THE DEVELOPMENT OF A PROCESS FOR THE PRODUCTION OF PHENYLCHLOROSILANES

by

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I. INTRODUCTION

The silicone (organosilicon) polymers are a new and remarkable development of the chemical industry. Filling the void between organic and inorganic products, they find a great variety of uses where their outstanding properties of heat and moisture resistance, general chemical inertness, and high electrical resistance can be applied. They are available as fluids for hydraulic and other uses, lubricants and greases, electrical sealing compounds, resins, and elastomers. Some of the intermediate compounds formed in the manufacture of these final products have also found uses.

Organic compounds of silicon have been known and studied for over one hundred years. Nearly all of the early study, however, was done on the chemical and physical properties of the monomers and low polymers and until very recently little was accomplished toward the practical application of this type of compound. In the United States, about 1935, impetus was furnished to research on the silicones by the need for a material suitable for binders, varnishes, and adhesives for newly-developed glass fabrics to be used in electrical insulation. The silicones are structurally analogous to glass and therefore seemed a likely starting point for the search. The monomers and low polymers are unsatisfactory and there were finally developed high polymers which proved to have outstanding heat and moisture resisting properties, in addition to the desirable qualities for electrical insulation. Since then research on silicones has progressed rapidly. The number of new products developed has created a demand that has far outstripped commercial production, begun in 1943.

All efforts are now being directed toward finding better commercial methods of production as present methods are expensive and relatively difficult to control. This seems to be particularly true of the initial step in silicone production, i.e., that of making the intermediate organochlorosilanes.

The purpose of this investigation is to develop a process for the production of phenylchlorosilanes by the phenyl substitution of silicon tetrachloride at high temperatures.

II. LITERATURE REVIEW

A. History of Organosilicon Compounds

Silicon is second in abundance among the elements on the earth, being found in greater amount than any other except oxygen. In spite of this abundance, the only compounds of silicon which have been important to man until very recently have been the natural forms, such as silica and the silicate minerals, which are used in building materials and ceramic ware(91).

Studies Prior to 1900. The first compound of silicon other than the siliceous minerals was prepared by Berzelius in 1823 - silicon tetrachloride. In the same year he became the first to isolate metallic silicon(22). The first organic compound of silicon, ethyl orthosilicate ($(C_2H_5O)_4Si$), was made about 100 years ago by Ebelmen(22). Friedel and Crafts made the first organosilicon compound containing a direct silicon-to-carbon linkage in 1863(22)(34)(91). The first aromatic organosilicon compound, phenyltrichlorosilane, was made in 1873 by Ladenburg(22). Several compounds of this type were synthesized and studied by Friedel, Crafts, and Ladenburg from 1871 to 1874. Polis, in 1885, made the first crystalline organosilicon compound, tetraphenylsilane, and devised several methods for synthesizing organosilicons(13)(83)(84). Thus, it may be seen that the early progress in this field was slow.

Rochow(91) concluded that the lack of natural products and methods of synthesizing the compounds were the principal hindrances to the early studies.

Kipping's Studies. At about the turn of the century Dr. Frederick S. Kipping began his studies of the organosilicon compounds(2)(13)(22)(87)(91)(117). He and his associates, in England, studied them for forty years(14)(91)(117) and this work has provided most of the present-day basic knowledge of the compounds(5)(91)(117). The original objective of Kipping's researches was to prepare an optically active silicon compound(57). His research was "more in the cause of pure science than with any commercial objective"(117).

Development of Organosilicons for Practical Applications. In 1935 Carleton Ellis(32) said, "The further development of the organic chemistry of silicon may lead to the production of cheap and readily prepared derivatives which can be applied as resins or binding agents". It was at about this time that the first work on the silicones, with the object of commercial applications, was begun (5)(21)(22)(87)(117).

The development of glass fabrics and the thought that organosiloxane derivatives might provide materials useful with glass provided the original stimulus for the research(5)(15). The need for insulating resins and varnishes with high heat resistance and water-repellent properties, coupled with the already known fact that silicon organics were sometimes based on a glass-like structure and should therefore have some glass-like properties, made it apparent that the silicones were the logical starting point for the research (5)(15). Kipping's silicones, monomers and low molecular weight condensation products, were unsatisfactory and the search turned to the more complex polymers(21).

The first silicone product of importance was a flexible, thermosetting, resinous polymer(87). Further research and development has produced such diverse forms of silicones as greases, oils, insulating materials of many kinds, and rubber-like materials(5). Today there are available a great variety of products for many different uses. Some of the intermediate compounds are coming into commercial importance also(91).

The second World War was largely responsible for the recent rapid development of silicone technology. The sudden demand for these products for war uses necessitated immediate commercial scale production and a corporation was formed to manufacture them(87). Commercial production was announced in 1943(2)(15)(130).

B. Commercial Production and Prices of Silicones

Commercial Production. Commercial production of silicones is still on a limited scale(108) in spite of the many rapid advances in silicone technology which have been made in the past few years and still lags far behind the demand for the products. Total production as of May, 1947, was about fifty tons per month for all types of silicone materials. Better and less expensive processes are needed to convert the raw materials into useful products(108).

Prices. Prices of silicone materials are still high, but may be expected to decrease rapidly as production increases and better production methods are developed. The following prices of various silicone products are as of October, 1945. They are about twenty per cent less than the prices of the first commercial products(58):

1. Resins- $3.00 to $4.00 per pound
2. Varnishes- $15.00 per gallon, 50% solids
3. Fluids- $6.00 per pound or $48.00 per gallon
4. Greases- $5.00 to $7.00 per pound
5. Ceramic treating solutions- $0.38 to $0.48 per pound
6. Elastomers- $3.00 to $4.00 per pound

C. Classification of Commercial Silicone Products

Silicones are generally classified according to their physical properties. There are several groupings used by different authors(2)(5)(11)(15)(22)(40)(52)(87)(117), but the system given by Collings(22) will be used for discussion purposes in this review. His groupings are as follows:

1. Fluids for hydraulic and other uses
2. Lubricants and greases
3. Sealing compounds mainly for electrical applications
4. Resins for laminating and for temperature-resistant varnishes and paints

5. Silicone rubber

A sixth grouping, the intermediates, is included in the discussion of the properties and uses of silicones. These compounds are organochlorosilanes rather than silicones, but a chemical reaction occurs during their application which converts them to true silicones.

D. Properties and Uses of Silicones

General. The outstanding characteristics of all silicones are heat stability(2)(5)(15)(28)(58)(87)(117), water repellency (2)(5)(58)(87)(117), and general chemical inertness(2)(5)(15)(87). In addition, all possess good electrical insulating properties (5)(15)(28)(58)(87). The basic structure of alternating silicon and oxygen atoms (Si-O-Si-O-, etc.) is responsible for the heat stability, electrical properties, and chemical inertness peculiar to these compounds(5)(15)(27)(87); while the water-repellent properties, plasticity, and similarity in other respects to organic compounds are due to the presence of organic groups attached to the silicon atoms(5)(22)(87)(117). Many silicones also possess excellent low-temperature characteristics, undergoing only very small changes in their properties at reduced temperatures.

Silicones extend the range of service temperatures considerably beyond the limits imposed by conventional organic compounds intended for similar uses(5)(58)(87)(117) because of their stability under "drastic thermal and chemical conditions"(27). They can now be made to fit predetermined specifications(28), depending on their eventual use.

For the above reasons it is likely that the silicones, in general, will find increasing use in chemical engineering applications such as temperature-resistant paints, valve greases, heat-resistant gaskets, anti-foam agents, and many others(22).

Fluids. The outstanding property of the silicone fluids is their exceptionally low rate of viscosity change over a wide temperature range(2)(5)(8)(14)(15)(21)(23)(40)(46)(87)(117). They are manufactured in a wide range of viscosities. The following actual and suggested uses illustrate their versatility:

1. Damping fluids(5)(15)(21)(23)(87)(117)
2. Hydraulic fluids(5)(23)(87)(117)
3. Liquid dielectrics(5)(15)(21)(46)(87)
4. Foam inhibitors(5)(21)(23)(87)(117)(131)
5. Waterproofing agents(5)(15)(77)(87)
6. Special lubricants(5)(40)(46)(87)(117)
7. Gage fluids(15)
8. Dashpot liquids(15)(21)
9. Impregnants for asbestos materials(15)
10. Mold release agents(15)(23)(87)(117)(131)
11. Impregnated paper raincoats(77)
12. Floating dry flies in fast water for fishing(77)
13. Heat transfer media(87)

14. High temperature baths(87)
15. Thermal expansion fluids(87)
16. High vacuum diffusion pump oils(87)(131)

The literature contains considerable detailed information on the chemical and physical properties and uses of the fluids(2)(5)(8)(11)(14)(15)(21)(23)(40)(43)(52)(77)(87)(97)(117)(131).

Lubricants and Greases. The silicone lubricants and greases are manufactured for use at high and low temperatures(5)(11)(21)(24)(58)(131). Some uses of the lubricants and greases are:

1. Stopcock and plugcock lubricants(11)(21)(24)(58)
2. Valve lubricants(11)(87)
3. Lubricant for glass and ceramic cocks(11)
4. Electrical machine lubricants(5)(21)(28)(131)
5. Ball bearing lubricants(24)(52)
6. Journal lubricant(24)

Considerable test data on silicone lubricants are available in an article by Kauppi and Pedersen(52). They are rated variously as being suitable for use over a temperature range from -170° to 500 °F.(2)(11)(19)(21)(87)(131). Other data on these compounds are available in the literature(2)(5)(11)(19)(21)(24)(28)(58)(87)(117)(131).

Electrical Sealing Compounds. Some silicones in paste form are used as electrical sealing compounds for spark plug wells, magneto connections, and radio connections(19)(21)(25)(52)(58)(87)(117). They were particularly successful in military and naval aircraft ignition systems during the past war(21)(52)(58)(87)(117). Arcing and corona resistance is said to be excellent(21)(25).

There is not too much information available on the sealing compounds as such. They have apparently been classified by many authors with the silicone greases.

Elastomers. A recent development in the field of silicones are the elastomers(6)(13). They are finding a great variety of uses: molding, extruding, coating, and laminating stocks are on the market(6)(87). Many applications have been developed for these stocks:

1. Gasket lamination(6)(13)(27)(52)(58)(87)(117)(131)
2. Fabrication of bushings and diaphragms(6)(52)
3. Electrical insulation(6)(27)(72)(87)(117)(131)
4. Tubing(6)(131)
5. Protective coatings(6)(26)(117)(131)
6. Printing rolls(6)(117)
7. Garden hose, gloves, golf balls, and other consumer uses(6)

The types of elastomers now available are not equal to natural and synthetic rubbers in tensile strength, shearing resistance, and abrasion resistance(6)(13)(87)(117). Resistance to compression set, however, is considerably better than that of the natural and synthetic rubbers(13)(131). The deficient properties are constantly being improved(6).

Other information on the elastomers is available from many sources(2)(6)(13)(21)(26)(27)(40)(52)(58)(72)(87)(98)(117)(131).

Resins. Some of the most spectacular successes among the silicone products have been the resins. They are manufactured in great variety for a wide range of uses, the principal of which is for electrical insulation(1)(2)(3)(5)(7)(9)(11)(12)(14)(15)(16)(17)(19)(21)(25)(27)(28)(29)(40)(48)(49)(50)(51)(52)(58)(77)(78)(85)(87)(88)(90)(103)(104)(106)(107)(117)(121)(131)(132). Their success in this application can best be measured by a statement of some of the findings. The operating temperatures permissible for electric motors insulated with silicone-impregnated materials is very high compared to motors insulated with conventional organic substances, because of the high heat-stability of the silicones(1)(2)(3)(5)(11)(21)(28)(49)(51)(78)(117). This property and their water-repellency, general chemical inertness, and excellent insulating properties can be utilized in some of the following ways:

1. To permit higher operating temperatures(21)(52)(58)
2. To permit higher ambient temperatures(16)(28)
3. To permit higher ambient humidities(16)(28)
4. To eliminate fire hazard from insulation failure (21)(27)(52)(58)
5. To lessen the possibilities of odor of burning insulation and toxic vapors, and thus promote safety(58)
6. To provide increased service life of insulation(16)(28)(58)

7. To provide greater protection against overload temperatures(21)(52)

8. To permit a reduction in weight and size of electrical equipment where operating temperatures may be increased(16)(21)(28)(52)

The Westinghouse Corporation has published test data(11)(17)(40) showing that as much as fifty per cent reduction in weight is possible in electrical equipment where design limitations are based on insulating temperatures by using silicone insulating varnishes. Silicone-insulated machines have been demonstrated to have outstanding moisture resistance(3)(5)(21)(49)(77)(87)(106), and this property is maintained under severe conditions over a long period of time(49)(77). Kauppi, et al.(48), call the results of the tests "remarkable", although they are not yet complete.

The enthusiasm about the silicone insulating resins is widespread. DeKiep, et al.(28), say, "The advent of silicones is an important milestone in insulation development". Moses(78) states that "unquestionably the new silicone resins constitute one of the greatest advances made in electrical insulations". The latter statement is somewhat broad, but it is nevertheless evident that insulation will continue to be one of the major uses for silicone products.

Silicone resins are available in several forms other than insulating materials. They are manufactured as thermosetting or laminating resins, and coating resins(5)(8)(12)(14)(21)(25)(40)(47)

(52)(85)(87)(88)(90)(103)(104)(106)(107)(117)(131), and are used as lens cement(5); bonding agents in the fabrication of glass fabric(5)(14)(21)(58), asbestos(21)(58), and mica(58) laminations; vehicles for paints and enamels(5)(117) which have high resistance to heat(5)(58)(117), oxidation(5)(58), ultraviolet rays(5), ozone (58), withstand severe blows without chipping, and do not yellow with age; impregnants for kraft paper used in condensers(14); and for bonding glass and ceramic surfaces(117). The paints and varnishes are used for protective coatings on furnace fronts, exhaust stacks, and the like(25)(52)(131).

The use of silicone resins in molding is still experimental (14).

Intermediates. As an example of applications of organosilicon intermediates, the organochlorosilanes, which are intermediates in the production of organosiloxane polymers, are used to apply water-repellent films to a variety of materials(14)(15)(79)(99). This interesting and unexpected development has been used experimentally to waterproof glass, paper, cotton surfaces, ceramic materials, wood, wool, silk, and leather(14)(79)(99). When used to coat radio ceramic coils, these materials are said to be six times as effective as conventional wax coatings in overcoming moisture of condensation(14).

The surfaces of materials to be treated usually contain some moisture which hydrolyzes the treating compound, usually a methylchlorosilane, to form the corresponding silanol. The silanol immediately condenses chemically to form a methyl silicone polymer which adheres tightly to the treated surface in the form of a film which is water-repellent and chemically stable(14)(79)(99).

Rochow(99) gives considerable information on the chemical and physical properties of the water-repellent films, and Norton (79) has published test data on silicone films applied in the manner described to a number of materials, illustrating their effectiveness.

E. Chemistry of Silicon and Its Organic Compounds

Silicon. "In its chemical behavior, silicon is usually tetracovalent"(91). Silicon, like carbon, remains tetracovalent in its organic compounds, but because it is electropositive and has a maximum covalency of six, reactions may occur under some conditions which are not analogous to carbon under the same conditions (91). Another difference which might account for many divergencies in the carbon and silicon series of compounds is the fact that the four valence bonds are symmetrically distributed in carbon, but not in silicon(125). A comparison between silicon and carbon chemistry shows no close parallel; silicon resembles boron and germanium as closely as it does carbon(91).

Stability of Silicon Compounds. One outstanding characteristic of silicon is its tendency to form the oxide(91), due to the great strength of the silicon-oxygen bond as compared with other silicon linkages(91)(117). A comparison between the heats of formation of silicon dioxide and carbon dioxide, as well as other silicon compounds, will illustrate this. The following heats of formation are given in the literature(37)(91)(128):

SiO_2 - 198 to 201 kcal/mole (different crystal forms)

CO_2 - 98 kcal/mole (gas)

SiF_4 - 377 kcal/mole (gas)

$SiCl_4$ - 155 kcal/mole (liquid)

$SiBr_4$ - 96.5 kcal/mole (liquid)

SiS_2 - 33 kcal/mole (crystalline)

SiC - 1.5 kcal/mole (crystalline)

According to these data, only silicon tetrafluoride is more stable than silicon dioxide.

Properties of Organosiloxane Polymers. The high heat-stability of the organosiloxane polymers is due to their fundamental structure, the silicon-oxygen or siloxane linkage(5)(87)(117). Since the polymers of this type are fundamentally oxides of silicon, their behavior is best understood on this basis(108). An organosiloxane may be compared to the silicate minerals, which sometimes contain metal ions that satisfy some of the valence bonds of the atoms and prevent formation of the completely cross-linked structure found in pure silica. In the organosiloxanes, the organic groups act in such a manner(95)(108), but perform the dissimilar function of giving the compounds some hydrocarbon characteristics such as solubility in certain organic solvents(95), plasticity(5)(87), and water repellency(95)(117).

Size of Organosiloxane Polymer Molecules. The size of the polymer molecules is dependent on the number of hydroxyl groups available for condensation in the polymerizing silanols(86)(95). These groups, called "functional groups", are those which can condense to form a bond with another molecule(86). Rapidity of condensation varies with the size of the organic groups and the number of organic and hydroxyl groups present(95).

Linkages Found in the Organosiloxane Polymers. There are several linkages and combinations of linkages which can form the polymer structure. Chain, cyclic, and cross-linkages, or combinations of these three will form, depending on the degree of substitution of organic groups on the silicon atoms and whether the polymerizing substance is a single compound or a mixture of compounds(95). Characteristics of the final product depend on the type of linkage and the nature of the appended organic radical(2).

Organosiloxane Polymer Structure. Little is known concerning the interatomic distances and bond angles in the organosiloxane polymers. For this reason the search for better structures has been on a purely empirical basis(95).

F. Methods of Synthesizing Organosilicon Compounds

Rochow(92) lists two general types of syntheses for producing organosilicon compounds: the substitution methods and the direct method. All these methods have as their object the establishment of direct carbon-silicon bonds.

Substitution Methods(92).

1. Substitution by alkyls of zinc, mercury, and aluminum.

The following reaction illustrates this substitution:

$$2Zn(C_2H_5)_2 + SiCl_4 \dashrightarrow 2ZnCl_2 + Si(C_2H_5)_4$$

zinc diethyl	silicon tetrachloride	zinc chloride	tetraethyl-silane

Mercury has proven most satisfactory in the substitution of aromatic groups:

$$Hg(C_6H_5)_2 + SiCl_4 \dashrightarrow C_6H_5SiCl_3 + C_6H_5HgCl$$

mercury diphenyl	silicon tetrachloride	phenyltri-chlorosilane	phenyl mercuric chloride

2. Substitution by Sodium Condensation. This substitution is effected by the well-known Wurtz reaction using metallic sodium.

$$SiCl_4 + 4C_4H_9Cl + 8Na \rightarrow Si(C_4H_9)_4 + 8NaCl$$

silicon tetrachloride	butyl chloride	sodium	tetrabutyl-silane	sodium chloride

Difficulty of control makes this method suitable only for the preparation of tetra-alkylsilanes. It was used by Polis(83) who followed this reaction with another to form organochlorosilanes(84):

$$(C_6H_5)_4Si + PCl_5 \dashrightarrow (C_6H_5)_3SiCl + C_6H_5Cl + PCl_3$$

tetraphenyl-silane	phosphorous pentachloride	triphenyl-chlorosilane	chloro-benzene	phosphorous tirichloride

3. Substitution by Organomagnesium Compounds. This is the Grignard reaction. It was used independently by Dilthey(30) and Kipping in the synthesis of organosilicon compounds shortly after its discovery by Victor Grignard. Kipping and his associates, as well as most other workers on organosilicons, depended greatly on this method in later work. This is a two-stage method. The first step is the preparation of the organic magnesium halide containing the alkyl or aryl group to be substituted. The second step is a reaction such as follows:

$$2C_2H_5MgCl + SiCl_4 \longrightarrow (C_2H_5)_2SiCl_2 + 2MgCl_2$$

ethyl magnesium chloride	silicon tetrachloride	dichlorodiethylsilane	magnesium chloride

Several variations of this basic method have been used in preparing organosilicon compounds.

4. Substitution by the Absorption of Hydrocarbons. One method of this type is the absorption of hydrocarbons by silicon tetrachloride under pressure, 10 to 100 atmospheres(92), and in the presence of metal chlorides or oxychlorides as catalysts(92)(118):

$$CH_2{=}CH_2 + SiCl_4 \xrightarrow{cat.} ClCH_2{-}CH_2{-}SiCl_3$$

ethylene	silicon tetrachloride	B-chloroethyltrichlorosilane

Another method of the same general type effects absorption by passing vapors of a suitable hydro-carbon and silicon tetrachloride over a heated surface to form the organochlorosilane plus hydrogen chloride gas (76)(92). The following reaction illustrates this method:

$$C_6H_6 + SiCl_4 \longrightarrow C_6H_5SiCl_3 + HCl$$

benzene — silicon tetrachloride — phenyltrichlorosilane — hydrogen chloride

Direct Method. The second general type of synthesis is the direct method in which hydrocarbon halides, in the liquid or vapor phase, are reacted with metallic silicon with or without a catalyst to form organosilicon halides(89)(92)(109)(112)(114)(122)(123). The general reaction is(92):

$$2RX + Si \longrightarrow R_2SiX_2 \text{ (with several side reactions)}$$

hydrocarbon halide — silicon — di-(hydrocarbon)-dihalogenosilane

Silicon is usually used in the form of a porous silicon-copper mass with the copper acting as a catalyst(89)(92)(109)(112)(114). Other metals, such as nickel, platinum, silver, and antimony have been tried, but copper has proven most satisfactory(112).

