter film had 1.63, 1.93 per cent. This indicates that only a small portion of the solvent ortho silicate is retained in the final film.

For the purpose of determining the increased flame resistance of halogens in the urea-silicate type of condensation product, a resin solution was made as above using dimethylol urea, ethylene chlorohydrin, and tetra-(β -chloroethyl) -orthosilicate.

The films from these urea-formaldehyde-orthosilicate mixtures resembled the standard urea-formaldehyde-alcohol resins in being clear, hard and brittle. Since these orthosilicate resins gave homogeneous

films, the burn test similar to that employed at Ault and Wiborg was used. A coarse steel wool is first cleaned with dilute hydrochloric acid, washed well with water, then dried by immersing in acetone and blowing air through the wool. A resin solution is then prepared by dilution of the condensation product to a 25 per cent solids content. The cleaned steel wool is dipped into this solution several times, allowed to drain, and then placed in an oven heated between 140-50° C for ten to fifteen minutes. The coated steel wool is then held directly in a 6 in. slightly yellow Bunsen flame. The combustibility is roughly divided into three obvious groups: whether it burns only when held in the flame but extinguishes when taken out of the flame, whether it does not burn when held in a flame, or whether it continues to burn when taken out of the flame. The standard urea-formaldehyde-alcohol film ignites easily and continues to burn once away from the flame. The urea-formaldehyde resin films made with methyl and ethyl orthosilicate are more difficult to ignite, but once started they will continue to burn out of the flame. The film made using the B-chloroethyl orthosilicate gave the best flame resistance. It was the most difficult to ignite and burned for only a short while when taken out of the flame. This was the best flame-resistant film prepared of this type.

12. Preparation of Butyl urea-formaldehyde-ethyl orthosilicate

Resin: - Twenty-five milliliters of 35 per cent formalin neutralized to approximately pH 7.0 with sodium hydroxide was added to 11.6 g. of butyl urea (Sharples Solvent Corp. product) (0.1 mole) in a 100-cc. flask. This mixture was refluxed for one hour by heating on an oil bath maintained at 150° C. The condenser was then arranged for distillation

and 16.5 cc. of distillate was collected. This resin was further dehydrated by twice adding 25-cc. portions of acetone and distilling over liquid until the resin frothed excessively. Films from this resin were thermoplastic even after heating at 150° C for one hour.

The resin was not very compatible with ethyl orthosilicate alone. A solution was prepared by using a mixture of 5 cc. of ethyl orthosilicate, 10 cc. of butyl alcohol and 5 g. of butyl urea-formaldehyde resin. Films from this mixture were less sticky and more thermoset than the pure butyl urea resins after heating at 150° C. for one hour.

IV. PREPARATION OF COMPOUNDS CONTAINING A SILICON-CARBON BOND

A. Discussion of Reactions with the Grignard Reagents:- The best known method of blocking some of the functionality of quadrivalent silicon is to form a silicon-carbon bond. From the present state of knowledge of the chemistry of silicon compounds, the most convenient method of forming a silicon-carbon bond is by the reaction of a Grignard reagent with silicon halides or esters. For commercial production and large scale laboratory preparation, the formation of this bond by the use of the Grignard reagent has disadvantages. The process is several steps removed from sand, the source of raw material; large quantities of anhydrous ethyl ether are required and magnesium halides are produced; the yield of the desired derivative is low because of the formation of silicon derivatives other than the desired ones and because of the tenacity with which the silicon compounds adhere to the magnesium halides. For these reasons it is desirable to either improve the present process or devise a new method of forming the silicon-carbon bond. Some of the time devoted to this thesis was given to both of these problems.

The initial research with the Grignard reagent was done with methyl magnesium bromide. Later most of the work was done with ethyl magnesium bromide because of the greater convenience of working with this compound.

Although silicon organic compounds had already been known for about eighty years, the methyl silicon halides were prepared pure for the first time in 1941 (127). The reason for this was the unexpected boiling points of the methyl derivatives in comparison to other alkyl derivatives:

Compound	Boiling Point	Compound	Boiling Point
SiCl_4	57.6°C	SiCl_4	57.6°C
MeSiCl_3	66-67 (127)	EtSiCl_3	100 (128)
Me_2SiCl_2	70 (127)	Et_2SiCl_2	128-30 (128)
Me_3SiCl	—	Et_3SiCl	143 (129)
Me_4Si	26 (127)	Et_4Si	152-154 (128)

Two conditions were established for the preparation of alkyl silicon chlorides by means of the methyl derivatives. These were: the proper amount of Grignard reagent to be added for the preparation of a certain derivative, and the best method of obtaining the silicon halides from the reaction mixture.

By varying the amount of preformed methyl magnesium bromide added to a constant amount of silicon tetrachloride-ethyl ether solution, it was found that the highest yield of dimethyl silicon dichloride was obtained when 2.3 moles of Grignard reagent was added to one mole of silicon tetrachloride. This is the amount used in the directions given by Gilliam, Liebhofsky and Winslow (127) and is approximately the best as indicated by the following table:

Amount of Grignard Moles/mole of SiCl_4	Weight of product b.p. 67-69°C.
2.0	28. g.
2.3	45.
2.57	24.

Methyl chloride was used in one run, but only 61 g. of product b.p. 36-68° C was obtained. Furthermore the difficulty of forming large amounts of methyl magnesium chloride without a dry ice cold finger was discouraging.

In carrying out the reaction between the Grignard reagent and silicon tetrachloride a large volume of ether is required because of the bulky

mass of magnesium halide formed. After the reaction is completed the ether solution can be separated from the magnesium halide by filtration, centrifuging, continuous extraction process, and distillation. All of these methods have been used by other workers. The method found most suitable was to distill off the ether at atmospheric pressure as rapidly as possible by heating with an oil bath until the magnesium halide appeared dry, and then the tenaciously held liquor was driven over by heating the oil bath up to 250°C under reduced pressure. Even under these conditions 5 to 10 g. of silicon compounds were still retained by the magnesium halide.

From information in the literature the length of time given for the Grignard reagent to react with silicon tetrachloride varied from two hours to several days. Actually the reaction with ethyl magnesium bromide was complete almost immediately after the addition of the reagent. The reaction was followed roughly by withdrawing some of the reaction mixture and measuring by means of a eudiometer the amount of ethane liberated by water.

Diethylsilicon dichloride was prepared in two ways; the preformed Grignard reagent was added to an ether solution of silicon tetrachloride, or the Grignard reagent was made in presence of silicon tetrachloride by adding an ether solution of ethyl bromide to a mixture of silicon tetrachloride, magnesium, and ether.