Commercial Methods of Organosiloxane Polymer Production. Commercial methods of organosiloxane polymer production first produce the organosilicon halides by one of the above syntheses. After the organosilicon halides are produced, they are treated with hydrolyzing agents to replace the halogen groups with hydroxyl groups. The organohydroxysilanes (silanols) are then chemically condensed to build the high molecular weight organosiloxane polymers, except in the case of the tri-substituted silanols. Polymerization and copolymerization of the silanols give rise to an extensive variety of products(15).

Commercial Production by the Grignard Synthesis. Commercial production in the past has been entirely by the Grignard synthesis(5)(22). This process has one great advantage over others in its high degree of flexibility(100). However, there are two major drawbacks to the process(100): first, the number of steps in the process, with resulting intermediate products and by-products, and second, the dependence on silicon tetrachloride or ethyl silicate, both low in silicon content, as a source of silicon. The flow diagram on page 21 illustrates the steps in the commercial Grignard process from raw materials to finished products(15)(100).

Commercial Production by the Direct Method. Synthesis by the direct method was scheduled to be in production by the fall of 1946. This date has now been advanced to early 1948(110). The treatment of the chlorides (halides), after their production to form the polymers is the same or similar for the direct process to that used in the Grignard process. The flow diagram on page 22 illustrates the steps in the commercial direct method, using the production of a methyl silicone polymer as an example(101). The direct synthesis of the chlorosilanes is to be carried out commercially by passing hydrocarbon halides through a silicon-copper mass containing

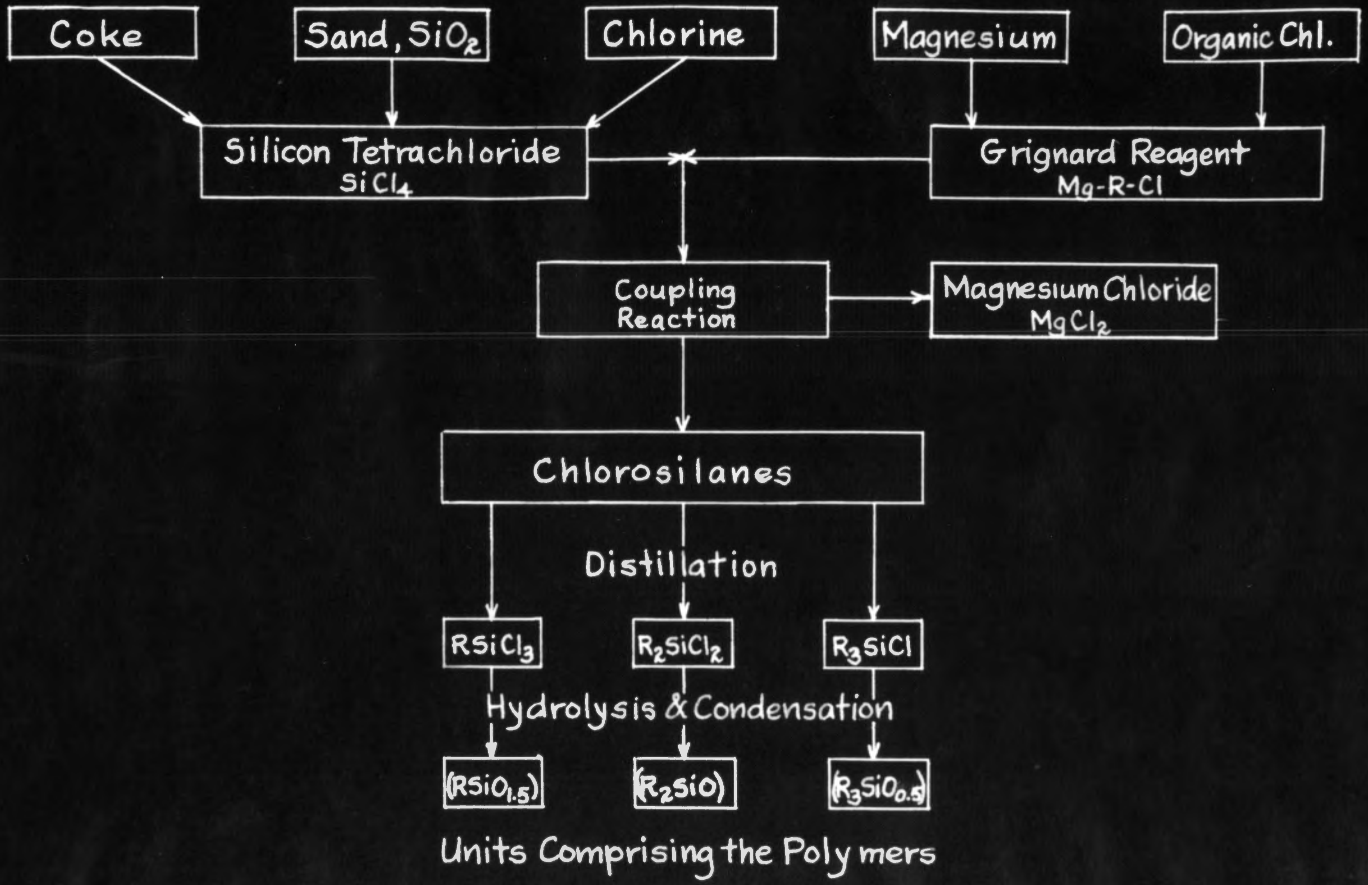

Fig. 1

Production of Silicone Polymers by the Grignard Method

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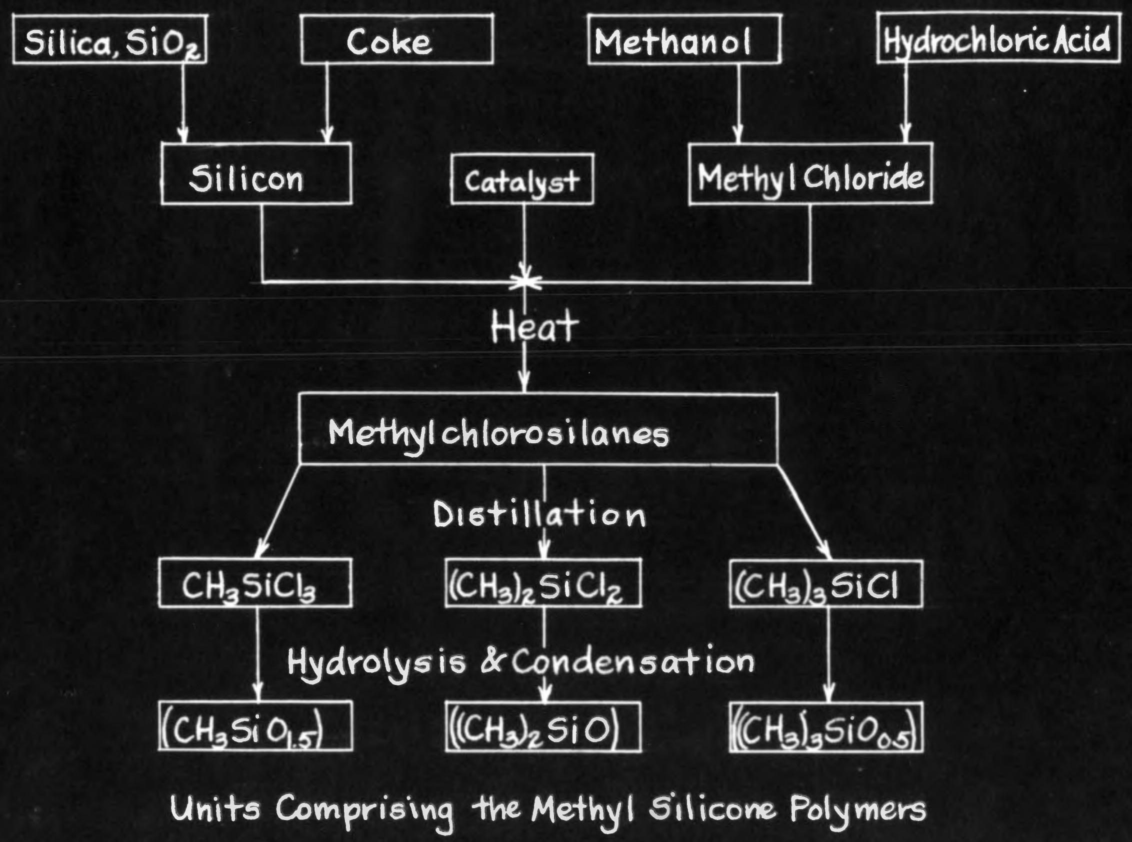

Fig. 2
Production of Silicone Polymers by the Direct Method

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100 pounds of available silicon. The mass is to be heated to 200°-250°C. and agitated. After two and one-half days of reaction, in the case of methyl chloride, using one batch of the mass, yields of methylchlorosilanes containing 70 to 90% of the available silicon are obtained. Dimethyldichlorosilane constitutes about 57% of the methylchlorosilane yield(110).

G. Nomenclature of Organosilicon Compounds

Use of the Term "Silicone". The term "silicone" was apparently first used by Wohler(134) to designate a product which he obtained by the action of concentrated hydrochloric acid on calcium silicide. The product was an oxyhydride with the approximate empirical formula $Si_3H_3O_2$. Kipping later used "silicone"(55) to desingnate the hydrolysis product of disubstituted silicon chlorides, because he thought them to be analogous to the organic ketones. This has been proven incorrect and Kipping later realized his mistake. The ketones are monomeric, while the "silicones" are always polymeric with the unit structure $-R_2-Si-O-$(96)(108). The name still persists because of long usage(108) and is now applied to all organosiloxanes.

Systems of Nomenclature. The nomenclature of the organosilicon compounds as a whole is in a state of flux. Sauer(115) lists four systems of naming them: Kipping's, Stock's, "other usage", and a proposed system. Chemical Abstracts(10) uses a system similar to Kipping's.

Kipping's System. Kipping(55) proposed that derivatives of silicon hydride (SiH_4), which he called "silicone", should receive names corresponding to those of analgous derivatives of methane. Thus:

SiH_4 - silicane
SiH_3OH - silicanol
$SiPh_3OH$ - triphenylsilicanol
$SiH_2(OH)_2$ - silicanediol

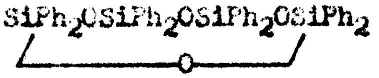
Kipping first used the term "cilicane" to "show the analogy with the corresponding derivatives of methane"(54) in the compound tetraphenylsilicane, formerly called silicon tetraphenyl.

Stock's System. Stock's naming(124) is based on the term "silane" in this manner:

SiH_4 - monosilane
Si_2H_6 - disilane

He also proposed the term "siloxane"(126) to refer to substances containing the -Si-O-Si-O- system and to specify the number of silicon and oxygen atoms in such terms as "disiloxane" and "disildioxane". Using this system the following names are given:

$(SiCl_3)_2O$ - Hexachlorodisiloxane



$\underbrace{SiPh_2OSiPh_2OSiPh_2OSiPh_2}_{O}$ - octaphenyltetrasiltetroxane

Chemical Abstracts System. Chemical Abstracts(10) uses "silicane" as the base word in naming organic silicon compounds:

SiH_4 - silicane
$ClSi(C_2H_5)_3$ - chlorotriethylsilicane

"Silico" is used to denote replacement of carbon by silicon:

H_3SiSiH_3 - disilicoethane

$H_3SiSiH_2SiH_3$ - trisilicopropane

These two compounds are not organosilicons, however, since there are no direct carbon-silicon linkages.

"Other Usage". The "other usage" given by Sauer(115) is a collection of miscellaneous terms applied to individual compounds and is in no particular order.

Sauer's Proposed System. Sauer's proposed system(115) is used by Rochow(91)(108) in naming organosilicon compounds. The "silane" root is used and "siloxane" is used to designate dehydration products of the silanols. This system of nomenclature will be followed in this thesis. The following rules are given for naming:

1. Organosilicon compounds of the general formula $R(SiR_2)_nSiR_3$, where R may be an organic radical, H, X, or alkoxy or aroxy group, and n is 0, 1, 2..., are named as silane derivatives.

2. Organosilicon compounds containing -Si-O-Si- linkages are named as siloxane derivatives.

3. Organosilicon ring compounds of the general formula $(R_2SiO)_n$, where R has some significance as in 1. (above), and n is 2, 3, 4..., are named as cyclosiloxanes.

4. In organosilicon compounds containing one or more OH groups attached to the silicon atoms the name is

formed by adding the suffices -ol, -diol, -triol, etc. (corresponding to the number of OH groups per molecule) to the proper root name.

5. Organosilicon compounds of the type formula $R(SiR_2NH)_nSiR_3$, where R has some significance as in 1. (above), and n is 1, 2, 3..., are named as silazine derivatives.

III. EXPERIMENTAL

A. Purpose of Investigation

The purpose of this investigation was to develop a process for the production of phenylchlorosilanes by the phenyl substitution of silicon tetrachloride at high temperatures.

B. Plan of Investigation

Construction of Apparatus. A gas-fired combustion furnace was constructed to heat combustion tubes 1-1/2" to 1-7/8" O. D. A phenyl substitution apparatus was assembled, consisting of a feed vessel, feed orifice, manometer to measure feed pressure, appropriate shutoff and control valves, carbon dioxide feed pressure system, combustion tube packed with quartz, product condensers, collecting vessels, and the combustion furnace. A thermocouple was installed in the combustion tube and connected to a pyrometer to measure the temperature of the phenyl substitution reaction.

Phenyl Substitution of Silicon Tetrachloride. An investigation was made of the process in which silicon tetrachloride and benzene are reacted at red heat in quartz tubes to form phenylchlorosilanes(76). A mixture of silicon tetrachloride and benzene in the gaseous phase in the molar ratio of 2:1, such as was held in a previous investigation of the method(76), was passed through a quartz-packed combustion tube at space velocities in the range 100 to 3500 liters gas per liter of reaction space per hour, calculated at the temperature of the reaction space of the combustion tube. The tube was heated to temperatures in the range 650°C. to 900°C., within the range of "red heat" used in the previous investigation(76), and was at approximately atmospheric pressure (713±7mm. Hg). The products of this reaction were condensed and collected. No investigation was made of any catalysts.

Separation of the Products of the Phenyl Substitution of Silicon Tetrachloride. The products of the phenyl substitution of silicon tetrachloride were separated by batch distillation at atmospheric pressure. Fractions were collected over the boiling ranges of silicon tetrachloride and benzene, intermediate boiling compounds, phenyltrichlorosilane, and diphenyl. Refer to Table I, page 29, for boiling points of some of the possible products.

Analysis of the Products. Analysis for chlorine was made of the fractions collected at the boiling point of phenyltrichlorosilane. Weighed samples of the fractions were hydrolyzed with aqueous sodium hydroxide; the excess alkali was neutralized with dilute sulfuric acid and a standard chloride analysis was made of the solution. From the chloride determination, knowing the theoretical chlorine content of phenyltrichlorosilane and assumihg all hydrolyzable chlorine in the fractions to be present in the compound, the amount of phenyltrichlorosilane in the fractions was calculated.

TABLE I

SOME PHYSICAL PROPERTIES OF SOME OF THE POSSIBLE PRODUCTS OF THE PHENYL SUBSTITUTION OF SILICON TETRACHLORIDE BY THE MILLER AND SCHREIBER PATENT METHOD(76) USED IN THIS INVESTIGATION

Substitution Products	Melting Point, °C.	Boiling Point, °C.
Tetraphenylsilane(94)	233	530
Triphenylchlorosilane(94)	111	365
Diphenyldichlorosilane(94)	-22	303
Phenyltrichlorosilane(94)	-	199
Unreacted Reactants		
Silicon tetrachloride(59)	-70	57.6
Benzene(60)	5.4-5.5	80.1
Benzene Pyrolysis Products		
Diphenyl(63)	69-71	254.9
1,3-diphenylbenzene(41)	86-87	363
1,4-diphenylbenzene(43)	213	427#
Triphenylene(44)	198.5	-
1,3,5-triphenylbenzene(42)	170	-
By-products		
Chlorobenzene(61)	-45.2	132.1
Dichlorobenzenes(62)	-24.8, 53	172-179
Trichlorobenzenes(66)	-63.5	208.5-219
Tetrachlorobenzenes(64)	46-140	240-254
Impurities from Reactants		
Toluene(65)	-95	110.8
Xylenes(67)	-47.4, 13.2	138.5-144

Sublimes

C. Materials

The following materials were required for the construction of the phenyl substitution apparatus:

Insulating Fire Brick. M-26, 2-1/2" x 4-1/2" x 9". Manufactured by the Ludowici-Celadon Co., Chicago, Illinois. Used in the construction of the gas-fired combustion furnace.

Mortar, Ready-Mixed. M-5. Manufactured by the Ludowici-Celadon Co., Chicago, Illinois. Used as sealing material in constructing the gas-fired combustion furnace.

Asbestos Board. One piece, 19" x 28" x 3/4". Used as insulation under the gas-fired combustion furnace.

Strap Iron. 3/4" x 1/8". Used in construction of gas-fired combustion furnace.

Angle Iron. 3/4" x 3/4" x 1/8". Used in constructing the gas-fired combustion furnace.

Carriage Bolts. 3/16" x 4". Used in constructing the gas-fired combustion furnace.

Machine Screws. 3/16"-32. Used in constructing the gas-fired combustion furnace.

Steel Rod. 1/4" mild steel. Used in constructing the gas-fired combustion furnace.

Pipe and Fittings. Standard black iron. Used in the construction of the burner assembly, gas-air mixing chamber, secondary air inlet pipes, and adapter for combustion tube metal connector-thermocouple mount connection.

Quantity	Size	Item
7	1/8"	elbow, std. (90°)
4	1/8"	tee
1	1/2"	tee
1	1/8"	union
2	3/8" x 1/8"	bushing
1	1/2" x 3/8"	bushing
1	1/2" x 1/8"	bushing
1	1"	coupling
1	3/8" x 1/8"	coupling, reducing
1	1/2" x 3/8"	coupling, reducing
1	3/8"	plug
4	1/8"	nipple, close
2	1/8"	nipple, 1-1/2"
4 in.	1/2"	pipe
5 ft.	1/8"	pipe

Tubing, Pyrex Glass. Standard wall, O.D. 5mm, 9mm, and 19mm. Used in constructing feed lines, exit lines, feed orifice, manometer, manometer connections, and other non-standard Pyrex glass portions of phenyl substitution apparatus.

Filter Plate. "Filtros" silica filtering material; grade "B". Manufactured by Filtros, Inc., Rochester, N.Y. Used to make filter cover for the feed line intake in the feed vessel.

Plaster of Paris. Dental grade. "Druggist" brand. Distributed by The Penslar Co., Inc., Detroit, Mich. Used to seal the combustion tube metal connectors to the combustion tube.

Acetic Acid, 2%. Made from glacial acetic acid and tap water.

Acid Acetic Glacial
CH_3COOH M.W. 60.05
Lot No. 82646
J. T. Baker Chemical Co.
Phillipsburg, N. J.

Used to make up Plaster of Paris for sealing combustion tube metal connectors to combustion tubes.

Quartz. Crystalline; crushed and screened on 1/4", through 1/2". Used as packing material in the combustion tube.

Tubing, Rubber. 5/16" O.D., heavy wall, black. Used to make connections between various portions of the phenyl substitution apparatus.

Litharge-Glycerin Cement. Used to seal metal to metal connections in the feed section of the phenyl substitution apparatus.

The following materials were used in the phenyl substitution of silicon tetrachloride:

Silicon Tetrachloride. Purchased from E. H. Sargent & Co., Chicago, Illinois; and Fisher Scientific Co., Pittsburgh, Pennsylvania. Technical grade; sp.gr. 1.480 to 1.490 at 20/15.5°C.; free chlorine not more than 0.01%; titanium tetrachloride not more than

0.10%; silicon tetrachloride not less than 99.50%. Used as a reactant in making phenylchlorosilanes.

Benzene. Purchased from E. H. Sargent & Co., Chicago, Illinois. Technical grade; impurities-toluene, xylene, tarry substances. Used as reactant in making phenylchlorosilanes.

Carbon Dioxide. One cylinder. Manufactured by the Southern Oxygen Co., Kingsport, Tennessee. Used to flush air from feed lines, combustion tube, exit lines, and condensers; and to maintain pressure in the feed vessel during phenyl substitution runs.

The following materials were used in distilling the products of the phenyl substitution reaction:

Sand. Used in the sand bath for heating the distilling flasks.

Quartz. Crystalline, through 8 mesh, on 20 mesh (U. S. Std.). Used in the distilling flasks to prevent "bumping".

The following materials were used in making chloride analyses of the phenylchlorosilanes:

Silver Nitrate.

Baker & Adamson
Meets A.C.S. Specifications
Silver Nitrate, Crystal
Reagent $AgNO_3$ Code 2179
General Chemical Company
New York, N.Y., U.S.A.

Used to make standard solution for titrating chlorides.

Sodium Chloride.

Sodium Chloride, C.P. Fine
1 lb. Crystal NaCl M.W. 58.45
J.T. Baker Chemical Co.
Phillipsburg, New Jersey

Used to make standard solution for the standardization of silver nitrate solution.

Sodium Chromate.

Phipps and Bird, Inc.
Richmond, Virginia

Used to make indicator solution for chloride tetrations.

Sodium Hydroxide.