The best yield of diethylsilicon dichloride obtained by the first method occurred when the ether solution of silicon tetrachloride was cooled with an ice bath. In this instance the reactants were stirred together at 0° C overnight. The yield was 38 per cent. Although by the one stage

procedure cooling could not be used, the yield was 41.4 per cent. The better yield by the latter method was probably due to the ease with which the reaction is performed.

The most convenient way of obtaining an alkyl silicon compound containing functional groups is to react a Grignard reagent with an orthoester. It is pleasanter to work with the orthoester, and the alkoxyl compound is less susceptible to hydrolysis than the halide. This latter property facilitates the isolation of alkyl silicon compounds, because the magnesium salt can be dissolved in dilute acid leaving the silicon compound in the ether layer. Diethyldiethoxysilicane and dibutyldiethoxysilicane were obtained in 45 and 50 percent yields respectively.

B. Discussion of Wurtz and Fittig Types of Reactions:— These reactions have been used to obtain yields of 80 to 90 per cent of the tetraalkyl - or arylsilicanes, but they have never been successfully used to prepare the silicon chlorides. Kipping and Lloyd (94) state that they performed many experiments to test the practicability of obtaining arylsilicon chlorides by altering the proportions of the reactants. However, even when the smallest proportion of chlorobenzene and sodium wire were used, the principal product was tetraphenylsilicane. An attempt was made in the laboratory to prepare diethylsilicon dichloride by modification of the Wurtz reaction. It was difficult to get a reaction started when ethyl bromide in ether was dropped into a mixture of ether, silicon tetrachloride, and sodium. When ethyl acetate, which is sometimes used as a catalyst for this reaction (130), was added, the ether would reflux for a short duration and a quantity of blue colored precipitate formed. When the stirring was

finally stopped, much unreacted sodium metal was still present and only a small amount of product boiling in the range of the ethyl silicon halides was obtained.

Some Russian workers (131) report the successful formation of silicon-carbon bonds by the reaction of benzyl magnesium halides with sodium fluosilicate. Tetrabenzylsilicane was obtained in 53 per cent yield by this method. This suggested a Wurtz type of reaction which was attempted with chlorobenzene, sodium, and sodium fluosilicate in various solvents. No aryl silicon compounds were formed as the sodium fluosilicate was entirely recovered.

C. Discussion of Reaction Between Diethylsilicon dichloride and Sodium malonate:- Kipping's (99) attempt to react sodio acetoacetate with triethylsilicon chloride in ethyl ether was unsuccessful. When diethylsilicon dichloride was added to sodio malonate suspended in benzene, a reaction took place as evidenced by the gradual disappearance of the sodio malonate and the simultaneous appearance of a gel-like precipitate. This reaction mixture was shaken with water and extracted with benzene. After drying the benzene was distilled off and the residue was hydrolyzed with concentrated ammonia. The products obtained from this hydrolysis were a silicon polymer and an ammonium salt not containing silicon which analyzed 27.2 per cent nitrogen. The structure of this compound cannot be predicted without further analysis.

D. Attempted Silicon-carbon Bond Formation from Magnesium Silicide and Compounds Containing Active Groups:- Magnesium reacts with silicon dioxide exothermally forming magnesium silicide and magnesium oxide. This mixture reacts with acids very vigorously giving silicon hydrides and polymeric prosiloxane. Because of the ease of preparing the silicide and

its pronounced reactivity with aqueous acids, it seemed possible that compounds containing active halides would react with magnesium silicide.

Johnson and Isenberg (35) made a rather thorough study of the preparation of mono- and disilane by the action of liquid ammonia-ammonium bromide solution on magnesium silicide and a few comparative runs using dilute acids. They reviewed the work done on the preparation of magnesium silicide and reported that at least three silicides have been shown to exist: MgSi , Mg_2Si and Mg_3Si_2 . MgSi is stable only above 800°C ; at lower temperatures it decomposes into Mg_2Si and silicon. Likewise, Mg_2Si decomposes to MgSi and magnesium above 800°C . Mg_3Si_2 has a stability range between 550 – 650°C . A silicide prepared at temperatures above $1,000^\circ\text{C}$ was found to produce only small amounts of silanes.

Some magnesium silicide was prepared by heating together the elements in an induction furnace under a hydrogen atmosphere. The temperature of the furnace read by an optical pyrometer was about 900°C . This would indicate the existence of MgSi and a large amount of magnesium, but this did not seem to be the case as indicated by its explosive reaction with hydrochloric acid and slight reaction with ethyl iodide indicating a small excess of magnesium.

With variation such as solvents and addition of compounds that might act as catalysts, the magnesium silicide was refluxed with compounds such as alkyl or aryl halides, acid chlorides, anhydrides, bromine, methyl sulfate, or alcohols. There was visible and quantitative evidence of reaction between the silicide and benzoyl chloride, methyl sulfate, and glycol.

The benzoyl reaction gave a brown amorphous product that possessed no

silicon, burned with a sooty flame, and was only slightly soluble in benzene. It was not possible to separate this product and the magnesium silicide of which there was a considerable quantity. The brown product was probably a polymeric ketone formed by a Friedel and Crafts type of reaction with benzoyl chloride.

The weight of the solid obtained after refluxing magnesium silicide with methyl sulfate in presence of a trace of pyridine was twice the weight of the starting silicide. This black product was a mixture containing magnesium silicide as could be determined by its reaction with water. This seems to indicate the presence of some acid or acidic forming compound such as magnesium methyl sulfate. Except for the presence of magnesium silicide no other compound was identified in this mixture.

A rapid reaction took place between magnesium silicide and glycol when heated to its boiling point. None of the other alcohols, low or high boiling or glycerol, had any effect upon the silicide. The product from ethylene glycol did not melt, burned, and was insoluble in all the common organic solvents except glacial acetic acid. Upon standing for one week the acetic acid solution gelled indicating the presence of silicates. Analysis gave 6.05 per cent silicon and 11.06 per cent magnesium. These figures give a ratio of atoms in a molecule of approximately 1 to 2 of silicon to magnesium. By assuming the remainder of the molecule was composed of glycol units hypothetical compounds can be constructed that fit all the figures.

The time devoted to the characterization of these products was scanty, but because of the lack of any evidence of silicon-carbon bond formation no further work was expended in their characterization.

E. Experimental:- The ether used in all of the preparations of the alkylsilicon halides was commercial anhydrous ether that was dried with sodium metal. The methyl bromide was generated by heating a mixture of aqueous methyl alcohol, sulfuric acid, and potassium bromide. The Grignard reagent and the dimethylsilicon dichloride were both formed in 2-l. three-necked flasks provided with spiral condensers, mercury sealed stirrers, and dropping funnels.