Baker & Adamson
Sodium Hydroxide, 76%
Lot No. C108J,Code 2256
General Chemical Company
New York, N.Y., U.S.A.

Used to make 5% aqueous solution for the hydrolysis of phenylchlorosilanes prior to the chloride tetrations.

Sulfuric Acid. Conc., 98%, C.P.

Baker & Adamson
Meets A.C.S. Specifications
Lot No. E-207018 Reagent
General Chemical Company

New York, N.Y., U.S.A.

Used to make 5% solution (by vol.) for neutralization of excess sodium hydroxide from the hydrolysis of phenylchlorosilanes.

Test Papers. "Hydrion A" and "Hydrion B" (pH range 1-11) wide range test paper. For rapid determination of approx. pH.

Micro Essential Laboratory
Brooklyn, New York

Used to determine the neutral point (pH 7) in neutralizing excess sodium hydroxide from the hydrolysis of phenylchlorosilanes.

Calcium Chloride.

Calcium Chloride, Purif., Anhyd., Granular
Lot No. 11242
J.T. Baker Chemical Co.
Phillipsburg, New Jersey

Used as a drying agent in the desiccator, and in the drying tube in the carbon dioxide line to the feed section of the phenyl substitution apparatus.

D. Apparatus

The following apparatus was used in the phenyl substitution apparatus assembly:

Flask, Three-Neck, Woulff. 2000 ml., Pyrex glass. Used as a feed vessel for the benzene-silicon tetrachloride reaction mixture.

Filter Cover. Made of "Filtros" silica filtering material. 1/2" dia., 3/8" thick, depression 9mm dia. by 3mm deep drilled in one face. Used as a cover on the feed line intake in the feed vessel.

Feed Orifice. Made of a length of 5mm O.D. Pyrex glass tubing, drawn out to form a capillary, sealed with both ends open into a length of 9mm O.D. Pyrex glass tubing as a reinforcement. Overall length- 3"; capillary length- 1-1/4". Used to restrict feed flow and as a means of measuring feed pressure.

Stopcock. Plug opening 3mm, 9mm O.D. connections, Pyrex glass. Used as shutoff valve in the feed line.

Stopcock. Plug opening 1mm, 6mm O.D. connections, Pyrex glass. Used as gas bleedoff valve in the feed line.

Connectors, Metal, Combustion Tube. Brass, for combustion tubes 1-1/4" to 1-1/2" O.D.; size B. Used to connect combustion (reaction) tube with the feed and exit lines; used as a point of entry for temperature measuring equipment at the feed end of the combustion tube.

Combustion Tube. Fused silica; "Vitreosil"; glazed inside and outside; 1-1/2" O.D., 1-1/8" I.D., 30" long; made in England. Used as a reaction tube in the phenyl substitution of silicon tetrachloride.

Combustion Tube. Fused silica; "Vitreosil"; glazed inside, sand-finished outside; 1-7/8" O.D., 1-1/2" I.D., 30" long; made in England. Used as a reaction tube in the phenyl substitution of silicon tetrachloride.

Adapter. Constructed from a bronze valve bonnet to which was brazed a truncated cone made of sheet copper. At the small end of the cone a 4" length of 5/16" O.D. copper tubing was brazed. Used to connect the combustion tube metal connector at the exit end of the combustion tube to the steam-cooled condenser.

Condensers, Liebig. Pyrex glass, 250mm jacket. Used to condense the products of the phenyl substitution reaction.

Heater, Steam (see drawing 5, page 50). Constructed from a section of an oil can, 6-1/2" dia. and 5" high, at one end of which was soldered a cone of galvanized iron, 3" high. Four-inch lengths of 1/4" galvanized pipe were soldered to openings 1-1/2" below the top of the can section and at the small end of the cone. A shield was made of two pieces of galvanized sheet iron cut to fit around the neck of a 500ml Erlenmeyer flask and inside the heater, just above the pipe in the can section. Used to maintain the collecting vessel for the steam-cooled condenser at temperatures between 95° and 100°C.

Water Bath (see drawing 5, page 50). Constructed from a can 6" dia., 4" high, and open at one end, to which were brazed two 2" lengths of 1/4" galvanized pipe. One was centered 1/2" below the top and the other 1/2" above the bottom of the can. Used to maintain the collecting vessel for the water-cooled condenser at temperatures of 20°C. or below.

Manometer. Water-filled; maximum reading 30 in.; scale graduations 1/20". Constructed from a length of 9mm O.D. Pyrex glass tubing bent into a U-shape and mounted on a suitable length of board. Used to measure pressure differences across the feed orifice.

Pinch Clamps. Screw type. Used as valves in rubber tubing portions of feed section.

Pressure Regulator. Bastian-Blessing Co., Chicago, Illinois. Russ-Knight. Gage graduated 0-300 psi. in 5 psi. increments. Used to control pressure and flow of carbon dioxide.

Adapter. Constructed from a bronze valve bonnet and a 1" standard black iron coupling, brazed together. Used to connect combustion tube metal connector and thermocouple mount.

Thermocouples. Chromel-Alumel; #14 gauge; 18" and 30" long; stainless steel wells; 1" S.T.P. mounting threads. Brown Instrument Co., Philadelphia, Penn. Used to determine temperature in the combustion (reaction) tube.

Pyrometer. Serial no. 238228; surface mounting type; 105X1P series; scale 0 to 2000°F. in 20° increments. Brown Instrument Co., Philadelphia, Penn. Used to determine temperature in the combustion (reaction) tube.

Switch. D.P.D.T.; key. Brown Instrument Co., Phildelphia, Penn. Used to control pyrometer-thermocouple connection.

Extension Lead Wire. #5W2B13 (AAR2-14); asbestos insulation, yellow; fur use only with M.A. (chromel-alumel) thermocouples; maximum ambient temperature 400°F. Brown Instrument Co., Philadelphia, Penn. Used to connect thermocouple, switch, and pyrometer.

Drying Tube. Calcium chloride filled. Made from a four-inch length of 19mm O.D. Pyrex glass tubing. Used to remove residual moisture from the carbon dioxide prior to its entry into the feed section.

Gas-Fired Combustion Furnace. A gas-fired combustion furnace was constructed to heat the combustion (reaction) tube in the phenyl substitution apparatus. Steps in the construction and assembly of the parts are given below.

Gas-Air Mixing Chamber. A gas-air mixing chamber (see drawing 1, page 41) was constructed of standard black iron pipe and fittings to provide gas-air mixtures for the burner assembly.

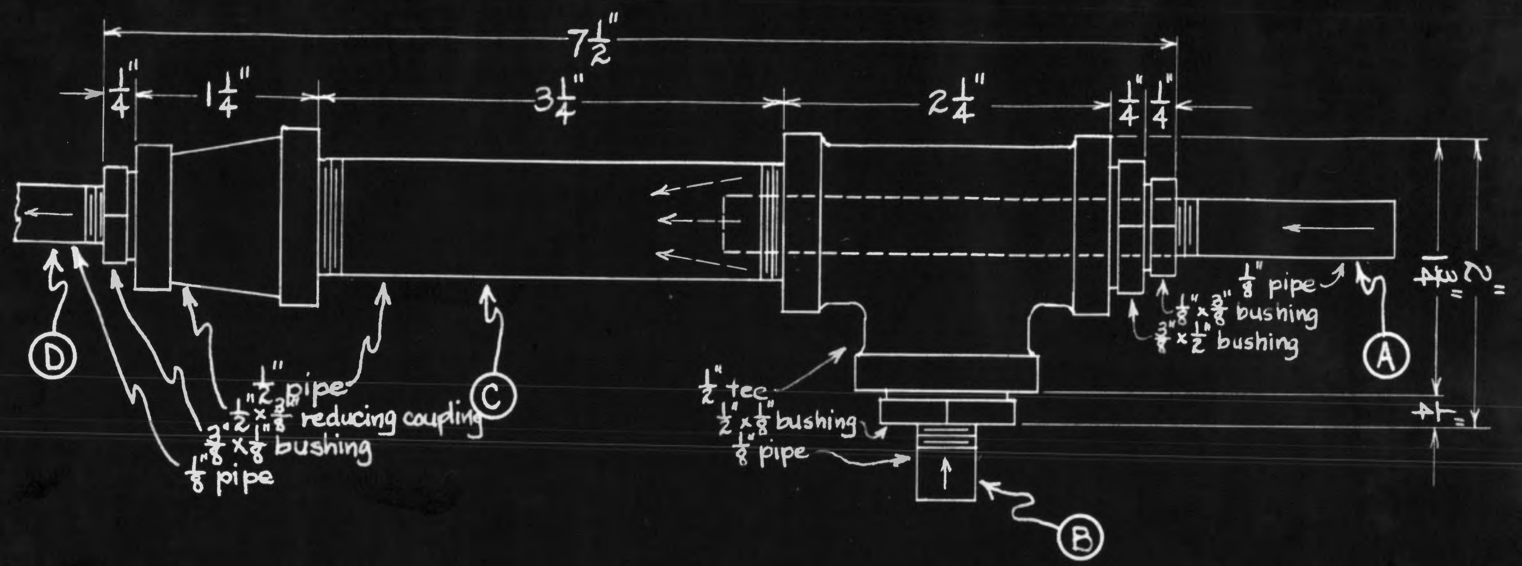
Burner Assembly. A burner assembly (see drawing 2, page 42) was constructed chiefly of standard black iron pipe and fittings. It consisted of three burners, spaced 3" center-to-center along an inlet pipe, on alternate sides of the inlet pipe. The burners were 1-1/2" center-to-center from the inlet pipe. A footing, made of 3/4" x 1/8" strap iron, was brazed to the 3/8" x 1/8" reducing coupling at the end of the inlet pipe to provide stability for the burner assembly inside the furnace. A brass collar was put on the end of each burner to fit a standard Bunsen burner fishtail.

The burner was revised uring the experimental runs as follows (see drawing 2a, page 43): the brass collars were removed from the burners and burner heads of 1/8" standard black iron pipe were brazed in their place. The burner head on the two-burner side was 9" long, centered between the burner head inlet pipes, and drilled 3/32" every 1/2" along the top except over the inlet pipes. The ends of the burner head were brazed shut. The burner head on the one-burner side was 4-1/2" long and centered on the burner head inlet pipe. It was the same in other respects as the two-burner head. The burner was further revised to include a third burner head, 7" long, centered between the other two. A hole 3/8" in diameter was drilled in the top of the middle tee of the inlet pipe (refer to drawing 2a) and a 2-3/4" length of 1/8" standard black iron pipe was brazed over the hole. The 7" burner head was brazed to the top of this pipe, completing the arrangement.

Furnace Proper. The furnace proper (see drawings 3a and 3b, pages 44 and 45) was constructed of M-26 insulating fire brick, each 2-1/2" x 4-1/2" x 9", sealed with M-5 ready-mixed mortar, as follows:

Two courses of brick were laid four rows wide with the bricks on the 4-1/2" x 9" side. Outside dimensions of each layer were 18-1/2" x 26-1/2" x 9". The rows were staggered to break mortar joints. These two courses formed the bottom of the furnace. For the sides, two more courses of brick were laid on the bottom courses with the bricks on the 2-1/2" x 9" side. Two rows of bricks were laid in each course with the outside of the bottom courses, leaving a chamber 8-1/2" x 8-1/2" x 16-1/2" open inside the furnace. The rows were again staggered to break mortar joints.

The bottom-most course was held in place by a binder of 3/4" x 3/4" x 1/8" angle iron, bent to conform to the outside dimensions of the course and tightened by a carriage bolt. The other three courses were held in place by binders of 3/4" x 1/8" strap iron, bent to conform to the outside dimensions of the courses and tightened by carriage bolts. Each binder was drilled and tapped for 3/16"-32 machine screws at points 7" from the ends on each 26" side and



Side Elevation

Legend

Ⓐ Gas inlet
Ⓑ Compressed air inlet
Ⓒ Mixing Chamber
Ⓓ Inlet to burner assembly

All pipe and fittings used in this device are standard black iron.

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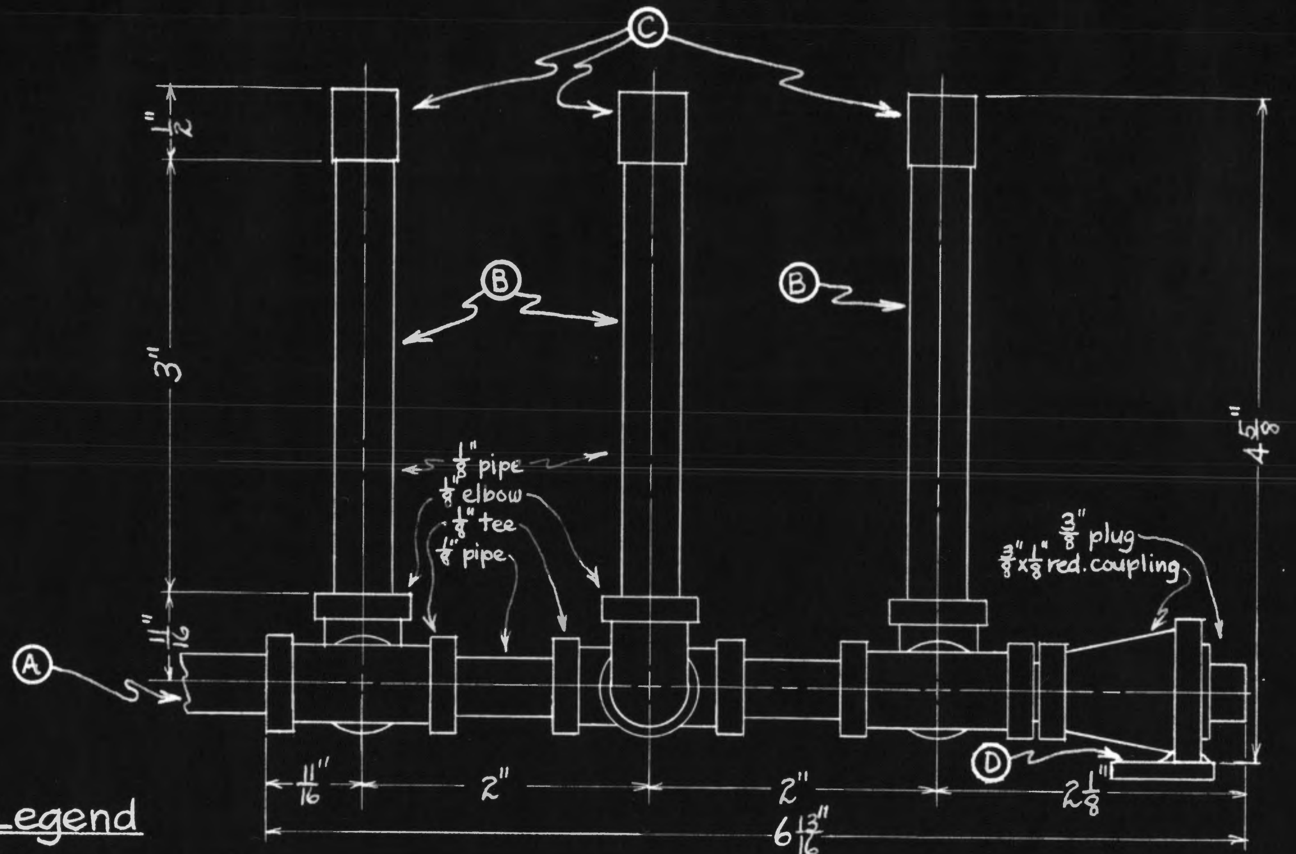
Virginia Polytechnic Institute
Blacksburg, Virginia

Drawing of
GAS-AIR MIXING DEVICE

Scale: 9"=1'-0"
Drawn by : W.A.G.,Jr. Date: 4/15/47
Checked by : W.A.G.,Jr. Date: 4/15/47
Approved by: F.W.B. Date: 4/16/47

Case: 47
File : 539
Dwng : 1



Legend

Ⓐ Inlet from gas-air mixing device
Ⓑ Burner pipes
Ⓒ Brass collars
Ⓓ Footing

Side Elevation

All pipe and fittings used in this device are std. black iron

Centers of burner pipes are offset $1\frac{1}{2}''$ from center of inlet pipe

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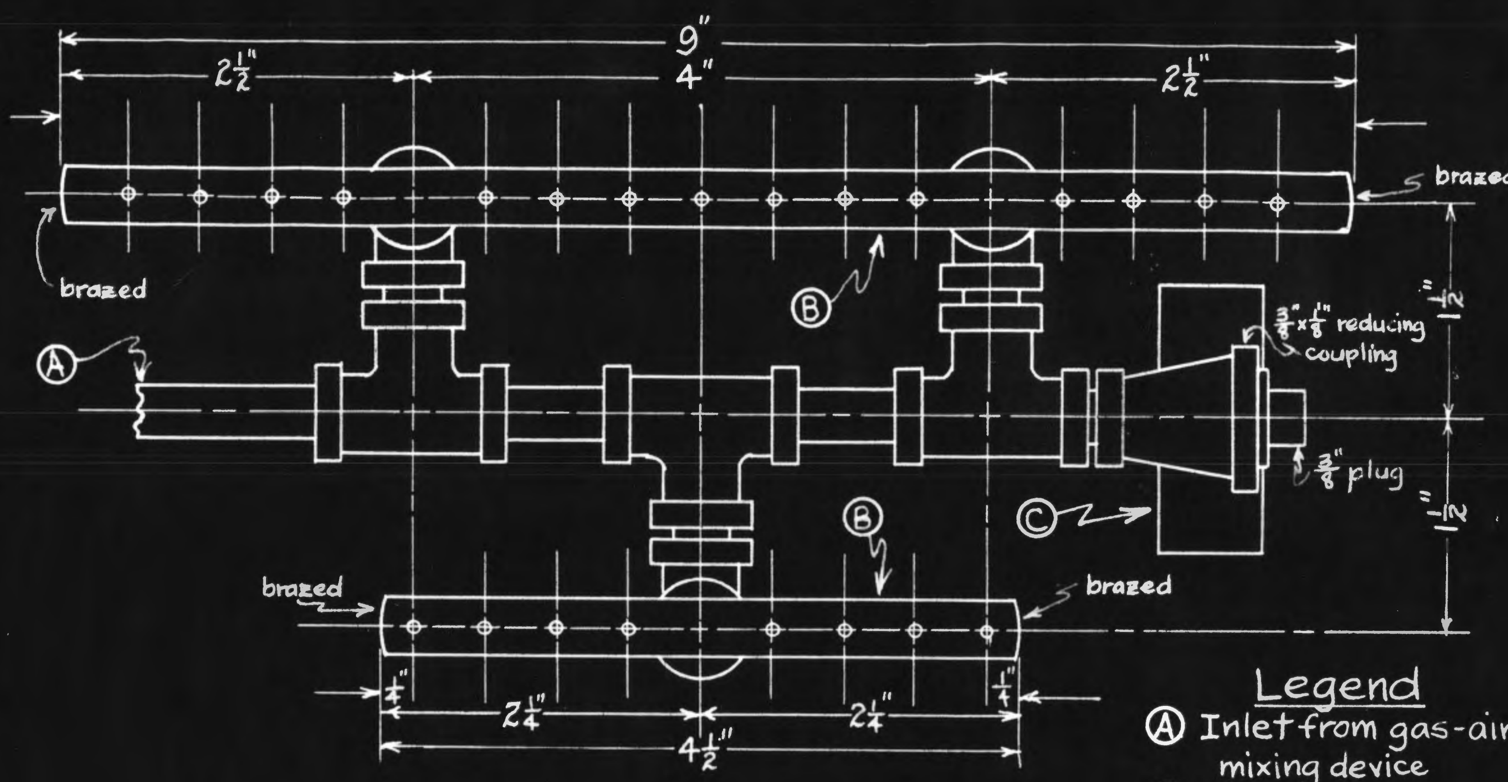
Blacksburg, Virginia

Drawing of
BURNER ASSEMBLY

Scale: 9"=1'-0"
Drawn by : W.A.G., Jr. Date: 4/14/47
Checked by : W.A.G., Jr. Date: 4/19/47
Approved by: F.W.B. Date: 5/7/47

Case: 47
File: 539
Dwg: 2



Plan View

All pipe and fittings used in this device are ⅛" standard
black iron, except as noted.