1. Dimethylsilicon dichloride:- The methyl bromide was generated by the method of Bygden (132). To 740 g. of concentrated sulfuric acid in a 2-l. flask, cooled by ice, 557 g. of commercial methanol was added with stirring so that the temperature never passed 60° C. After this mixture cooled 284 g. of water was also added slowly to prevent excessive heat generation. Now 371 g. (3.12 moles) of potassium bromide was gradually added. The flask was placed on a sand bath and provided with a 50-cm. spiral condenser. The top of the condenser was connected to a train which consisted of a safety bottle, two 500-cc. water wash bottles, two 500-cc. concentrated sulfuric acid washbottles, a sodium hydroxide drying bottle, a mercury pressure regulator, and finally a magnesium perchlorate drying bottle. The methyl bromide was generated at such a rate, by regulating the temperature of the sand bath, that kept the ether refluxing.

The methyl magnesium bromide was prepared by the method described by Kharasch and Tawney (133). The three-necked 2-l. flask was provided with a 50-cm. spiral condenser, Hershberg stirrer, a 500-cc. pear-shaped funnel having connections for pressure equalization, and an inlet tube extending to the bottom of the flask. The top of the condenser was provided with a

mercury escape valve as recommended by Fieser (134).

Before adding the magnesium to the flask, dry nitrogen was allowed to sweep through the apparatus and escape at the mouth of the dropping funnel. At the same time the flask was heated by means of a flame to drive out the surface condensed water.

Fifty- six grams (2.3 moles) of magnesium was placed in the flask. This was covered with 270 cc. of anhydrous ether and 455 cc. of absolute ether was also poured into the dropping funnel. Fifteen minutes after the Grignard reagent formation started, about 270 cc. of ether was added. At the end of one hour from the start of the reaction, 185 cc. more of ether was added. Methyl bromide was passed in until practically all the magnesium was used up. A 5-cc. portion analyzed as recommended by Fieser (134), indicated a 97 per cent yield of Grignard.

The 2-l. three-necked flask containing the silicon tetrachloride was provided in the same manner as the flask for the Grignard reagent preparation except there was no gas inlet tube, and the top of the dropping funnel was connected to calcium chloride drying tube filled with glass wool for filtering. A rubber tube connection with the filter tube and the methyl bromide inlet tube served to transfer the Grignard reagent (under nitrogen pressure) to the second dropping funnel.

The second flask was dried by means of nitrogen and heat as previously. This apparatus was also under a continuous nitrogen pressure. A mixture of 170 g. (1.0 mole) of distilled silicon tetrachloride and 250 cc. of anhydrous ether were poured into the flask. The Grignard reagent was added dropwise at such a rate that only a slight reflux was noticeable. Immediately upon addition of the methyl magnesium bromide, the precipitated magnesium halide

was evident. Because of the bulky nature of this precipitate vigorous stirring was needed during the entire reaction. All of the Grignard reacted within a short time after the addition of the final portion. However, the mixture was usually allowed to stand overnight because the entire preparation took about 8 hours after the apparatus was set up.

After the reaction was completed the entire contents of the second flask were transferred as rapidly as possible to a 2-l. distilling flask. The side-arm was connected to a condenser provided with an adapter. A 500-cc. filtering flask protected with a drying tube served as a receiver which was partly immersed in an ice bath. An oil bath heated to about 70° C distilled over the bulk of the ether solution and as the distillate started to come over slower the temperature of the bath was slowly raised. The bath temperature was brought to about 230° C in this manner and when the distillate slowed to about one drop in five seconds, the side arm of the receiving flask was connected to a source of reduced pressure. A water pump served well, but for best yields a mechanical pump was used. The pressure was slowly reduced until about 10 mm. of mercury was attained. All the distillates were poured into a 2-l. round-bottomed flask, and the mixture was fractionated through a 22-cm. column filled with glass beads and provided with a partial condensation partial take off head. Three fractions were usually obtained, as for example for the best run:

Boiling point	Weight
35-67° C	39 g.
67-69	45
Residue	22

The procedure used for this preparation is essentially the same as that given by Gilliam, Liebhofsky, and Winslow (127), but in much greater detail.

The yield of pure dimethylsilicon dichloride reported by these workers was 11.2 per cent. The weight of product obtained in this run amounts to 35.2 per cent. This product was rather pure as was evident from the difficulty of gelling the hydrolysis product.

2. Diethylsilicon dichloride:- This compound was prepared by two methods: a two stage procedure in which the preformed ethyl magnesium bromide was added to silicon tetrachloride, and by the second method, the Grignard reagent was formed in presence of silicon tetrachloride.

The procedure followed for the preparation of diethylsilicon dichloride by the first method was similar to that used for dimethylsilicon dichloride except that an ether solution of the halide was employed. Thus, after the flask was dried 400 cc. of anhydrous ether was poured over 56 g. (2.3 moles) of magnesium. Then 5 cc of ethyl bromide (b.p. 38.4-38.6°C) was added to start the reaction (135) and then 250 g. (2.3 moles) more of ethyl bromide in 500 cc. of ether was dropped in at such a rate that kept the ether refluxing. This required about two and one-half hours.

The directions followed for the reaction of the Grignard reagent and the silicon tetrachloride were those of Martin and Kipping (114). However, instead of allowing the reaction to take place at room temperature, the flask containing the solution of one mole of silicon tetrachloride in 250 cc. of ether was immersed in an ice-bath. The Grignard reagent was then added over a period of three hours and the mixture was stirred twelve hours more while remaining in the ice bath.

The completion of the reaction was determined in the following manner. Both calibrated and cup portions of an eudiometer were filled with water and stoppered. Then the cup portion was immersed under water where

the stopper was removed. Five cubic centimeters of reaction mixture was pipetted into a 10-cc. weighing bottle. The weighing bottle was then inserted inside the cup portion of the eudiometer where the lid was pushed off with the aid of a piece of wire. After opening the stopcock, the gas in the cup portion was forced into the calibrated portion of the apparatus. The reaction was completed when the volume of the gas reached a constant minimum volume.

The ether and silicon halides were distilled from the magnesium halides using reduced pressure as for the methyl derivatives. After stripping off the ether from the silicon halides with the aid of a fractionating column, the ethyl silicon chlorides were fractionated in a 20 cm. Vigreux apparatus. The best run using the two stage procedure gave the following fractions:

Boiling Point	Weight
30-95°C	2.6 g.
95-125	2.0
125-132	59.5
136-147	47.8
Residue	<u>19.1</u>
	131.0

The fraction boiling between 125-132° C amounts to 38 per cent of diethyl-silicon dichloride. Recorded b.p. 128-30° C (114). This material was also rather pure as was evident by the long heating that was required to gel its hydrolysis products.

The one stage procedure for the preparation of alkylsilicon halides was first used by Martin and Kipping (114) and is the most suitable for these compounds as it gives the best yields, saves time, and is the more pleasant to carry out.

The 2-l. three-necked flask was set up and dried as for the preparations of the methyl derivative. Then 56 g. (2.3 moles) of magnesium, 400 cc. of anhydrous ether, and 170 g. (1.0 mole) of silicon tetrachloride were placed in the flask. To this mixture a solution of 250 g. of ethyl bromide (2.3 moles) in 500 cc. of absolute ether was added dropwise. The rate of addition was rapid enough (requiring five to six hours) to keep the ether refluxing. After standing with stirring overnight, the ether and halides were distilled under reduced pressure. The best run gave the following fractions:

Boiling point	Weight
37-125°C	7.5 g.
125-132	65.0
Residue	<u>27.1</u>
	99.6

The yield is 41.4 per cent. If the magnesium halides which weighed 341 g. (2.3 moles of MgBrCl weigh 321 g.) were dissolved in water, a layer consisting of a silicon polymer and ether floated to the surface. This silicon polymer weighed from five to ten grams. This was an indication of how completely the silicon chloride had been driven from the magnesium halides.

3. Diethyldiethoxysilicane:- The reaction between a Grignard reagent and silicon orthoester can be either a one or a two stage procedure. There are several examples of the two stage procedure (136) in literature, but only one was found for the one stage procedure (137). In this latter reaction, allyl bromide or chloride was condensed with ethyl orthosilicate in presence of magnesium forming allyltriethoxysilicane.

No investigator's directions were followed for the preparation of diethyldiethoxysilicane by the one stage procedure. The ratio of the reactants

was the same as for the previous experiments except all were halved. Thus, 28 g. (1.15 moles) of magnesium, 104 g. (0.5 moles) of ethyl orthosilicate, and 200 cc. of absolute ether were placed into a 1-l. three-necked flask as for the preparation of dimethyl silicon dichloride. A mixture of 125 g. (1.15 moles) of ethyl bromide in 200 cc. of anhydrous ether was dropped into the magnesium, ether, and silicate mixture. The reaction started almost immediately with the formation of a white precipitate and a gentle refluxing of the ether. After the halide addition, which took about two hours, the mixture was allowed to stand with stirring overnight. The white solid was collected on a filter and weighed 153 g. (1.0 mole of MgOEtBr weighs 149 g.). The ether was distilled off by means of an oil bath, the temperature of which was allowed to reach 120°C . The weight of the higher boiling residue was 56.6 g. This was fractionated in a 22 cm. Vigreux column and the fractions collected were:

Boiling point	Weight
35-154° C	10.0 g.
154-155	40.7
Residue	5.

The yield is 46 per cent. Recorded b.p. 155.5 (138).

4. Dibutyldiethoxysilicane:- Although this compound was prepared by the procedure used for diethyldiethoxy silicane, its isolation was different. In the flask were placed 28 g. of magnesium, 200 cc. of absolute ether, and 104 g. of ethyl orthosilicate. The dropping funnel contained a solution of 164 g. (1.2 moles) of butyl bromide (b.p. $101.6-101.8^\circ \text{C}$) and 200 cc. of anhydrous ether. The Grignard reagent formed immediately but the reaction with the silicate was slow. After all the halide had been added the mixture

was refluxed for twenty-four hours with stirring. The reaction mixture was poured onto 1.5 l. of crushed ice. The aqueous layer was acidified to break an emulsion that formed and to dissolve the suspended solids. After decanting the ether layer, the aqueous layer was extracted twice with 100-cc. portions of ether. This was dried with calcium chloride overnight, the ether was removed by distillation, and the residue distilled under reduced pressure. This high boiling residue weighed 88.1 g. The fraction b.p. 210-15° C weighed 49.5 g. yields 25 per cent of dibutyldiethoxysilicane.

It is difficult to hydrolyze these alkylethoxyl compounds as is evident from the manner in which they can be isolated. To form a film these compounds must first be hydrolyzed by refluxing with an alkali or acid for at least fifteen minutes. This hydrolysis product can be baked to a film which resemble those obtained from the alkylsilicon halides.

5. Attempted Wurtz Type of Reaction:- A one stage procedure for forming silicon-carbon bond would be the modified Wurtz reaction between silicon tetrachloride, sodium, and ethyl bromide. Thus to a mixture of 84 g. (0.5 moles) of silicon tetrachloride, 46 g. (2.0 moles of finely divided sodium metal, and 100 cc. of anhydrous ether was added a solution consisting of 109 g. (1.0 mole) of ethyl bromide in 300 cc. of ether. When the halide was first dropped in no reaction started until 1 cc. of ethyl acetate was added. However, the reaction was of about three minute duration as indicated by the refluxing ether. Subsequent additions of halide gave no further evidence of reaction and only when ethyl acetate was added did the ether reflux. In all, about 10 cc. of ethyl acetate was added. The mixture was heated with stirring overnight and next morning the ether and products were

distilled under a nitrogen atmosphere by means of an oil bath heated finally to 220° C. The ether was stripped off and the following fractions were collected:

Boiling point	Weight
36-70° C	27. g.
70-120	27.7
Residue	-----

The first cut consisted largely of silicon tetrachloride and the second cut contained no constant boiling portion. The reaction as described is a failure for the preparation of diethyl silicon dichloride.

About the same results were obtained using benzene as a solvent.

6. Attempted Fittig Type of Reaction:- A 250 cc. three-necked flask was set up as were the flasks for the preparation of the Grignard reagents. Eighteen and eight-tenths grams (0.1 mole) of sodium fluosilicate (obtained from Harshaw Chemical Company), 19.2 g. (0.8 moles) of sodium, and 50 cc. of xylene dried over sodium were placed into the flask. The sodium was beat into finely divided "bird shot" according to the directions in Fieser (134). Forty-four and eight tenths grams (0.4 moles) of chlorobenzene b.p. 128-129° C was added slowly. During this addition a white precipitate formed and the solvent refluxed. After all the chlorobenzene had been added, the mixture was heated for several more hours. There seemed to be a great deal of unreacted metallic sodium which was destroyed by methyl alcohol. This mixture was poured into 100 g. of water, the layers were separated, and the bottom layer extracted with two 25-cc. portions of xylene. A tan precipitate was present in the aqueous layer. This was collected on a filter, washed with water, and dried. The precipitate weighed 22.6 g. and was composed largely

of sodium fluosilicate as was evident from the large volume of silicon fluoride evolved when heated with concentrated sulfuric acid. The xylene solution contained biphenyl which was identified by its odor and melting point. Very little if any tetraphenyl silicane was formed.