Holes in burner heads are drilled $\frac{3}{32}$", ½" on centers

Burner Heads are brazed to tops of burner pipes

Legend

Ⓐ Inlet from gas-air mixing device

Ⓑ Burner heads

Ⓒ Footing

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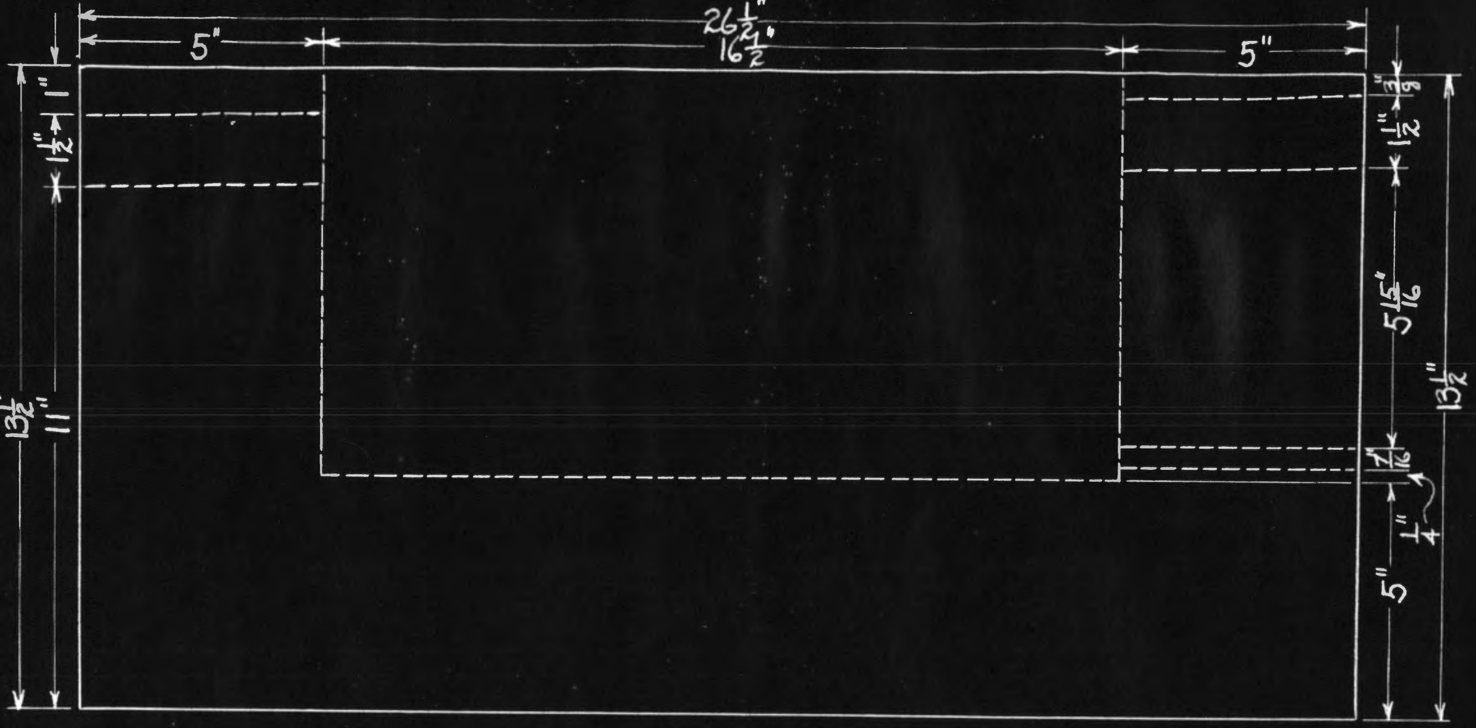
Drawing of
BURNER ASSEMBLY REVISION

Scale: 9"=1'-0"
Drawn by : W.A.G.,Jr. Date: 9/6/47
Checked by : W.A.G.,Jr. Date: 9/7/47
Approved by: Date: 9/8/47

Case : 47
File : 539
Dwng: 2a



Side Elevation

Outline of bricks not shown
Binder straps not shown

Material of construction: M-26 insulating fire brick, sealed with
M-5 ready-mixed mortar

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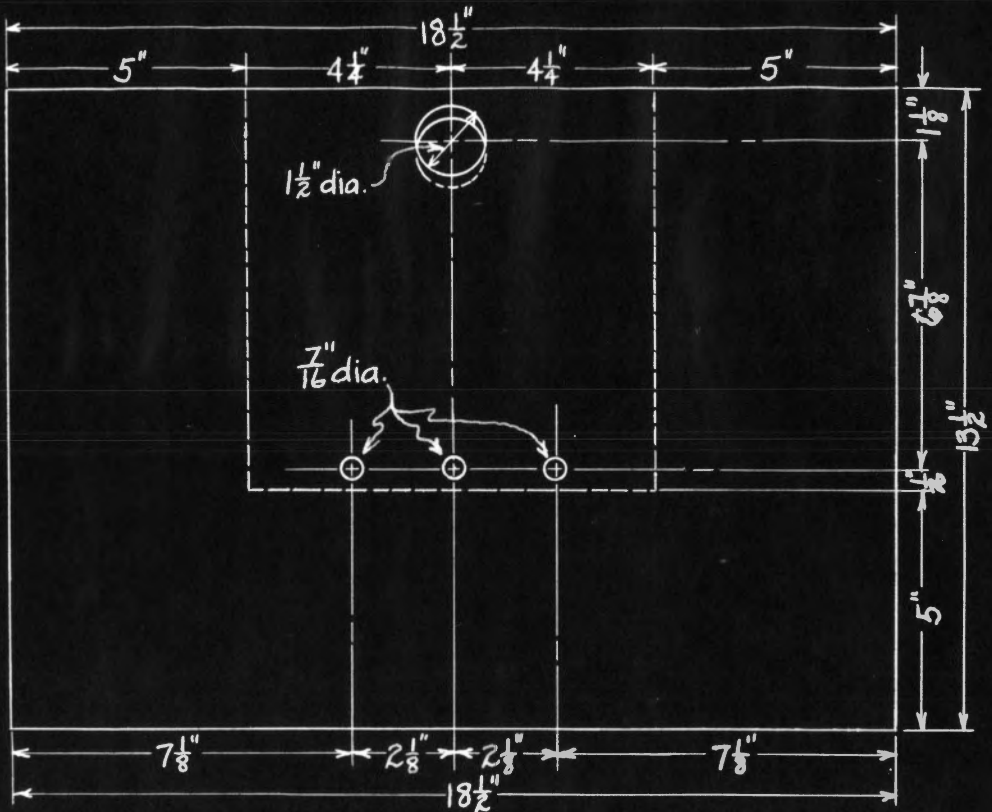
Drawing of
GAS-FIRED COMBUSTION FURNACE

Scale: 3"=1'-0"
Drawn by : W.A.G., Jr. Date: 4/18/47
Checked by: W.A.G., Jr. Date: 4/19/47
Approved by: FoB. Date: 5/7/47

Case: 47
File: 539
Dwng: 3a

Material of construction:
M-26 insulating fire brick, sealed with M-5 ready-mixed mortar



End Elevation

(entering end)

Outline of bricks not shown
Binder Straps not shown

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Drawing of
GAS-FIRED COMBUSTION FURNACE

Scale: 3" = 1'-0"
Drawn by : W.A.G., Jr. Date: 4/18/47
Checked by : W.A.G., Jr. Date: 4/19/47
Approved by: FW-B Date: 5/7/47

Case : 47
File : 539
Dwng: 3b

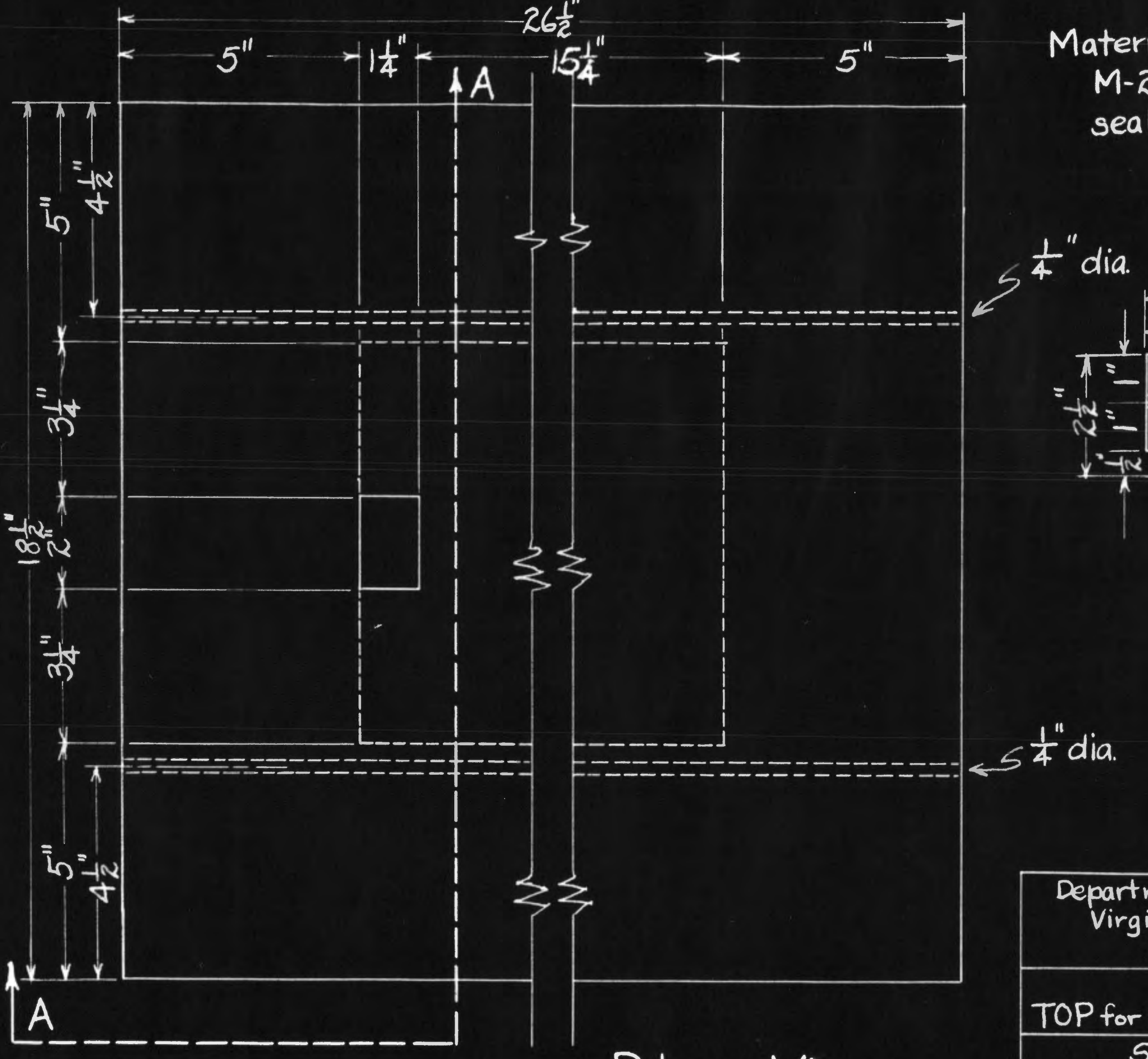
secured in place around the courses of brick by four pieces of 3/4" x 1/8" strap iron, each 11" long, placed vertically.

One end of the furnace, designated the entering end, was drilled as follows: one, 1-1/2" diameter hole, centered 1-1/8" from the top, for the combustion tube; one, 7/16" diameter hole, centered 1/2" above the floor of the furnace chamber, for the burner inlet pipe; two, 7/16" diameter holes, centered 1/2" above the floor of the furnace chamber and 2-1/8" center-to-center on either side of the burner inlet pipe hole, for the secondary air inlet pipes. The other end of the furnace, designated the exit end, was drilled as follows: one, 1-1/2" hole, centered 1-3/4" below the top, for the combustion tube. The 1-1/2" holes in each end were drilled along the same axis. The 1-1/2" holes in both ends of the furnace were enlarged during the experimental runs to 1-7/8" diameter to accommodate a larger size (1-7/8" O.D.) combustion tube. The locations of the centers for the holes and the common axis were not changed.

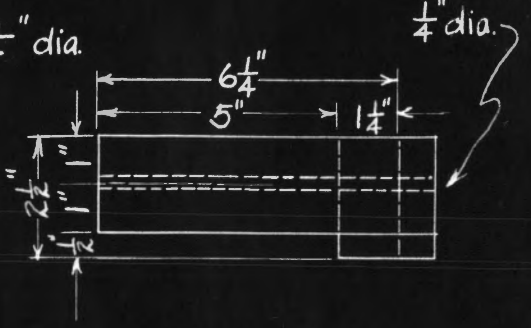
<u>Top of Furnace</u>. A removable top (see drawing 3c, page 47) for the furnace was constructed of M-26 insulating fire brick, each 2-1/2" x 4-1/2" x 9", sealed with M-5 ready-mixed mortar, as follows:

Two rows of brick, laid on the 4-1/2" x 9" side, with the 4-1/2" x 2-1/2" sides of bricks in the adjacent rows together, were held in place by a binder of 3/4" x 1/8" strap iron bent to conform to the outside dimensions of the top and tightened by two carriage bolts, one on each end. Each row of bricks was drilled through the

Material of construction:
M-26 insulating fire brick,
sealed with M-5 ready-mixed mortar



Plan View



Section A-A

Outline of bricks not shown
Binder strap not shown

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Virginia Polytechnic Institute
Blacksburg, Virginia

Drawing of
TOP for GAS-FIRED COMBUSTION FURNACE

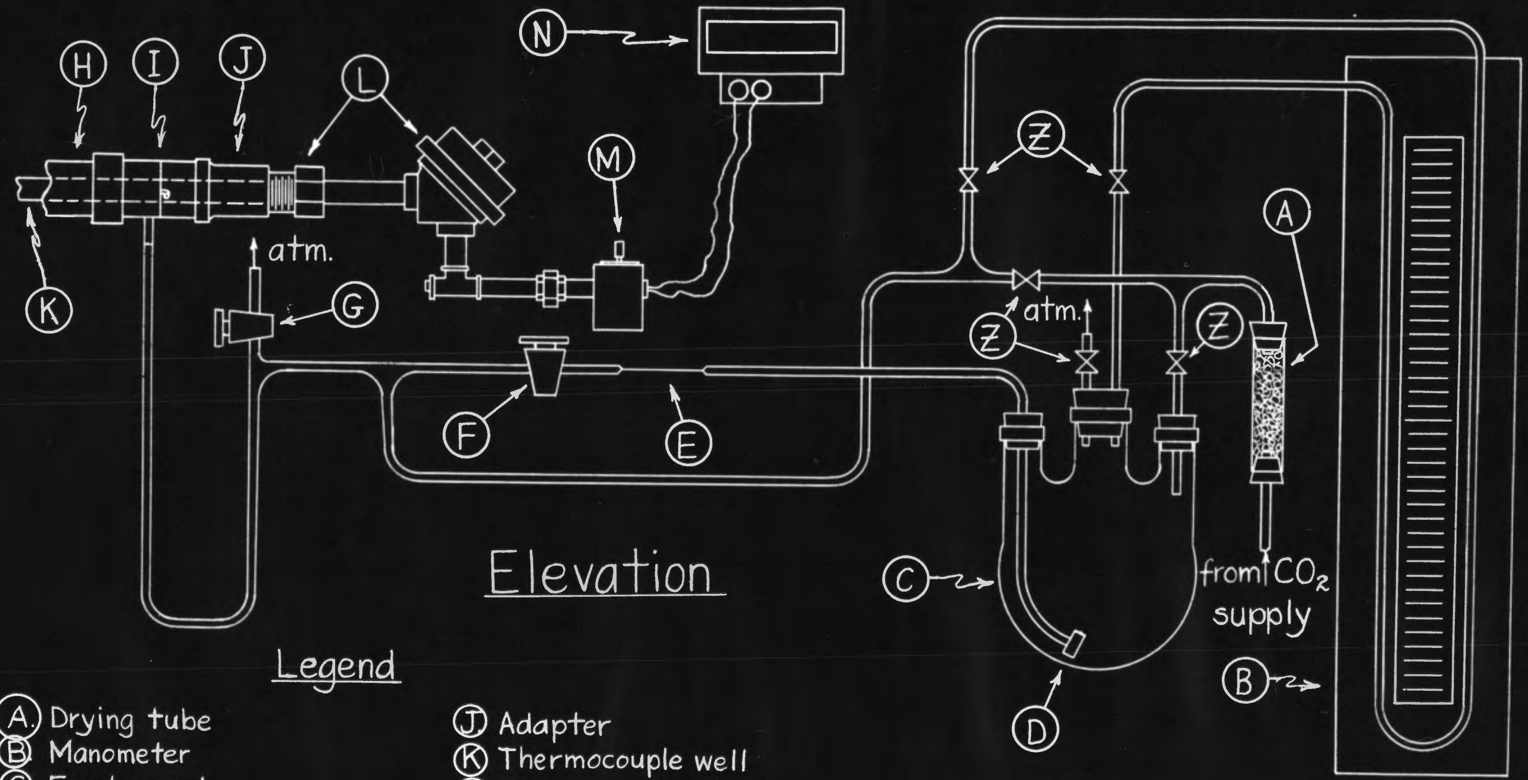
Scale: 3"=1'-0"
Drawn by : W.A.G., Jr. Date: 4/9/47
Checked by : W.A.G., Jr. Date: 4/19/47
Approved by: J.W.B. Date: 5/7/47

Case : 47
File : 539
Dwng: 3c

center of the 4-1/2" x 9" side, 1" from the top, to accommodate a 1/4" steel supporting rod, 28" long, threaded at both ends. The binder was drilled at the appropriate points to accommodate the supporting rods, and the rods were then inserted through these holes and secured by nuts. Overall dimensions were 18-1/2" x 26-1/2" x 2-1/2". The bricks were cut to allow the top to protrude 1/2" into the furnace chamber when in place. A 1-1/4" x 2" opening was cut through the top at a point corresponding to the exit end of the furnace chamber and centered on the end, to allow the burner gas combustion products to escape.

Assembly of Furnace. The burner assembly was placed in the furnace chamber with the inlet pipe projecting through the inlet pipe hole. The gas-air mixing chamber was then connected to the burner assembly by a standard 1/8" black iron screwed union. One-eighth inch pipes were inserted through the secondary air inlet pipe holes and joined to a common compressed air supply inlet through a 1/8" tee. The furnace top was then set in place.

Assembly of Phenyl Substitution Apparatus (For schematic elevations of the feed end and condensing and collecting end of this apparatus, refer to drawings 4 and 5, respectively, pages 49 and 50). The combustion (reaction) tube was inserted through the combustion tube holes in the ends of the gas-fired combustion furnace proper so that an equal length protruded from each end. The combustion tube metal connectors were disassembled. The combustion tube well portions of the connectors were cemented to the ends of the combustion



Legend

Ⓐ Drying tube
Ⓑ Manometer
Ⓒ Feed vessel
Ⓓ Filter cover
Ⓔ Feed orifice
Ⓕ Feed shutoff stopcock
Ⓖ Gas bleedoff stopcock
Ⓗ Combustion tube
Ⓘ Combustion tube metal connector
Ⓙ Adapter
Ⓚ Thermocouple well
Ⓛ Thermocouple mount
Ⓜ Switch
Ⓝ Pyrometer
Ⓩ Shutoff valves (pinchclamps)

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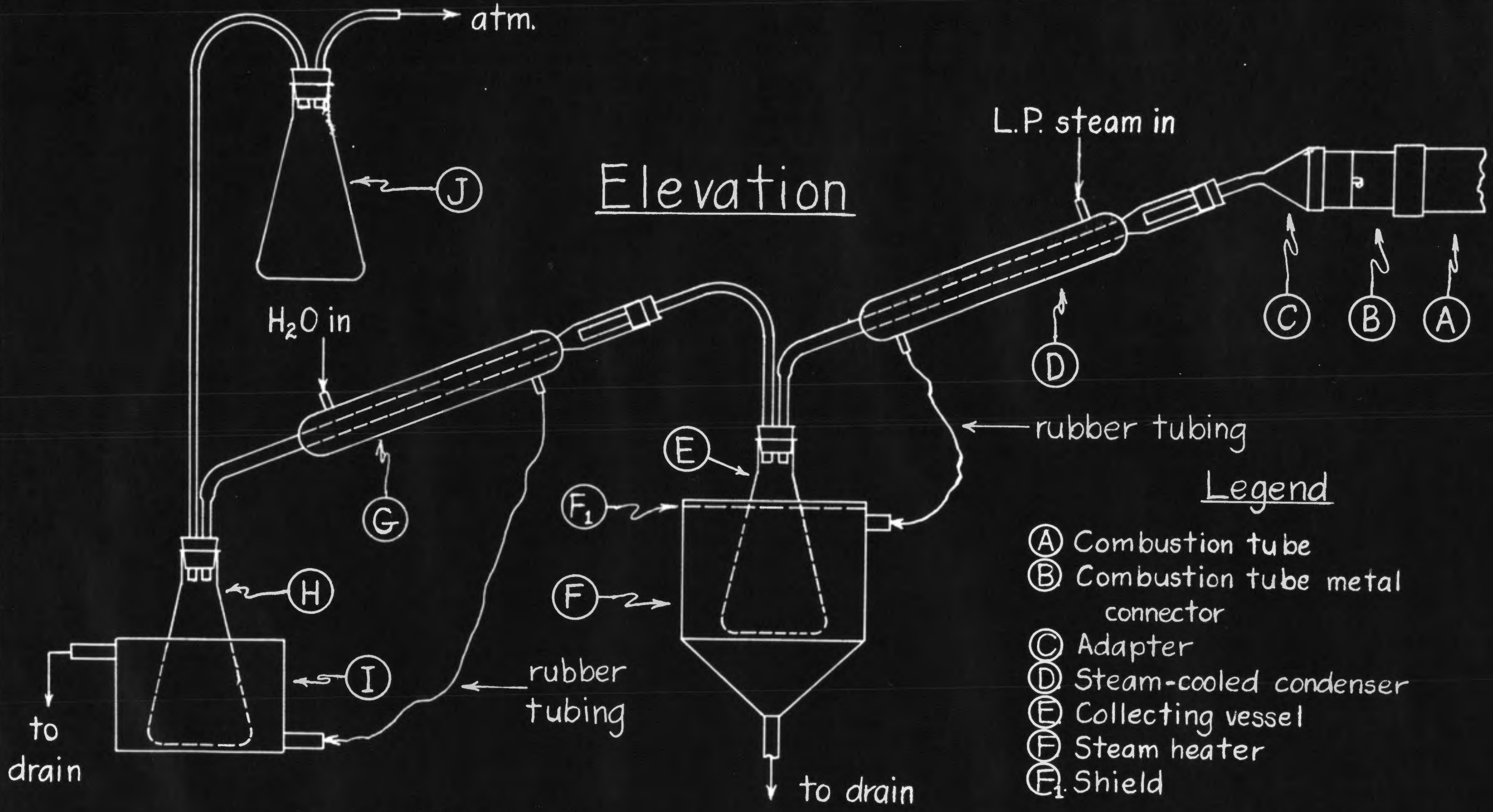
Virginia Polytechnic Institute
Blacksburg, Virginia
Schematic Drawing of
FEED END of
PHENYL SUBSTITUTION APPARATUS

Scale: none
Drawn by : W.A.G., Jr. Date: 9/6/47
Checked by : W.A.G., Jr. Date: 9/6/47
Approved by: Date: 9/8/47

Case: 47
File : 539
Dwng: 4

Elevation



Legend

Ⓐ Combustion tube
Ⓑ Combustion tube metal connector
Ⓒ Adapter
Ⓓ Steam-cooled condenser
Ⓔ Collecting vessel
Ⓕ Steam heater
F$_1$ Shield

Legend (cont.)