7. Attempted Reactions of Magnesium silicide with Organic Compounds Containing Active Groups:- The magnesium silicide (†) was prepared in a 400 cc. graphite crucible, covered with a graphite lid through which ran a porcelain tube for the hydrogen. Into the crucible was placed a mixture consisting of 136 g. (5.68 moles) of magnesium filings (Dow magnesium containing 97 per cent magnesium and 3 per cent manganese) and 66 g. (2.35 moles) of powdered silicon (Electro Metallurgical Company product consisting of 97.9 per cent silicon). To decrease the loss of magnesium by volatilization, 10 g. more of silicon was spread on top of the mixture making a total of 2.72 moles of silicon. The temperature (which was determined by an optical pyrometer) of the induction furnace was brought to about 900° C in one-half hour. This heat was maintained for twenty minutes, and then the product was allowed to cool under a hydrogen atmosphere for thirty minutes. The blue-black crystalline material weighed 186.3 g. indicating a 15.3 g. loss of mostly magnesium. When this silicide was powdered and thrown on dilute hydrochloric acid the gases exploded spectacularly.

(†) J. Stansbury and the Metallurgy Department are thanked for this willful cooperation during the preparation of the silicide.

The silicide still contained free magnesium as could be determined by reacting it with compounds containing active halides. When the silicide was used in place of magnesium in a Grignard reaction, the other refluxed for a short time. Then no heating or stirring could induce any further reaction. The solid residue collected by filtration would always weigh more than the magnesium silicide initially used. Thus 3.9 g. of magnesium silicide, 31.2 g. of ethyl iodide (b.p. 72.3° C), and 140 cc. of anhydrous ether were heated for 16 hours. The solid collected on a filter reacted with acids to give a gas that exploded, was blue-gray in color, and weighed 4 g.

Other halides that behave similarly were butyl bromide, heptyl chloride, allyl bromide, benzyl chloride, phenyl bromide and phenyl iodide.

The reaction with methyl sulfate was performed in the following manner. Seven and eight-tenths grams of magnesium silicide and 25.2 g. of commercial methyl sulfate were placed in a 100 cc. flask. These were refluxed for ten hours without any visible evidence of a reaction. However, when 1 cc. of pyridine was added to the boiling mixture, some gas seemed to be formed. The weight of the solid residue after washing with benzene and drying on a steam plate was 15.5 g. It still contained magnesium silicide as indicated by the explosion when thrown into dilute acids. When the black residue was added to distilled water, gas which exploded was again generated. This indicates the presence of an acid which could have come from occluded methyl sulfate, magnesium sulfate, sulfonated pyridine or pyridinium salts, or mixtures of these.

Neither the benzene solution nor any of the fractions obtained by

distillation contained any silicon.

The procedure with benzoyl chloride (b.p. 191,5-93° C) was identical to that with the methyl sulfate except no pyridine was added. The brown product collected contained magnesium silicide and weighed 20 g. The brown portion of the solid was difficultly soluble in benzene, but since it did not contain any silicon it must have been a polymeric compound formed by the self condensation of benzoyl chloride. There was no visible evidence of reaction with acetyl chloride, chloracetyl chloride, acetic anhydride, and phthallyl dichloride. Pyridine was used with some of these compounds.

The reaction with glycol was definite but unexplainable. Seven and eight-tenths grams of magnesium silicide and 200 cc. of pure glycol were placed in a 500-cc. round-bottomed flask provided with a water-cooled condenser. The reaction was rapid near the boiling point of the glycol and cooling with ice was necessary to control the reaction. A gas, which was not collected, was generated, but the lack of any explosion probably indicated pure hydrogen. After the initial reaction had subsided, the mixture was refluxed until no colored specks of silicide were visible. A white precipitate was formed. This precipitate was insoluble in water, acetone, ethyl acetate, and alcohols. Glacial and aqueous acetic acid gave a clear solution which was stable for about a week after which it gelled.

The white solid weighed 32 g. and contained 6.03, 6.06 per cent silicon and 10.94, 10.81, 11.43 per cent magnesium.

It was surprising that none of the other alcohols tried, including phenol, reacted. The alcohols were ethyl alcohol, butyl alcohol, Cellosolve, Carbitol, diethylene glycol, propylene glycol, ethanol amine, and glycerine.

Glycerine was reacted with the magnesium silicide in the presence of a small amount of water, glycol, dilute hydrochloric acid, dilute sodium hydroxide, and a mixture of bromine in water. These had no catalytic action.

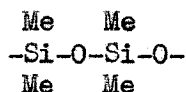
Aniline did not react, but an aqueous solution of aniline hydrochloride slowly generated silane. This might be a convenient way of obtaining this gas as it seems to be controllable.

Bromine had no effect by itself or in presence of carbon tetrachloride or pyridine.

More work with magnesium silicides prepared at lower temperatures or other metallic silicides should be carried out before this method of forming a silicon carbon bond can be proven a failure.

V. PREPARATION OF PRODUCTS CONTAINING A SILICON-OXYGEN-PHOSPHOROUS BOND

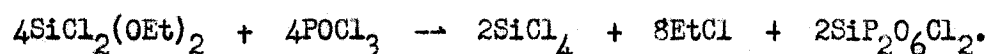
A. Discussion:- The silicon film containing the lowest carbon content should be the most fire-resistant. Thus films made from the silicols of methylsilicon chlorides should be the most desirable. These silicols undoubtedly combine by splitting out water and by oxidizing off methyl groups to form siloxane linkages. Pure dimethylsilicon dichloride would give a siloxane unit containing methyl groups:



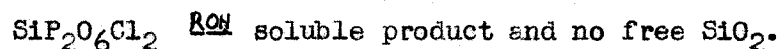
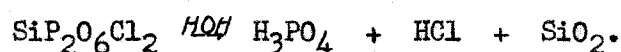
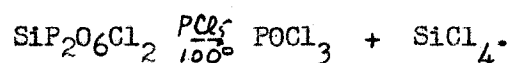
The carbon content of one of these units is 32.5 per cent. However, it would be possible to reduce the carbon content of one of these units in the final polymer if some larger group other than oxygen was the connecting radical between two silicon atoms. From the review of silicon chemistry it was apparent that none of the other silicon-element bonds (Si, N, or S) would be sufficiently stable to bind silicon atoms in paint films. This lead to a consideration of the possibility of some inorganic compounds for this purpose. Of the acids, bases, and salts considered, phosphoric acid appeared to be the most promising for several reasons: a). orthophosphoric acid derivatives are being used for flame proofing purposes; b). the functionality of orthophosphoric acid can be controlled; and c). some silicon-phosphorous-oxygen containing compounds have been formed.

Hautefeuille and Margottet (139) studied the reaction between silica and phosphoric acids. From a fusion mixture of silica and metaphosphoric acid they were able to extract with water a product which crystallized. This substance scratched glass, melted to a glass which did not devitrify on cooling, and its composition corresponded with $\text{SiO}_2 \cdot \text{P}_2\text{O}_5$. Stokes (140)

obtained a product giving the same analysis when he heated the compound obtained by reacting together ethyl orthosilicate or chloroethoxysilanes and phosphorous trichloride. For example:



Some of the reactions besides decomposition are:



The structure of this compound was not elucidated, but it was named silicopyrophosphoryl chloride as it seemed to contain a pyrophosphoryl group: $-\text{O} \cdot \text{PO} \cdot \text{O} \cdot \text{PO} \cdot \text{O}-$.

With this evidence for the existence of compounds containing silicon, oxygen, and phosphorous it was hoped that a controllable condensation might be realized between difunctional phosphoric acid esters and organo silicon compound. Dimethylsilicon dichloride and monomethyl orthophosphoric acid or fluorophosphoric acid could form a unit containing less carbon than the condensation product of dimethylsilicanediol:

Unit	Per cent carbon
Me -Si-O- Me	32.5
Me O -Si-OP-O- Me OMe	21.4
Me O -Si-OP-O- Me F	15.4

There is ample evidence that resins can be formed from alkylsilicon chlorides and diacidic phosphoric compounds, but the silicon-oxygen-phosphorous bond is not sufficiently stable to resist hydrolysis nor to withstand the heat that would be required for thermosetting. The manner in which these facts were determined is discussed below.

There are three ways in which resins containing silicon-oxygen-phosphorous bonds could be formed: a). the difunctional phosphoric acid or its salts could be reacted with silicon chlorides; b). alkoxy-silicanes; and c). silicanediols might be reacted with phosphoric anhydride or phosphorous oxychloride.

When monomethyl orthophosphoric acid dissolved in a small amount of methanol was dropped into silicon tetrachloride, a reaction resembling the addition of glycol in methanol to the silicon halide was obtained. A gel would form which could be put into solution by adding excess alcohol, but upon standing this alcoholic solution solidified within one-half hour. The gel when dried would flare momentarily when put in a flame, but then would only char and intumesce, i.e., when heated it swelled to a mass which hardened.

To prove more definitely that compounds containing silicon-oxygen-phosphorous bonds exist, silicon tetrachloride was refluxed with excess diethylphosphoric acid in dioxane. An amorphous white solid was obtained which hydrolyzed in water to give an acid reaction, and contained a ratio of silicon to phosphorous of 1 to 1. This compound flared momentarily when held in the direct flame, then charred, and melted only at the highest temperature of the Mecker burner. During ignition the residue would lose weight steadily indicating the sublimation of some material.

Dimethylsilicon dichloride and monomethyl phosphoric acid are not miscible at room temperature, but if heated to 35° C for three hours they become homogeneous. If these two reactants are heated at 90-100° C while stirring they become homogeneous in fifteen minutes with the simultaneous evolution of hydrochloric gas. With continued heating, the mixture increases in viscosity until the product becomes too hard to stir. This material is deliquescent as is the film which is formed upon baking at 120° C for twenty-four hours. If the film is baked for about three days, the deliquescent tendency is slowly lost and the film becomes brittle resembling the silicol films.

It was thought that the water absorption of the film was due to an incomplete condensation leaving free acidic groups. Therefore, attempts were made to use larger amounts of silicon dichloride and higher temperatures during the resin formation. However, when the mixture of diethylsilicon dichloride and monoethylphosphoric acid was heated to 150° C, a large volume of gas other than hydrochloric acid was evolved. This other gas was ethylene formed by the decomposition of monoethyl phosphate. This resinous product was deliquescent as was the resin formed by heating the mixture at 320° C until stirring became difficult. This product was decomposed slowly by alcohol into two layers. The top layer consisted of an alcohol-phosphoric acid mixture while the bottom layer was a silicon polymer. This polymer baked to a very clear film possessing 32.6 per cent silicon and 1.0 per cent phosphorous. A unit, $-\text{Si}(\text{Et})_2-\text{O}-$, formed from the condensation of diethylsilicanediol contains 27.5 per cent silicon. The film analyzed above is the condensation product of diethylsilicanediol that cross condensed by oxidizing off ethyl groups, thereby increasing the silicon content.

It was hoped that fluorophosphoric acid would be sufficiently different to form a stable silicon-oxygen-phosphorous bond. However, when 0.1 moles of diethylsilicon dichloride and 0.1 moles of monofluorophosphoric acid were heated together up to 200° C, .27 moles of sodium hydroxide were neutralized by the gases evolved, indicating that at least .007 moles of hydrofluoric acid was liberated. These films were also acidic and deliquescent.

Attempts were made to form phosphoric acid and ethylphosphate in presence of the silicon halide, by adding water or ethyl alcohol to a mixture of diethylsilicon dichloride and phosphoric anhydride. The water or alcohol reacted first with the anhydride forming metaphosphoric acid or the ester which reacted with the silicon halide evolving hydrochloric gas and eventually forming a product that was deliquescent and acidic in the presence of water.

To determine whether alkylethoxysilicanes behaved differently, diethyl-diethoxy- and dibutyldiethoxysilicanes were refluxed with diethyl phosphate. This formed a homogeneous solution which did not harden as did the silicon chloride mixture on prolonged heating, but the films formed were deliquescent which property was lost on prolonged heating. When tetraethyl orthosilicate and monomethyl phosphate were refluxed together, a white solid was formed. This amorphous solid hydrolyzed to give an acid reaction in water, charred but did not burn, and contained 12.8 per cent silicon and 18.4 per cent phosphorous. The atomic ratio of silicon to phosphorous in any molecule or polymeric unit is 1 to 1.3. Hypothetical structures cannot be proposed without more analyses.

The final attempts to form silicon-oxygen-phosphorous bonds were to

react together diethylsilicanediol and phosphoric anhydride and phosphorous oxychloride. The latter compound did not react appreciably upon heating the solution of the reactants. When baking a layer of the mixture, phosphorous chloride was volatilized off leaving behind a silicon polymer that finally baked to a silicol-like film. Phosphoric anhydride seemed to have a plasticizing action on the silicols. Films of this mixture remained appreciably sticky after over twenty-four hours of baking at 130-150° C. Continued baking eventually gave a hard brittle film which absorbed a surface layer of water indicating the presence of phosphoric compounds.