Ⓖ Water-cooled condenser
Ⓗ Collecting vessel
Ⓘ Water bath
Ⓙ Trap flask

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Blacksburg, Virginia

Schematic Drawing of
CONDENSING & COLLECTING END of
PHENYL SUBSTITUTION APPARATUS

Scale: none
Drawn by : W.A.G. Jr. Date: 9/7/47
Checked by: W.A.G. Jr. Date: 9/7/47
Approved by: JWB Date: 9/8/47

Case: 47
File: 539
Dwng: 5

tube with a Plaster of Paris-2% acetic acid mixture so that the side arm inlet of the entering end connector was vertically downward and that of the exit end connector was horizontal. These were allowed to stand for 24 hours so that the Plaster of Paris would set.

The thermocouple mount, with the 18" thermocouple, well, cover, and switch attached, was screwed into the coupling portion of the adapter for this connection. The thermocouple projected to a point inside the combustion tube three inches within the furnace chamber. The adapter and view port section of the metal connector were then screwed together. The thermocouple well was inserted into the combustion tube and the sections of the connector were attached together, completing the thermocouple mounting arrangement in the combustion tube. The thermocouple was then connected through the switch to the pyrometer by means of a three-foot length of extension lead wire. The 18" thermocouple was later replaced by the 30" thermocouple to measure temperatures at different points inside the combustion tube.

The combustion tube was packed tightly with pieces of quartz (on 1/4", through 1/2") through the exit end metal connector.

The adapter for the exit end was screwed into place on the assembled metal connector. The side arm inlet of the metal connector was sealed. The outlet tube on the adapter was bent downward at an angle of 20° and inserted into the inlet end of the steam-cooled condenser. The exit end of the condenser was previously welded to a 2" length of 9mm O.D. Pyrex glass tubing, bent so that its position in the final assembly would be vertically downward. This tube was connected to a collecting vessel from which a tube, also of 9mm O.D. Pyrex glass tubing, led into the water-cooled condenser. The steam heater was placed under the exit end of the steam cooled condenser, around the collecting vessel. The exit end of the water-cooled condenser was previously welded to a 2" length of 9mm O.D. Pyrex glass tubing, bent so that its position in the final assembly would be vertically downward. This tube was connected to a collecting vessel from which connections were made to a trap flask and thence to the atmosphere. The water bath was placed under the exit end of the water-cooled condenser, around the collecting vessel.

Weighed 500 ml Pyrex Erlenmeyer flasks were used as collecting vessels. A similar flask was also used as the trap flask.

The steam-cooled condenser was connected to the laboratory low pressure steam supply. Exit steam from the condenser was introduced into the steam heater and from there was sent to the drain.

The water-cooled condenser was connected to the laboratory watter supply. Exit water from the condenser was introduced into the water bath and from there was sent to the drain.

The carbon dioxide tank was connected to the feed section of the apparatus through the pressure regulator and the drying tube which had been previously filled with calcium chloride. Connections were made to the feed vessel and to the feed line through the low pressure manometer tap.

The feed line was constructed of 9mm O.D. Pyrex glass tubing. It included the low pressure manometer tap and a U-trap. In it were attached the feed orifice, feed shutoff stopcock, and gas bleedoff stopcock. The filter plate was attached to the intake end of the feed line which was then inserted into the feed vessel. The other end of the feed line was attached to the side arm inlet of the entering end combustion tube metal connector.

The feed vessel was provided with a pressure relief valve.

The manometer was connected to the feed vessel and to the low pressure manometer tap. Valves were provided in both manometer connections and in the carbon dioxide lines to the feed vessel and low pressure manometer tap.

The following apparatus was used in distilling the products of the phenyl substitution reaction:

Flasks, Distilling, Ladenburg. Pyrex glass. 125ml, 250ml, and 500ml.

Flask, Distilling, Standard. Pyrex glass. 50ml.

Thermometers. General laboratory, 0 to 360°C. by 1° increments; chemical, mercury, nitrogen-filled. Used to make temperature measurements during distillations.

Condenser, Liebig. Pyrex glass, 250mm jacket. Used to condense vapors from the distilling flasks.

The following apparatus was used in making chloride analyses of the phenylchlorosilanes:

Burette. Kimble glass; 50ml at 20°C.; stopcock type; graduated in 0.1ml. Used to measure standard silver nitrate required for chlorine titrations.

Lamp. Yellow, 60 watts, 120 volts. Used to light titrating vessel in chloride titrations.

Electric Heater.

Autemp Heater 15v. A.C.
Fisher Scientific Co.
Pittsburgh, Pennsylvania

Used to heat phenylchlorosilanes during hydrolysis.

The following apparatus was used for miscellaneous purposes:

Desiccator. Pyrex glass, 250mm; and **Desiccator Plate.** 230mm, porcelain. Used to store products of phenyl substitution runs and subsequent distillations.

Hydrometers. Ranges: 0.800-0.900, 0.900-1.000, 1.000-1.200, 1.200-1.400, 1.400-1.600 at 60°/60°F. Graduated to 0.002 below 1.000; to 0.005 above 1.000. Fisher Scientific Co., Pittsburgh, Penn. Used to determine specific gravities of benzene-silicon tetrachloride mixtures.

Balance. Analytical; chainamatic, magnetic damper; capacity 200 grams; sensitivity 0.0001 gram. With weights.

Wm. Ainsworth & Sons, Inc.
Denver, Colorado Made in U.S.A.
Type DLB No. 15345
Will Corporation

Rochester, N.Y.

Balance. Triple beam; capacity 600 grams; sensitivity 0.05 gram.

Ohaus
Newark, N.J.
U.S.A.

Balance. Double beam; porcelain pans; capacity 2 kilograms; sensitivity 0.05 gram. With weights.

Ohaus
made for
Fisher Scientific Co.
Pittsburgh, Pa.

Glass Working Tools. Glass cutter and glass blowers' shaper. Used in making non-standard Pyrex glass portions of the phenyl substitution apparatus.

Blowpipe. "National"; #3-A; OX-2 tip, for gas and oxygen. Prevision Scientific Co., Chicago, Illinois. Used in making non-standard Pyrex glass portions of the phenyl substitution apparatus.

Miscellaneous Laboratory Apparatus and Glassware. Clamps, ringstands, rings, wire gauze, rubber stoppers, cork stoppers, Bunsen burner, Meker burner, beakers, flasks, volumetric flasks, pipettes, test tubes, evaporating dishes, graduated cylinders, watch glasses, adapters, vials, and bottles.

B. Methods of Procedure

The following procedures were used in preparing, separating and analyzing the phenylchlorosilanes:

Preliminary: Specific gravities were taken of mixtures of silicon tetrachloride and benzene at 25°C. in gram-molar ratios from 2:0 to 2:8 ($SiCl_4$:C_6H_6). A curve was plotted (figure 3, page 57) showing specific gravities vs. gram-molar ratios so that the composition of mixtures of these two compounds could be determined.

Phenyl Substitution of Silicon Tetrachloride (numbers and letters in parentheses refer to drawings 4 and 5, pages 49 and 50, and items in the respective legends):

a) Prior to each run, about 1200ml of a reaction mixture of silicon tetrachloride and benzene in the gram-molar ratio of 2:1 was prepared and put in the feed vessel (4C). The vessel was weighed and installed in the phenyl substitution apparatus. Two 500ml Pyrex Erlenmeyer flasks were weighed and installed as collecting vessels (5E & H) for condensate from the two condensers (5D & G) in the apparatus. The shield ($5F_1$) was placed around the steam-cooled condenser collecting vessel.

b) The burner in the gas-fired combustion furnace was lighted and the gas and air flows were adjusted until the pyrometer (4N) indicated that the heated zone of the combustion tube (4H, 5A) was at the desired temperature.

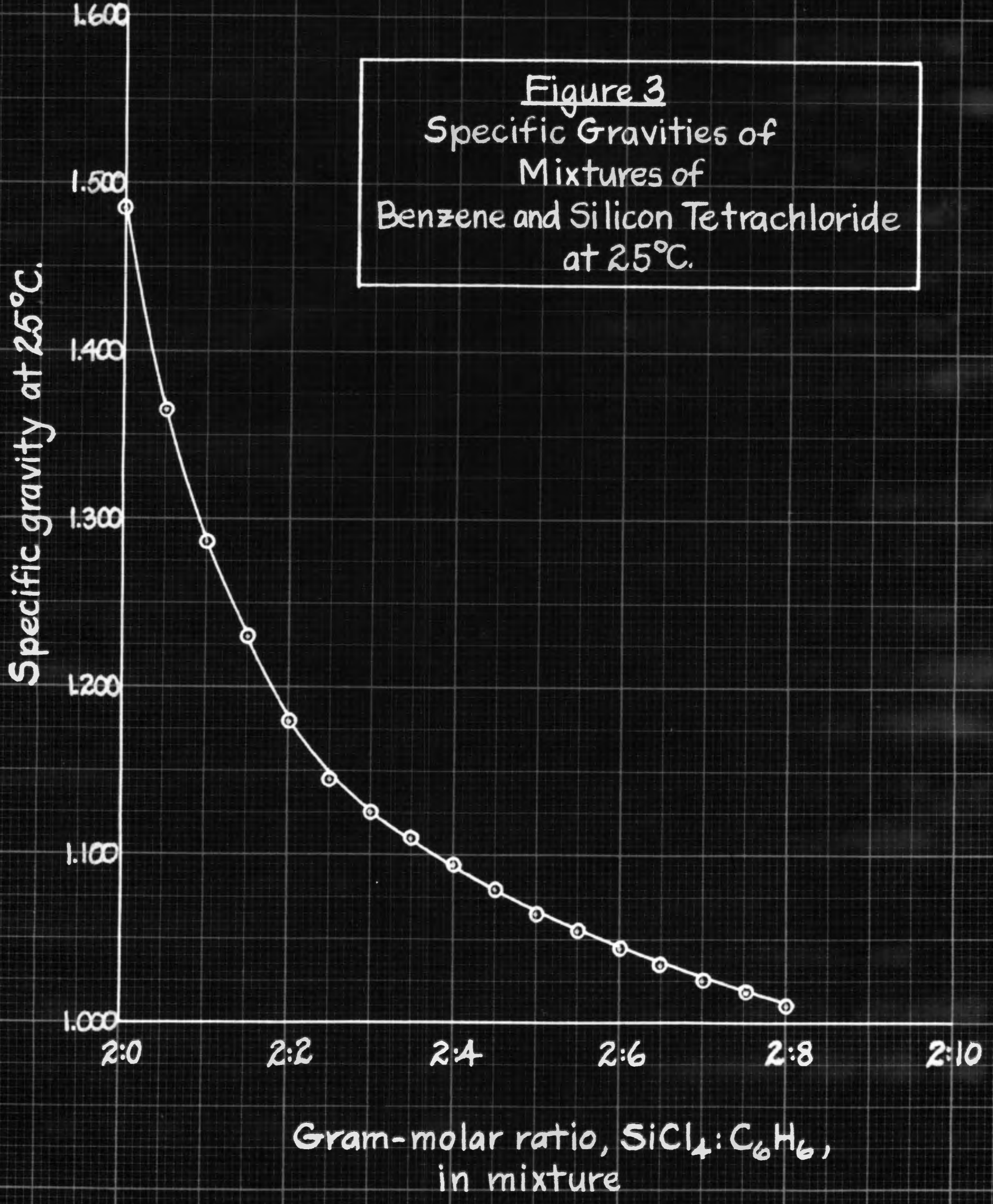

Figure 3
Specific Gravities of
Mixtures of
Benzene and Silicon Tetrachloride
at 25°C.

W.A.G., Jr.
7/28/47

gwb 9/8/47

c) About one-half hour before reaction mixture flow into the combustion tube was started, low-pressure steam was turned on to the steam-cooled condenser (5D) and steam heater (5F); and water was turned on to the water-cooled condenser (5G) and water bath (5I). Carbon dioxide gas was passed through the system for about five minutes before starting reaction mixture flow by opening the valve (pinchclamp) by-passing the feed vessel (4C) and turning on the regulating valve on the carbon dioxide cylinder (not shown). The feed vessel by-pass valve was then turned off.

d) The two valves (pinchclamps) in the manometer connections and the feed stopcock (4F) were turned on. Reaction mixture was forced through the feed orifice (4E) and combustion tube metal connector (4I) into the combustion tube (4H, 5A) by introducing carbon dioxide gas, under pressure, into the feed vessel (4C). Carbon dioxide pressure was varied until the desired manometer (4B) reading was obtained. The manometer reading served to indicate the uniformity of the reaction mixture flow rate for entire runs.

e) At fifteen-minute intervals throughout the runs, starting at the time the reaction mixture started flowing into the combustion tube, temperature of the reaction zone in the combustion tube and the manometer reading were recorded. Final readings were taken just before the apparatus was shut down. No time limit was set on the runs. Rather, the length of any run was determined by the time taken to obtain a sufficiently large quantity of products (over 100 grams) to distil and examine conveniently, and at the same time to allow the system to approach equilibrium.

f) Carbon dioxide gas bubbles seeping into the feed line through the manometer connection were vented slowly to the atmosphere through the gas bleedoff stopcock (4G) as they accumulated at this point.

g) The apparatus was shut down as follows: Carbon dioxide pressure on the feed vessel was relieved by turning off the regulating valve on the carbon dioxide cylinder and venting the gas remaining in the feed vessel to the atmosphere. This immediately stopped the flow of reaction mixture into the combustion tube. The furnace gas and air supplies were turned off. Steam to the steam-cooled condenser and steam heater was turned off. Water to the water-cooled condenser and water bath was turned off. Reaction mixture remaining in the feed line was drained back into the feed vessel. The collecting vessels for the two condensers were removed from the system and weighed. The feed vessel was removed from the system and weighed.

Separation of the Products of the Phenyl Substitution of Silicon Tetrachloride:

a) The contents of the two condenser collecting vessels (5E & H) were combined and placed in a Pyrex Ladenburg distilling flask of suitable size (125, 250, or 500ml). A few small chips of crystalline quartz were put into the flask to prevent "bumping". The flask was fitted with a cork and a 360°C. thermometer. The side arm was connected to a water-cooled, 250mm jacket, Pyrex

Liebig condenser. The exit end of the condenser was connected through a Pyrex adapter to a weighed collecting flask. The reflux bulbs in the neck of the distilling flask were wrapped with asbestos insulating tape. The distilling flask was placed in a sand bath and heated by means of a Fisher burner. Distillations were carried out at atmospheric pressure (713 ±7mm Hg).

b) The first fraction was collected over the boiling ranges of silicon tetrachloride and benzene mixtures (about 55° to 80°C.). After this fraction, about 80 to 95% of the original charge, was collected, the condenser and adapter were removed and the higher-boiling fractions were condensed by air cooling of the distilling flask side arm. Weighed glass vials, 5ml size, were used as collecting vessels for the higher boiling fractions. The second fraction was collected over the temperature range between the end of the first fraction and 180°C. Benzene was added in several runs to wash the residue left from the first fraction into a smaller distilling flask. The third fraction was collected over the temperature range of 190° to 250°C., although it was attempted to limit the upper temperature to 220°C. A fourth fraction was collected over the temperature range between the end of the third fraction and 265°C. No material boiling over 267°C. was obtained in any of the runs. The table on the following page shows the probable composition of the various fractions. Actual temperature ranges varied somewhat from run to run from those given in the table.

TABLE II

PROBABLE COMPOSITION OF THE FRACTIONS COLLECTED DURING THE DISTILLATION OF THE PRODUCTS OF THE PHENYL SUBSTITUTION OF SILICON TETRACHLORIDE

Fraction	Approximate temperature range, °C.	Probable principal components	Some possible secondary components	Remarks
1	55-80	$SiCl_4, C_6H_6$	HCl	Contained recoverable reactants
2	81-190	C_6H_6	Chlorinated benzenes, toluene, xylenes	-
3	191-250	$C_6H_5SiCl_3$	Diphenyl, chlorinated benzenes	Contained phenyltrichlorosilane
4	251-265	$C_6H_5-C_6H_5$	Chlorinated benzenes	-
5	above 265	no fractions expected		-

Analysis of the Products: Fraction 3, obtained in the distillation of the products of the phenyl substitution of silicon tetrachloride (B.P. range approx. 190°-250°C.), was considered to contain the yield of phenyltrichlorosilane. This fraction was analyzed for chlorine content to indicate the true yield of phenyltrichlorosilane, assuming that all chlorine in the fraction was present in phenyltrichlorosilane and knowing the theoretical chlorine content of this compound, 50.4%(76). The method used was based on that of Stock and Somieski(127), suggested by Rochow(102).

a) Two liters of a 0.1N solution of silver nitrate ($AgNO_3$) were prepared and standardized against sodium chloride(120). Two hundred ml of sodium chromate indicator solution was prepared(38). One liter each of 5% aqueous solutions of sodium hydroxide (NaOH) and sulfuric acid (H_2SO_4) was prepared.

b) Approximately 0.200 gram of fraction 3 was weighed accurately in a 250ml Pyrex beaker. To this was added 25ml of 5% NaOH solution.

c) The mixture was heated for five minutes at about 90°C. to hydrolyze the phenyltrichlorosilane and convert the chlorine to the form of sodium chloride.

d) A solution of 5% H_2SO_4 was added to the solution until pH paper showed it to be neutral (pH 7).

e) A standard chloride analysis(119) was made of the neutral solution.

The chlorine content of the sample was calculated in the following manner:

$$\frac{(\text{ml AgNO}_3)\ (\text{normality})(\text{M.E. of Cl})(100)}{(\text{wt. of sample})} = \%\text{Cl}$$

Knowing the theoretical chlorine content of phenyltrichlorosilane, the weight of the compound present in fraction 3 was calculated as follows:

$$\frac{(\%\ \text{Cl in sample})(\text{wt. of fraction 3})}{(\text{theoretical Cl}\ \%\ \text{in phenyltrichlorosilane})} = \begin{array}{l}\text{wt. of phenyl-}\\ \text{trichlorosilane}\\ \text{in fraction 3}\end{array}$$

Check on Temperature Variations Along Reaction Space: In order to check on temperature variations along the reaction space of the combustion tube, a thirty-inch thermocouple and well was installed in the combustion tube after the completion of the phenyl substitution runs in place of the eighteen-inch thermocouple used during the runs. This thermocouple was mounted so that it could be moved to take temperature readings at any point up to twelve inches within the furnace chamber inside the combustion tube, measured from the entering end wall. The furnace was lighted and allowed to heat up to a temperature within the range of those of the phenyl substitution runs. Temperature readings were taken at one inch intervals for a distance of twelve inches within the furnace chamber, starting at the entering end wall.

F. Sample Calculations

1. Calculation of Reaction Space in the Combustion Tube:

It was assumed, on the basis of visual observation of the length of the combustion tube heated to the same degree of redness, that the effective heated length of the combustion tube was eight inches for the original burner assembly and ten inches for the two revisions, both measured from the entering end wall of the furnace chamber. Reaction space was then calculated as follows:

I.D. combustion tube (small) - 1-1/8"
O.D. thermocouple well - 0.54"
Length heated area - 8"
Thermocouple well in heated area - 3"

(volume heated area) - (volume thermocouple well in heated area) = reaction space

$$\frac{\frac{(8)(81)(3.1416)}{(64)(4)} - \frac{(3)(0.54)^2(3.1416)}{4}}{1728} =$$

0.00421 cu. ft. = 0.119 liters

The following calculations are based on revisions in the equipment in the order in which they were installed. Nothing was altered after its installation.

a) For an effective heated length of ten inches, reaction space was calculated:

0.00536 cu. ft. = 0.152 liters

b) For the large combustion tube with an inside diameter of 1-3/8", reaction space was calculated:

0.00984 cu.ft. = <u>0.278 liters</u>

c) For the thermocouple well extending all the way through the reaction space, reaction space was calculated:

0.00891 cu.ft. = <u>0.252 liters</u>

2. <u>Calculation of Approximate Space Velocity at the Temperature and Pressure of the Reaction Space in the Phenyl Substitution of Silicon Tetrachloride:</u> Dodge(31) gives a method for the calculation of the specific volumes of mixtures of gases where the mole fraction, molecular weight, critical temperature, and critical pressure of each component are known. The critical temperature and pressure for benzene were found in Perry's(82). Mol fractions and molecular weights of both components are known. It was necessary to calculate the critical values for silicon tetrachloride since these could not be found in the literature. The methods of Meissner and Redding were used as follows:

a) <u>Calculation of Sugden's Parachor-</u>

$$P = \frac{M(\gamma)^{0.25}}{D - d}$$

where:

P = parachor

M = molecular weight = 169.9(59)

γ = viscosity, dynes/cm. = 16.9 at 18.9°C.(128)

D = density of liquid, grams/cc. = 1.483(59)

d = density of saturated vapor, grams/cc. = 2.65×10^{-4} (75),

negligible at low pressures

$$P = \frac{(169.9)(16.9)^{0.25}}{(1.483)}$$

$$P = 232.1$$

b) Calculation of Critical Volume-

$$V_c = (0.377P \quad 11.0)^{1.25}$$

where:

V_c = critical volume, cc./gram-mole

P = parachor = 232.1

$$V_c = ((0.377)(232.1) \quad 11.0)^{1.25}$$

$$V_c = 309$$

c) Calculation of Critical Temperature-

For compounds boiling over 235°K and containing sulfur or halogen:

$$T_c = 1.41T_B \quad 66 - 11F$$

where:

T_c = critical temperature, °K

T_B = boiling point, °K = 330.6 (59)

F = no. fluorine atoms = 0 for $SiCl_4$

$$T_c = (1.41)(330.6) \quad 66 - 0$$

$$T_c = 532$$

d) Calculation of Critical Pressure-

$$P_c = \frac{20.8T_c}{V_c - 8}$$

where:

P_c = critical pressure, atmospheres

T_c = critical temperature, °K = 532

V_c = critical volume, cc./gram-mole = 309

$$P_c = \frac{(20.8)(532)}{(309 - 8)}$$

$$P_c = 36.8$$

The critical values for both benzene and silicon tetrachloride were converted to degrees Rankine and pounds per square inch absolute. They were then substituted in the equations of Dodge's method(31) to find the specific volume.

Then:

$$v = \frac{CRT}{pM}$$

where:

v = specific volume, cu.ft./lb.

C = compressibility factor - 1.0 for the temperatures and pressure of the experimental work

R = gas constant, psia-cu.ft./lb.mole-°R = 10.73

T = temperature of gas mixture, °R.

p = pressure of gas mixture, psia = 13.8 for the experimental work (assumed)

M = molecular weight of the gas mixture, lbs. = 139.3

$$v = \frac{(1.0)(10.73)\ T}{(13.8)(139.3)}$$

$$v = \frac{10.73\ T}{1902}$$

Converting v to liters/gram:

$$v = \frac{(10.73)(0.0624)\ T}{1902}$$

$$v = \frac{0.67\ T}{1902}$$

Knowing the specific volume, space velocity can be calculated as follows:

$$U = \frac{vw}{St} = \frac{0.67\ Tw}{1902\ St}$$

where:

U = space velocity, liters gas/liter catalyst space/hour

T = temperature of catalyst space (reaction space), °R

w = total weight of reaction mixture used, grams

S = catalyst space (reaction space), liters

t = time of run, hours

G. Data and Results

The data and results obtained in the experimental work on the development of a process for the production of phenylchlorosilanes are given in the form of tables, as follows:

1. Data and results of the phenyl substitution of silicon tetrachloride and subsequent distillation and analysis of the products, including operating conditions for the phenyl substitution, temperature ranges and weights of the fractions collected during the distillations, analysis of the fraction believed to contain the phenyltrichlorosilane, yields of phenylchlorosilanes, and losses of reaction mixture incurred during phenyl substitution and distillation, are given in:

Table III Data and Results for the Phenyl Substitution of Silicon Tetrachloride and Subsequent Distillation and Analysis of the Products. Page 70.

2. The results of the check on temperature variations inside the combustion tube to determine the actual effective heated length of the tube are given in:

Table IV Temperature Variations Inside the Combustion Tube Used for the Phenyl Substitution of Silicon Tetrachloride. Page 71.

TABLE III

DATA AND RESULTS FOR THE PHENYL SUBSTITUTION OF SILICON TETRACHLORIDE AND SUBSEQUENT DISTILLATION AND ANALYSIS OF THE PRODUCTS

Phenyl Substitution of Silicon Tetrachloride						Distillation of the Products of the Phenyl Substitution of Silicon Tetrachloride												Results of the Phenyl Substitution of Silicon Tetrachloride						Losses of Reaction Mixture				
						Fraction 1 #		Fraction 2 ##		Fraction 3 ###		Fraction 4		Fraction 5											Lost during phenyl substitution reaction		Lost during##### distillation of the products	
Run no.	Reaction space, liters	Time of run, hours	Reaction mixture, grams	Total products, grams	Average temp. of run, °C.	Temperature, °C.	Weight grams	Temperature, °C.	Weight, grams	Temperature, °C.	Weight, grams	Temperature, °C.	Weight, grams	Temperature, °C.	Weight, grams	Benzene added as wash, grams	Total weight of fractions collected, grams	Chlorine in fraction 3, %	Theoretical yield of $C_6H_5SiCl_3$, grams	Corrected yield of $C_6H_5SiCl_3$, grams	Corrected yield, % of theoretical	Space velocity, liters gas per liter reaction space per hour	Yield of polysubstituted $SiCl_4$ compounds, grams	#### Total losses, grams	grams	%	grams	%
S-1	0.119	2.0	719.70	703.15	790	57-80	579.70	85-140	14.15	195-250	9.35	251-264	4.10	above 264	0	49.00	607.30	18.34	363.50	3.40	0.94	2020	0	185.60	16.55	8.9	169.05	91.1
S-2	0.119	1.5	739.50	558.05	683	56.5-80	523.65	78-120	11.65	195-230	0.75	above 230	0	-	-	42.35	536.05	43.15	374.00	0.64	0.17	2510	0	257.56	181.45	70.6	76.11	29.4
S-3	0.119	1.0	581.05	489.20	749	55-74	454.15	76.5-115	59.40	198-235	2.90	236-256	1.65	above 256	0	53.60	518.10	30.82	294.00	1.77	0.60	3165	0	178.73	91.85	51.3	86.88	48.7
S-4	0.119	1.0	656.25	549.45	718	55-80	504.70	77.5-150	67.75	195-245	2.80	above 245	0	-	-	69.25	575.25	21.10	332.00	1.17	0.35	3460	0	220.63	106.80	48.4	113.83	51.6
S-5	0.119	2.0	334.20	317.90	718	55-70	287.15	76-112	65.95	198-235	3.45	above 235	0	-	-	66.35	356.55	32.50	171.30	2.22	1.30	880	0	111.18	16.30	14.7	94.88	85.3
S-6	0.152	1.0	816.60	660.05	741	55-70	517.50	74-120	74.70	above 120	0	-	-	-	-	59.95	592.50	-	412.00	0	0	3450	0	359.05	156.55	43.6	202.50	56.4
S-7	0.278	3.5	200.50	125.60	765	57-77	101.70	78-84	0.80	above 84	0	-	-	-	-	0	102.50	-	101.30	0	0	135	0	98.80	74.90	75.8	23.90	24.2
S-8	0.278	3.0	494.50	408.45	690	56-80	369.20	80-180	5.60	196-207	0.80	above 207	0	-	-	0	375.60	48.30	250.20	0.77	0.31	360	0	124.53	86.05	69.01	38.48	30.9
S-9	0.278	2.5	366.20	273.35	777	56-80	142.80	81-180	3.55	190-211	3.80	above 211	0	-	-	0	250.15	43.60	185.10	3.29	1.78	350	0	220.11	92.85	42.2	127.26	57.8
S-10	0.278	3.0	505.00	325.55	890	55-81	269.95	82-180	3.90	196-230	5.65	231-241	1.05	above 241	0	0	280.55	48.10	255.40	5.38	2.11	445	0	229.67	179.45	78.2	50.22	21.8
S-11	0.278	2.0	213.15	142.80	863	56-80	116.60	81-172	1.65	194-233	2.15	above 233	0	-	-	0	120.40	40.50	107.80	1.73	1.60	290	0	109.27	80.35	73.5	28.92	26.5
S-12	0.252	1.5	625.50	437.15	877	55-80	339.05	81-181	3.45	193-229	7.40	231-267	10.85	above 267	0	0	360.75	37.50	316.40	5.50	1.74	1205	0	280.95	188.35	67.0	92.60	33.0

Constant Conditions

Pressure of reaction space - 13.8 psia (assumed)

Sp.gr. of reaction mixture at 25°C. - 1.287

Molar ratio $SiCl_4:C_6H_6$ in reaction mixture - 2:1

Considered to contain the recoverable unreacted $SiCl_4$ and C_6H_6

Benzene added to residue from fraction 1 to wash into smaller distilling flask before collecting this fraction

Considered to contain the phenyltrichlorosilane yield

In runs S-1 to S-6 the weight of wash benzene used was added to the weight of material distilled in calculating total losses

Includes all material boiling over 80°C. which was not phenyltrichlorosilane as indicated by analysis

TABLE IV

TEMPERATURE VARIATIONS INSIDE THE COMBUSTION TUBE USED FOR THE PHENYL SUBSTITUTION OF SILICON TETRACHLORIDE

Distance within furnace chamber, inches	Pyrometer reading, °F.	Temperature (converted), °C.
0	1450	788
1	1540	838
2	1590	866
# 3	1610	877
4	1640	893
5	1610	877
6	1600	871
7	1600	871
8	1580	860
9	1550	843
10	1540	838
11	1510	821
12	1490	810
average, 1-11	1580	860

Position of thermocouple for all phenyl substitution runs.

Reaction space was originally considered to be from 0 to 10 inches within the furnace chamber.

IV. DISCUSSION

A. Discussion of Results

The object of this investigation was to develop a process for the production of phenylchlorosilanes. Little progress was made in this direction. The experimental data and results indicate trends in the phenyl substitution reaction rather than optimum conditions. The results were so scattered that it was not practical to plot yields *vs.* temperature or space velocity to show the trends graphically.

A total of forty-two phenyl substitution runs were made. Thirty runs were useful only in improving operating technique or were worthless because of operating difficulties such as leaks, clogging or parts of the apparatus, lack of control, excessive temperature variations, and so on. The remaining twelve runs were those from which the data and results are given in the tables.

Space Velocity

Definition. Perry's handbook(82) defines space velocity as "...the volume of gas (S.T.P.) or liquid passing through a given volume of catalyst space... in unit time divided by the latter...". In this investigation no catalyst was used. Space velocities were calculated for the effective heated length of the combustion tube, called the reaction space, to give an indication of the time of contact of the reaction mixture with this length. Measurement of feed rate alone would indicate nothing since contact time varies considerably with temperature, assuming a constant pressure, even at a constant feed rate, because of the variation in volume of the gaseous reaction mixture.

The comment was made(82) that it would seem to be more correct to measure the volume of the gas at the temperature and pressure of the reaction space. On this basis it was decided to calculate space velocities at the temperatures and pressure of the phenyl substitution runs. A calculation of space velocity at standard conditions would indicate no more than a feed rate measurement.

Equations for Calculation of Space Velocity. Use of the equation given by Dodge(31) to calculate specific volumes of the reaction mixture at the temperatures and pressure of the phenyl substitution runs, as a step in determining space velocities, is open to question. This method was devised for calculations of hydrocarbon mixtures. Nevertheless, it is undoubtedly more accurate for this use than making the assumption that the reactants have molar volumes of 22.4 liters (S.T.P.) to determine space velocities, as was considered.

Sugden's parachor was calculated as one step in finding the critical values for silicon tetrachloride by the methods of Meissner and Redding(74). The parachor, calculated to be 232.1, was later found to have been experimentally determined as 229.2(138).

Temperature as Related to Space Velocity. In calculating reaction space (see page 64) it was assumed that the space was eight inches long for the original burner assembly and ten inches long for the two revisions. Both measurements were made from the entering end wall of the furnace chamber. The assumption was based on visual observation of the length of the combustion tube heated to redness. In order to justify the assumption, after the completion of the phenyl substitution runs, a thermocouple long enough to project twelve inches into the furnace chamber was installed inside the combustion tube. Temperature readings were taken at one-inch intervals throughout the twelve-inch distance, starting at the entering end wall of the furnace chamber (Table IV, page 71). These data show that there was a ten-inch length of the combustion tube which was at or near the so-called reaction temperature indicated by the fixed thermocouple, three inches from the entering end wall, used in the phenyl substitution runs. The higher temperatures started and ended one inch further within the furnace chamber than was originally assumed. There appears to be a sharp drop in temperature on either side of this section of the tube. However, the question remains as to whether these adjacent sections were at high enough temperatures to cause the phenyl substitution reaction to proceed, particularly in those runs where the reaction temperatures were above 800°C., thus changing the volume of the reaction space and the space velocities. No temperature checks of this nature were made while the original burner assembly was in use.

Channelling. Another complicating possibility in the calculation of space velocity was channelling. All calculations were made on the assumption that the reaction space was filled with gaseous reaction mixture. Channelling might well have occurred since the tube was heated unevenly from top to bottom and rested on its side.

Pressure as Related to Space Velocity. Pressure of the reaction space was assumed to be constant at 13.8 psia, the approximate average atmospheric pressure of the location in which this investigation took place. The assumption is valid in this case since it was never necessary to apply a pressure of more than twenty inches of water (0.72 psig), measured against the atmosphere, to the feed vessel to force the reaction mixture into the combustion tube. Part of this feed vessel pressure was needed to overcome filter plate resistance, orifice resistance, and feed line frictional resistance to flow. The condensers at the exit end of the combustion tube had some effect in lowering tube pressure, but no measurement or calculation of the effect was practical. Normal variation in atmospheric pressure has a negligible effect in the space velocity calculation.

Loss of Reaction Mixture. It will be noted that the formula used to calculate space velocity (page 68) contains the term "w", defined as the weight in grams of reaction mixture used. This was measured by difference of the weight of the feed vessel before and after the phenyl substitution runs. This quantity was considered in the calculations of both yield and space velocity to have passed from the feed vessel through the feed line and combustion tube without loss. This was never the case, but since no method of measuring leakage from the system could be devised, the error was not considered.

Surface Area of Packing. The use of space velocity as a factor in evaluating the data of these experiments is subject to a limitation: no account is taken of the surface area of the packing material. The seriousness of the limitation is diminished when it is considered that the packing size was the same for all the phenyl substitution runs and the quartz packing was packed to about the same degree of tightness in all cases. In effect, the surface area of the packing per unit volume of the reaction space remained constant, although no measurement was made of it.

Because of the many sources of possible error in the calculations, space velocities were calculated only to the nearest 5 liters gas/liter reaction space/hour.

Phenyl Substitution Apparatus

The phenyl substitution apparatus was not satisfactory in its operation. Control of both temperature and flow rates of the reaction mixture within narrow limits was impossible.

Temperature Readings. Temperature was determined at only one point in the combustion tube reaction space during the phenyl substitution runs because of the inflexibility of the thermocouple installation. The thermocouple should have been mounted so that the temperature in any part of the combustion tube could have been determined during the runs. Another disadvantage of this arrangement was the large size of the thermocouple well (0.54" O.D.) as compared to the inside diameters of the combustion tubes used

(1-1/8" and 1-1/2" I.D.). This decreased the reaction space by about 20% for the length occupied by the well in the case of the ten-inch reaction space and 1-1/2" I.D. combustion tube.

Control of Temperature. Temperature control during the phenyl substitution runs was poor in most cases. Gas and air supplies to the furnace and burner assembly were subject to considerable fluctuation and this in turn caused temperature variations in the combustion tube. In addition, heat losses through the walls, top, and combustion products opening in the top of the furnace could have caused considerable temperature variation, especially if there were drafts around the outside of the furnace. Attempts to maintain a constant temperature in the combustion tube by varying gas and air supplies were largely unsuccessful.

Temperature Variations. Temperature variations from maximum to minimum during the phenyl substitution experiments were not consistent from run to run. They ranged from 295°C. for one of the thirty discarded runs down to 11°C. for several of the twelve reported runs. These variations cannot be entirely assigned to lack of temperature control, but were partly due to variations in flow rate of the reaction mixture into the combustion tube. In general, it may be said that temperature control was better for the twelve reported runs than for the thirty which were discarded. Average variation from maximum to minimum in the former was 36°C., while in the latter it was 100°C. Of the twelve reported runs, those in which the 1-1/2" I.D. tube was used showed a lower average variation, 24°C., than those in which the 1-1/8" I.D. tubes were used, 46°C. The damping effect of the 3/16" thick wall of the larger tube on the transmission of heat causing temperature variations from the furnace chamber to the inside of the combustion tube was probably greater than that of the 1/8" thick wall of the smaller tube. The actual dimensions of the tubes did not correspond to the catalog specifications.

Efficiency of the Furnace as a Heating Unit. The combustion furnace assembly was not satisfactory as a heating unit for the combustion tubes. The effective heated lengths of the combustion tubes for the original burner assembly and the two revisions were eight and ten inches, respectively. The burner assemblies were not long enough to heat the tubes along the sixteen-inch length of the furnace chamber. Those portions of the tubes outside the heated zone acted only as vaporizers for the reaction mixture on the entering end or as partial condensers on the exit end. The five-inch lengths of the tubes passing through the end walls of the furnace were also ineffective as reaction space.

Flames from the burner assemblies impinged upon only a small segment of the periphery of the tubes. A "hot spot" resulted in all runs at the bottoms of the tubes directly over the burner assemblies.

Leakage. The apparatus developed numerous leaks during the experimental work. Some were evident only because of the odor of escaping silicon tetrachloride. Principal sources of leakage were the connections between various parts of the feed end of the apparatus. Several sealing compounds were tried, such as De Khotinsky cement, glycerin-litharge cement, and silicone stopcock lubricant, but none proved entirely successful. Leaks serious enough to necessitate shutting down the apparatus occurred in eight of the thirty discarded runs.

Condensed, unreacted reaction mixture was lost by vaporization from the water-cooled condenser collecting vessel. The temperature of the water bath was not low enough to prevent the highly volatile mixture from passing off to the atmosphere through the trap flask.

Clogging of Process Lines. Clogging of the feed or product lines occurred in eleven of the thirty discarded runs. In both lines the principal trouble points were constrictions and bends. Although precautionary steps were taken to eliminate moisture from the system, stoppage in the feed line was caused mostly by the hydrolysis of the silicon tetrachloride in the reaction mixture to form a silica sludge. It was not discovered how the moisture entered the feed line. In the product lines, clogging was caused entirely by the caking of benzene pyrolysis products on the walls. The line from the steam-cooled condenser collecting vessel to the water-cooled condenser was particularly subject to this, indicating that the collecting vessel probably should not have been heated.

Materials of Construction. The materials of construction of the apparatus in contact with reactants and products at temperatures below 100°C. were generally satisfactory. Fused silica, quartz, Pyrex glass, brass, copper, and stainless steel were all used without serious deterioration. Brass and copper were observed to have been corroded by prolonged contact with reactants and products at temperatures above 350°C. Stainless steel was corroded by temperatures of 600°C. or higher. Natural rubber tubing was readily decomposed by the action of the compounds at temperatures above 100°C. and more slowly at lower temperatures. None of the Pyrex glass parts of the apparatus were subjected to contact at temperatures above 300°C. and no deteriorative action was noted. The fused silica combustion tubes and quartz packing were in contact with reactants and products at temperatures up to 900°C. with no noticeable effect. Observations of the action of products and reactants on the materials of construction indicate that fused silica and quartz were most satisfactory for temperatures above 300°C., while stainless steel and Pyrex glass are the most satisfactory of the remainder of the materials at temperatures below 300°C. The use of natural rubber is not feasible for prolonged contact at any temperature.

Phenyl Substitution of Silicon Tetrachloride

Variables Studied. The variables studied in the phenyl substitution of silicon tetrachloride to produce phenylchlorosilanes were (1) space velocity of the reaction mixture in the gaseous phase through the reaction space of the combustion tube and (2) temperature of the reaction as measured by a thermocouple placed inside the combustion tube at a point within the furnace chamber three inches from the entering end wall. Pressure of the reaction was considered to be constant at 13.8 psia and the gram-molar ratio of the reactants in the reaction mixture was constant at 2:1 ($SiCl_4$:C_6H_6).

Reaction Temperature. The average temperatures of the runs, given in Table III (page 70), are the averages of the readings taken every fifteen minutes during the runs, disregarding the initial readings. The error in assuming the averages to be the reaction temperatures is not known, but may exceed five per cent in all cases. The initial readings in all runs were not averaged with the rest. In most runs there was a large decrease in temperature during the first five to ten minutes, caused by the entry of cold liquid reaction mixture into the combustion tube. Magnitude of the drop varied approximately with the feed rate (grams per hour) of the reaction mixture. In run S-7, for a feed rate of 57.2 grams/hour, the drop was 11°C.; in runs S-4 and S-6, for feed rates exceeding 650 grams/hour, the drop was about 120°C. No drop was noted in runs S-10 and S-12 as the combustion tube was not at its maximum temperature when the runs were started.

Theoretical Yields. Theoretical yields of phenyltrichlorosilane (Table III, page 70) were calculated on the basis of 100% reaction of the benzene to form the compound. Benzene was the limiting component of the reaction mixture. This was used as a basis for determining the efficiency of the phenyl substitution runs (0 to 2.11%), as measured by per cent-of-theoretical yields, since no polysubstituted silicon tetrachloride was produced.