B. Experimental:- All of the reactions of the silicon halides with phosphoric acid compounds were performed in a 250-cc. three-necked flask provided with a 100-cc. dropping funnel with a pressure equalization attachment, a mercury-sealed stirrer, and a 20-cm. condenser the top of which held a stopper through which a glass tube ran for conducting the hydrochloric gas through either a sodium hydroxide wash bottle or a gas trap.

For some of the preliminary experiments a mixed mono- and dimethyl orthophosphoric acid ester (Monsanto Chemical Co. product) was used. All of this preliminary work was repeated with pure mono- and diacids obtained from the Victor Chemical Works. The silicon halides used were those described in the section IV.

1. Monomethyl orthophosphoric acid ester, Silicon tetrachloride, and Methyl alcohol:- Seventeen grams (0.1 mole) of silicon tetrachloride was weighed directly in the 250-cc. three-necked flask. Then a mixture of 23 g. (0.2 moles) of monomethyl phosphate and 6.3 g. (0.2 moles) of 99.5 per cent

methyl alcohol was placed in the 100 cc. dropping funnel. As the acid solution was dropped into the silicon tetrachloride, vapors of the latter immediately reacted with each drop forming a gel-bag into which more solution flowed until it broke from the weight. The bag was broken by the agitation and more gel would be formed in the silicon tetrachloride. When all the solution had been added, the gel could be brought into solution which was stable for about one-half hour by adding more alcohol. This gel would not burn and upon direct heating in a flame would swell into a white noncombustible foam.

2. Silicon tetrachloride and Diethyl orthophosphoric acid ester:-

Fifteen grams (0.1 moles) of diethyl phosphate with 15 cc. of anhydrous dioxane were placed in the 250-cc. flask. Into this mixture was dropped 4 g. (0.025 moles) of silicon tetrachloride in 10 cc. of dioxane. At first the precipitate that formed dissolved, then the solution became cloudy, and finally a permanent precipitate formed. The mixture was refluxed until only a slight amount of the hydrochloric gas as detected with ammonia was evolved. The white solid was collected on a filter, dried on a steam plate, and analyzed for silicon and phosphorous which gave 11.39, 11.43 and 12.45, 12.28 per cent respectively. This gives an exact ratio of silicon to phosphorous atoms in a molecule or unit of 1 to 1.

3. Dimethylsilicon dichloride and Monomethyl orthophosphoric acid ester:- Twelve and eight tenths grams (0.1 mole) of dimethylsilicon dichloride was weighed directly into the flask. To this over a period of one-half hour was added 11 g. (0.1 mole) of monomethyl phosphate. The liquids were not homogeneous and stirring at room temperature for six hours caused

no visible change. However, heating at 35° C for three hours while stirring caused the reactants to become homogeneous. During this treatment hydrochloric gas came off slowly. The rate of evolution was appreciably increased when the temperature of the oil bath was raised to 90-100° C. While heating at this temperature for six hours the product became more and more viscous until at the end of the time it was too hard to stir. The solid weighed 15.7 g. indicating an 8.1 g. loss of gas (0.2 moles of HCl weigh 7.3 g.).

This deliquescent resin after being ignited in a porcelain crucible, left a residue which amounted to 75.3-78.0 per cent of the product. The residue upon continued ignition slowly lost weight, thereby indicating products other than silica.

Variations of the above resin formation were attempted such as the use of an inert solvent, addition of excess diethylsilicon dichloride, adding the silicon dichloride into heated phosphate, and completing the condensation at temperatures up to 320° C. None of these overcame the deliquescent nature of the resin.

4. Diethylsilicon dichloride and Monoethyl orthophosphoric acid ester:- Although there was evidence of excess nonacidic gas evolution during the high temperature treatment of the previous run, none was identified. It was suspected that phosphate was decomposing; so to prove this the following run was performed.

The gas that came out of the top of the condenser passed through a wash bottle containing 100 cc. of 2.95 N sodium hydroxide and any excess gas was collected over distilled water in a 2.5 l. inverted bottle.

To 19.2 g. (0.122 moles) of diethylsilicon dichloride was slowly

added 15.4 (0.122 moles) of monoethylphosphate. After the initial evolution of gas had subsided, the temperature of the oil bath was slowly increased (temperature above 200°C was attained by use of a metal bath.) The gas was evolved according to the following rate:

Time	Temp of bath	Vol. of gas at $21.0-22.8^{\circ}\text{C}$
0.0	Room	0.0 cc.
0.5	105°C	605
1.75	140	1000
2.33	170	1617
3.26	310	2447
4.24	330	3200
6.00	330	3659

The partially neutralized sodium hydroxide was titrated, and 0.180 equivalents of base had been neutralized. Originally there had been 0.244 equivalents of chloride in the diethylsilicon dichloride indicating an unfound 0.064 equivalents of hydrochloric gas.

In a similar experiment previous to this run, all the gas was bubbled through a carbon tetrachloride-bromine solution. The bromine was used up and 1,2-dibromoethane was isolated.

To determine the amount of ethylene in the gas collected in this experiment, an Orsat gas analysis apparatus was employed. By exposing the gas sample to a saturated aqueous bromine solution, the first 2,447 cc. of gas collected contained 66.5 per cent ethylene and the second 1,212 cc. contained 8.8 per cent making a total of 1,730 cc. of ethylene. The volume of the gas was measured and the analyses were made when the room temperature was approximately 22.5°C and barometric pressure was 745 mm. Under these conditions if all the ethyl phosphate had decomposed to ethylene gas, there should have been 3,100 cc. The discrepancy of these two values for ethylene, 1,730 cc. found and 3,100 cc. theoretical can be

accounted for by the fact that decomposition of the ethyl phosphate produced free ethyl radical which started chain reactions forming besides ethylene some hydrogen, methane and ethane. Furthermore, ethylene and hydrochloric gas might have reacted to produce ethyl chloride.

The weight of the final resin was 21.8 g. representing a decrease of 12.8 g. Of this decrease, 8.9 g. may be accounted for by the evolution of hydrochloric gas, leaving 3.89 g. for the ethyl radical formation (0.122 moles of ethyl radical weigh 3.54 g.). These values are checked well by a previous run in which the weight of the final resin was 21.5 g. This resin would dissolve in ethyl alcohol forming two layers. The top layer contained phosphoric acid, while the bottom layer was composed of 84.5 per cent nonvolatile material. A film baked for forty-eight hours contained 32.57, 32.52 per cent silicon and 0.90, 1.20 per cent phosphorous. The film was hard, brittle and remarkably glass clear. Further substantiating data that the gas evolved came only from the ethyl phosphate and not the diethylsilicon dichloride were obtained when the resin was prepared from fluorophosphoric acid in place of the ethyl ester.