Effect of Space Velocity. The effect of space velocity on the phenyl substitution reaction is shown by the results in Table III, page 70). In order to examine the effects of space velocity, the runs are grouped by temperature as follows: roughly, runs S-10, S-11, and S-12 are at the same temperature; 890°C., 863°C., and 877°C., respectively. Likewise, runs S-1, S-7, and S-9 can be grouped by temperature (790°C., 765°C., and 777°C.), as can runs S-3, S-4, and S-5 (769°C., 718°C., and 718°C.); and runs S-2 and S-8 (683°C. and 690°C.). These groupings are not sharply defined and no quantitative conclusions can be drawn by a comparison of the results within them.

From the yield percentages of runs S-10, S-11, and S-12, 2.11%, 1.60%, and 1.74%, respectively, it can be seen that the optimum space velocity for the formation of phenyltrichlorosilane is an intermediate value. For a space velocity of 445#, run S-10, the yield was higher than for a space velocity of 290 (S-11) or 1205 (S-12). This is also shown by the results of runs S-1, S-7, and S-9: yields of 0.94%, 0%, and 1.78% were obtained for space velocities of 2020, 135, and 350, respectively. Although it would

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\# Units for all space velocities are liter gas per liter reaction space per hour seem that very low space velocities, giving long contact times, would produce better yields, the results point to the opposite effect. At very low space velocities some other reaction, probably the pyrolysis of benzene, proceeds more rapidly and suppresses the phenyl substitution of silicon tetrachloride. At higher space velocities than the optimum, the contact time is probably not long enough to cause the phenyl substitution reaction to take place. The effect of lowering space velocities seems to be greater than that of raising space velocities in suppressing the desired reaction. Runs S-3, S-4, and S-5 show the increase in yield with lowering of space velocity, but more runs at still lower space velocities are needed to establish the optimum point for this group. Yields of 0.60%, 0.35%, and 1.30% were obtained for space velocities of 3165, 3460, and 880, respectively, for the runs in the order given. More runs are also needed in the group with runs S-2 and S-8 which have yields of 0.17% and 0.31% for space velocities of 2510 and 360, respectively.

No explanation is offered for the inconsistency of the results of run S-6 with those of run S-4. These two runs are closely comparable in both space velocity, 3460 and 3450, and temperature, 718°C. and 741°C., and the yield for S-6 should have been the same as for S-4, 0.35%. A mistake in operating technique could have been made undetected in any part of run S-6 to cause the loss of material boiling over 120°C. (Table III, page 70).

Effect of Temperature. The results of the runs cannot be easily grouped for a comparison of temperature effects on yields as was done for space velocity. The space velocities are rather widely scattered. However, some general observations on the effect of temperature can be made.

Runs S-8 and S-9 were made at about the same space velocity (360 and 350) and at temperatures of 690°C. and 777°C., respectively. The yield for run S-9, 1.78%, was almost six times that of run S-8 which was 0.31%. Run S-10, although at the higher space velocity of 445, can be used here to illustrate a point: for a temperature increase from 777°C. to 890°C. from run S-9 to run S-10, 23°C. greater than that from S-8 to S-9, the yield increased only from 1.78% to 2.11%, or about one-fifth. The increase in space velocity could hardly have suppressed the increase in yield to this extent as is shown by run S-5: at a space velocity of 880 the yield was 1.30%, still better than two-thirds that of S-9, even though the temperature was only 718°C. A comparison between runs S-1 and S-2, disregarding the difference in space velocity, shows a sharp increase in yield (from 0.17% to 0.94%) for a temperature rise beyond 700°C. S-2 was at 683°C. and S-1 was at 790°C. This compares with runs S-8 and S-9. Comparison of runs S-3 and S-4, again neglecting the difference in space velocity, shows that the increase in yield is not as pronounced for temperature increases after the temperature has risen above about 700°C. Yields of 0.35% and 0.60% were obtained at temperatures of 718°C. and 749°C. for runs S-4 and S-3, respectively. This compares with the case of runs S-9 and S-10. Evidently there is a "break point" at about 700°C., representing the minimum effective temperature for the phenyl substitution reaction, regardless of space velocity.

Graphical Evaluation of Space Velocity and Temperature Effects. It would be desirable to plot variations in yield versus temperature at constant space velocity for comparison with plots of yields versus space velocity at constant temperature. In this manner the optimum space velocity and temperature for the production of phenyltrichlorosilane could be determined graphically. The results obtained in this experimental work are too scattered to make such a graphical evaluation practical and not enough results were obtained to plot a three-dimensional diagram. The limits of space velocity investigated probably encompass the optimum, as is evidenced by the low yield percentages of phenyltrichlorosilane at both extremes. The lower limit on temperature seems to be about 700 °C. The upper temperature limit is controlled by the degree of pyrolysis of the benzene which will occur(76).

Pyrolysis of Benzene. Egloff(33) and Hurd(45) state that the pyrolysis of benzene in the absence of oxygen to form complex molecules commences at about 500 °C. It continues with increasing rapidity as the temperature rises without cracking of the benzene ring until the temperature reaches about 750 °C. Diphenyl is the principal product up to 750 °C., optimum temperature for its formation. Small amounts of benzene are cracked at temperatures above 750 °C. As the temperature increases, more complex molecules are formed at the same time as diphenyl. Highly complex polymeric pyrolysis products of benzene are tars.

Pyrolyzed benzene was obtained in all phenyl substitution runs. The amounts produced were not collected or weighed, but it was evident by visual observation of the volumes formed that more pyrolysis products were obtained as the temperatures of the runs increased. This was especially noticeable above 750°C. Pyrolysis products also increased as space velocity decreased, particularly above 750°C. None of these products was isoluated from the dark brown, tarry mass remaining as residue from the distillations of the phenyl substitution products except small amounts of diphenyl (B.P. 254.9°C.) in four runs (Table III, page 70). Some pyrolyzed benzene was deposited on the walls of the product lines, the inside of the combustion tubes, the thermocouple well and the quartz tube packing in the phenyl substitution apparatus. None of this material was recovered. No study was made of the effect of the coating on the inside of the tube or the packing on the phenyl substitution reaction; or of the effect of the thermocouple well coating on temperature readings.

Since pyrolyzed benzene is a loss of unreacted material to possible recycling, the highest temperature practical for the phenyl substitution reaction (and the lowest space velocity) is that which will produce a minimum of pyrolysis products for a high (relative) percentage yield of phenyltrichlorosilane. For this investigation, by visual observation only, the smallest yield of pyrolyzed benspace velocity of 350 liters gas/liter reaction space/hour and a temperature of 777°C.

Yields in Commercial Processes. There is little information available on yields of commercial processes producing any type of organochlorosilane with which to compare the results of this investigation. Rochow(110) has given some information on yields of methylchlorosilanes from the direct synthesis, a batch process: in two and one-half days of reaction, an average of 85% of the available silicon in the reactants is converted to a mixture of methylchlorosilanes. The best yield of phenyltrichlorosilane obtained from the continuous process used in this investigation was 2.11% (Table III, page 70). One advantage of the process studied is that recycling of the unreacted material is possible by separating it from the higher-boiling products. Recycling would offset the disadvantage of the low one-pass yields. No yield percentages for the commercial Grignard process were found in the literature. Laboratory preparation of phenylchlorosilanes by the Grignard synthesis has been carried out at 0°C., the reaction being allowed to proceed for twelve hours(56). Sixty-three per cent of the available silicon was converted to a mixture of phenylchlorosilanes(35)(56).

Thermochemistry. The small yields of phenyltrichlorosilane and the complete lack of polyphenylchlorosilanes is best explained by a consideration of the thermochemistry of the phenyl substitution reaction. The phenyl substitution of silicon tetrachloride to form these products is a highly endothermic reaction according to theoretical calculations. It becomes more endothermic in a one-pass process as the degree of substitution of organic groups on the silicon atom increases. The fact that no appreciable temperature rises were encountered in the phenyl substitution runs might bear this out. However, the quantities of phenyltrichlorosilane formed were so small that the effect of an exothermic reaction, if the reaction were exothermic, would be obscured by temperature variations caused by external conditions. No check was made for "hot spots" during the phenyl substitution runs. The existence of these would also have indicated an exothermic reaction.

The method given by Wenner(133) for the calculation of heats of formation of compounds from the bond energies(18)(92)(133) and heats of formation of the atoms(18)(133) composing them was used for the phenylchlorosilanes. Heats of formation were found to be +107.4 kcal/mole for phenyltrichlorosilane and +328.3 kcal/mole for diphenyldichlorosilane. The accuracy of this method is questionable(133). Heats of reaction were then calculated in the following manner(133):

$$\underline{(A)}\quad C_6H_6(g) + SiCl_4(g) \dashrightarrow C_6H_5SiCl_3(g) + HCl(g)$$

$$\Delta H_f:\ +44.6 \qquad -142.5 \qquad +107.4 \qquad -22.1$$

$$\Delta H_R = \underline{+183.2\ \text{kcal}}.$$

$$\underline{(B)}\quad 2C_6H_6(g) + SiCl_4(g) \longrightarrow (C_6H_5)_2SiCl_2(g) + 2HCl(g)$$
$$\Delta H_f:\ (2)(+44.6) \quad -142.5 \quad +328.3 \quad (2)(-22.1)$$
$$\Delta H_R = \underline{+337.4\ \text{kcal.}}$$

Heat of formation of benzene was calculated from the heat of combustion(68)(70) and heats of formation for silicon tetrachloride and hydrogen chloride were found in the literature(18).

Fuoss(35) states that the formation of diphenyldichlorosilane takes place stepwise, rather than as shown in (B), the reaction proceeding from silicon tetrachloride to phenyltrichlorosilane to diphenyldichlorosilane. His statement is based on a Grignard synthesis performed by Kipping(56), but it believed that an analogy can be drawn with the phenyl substitution method investigated. The first step is reaction (A) and the second step, with heat of reaction calculated, would be as follows:

$$\underline{(C)}\quad C_6H_6(g) + C_6H_5SiCl_3(g) \longrightarrow (C_6H_5)_2SiCl_2(g) + HCl(g)$$
$$\Delta H_f:\ +44.6 \quad +107.4 \quad +328.3 \quad -22.1$$
$$\Delta H_R = \underline{+154.2\ \text{kcal.}}$$

Reactions (B) and (C) are both endothermic. Assuming that the phenyl substitution method used in this investigation proceeds stepwise, it follows that, even though the heat of reaction is less for the formation of diphenyldichlorosilane from phenyltrichlorosilane than for the formation of the latter compound, the energy was not available to cause the second step, (C), to take place. This was evidenced by the absence of diphenyldichlorosilane in the products (Table III, page 70). The same statements may be made for the formation of triphenylchlorosilane, a third step in the series of reactions. Rygden(20) states that mono-derivatives of silicon tetrachloride are easily obtained in most cases, this also with reference to a Grignard synthesis, a fact which seems to be true of the substitution method investigated.

In reaction (C), given in the preceding paragraph, the theoretical heat of reaction for the formation of diphenyldichlorosilane from phenyltrichlorosilane, +154.2 kcal., is shown to be less than the heat of reaction for the initial formation of phenyltrichlorosilane, +183.2 kcal. This seems to indicate that it would be possible to produce diphenyldichlorosilane by a second phenyl substitution reaction, using the same methods of procedure by replacing the silicon tetrachloride with phenyltrichlorosilane in the reaction mixture.

The small percentage yields obtained in this investigation indicate that energy was not furnished efficiently enough to the reaction mixture at the temperatures and space velocities studied. This, in turn, points to a need for lower space velocities and higher temperatures. However, as was pointed out previously, there is a limit imposed upon both variables by the degree of pyrolysis of the benzene.

<u>By-products and Impurities</u>. (refer to Table I, page 29; Table II, page 61; and Table III, page 70). Technical grades of

silicon tetrachloride and benzene were used in this investigation (pages 32 and 33). These grades were selected because the patent on the process(76) reported them as satisfactory. The reactants contained small amounts of impurities in the form of free chlorine and titanium tetrachloride in the silicon tetrachloride; and toluene, xylene, and "tarry substances" in the benzene. Some of the impurities were capable of reacting with each other or the reactants to form by-products.

Hydrogen chloride is a principal by-product of the phenyl substitution method investigated. Its formation undoubtedly took place, but none was isolated or identified in the products. No investigation was made of possible action of the compound on others present in the process.

The presence of small amounts of chloride (0.10%) in the silicon tetrachloride made possible the formation of chlorobenzenes. Benzene is easily halogenated by direct action of halogens(136). Mono-, di-, tri-, and tetrachlorobenzenes all have boiling points within the temperature range of the fractions collected in distilling the products of the phenyl substitution reaction. A drop or two of some compound was observed to have distilled over at the boiling points of both mono- and dichlorobenzenes in several runs. There was also a possibility that the chlorobenzenes, if formed, would enter into the substitution reaction to produce chlorophenylchlorosilanes. These compounds have been prepared and are desirable(90). The boiling points were not known, however, and no attempt at isolation or identification was made.

Toluene and xylene both have boiling points within the temperature range of the fractions collected in distilling the phenyl substitution products. A few drops of some material was observed to have distilled over at the boiling points of both compounds in several runs.

Chlorination of toluene and xylene is also possible. Chlorine can be added both to the aromatic nucleus and to the side chains. These compounds were not considered in the investigation. Toluene and xylene can also take part in substitution reactions of their own(76). Substitution of these compounds on silicon tetrachloride can take place either on the aromatic nucleus or on the side chains. No study was made of these possible reactions.

Possible reactions of titanium tetrachloride and the "tarry substances" were not considered.

Only a few of the possible by-products have been discussed. They are believed to be of minor importance because of the small quantities which could form. A great many have boiling points within the temperature range of the fractions collected in distilling the phenyl substitution products, but it was not practical because of the very small quantities obtained to attempt a separation for identification purposes.

<u>Losses</u>. Large losses of material occurred during most of the phenyl substitution runs (Table III, page 70). Only a small part of these losses can be attributed to the formation of hydrogen

chloride in the phenyl substitution reaction and to pyrolyzed benzene remaining in the system. The larger part was caused by leaks and vaporization of material from the water-cooled condenser collecting vessel. The losses bear no relation to the operating condicitions or results of the phenyl substitution runs. Most of the losses could be eliminated by refinements in the apparatus.

Distillation of the Products of the Phenyl Substitution of Silicon Tetrachloride

Method Used in this Investigation. The separation in this investigation was effected by collecting the material boiling over specified temperature ranges as temperature in the distilling flask increased. Considerable difficulty was experienced in maintaining the temperature limits for the fractions from run to run and the compositions of the same numbered fraction varied as a result.

Distillation was carried out at atmospheric pressure as this seemed at first to be the most convenient means. Kipping(56) reported distillations to obtain phenyltrichlorosilane, the principal product expected in this investigation, at atmospheric pressure. For polysubstituted compounds he stated that distillation was carried out "preferably under diminished pressure". The Miller and Schreiber patent(76), on which this investigation was based, states that fractional distillation at 25mm pressure was used to separate phenyltrichlorosilane.

Temperature divisions between the four fractions collected were not marked except between fractions 2 and 3. There was at least 10°C. difference between these two fractions in all distillations (Table III, page 70). The end point of the first fraction was chosen as 80°C. to separate the unreacted benzene and silicon tetrachloride from the remainder of the material. In several cases the end point of fraction 1 was well below 80°C. Here the bulk of the charge had distilled over and the residue was washed into a smaller distilling flask with additional benzene. The additon of benzene caused a gap between fractions 1 and 2 in several runs. Possible superheating was not considered.

Fraction 1. Fraction 1 was considered to contain the recoverable silicon tetrachloride and benzene. This fraction always composed the greatest part of the fractions collected during distillation.

Fraction 2. Fraction 2 consisted principally of benzene, both in those runs where benzene was added as wash and those where no wash was used. A few drops of higher-boiling material were noted in all runs except S-7. No analysis was made of the fraction.

Fraction 3. Fraction 3 was considered to contain the yield of phenyltrichlorosilane. Chlorine content of the fraction (Table III, page 70) showed a definite relationship to the temperature range over which the fraction was collected. It will be noted that for temperatures below 195°C. and above about 210°C. there was a definite decrease in chlorine content. The effect at temperatures above 210°C. did not become pronounced until the temperature increased above 230°C. Therefore, the ideal temperature range for the separation of phenyltrichlorosilane by the distillation method used was between 195°C. and 210°C. Impurities causing a decrease in chlorine content below 195°C. were probably chlorobenzenes and those causing a decrease above 210°C. probably consisted principally of diphenyl.

Fraction 4. Fraction 4 was believed to consist principally of diphenyl. The material collected over the temperature range between the end of fraction 3 and the maximum temperature obtainable in the distillations was a white solid, structure undetermined, with a sweetish smell. Fraction 4 was obtained in only four runs.

Higher Boiling Material. No material boiling above 267°C. was obtained. The lack of fractions at higher temperatures could have been due to inefficient heating of the distilling flasks. It was noted, however, that increasing the temperature of the flask seemed to thicken the remaining material rather than to vaporize any of it. A temperature drop always occurred, either after fraction 4 was collected or after fraction 3 if fraction 4 were not obtained.

Losses. Losses during distillation of the products of the phenyl substitution of silicon tetrachloride were caused principally by vaporization of material from the receivers. They bear no relation to the conditions of the distillations or composition of the products. A small part of the losses was caused by the presence of pyrolyzed benzene in the residue remaining after the distillations and another small part by the material boiling at temperatures over 80°C. which was not phenyltrichlorosilane. The magnitude and percentage of the total of the distillation losses is given in Table III, page 70. Most of the losses could be prevented by refinements in the equipment.

Analysis of the Products

True Yield of Phenyltrichlorosilane. The purpose in analyzing fraction 3 obtained in the distillation of the products of the phenyl substitution runs was to determine the true yield of phenyltrichlorosilane by a comparison between the analytically determined chlorine content of the fraction and the theoretical chlorine content of the compound, 50.4%(76).

Sources of Error. It was assumed that all hydrolyzable chlorine found in fraction 3 was present in phenyltrichlorosilane. It is possible that small quantities of silicon tetrachloride were present also. Since chlorine in this compound is very readily hydrolyzed, the presence of silicon tetrachloride would seriously limit the value of the chlorine analysis. However, the difference in boiling points of silicon tetrachloride and phenyltrichlorosilane is large (over 140°C.) and the possible compounds with intermediate boiling points so numerous that it is doubtful whether any appreciable quantity of the former compound was present.

Chlorine in fraction 3 could have also been present in the form of chlorobenzenes with boiling points close to that of phenyltrichlorosilane (Table I, page 29). Halogen attached to a benzene ring, however, is hydrolyzed only under conditions much more severe than were imposed upon fraction 3 in this investigation, even in the presence of aqueous alkali(135)(136).

Identification of Phenyltrichlorosilane by Hydrolysis. Furthur substantiation of the presence of phenyltrichlorosilane in fraction 3 was furnished by the nature of the hydrolysis products other than chlorine compounds. In hydrolyzing the samples of the fraction weighed for analysis, a white substance of the consistency of thick glue was observed to form in all cases. The substance hardened in a few minutes and could then be broken into small bits in the sample contained with a stirring rod. Such a substance has been previously observed to form in the hydrolysis of phenyltrichlorosilane in an alkaline medium(137).

B. Limitations

Phenyl Substitution Apparatus

Flow Rate and Temperature Control. Close control of temperature and flow rate was impossible with the apparatus used in this investigation. Fluctuations in gas and air supplies to the combustion furnace and burner assemblies could not be eliminated. Feed rate could only be measured by a difference in the weight of the feed vessel before and after each phenyl substitution run. No measurement of feed rate was possible while runs were in progress.

Temperature was taken at only one point in the reaction space during the phenyl substitution runs because of the inflexibility of the thermocouple installation. The large size of the thermocouple well reduced the reaction space in the combustion tube approximately 20%. Burner assembly and furnace design were such that a maximum of only ten inches of the thirty-inch combustion tube was directly heated.

Equipment Leaks. Leaks in the feed end of the apparatus and vaporization of the unreacted material from the water-cooled condenser collecting vessel caused large losses of reaction mixture. The former source of loss made the space velocity calculations inaccurate; while both sources of loss made an evaluation of the amount of recovered unreacted reaction mixture and its composition for purposes of recycling impractical.

Materials of Construction. Brass, copper, and stainless steel in the materials of construction were corroded by the action of the reactants and products at the higher temperatures to which they were subjected. Natural rubber deteriorated at all temperatures in contact with products and reactants. No investigation was made of the effects of these materials or their corrosion or decomposition products on the phenyl substitution reaction.

Phneyl Substitution of Silicon Tetrachloride

Variables Studied. Space velocity and temperature only were studied in this investigation. The effect of pressure variations was not investigated. Only one molar ratio of silicon tetrachloride to benzene (2:1) was used in the reaction mixture and no catalysts for the reaction were investigated.

Reaction Temperature. The method of determining reaction temperature, that of averaging the temperature readings for the run, was probably inaccurate. In addition, the fixed thermocouple did not show the average temperature of the reaction space. Temperatures investigated were scattered and no investigation of the effect of temperature variations at constant space velocity was possible because of the lack of control of feed rate and therefore space velocity. The range of temperatures investigated was from 683°C. to 890°C.

Space Velocity. The range of space velocities investigated was from 135 to 3460 liters gas per liter reaction space per hour. Although this range seemed to encompass the optimum, insufficient intermediate values were studied to draw quantitative conclusions. No investigation of the effect of space velocity variations at constant temperature was possible because of the lack of control of temperature.

Pyrolysis of Benzene. No investigation was made of the actual degree of pyrolysis of benzene at the temperatures and space velocities of the phenyl substitution runs. The degree of pyrolysis was estimated by visual observation only.

Polysubstituted Compounds. No investigation was made of the possibility of reacting phenyltrichlorosilane with benzene in a second substitution step to form diphenyldichlorosilane, although the reaction is possible according to thermochemical calculations.