5. Diethylsilicon dichloride and Monofluorophosphoric acid:- This reaction was performed in the same manner as No. 4. Ten grams (0.1 mole) of fluorophosphoric acid (prepared by Dr. Ralph Livingston and was found to be 96.5 per cent pure) was placed in the three-necked flask. Fifteen and seven-tenths grams (0.1 mole) of diethylsilicon dichloride was added dropwise. After the oil bath temperature had reached about 200° C, the mixture was too viscous to stir so heating was stopped. From an analysis of the sodium hydroxide solution, it was found that 0.270 equivalents of base had been neutralized, indicating that at least 0.07 equivalents came

from the fluorophosphoric acid. The volume of gas collected was 240 cc. and none of this was absorbed by potassium hydroxide or bromine-water in the Orsat apparatus.

The solid resin was deliquescent as was its film. Water decomposed it into two layers, the top layer was the silicon resin and the bottom layer was phosphoric acid.

6. Diethylsilicon dichloride, Phosphoric anhydride, and Water or Ethyl alcohol:- Fifteen and four-tenths grams of diethylsilicon dichloride (0.1 moles) and 5.1 g. (enough to prepare 0.185 equivalents of phosphoric acid) of phosphoric anhydride were weighed directly into the three-necked flask. To this stirred mixture was slowly added 3.4 cc. of water in enough dioxane to give a 10 cc. solution. The first reaction of the water was with the phosphoric anhydride as indicated by the heat generated and the formation of a ball of acid around the stirrer blade. After the ball was formed hydrochloric gas came off; simultaneously the ball began to decrease in size until overnight it almost had disappeared. Heating the resultant mixture drove off more hydrochloric gas and the mixture began to turn brown. The cooled solution was viscous giving baked films that were tacky and deliquescent.

With the intention of forming methyl orthophosphate in the presence of the silicon halide, a solution of 4.6 g. (0.1 mole) of absolute ethyl alcohol and 0.9 g. (0.05 mole) of water were dropped into a slurry of 15.4 g. (0.1 mole) of diethylsilicon dichloride, 7.1 g. (0.05 mole) of phosphoric anhydride, and 10 cc. of dioxane. The reaction ran smoothly and the mixture was refluxed until hydrochloric gas no longer was evolved. The film obtained after forty-eight hours baking at 130-150° C was hard, but was slightly deliquescent.

7. Dialkyldiethoxysilicanes, Tetraethyl orthosilicate, and Monoethyl orthophosphoric acid ester:- Refluxing together 18.7 g. (0.1 mole) of dibutyldiethoxysilicane and 12.6 g. (0.1 mole) of ethyl phosphate for three hours gave a clear stable solution that produced a film at 130° C, which was deliquescent and tacky. Prolonged heating gave a hard brittle film that would cloud slightly when immersed in water.

When the same proportions of material were used together with 10 g. (0.5 mole) of tetraethyl orthosilicate, a clear solution was again obtained. This mixture produced a hard film sooner than the solution above, but the film had poor adherence and crazed.

Diethyldiethoxysilicane gave products that had the same properties as those from the dibutyl compounds.

The greater the amount of monomethyl orthophosphoric acid added to a constant amount of ethyl orthosilicate, the greater the volume of white precipitate produced. This white precipitate is difficult to isolate because it is of a resinous nature. After repeated washings by decantation with ~~dioxane~~, a clean precipitate that was free of ethyl silicate odor was obtained. An analysis showed this to contain 12.81 per cent silicon and 18.43 per cent phosphorous, giving an atom ratio of 1 to 1.3 respectively. The white precipitate was obtained by refluxing a mixture of 10 g. of methyl phosphate with 40 g. of ethyl orthosilicate with an oil bath at 150° C for one and one-half hours. The precipitate was hydrolyzed by water, did not burn, but charred.

8. Diethylsilicanediol and Phosphoric anhydride:- A patent (141) has been obtained for the condensation of silicols in presence of dehydrating agents. All possible dehydrating agents from sulfuric acid to Portland

cement are mentioned. Examples were given using antimony pentachloride, sulfuric acid, ethylene diamine, and borate esters. Special emphasis was given to this latter compound and the boric acid formed by the hydrolysis was an integral part of the final film. Phosphoric anhydride was mentioned as one of the dehydrating agents that could be used, but no example of its use was given.

In the expectation of forming a silicon-oxygen-phosphorous bond, 18.g. (0.15 moles) of the silicanediol and 7.1 g. (0.05 moles) of phosphoric anhydride were weighed directly into the three-necked flask. Some heat was generated while these products were stirred at room temperature and the mixture became viscous. Heating for one and one-half hours at an oil bath temperature of 180° C increased the viscosity to almost a solid. The product formed two layers with ethyl alcohol; the top was phosphoric acid and the bottom contained the silicon polymer. These two layers were soluble in dioxane and a layer of this solution was liquid at 150° C after fifteen minutes and sticky at room temperature. Continued heating at 150° C for three days gave a hard homogeneous film which on standing adsorbed moisture forming in droplets which were acidic.

When the amount of phosphoric anhydride was halved, a tacky film would be produced after heating for one hour at 150° C. This tacky film was not very deliquescent, but would cloud when covered with water.

VI. SUMMARY AND CONCLUSION

1. Orthoesters prepared by dropping alcohol through a condenser filled with glass beads and countercurrent to the gas evolved, gave no better yields than those reported in literature. A new method of forming mono-(B-chloroethyl)-silicon trichloride was developed, which consisted in adding ethylene oxide to silicon tetrachloride. Bromination of tetraethyl orthosilicate gave a product which analyzed for pentaethoxydisilicane bromide.
2. Baking films of alkyl orthosilicates or their condensation products, gave inferior coatings of no value as protective films. The silicon-oxygen-carbon bond is not sufficiently stable to withstand the baking process necessary for thermosetting. Films formed from the urea-formaldehyde-orthosilicate solutions greatly resembled the straight urea-formaldehyde-alcohol films except the former were more difficult to ignite.
3. Methods of obtaining higher yields of dimethyl- and diethylsilicon dichlorides and diethyl- and dibutyldiethoxysilicanes were developed. The best way of obtaining an alkylsilicane containing functional groups is to form a Grignard reagent in presence of ethyl orthosilicate. It was not possible to obtain a silicon-carbon bond compound from magnesium silicide.
4. Diacidic phosphate esters and fluorophosphoric acid reacted with dialkylsilicon dichlorides to form resins containing silicon-oxygen-phosphorous bonds. These products have excellent fire-resistance but the silicon-oxygen-phosphorous bond is not sufficiently stable to resist hydrolysis or high temperatures. Phosphoric anhydride has a plasticizing effect upon silicol condensation products.

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