Energy Balance. Because of the scattered nature of the data and results of this investigation no energy balances were calculated. The apparatus was not suitable for such a calculation.

By-products. No attempt at separation of identification of the by-products of the phenyl substitution reaction was made. Their effect on the reaction and subsequent distillation was not considered.

Losses. The proportions of the losses in the phenyl substitution process caused by leaks, loss by vaporization, and pyrolysis of the benzene were not determined separately. No evaluation of the losses to determine the amount of unreacted material available for recycling could be made.

Distillation of the Products of the Phenyl Substitution of Silicon Tetrachloride

Method Used in this Investigation. The distillation method used in this investigation did not permit close control of the temperature ranges, and therefore composition, of the fractions collected. Collection of fractions with boiling points of some of the by-products was impossible because of the lack of control. The method of heating the distilling flasks was not efficient.

Losses. The proportions of the losses caused by vaporization from the receivers, pyrolyzed benzene residue, and materials boiling at temperatures above 80 °C. which were not phenyltrichlorosilane were not determined separately. Therefore, the recoverable material contained in fraction 1 could not be evaluated for recycling purposes.

Analysis of the Products

The only analysis made of any of the fractions collected during the distillation of the products of the phenyl substitution of silicon tetrachloride was for the chlorine content of fraction 3. No analysis was made for silicon content of fraction 3 to show the proportion of the hydrolyzable chlorine present in phenyltrichlorosilane, assuming no silicon tetrachloride was present. It was not known definitely that the method of hydrolysis used was effective in hydrolyzing all the chlorine present in phenyltrichlorosilane. No reference was found in the literature to previous use of the method in chlorine analysis of phenylchlorosilanes.

C. Recommendations

Phenyl Substitution Apparatus

It is recommended that the phenyl substitution apparatus be changed as follows to provide for better operation and closer control:

Combustion Furnace and Controls. An electrically heated combustion furnace, provided with a rheostat for coarse temperature control, should be used to heat the combustion tube. It should be long enough to heat the entire length of the tube except that needed to make connections to other parts of the apparatus. The construction of the furnace should be such that the combustion tube would be in a vertical position to prevent settling of the packing in a manner which would leave open spaces in the reaction space. The furnace should heat the periphery of the tube evenly. Some type of automatic temperature controlling device should be used in conjunction with the thermocouple-pyrometer connection for close temperature control.

Feed Rate Measurement. A recording flow meter, if such a device is available, should be used to determine accurately the total weight of reaction mixture used in each phenyl substitution run, and at the same time measure feed rates during the runs. A valve suitable for feed rate control should be installed in the feed line. The feed end of the apparatus should be permanently set up and tightly sealed. The sources of leakage experienced in this investigation would then be eliminated.

Products Condenser. A single water-cooled condenser should be used to condense the phenyl substitution products emitting from the exit end of the combustion tube. If the products are to be collected here, the collecting vessel should be cooled by an ice bath or similar device to prevent vaporization of the volatile components.

Materials of Construction. Fused silica or quartz should be used as materials of construction where contact with products and reactants is at temperatures of 300°C. or higher. Stainless steel or Pyrex glass can be used where contact with products and reactants is at temperatures below 300°C. Natural rubber should not be used for contact at any temperature. The effect of the materials of construction on the phenyl substitution reaction should be studied.

Thermocouple Installation. The thermocouple should be so arranged that temperatures could be taken at any point inside the combustion tube during the phenyl substitution runs. The well should be constructed of a thin-walled fused silica tube of the smallest diameter which could accommodate the thermocouple to provide a minimum reduction in reaction space in the combustion tube.

Phenyl Substitution of Silicon Tetrachloride

It is recommended that further investigation of the phenyl substitution of silicon tetrachloride to produce phenylchlorosilanes be made. The following specific recommendations are made:

Variables. In addition to temperature and space velocity, the effect of pressure on the phenyl substitution reaction should be studied. Sub- and superatmospheric pressures should be investigated. The effect of varying the molar ratio of silicon tetrachloride and benzene in the reaction mixture should also be studied with the object of increasing yields of phenylchlorosilanes.

Catalysts. Catalysts for the phenyl substitution reaction should be studied to promote better yields of phenylchlorosilanes at lower reaction temperatures than were investigated. Temperatures below about 500°C., the lowest temperature at which the pyrolysis of benzene occurs, should receive particular attention.

Reaction Temperature. The effect of reaction temperature on yields of phenylchlorosilanes at constant space velocities should be more thoroughly investigated. In the absence of catalysts, temperatures between 700°C. and 900°C. should receive particular attention with the object of determining optimum temperature.

Space Velocity. The effect of space velocity on yields of phenylchlorosilanes at constant temperatures should be more thoroughly investigated. In the absence of catalysts, space velocities between 300 and 500 liters gas per liter reaction space per hour, measured at the temperatures and pressures of the reaction space, should receive particular attention with the object of determining optimum space velocity.

Pyrolysis of Benzene. The pyrolysis products of benzene obtained in the phenyl substitution runs should be collected and the degree of pyrolysis of the benzene at different temperatures and space velocities should be determined. These data should be correlated with the data on yields of phenylchlorosilanes at different temperatures and space velocities with the object of determining the conditions at which a minimum of pyrolysis occurs for a high phenylchlorosilane yield.

Polysubstituted Compounds. An investigation should be made of the possibility of a second substitution reaction, involving phenyltrichlorosilane and benzene as reactants, to produce diphenyldichlorosilane, since none was obtained in the one-pass process studied in this investigation.

Energy Balance. An energy balance should be calculated for the optimum conditions of the phenyl substitution reaction with the object of increasing the efficiency of the process.

By-Products. The by-products, if not isolated, should at least be identified so that their effect on the phenyl substitution reaction and subsequent distillation could be studied.

Losses. If refinements in the phenyl substitution apparatus eliminate leaks which cannot otherwise be determined, the losses in the process should then be evaluated to determine the amount of unreacted benzene and silicon tetrachloride available for recycling.

Distillation of the Products of the Phenyl Substitution of Silicon Tetrachloride

It is recommended that a more thorough investigation be made of the distillation of the phenyl substitution products. The following specific recommendations are made:

Method. Fractional distillation should be used to separate the phenyl substitution products. An effort should be made to obtain in separate fractions as many of the compounds present as possible. Fractional distillation should facilitate control of the temperature ranges of the fractions. The unreacted silicon tetrachloride and benzene could be driven off from the fractionating section since they are the lowest-boiling of the materials which probably compose the phenyl substitution products. They could be condensed and collected as a mixture. A receiver cooled by an ice bath or similar device should be used for silicon tetrachloride-benzene mixtures to prevent vaporization.

It would be desirable if the fractionating apparatus could be connected to the condenser at the exit end of the phenyl substitution apparatus. The phenyl substitution products could then be introduced directly into the distilling apparatus. This would eliminate a source of losses in the transfer process and from the collecting vessels used in this investigation. The fractionating apparatus would have to be of small capacity if continuous operation at the same time as the phenyl substitution reaction were to be attempted since the feed rates for the space velocities recommended for study would be quite small.

Losses. If refinements in the distillation apparatus eliminate sources of loss which cannot otherwise be determined, the losses in the process should then be evaluated to determine the amount of unreacted benzene and silicon tetrachloride available for recycling.

Analysis of the Products

If fractions could be obtained at the boiling points of some of the by-products in the distillation of the phenyl substitution products, these should be analyzed to determine their composition with the object of determining possible effects of the compounds on the phenyl substitution reaction.

Fraction 3 obtained in the distillation of the phenyl substitution products should be analyzed for silicon content as well as chlorine content with the object of determining the proportion of hydrolyzable chlorine present in phenyltrichlorosilane. Some study should be made of the possibility of the presence of silicon tetrachloride in fraction 3 with the object of increasing the accuracy of the chlorine analysis as a means of determining the amount of phenyltrichlorosilane present.

V. CONCLUSIONS

Phenyl Substitution of Silicon Tetrachloride to Produce Phenylchlorosilanes

On the basis of the results of the phenyl substitution of silicon tetrachloride in the absence of catalysts, effected by passing a mixture of gaseous silicon tetrachloride and benzene, in the molar ratio of 2:1 ($SiCl_4$:C_6H_6), at atmospheric pressure through fused silica combustion tubes, packed with quartz chips (through 1/2", on 1/4"), at temperatures between 683°C. and 890°C. and space velocities between 135 and 3460 liters gas/liter reaction space/hour, and condensation of the products; the following conclusions are drawn:

1. The highest yield of phenyltrichlorosilane, based on chlorine content of the fraction collected between 190°C. and 250°C., during the distillation, and on 100% reaction of the benzene, was 2.11%, where phenyl substitution was carried out at a temperature of 890°C. and a space velocity of 445 liters gas/liter reaction space/hour.

2. Maximum yield of phenyltrichlorosilane was obtained for space velocities between 300 and 500 liters gas/liter reaction space/hour.

3. Minimum effective temperature for the phenyl substitution of silicon tetrachloride was approximately 700°C.

4. No polysubstituted compounds of silicon tetrachloride were obtained within the limits of the conditions investigated.

5. Pyrolysis products of benzene were obtained for all sets of conditions within the limits investigated.

VI. SUMMARY

The silicone (organosiloxane) polymers are a new and remarkable development of the chemical industry. They are available as fluids, lubricants and greases, electrical sealing compounds, resins, and elastomers. Their outstanding heat and moisture resistance, chemical inertness, and electrical resistance make them suitable for a great variety of uses. However, present commercial methods of production do not meet the demand for these products. The production methods are expensive and difficult to control, particularly during the initial step of converting the raw materials to the intermediate organochlorosilanes.

Investigation was made of the process to product phenylchlorosilanes, one type of organochlorosilanes, in which a mixture of silicon tetrachloride and benzene, in the molar ratio of 2:1 ($SiCl_4$:C_6H_6), was passed through fused silica tubes packed with quartz chips at temperatures from 683°C. to 890°C. at space velocities, calculated at the temperatures and pressure of the reaction space, from 135 to 3460 liters gas per liter reaction space per hour. The reactants were in the gaseous phase during the reaction, which was carried out at atmospheric pressure (approximately 13.8 psia). The products were collected and batch distilled at atmospheric pressure. The fraction collected during distillation which was believed to contain the phenyltrichlorosilane yield was analyzed for chlorine content to indicate the amount of phenyltrichlorosilane present. No material boiling at temperatures above 267°C. was obtained. A total of forty-two phenyl substitution runs were made, of which twelve were useful in collecting data on the process. The remaining thirty runs were discarded because of equipment operating difficulties.

The highest yield of phenyltrichlorosilane, based on 100% reaction of the benzene, was 2.11%, where phenyl substitution was carried out at a temperature of 890°C. and a space velocity of 445 liters gas per liter reaction space per hour. No polysubstituted compounds of silicon tetrachloride were obtained from any of the phenyl substitutions.

Maximum yield of phenyltrichlorosilane was obtained for space velocities between 300 and 500 liters gas per liter reaction space per hour.

Minimum effective temperature for the phenyl substitution of silicon tetrachloride to produce phenyltrichlorosilane was approximately 700°C.

Pyrolysis products of benzene were obtained for all sets of conditions within the limits investigated. By visual observation only, the quantities were observed to increase as temperature increased or space velocity decreased.

Batch distillation at atmospheric pressure was found to be unsuitable where close control of the temperatures at which the fractions were collected was desirable. Compositions of the fractions varied considerably as a result.

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VIII. ACKNOWLEDGEMENTS

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APPENDIX

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UNITED STATES PATENT OFFICE

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COMPOUNDS

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4 Claims. (Cl. 260—607)

This invention relates to the preparation of organic compounds and more particularly to the preparation of organic compounds of silicon.

Organic compounds of silicon have hitherto been made by the reaction of silicon halides with organomagnesium compounds or with hydrocarbon halides and alkali metals. Both of these methods require expensive reagents and are therefore disadvantageous.

This invention has as an object the provision of a new process for the manufacture of organic silicon compounds. A further object is the provision of a process for preparing organic silicon halides. Other objects will appear hereinafter.

These objects are accomplished by the following invention wherein an inorganic silicon halide containing silicon, a halogen of atomic weight above twenty and preferably free from elements other than silicon, hydrogen, and halogen is reacted in the vapor phase at temperatures of at least 450° C. with a hydrocarbon. The silicon halide and the hydrocarbon are volatile under the pressure and at the temperature used.

The preferred method of practicing this invention involves heating a mixture of a hydrocarbon and the silicon halide to a temperature of 600 to 850° C. This is preferably carried out by passing the vapors of the reactants through a heated reaction zone or over a heated surface, condensing the vapor and separating the hydrocarbon substituted silicon halide from the liquid so obtained by fractional distillation or other suitable means.

The more detailed practice of the invention is illustrated by the following examples, wherein parts given are by weight. There are of course many forms of the invention other than these specific embodiments.

Example I

This example illustrates the preparation of phenyl-silicon trichloride by passing a mixture of benzene and silico-chloroform, $HSiCl_3$, through a heated zone.

A mixture of 1 part of benzene and 1.5 parts of silicochloroform was introduced into a tube, heated externally to 750–770° C., of fused quartz and filled with small pieces of clay plate. The rate of addition was controlled so that the space velocity was of the order of 80 to 90 per hour. The vapors issuing from the heated tube were condensed by a water cooled condenser. The condensate was fractionally distilled to isolate phenylsilicon trichloride, $C_6H_5SiCl_3$, boiling point 71–74° at 11 mm.

Example II

This example illustrates the preparation of an aryl silicon trichloride by passing the vapors of an aromatic hydrocarbon and silicon tetrachloride over a heated surface.

Benzene and silicon tetrachloride in the ratio of 1 to 2 were conducted in the vapor phase over a fused quartz tube heated to bright redness. The system was so arranged that substances boiling above 100° C. were condensed but the unchanged reactants were continuously recycled over the heated tube. The higher boiling material was removed and fractionally distilled under reduced pressure to obtain pure $C_6H_5SiCl_3$ which boils at 90 to 100° at 25 mm. mercury pressure. The product was a colorless liquid which fumed in moist air and had a sharp odor. It contained 13.01% silicon and 48.4% chlorine. The theoretical values for $C_6H_5SiCl_3$ are 13.24% silicon and 50.4% chlorine.

Example III

This example illustrates the preparation of a hydrocarbon substituted silicon halide from a polycyclic aromatic hydrocarbon and silicon tetrachloride.

A solution of 1 part naphthalene in 4 parts of silicon tetrachloride was treated as described in Example I at a temperature of 850 to 870° C. The product, isolated by fractional distillation under reduced pressure, fumed in moist air and reacted vigorously with water to give an ether-soluble naphthalenesiliconic acid.

Example IV

This example illustrates the preparation of a hydrocarbon substituted silicon halide from an olefin and silicon tetrachloride.

Two parts of octene-1 and 3 parts silicon tetrachloride were mixed and treated as described in Example I at a temperature of 700–720° C. The unchanged silicon tetrachloride was removed from the condensate by fractional distillation leaving a dark colored oil which reacted vigorously with water and contained 4.21% silicon.

Example V

This example illustrates the preparation of a hydrocarbon substituted silicon halide from an olefin and silicochloroform.

A mixture of 11 parts of silicochloroform, $SiHCl_3$, and 9 parts of n-octene-1 was treated as described in Example I at a temperature of 600 to 610° C. The unchanged silicochloroform was removed from the condensate by fractional distillation. The residue boiled in the range of 140–200° C. and reacted vigorously with water to give an ether soluble precipitate which contained silicon.

Example VI

This example illustrates the preparation of a hydrocarbon substituted silicon halide from a paraffin hydrocarbon and silicon tetrachloride.

One part of isobutane as a gas and 4 parts of silicon tetrachloride as a liquid were introduced into a fused quartz tube packed with clay plate, heated to 800° C. as described in Example I. The unchanged silicon tetrachloride was removed from the condensate by fractional distillation. There remained a green oil which was distilled at atmospheric pressure. The fraction boiling above 90° C. contained 12.42% silicon and 46.99% carbon. This corresponds approximately to dibutylsilicon dichloride.

The examples disclose the reaction of inorganic silicon halides with aromatic and aliphatic saturated and unsaturated hydrocarbons but the invention is generic to hydrocarbons, including saturated and unsaturated, cyclic and acyclic, straight chain and branched chain, aliphatic, aromatic and mixed aromatic aliphatic hydrocarbons and mixtures of hydrocarbons including methane, propane, dodecane, isobutane, neopentane, ethylene, octene, decadiene-1,9, butadiene, acetylene, hexine, cyclopentane, cyclopentadiene, cyclohexane, cyclohexene, p-menthane, p-menthene, pinene, dipentene, alpha-terpinene, benzene, diphenyl, naphthalene, anthracene, toluene, styrene, and diphenylmethane.

Commercial grades of hydrocarbons are satisfactory if they do not contain excessive amounts of water, alcohol, amines or other substances capable of giving rise to undesirable side reactions with silicon tetrachloride. Aromatic hydrocarbons are preferred. The hydrocarbons may be substituted with any group which is non-reactive toward silicon halide, as for example, halogen.

The inorganic silicon halides useful in the process of this invention contain at least one halogen of atomic weight above twenty and preferably no element other than silicon, hydrogen, and the halogens. The preferred silicon halides have the formula

$$Si_nH_aX_b$$

where $a+b$ is $2n+2$, n and b are intergers greater than 0 and not more than 6 and a may be zero or an integer whose value depends then on n and b. At least one X atom is a halogen of atomic weight above twenty. Thus, the invention is preferably practiced with $SiFCl_3$, SiF_3Cl, SiF_2Br_2, $SiFBr_3$, $SiCl_4$, SiH_2Cl_2, $SiHCl_2$, Si_3Cl_8, $Si_2H_4Cl_2$, Si_6Cl_{14}, $SiBr_4$, $SiHBr_3$, $SiClBr_3$, $SiBrCl_3$, Si_2HBr_5, Si_4Br_{10}, $SiCl_2I_2$, $SiBrI_3$, Si_2I_6, although silicon oxyhalides such as Si_2Cl_6O, $Si_3O_3Cl_6$, $Si_6O_7Cl_{10}$, $Si_4O_4Cl_8$, can also be used. Mixtures of silicon halides may be employed.

Commercial grades of inorganic silicon halides have been found to be satisfactory. Those not available commercially can be prepared by methods described in J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," vol. 6, part 2, pages 960 to 985, Longmans, Green and Co., London, England; W. C. Schumb & H. H. Anderson, J. Am. Chem. Soc., 58, 994 (1936); H. S. Booth and C. F. Swinehart, J. Am. Chem. Soc., 57, 1333 (1935); or Friend, Textbook of Organic Chemistry, vol. V (1917), pages 187 to 192, 194 to 202.

The method of mixing the reactants or the introduction of them into the reaction zone may be accomplished by any convenient means. The reaction may be carried out at subatmospheric, atmospheric or superatmospheric pressure. The reaction takes place at temperatures as low as 450° C. but proceeds more rapidly at higher temperatures and is operable even as high as 1000° C. The upper limit of temperature is determined by the stability of the hydrocarbon under the reaction conditions and the product and generally is below the temperature at which excessive decomposition sets in. The upper limit of the temperature depends upon the rate at which the reactants are passed through the heated zone and in general varies directly with the space velocity. The space velocity itself can be varied over wide limits but the optimum space velocity depends upon the nature of the reactants and the temperature of the reaction zone and is readily determined in any given case.

The tube may be made of any material impermeable to gases and capable of withstanding the elevated temperature and the action of silicon halide. It is preferred but not at all necessary to fill the heated zone loosely with an inert material to aid in uniform heating of the gases. Although the examples illustrate the use of clay plates for filling the heating zone, the process is not limited to the use of such filler. Carborundum, heat resistant glass beads, carbon, silica gel or any material resistant to silicon halides at elevated temperatures may be used.

The material may be collected in any convenient manner after it has passed through the heated zone and may be isolated from other products and unreacted materials in any suitable way. Fractional distillation is ordinarily used.

The process of this invention is of use in the preparation of products hitherto obtainable only through expensive processes such as the Grignard reaction. The products obtained may be used as intermediates for the preparation of organosilicon acids, esters, etc., and upon hydrolysis give rise to polymers from which coating compositions unusually resistant to high temperature and chemical attack can be prepared.

The above description and examples are intended to be illustrative only. Any modification of or variation therefrom which conforms to the spirit of the invention is intended to be included within the scope of the claims.

What is claimed is:

1. A process for the preparation of organosilicon compounds which comprises reacting an inorganic silicon halide having at least one halogen atom of atomic weight above twenty with an aliphatic hydrocarbon in the vapor phase at a temperature of at least 450° C. and below the decomposition temperatures of the reactants under the reaction conditions and isolating the organosilicon compound.

2. A process for the preparation of organosilicon compounds which comprises reacting an inorganic silicon halide having at least one halogen atom of atomic weight above twenty and which is free from atoms other than silicon, hydrogen, and halogen atoms, with an aliphatic hydrocarbon in the vapor phase at 600–850° C. and isolating the organosilicon compound.

3. A process for the preparation of organosilicon compounds which comprises reacting a silicon halide containing only silicon and halogen atoms, at least one of which has an atomic weight above twenty, with an aliphatic hydrocarbon in the vapor phase at 600–850° C. and isolating the organosilicon compound.

4. A process for the preparation of organosilicon compounds which comprises reacting silicon tetrachloride with an aliphatic hydrocarbon in the vapor phase at 600–850° C. and isolating the organosilicon compound.

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