

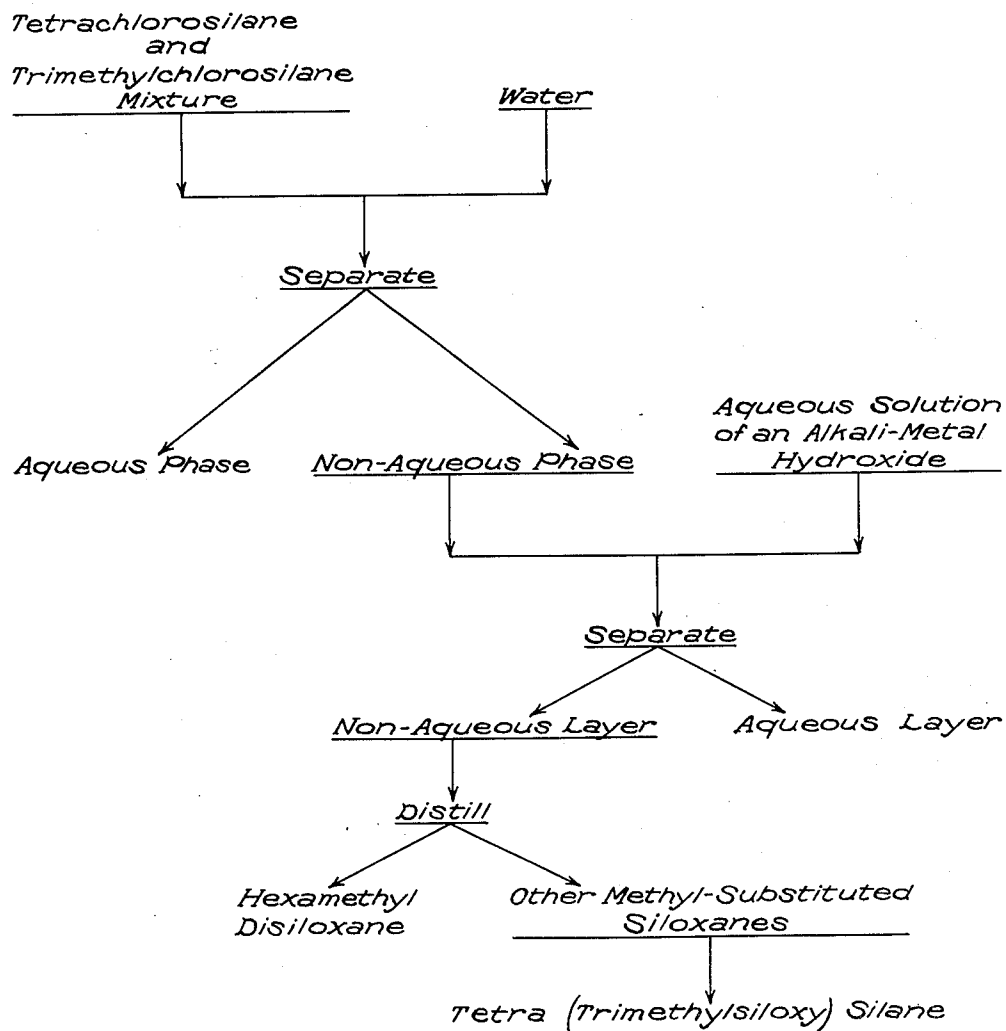
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W. I. PATNODE ET AL

2,519,926

RESOLUTION OF CHLOROSILANE MIXTURES

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Inventors:
Winton I. Patnode,
John R. Elliott,
by *Arthur G. Shaw*
Their Attorney.

UNITED STATES PATENT OFFICE

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RESOLUTION OF CHLOROSILANE
MIXTURES

Winton I. Patnode, Richland, Wash., and John R. Elliott, Schenectady, N. Y., assignors to General Electric Company, a corporation of New York

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7 Claims. (Cl. 260-448.2)

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The present invention relates to a process for resolving mixtures of tetrachlorosilane (silicon tetrachloride) and trimethylchlorosilane, particularly azeotropic or constant boiling mixtures of these two chlorosilanes. More particularly, the invention is concerned with the process which comprises (1) hydrolyzing a mixture of tetrachlorosilane and trimethylchlorosilane and (2) contacting the hydrolysis reaction product in an aqueous medium with an alkali-metal hydroxide, preferably in the form of an aqueous solution, thereby to obtain a layer comprising hexamethyl disiloxane.

Mixtures of the above-mentioned chlorosilanes cannot be completely separated into their various components by fractional distillation because tetrachlorosilane (B. P. 57.6° C. at 760 mm.) and trimethylchlorosilane (B. P. 57.5° C. at 760 mm.) not only have approximately the same boiling points, but also form a constant boiling mixture or azeotrope which consists substantially of about 45 to 55 mol per cent trimethylchlorosilane and 55 to 45 mol per cent tetrachlorosilane. Usually these two chlorosilanes are present in approximately equimolecular proportions in a constant boiling mixture which distills at about 54.5° C. at 760 mm. and contains about 65.8 per cent by weight of chlorine.

Various standard methods are known for resolving an azeotrope. One of the more common methods is to fractionally distill the azeotrope at pressures other than atmospheric pressure. However, with this method no appreciable change in the composition of the tetrachlorosilane-trimethylchlorosilane azeotrope is effected at practical super- or sub-atmospheric pressures. Another method involves fractionally distilling the mixture of chlorosilanes in the presence of a nitrile selected from the group consisting of acetonitrile and acrylonitrile as disclosed and claimed in Sauer et al. Patent 2,388,575, issued November 6, 1945, and assigned to the same assignee as the present invention. This latter method is, however, complicated by the fact that because of the corrosion of the iron equipment by the ingredients employed in this method, it has been necessary to use an all glass still which is expensive.

In accordance with the process of our invention which is diagrammatically illustrated in the accompanying drawing, we have discovered a process for separating the components of a mixture of tetrachlorosilane and trimethylchlorosilane thereby to obtain the latter component in the form of hexamethyl disiloxane substan-

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tially free of the former component, which process comprises first hydrolyzing the mixture of chlorosilanes with an amount of water at least in excess of that calculated as necessary to effect complete hydrolysis of the chlorosilanes, secondly, removing the resulting aqueous layer from the hydrolysis mixture and contacting the substantially non-aqueous phase resulting from the hydrolysis step with an aqueous solution, preferably a concentrated aqueous solution, of an alkali-metal hydroxide, for example, sodium hydroxide, potassium hydroxide, lithium hydroxide, etc., and finally, separating the resulting substantially non-aqueous layer from the reaction product obtained in the previous alkalizing step, and isolating the hexamethyl disiloxane present in the previously obtained non-aqueous layer, for instance, by fractional distillation.

The steps whereby our claimed process may be carried out may be varied. The mixture of chlorosilanes may be hydrolyzed by either adding water to the mixture or adding the mixture to water. We have discovered that when an azeotrope of tetrachlorosilane and trimethylchlorosilane is employed in the process, it is desirable that the amount of water employed in hydrolyzing the mixture of chlorosilanes be present in an amount equal to, by weight, from about 75 to 90, preferably from 80 to 85, per cent of the total weight of water and mixture of chlorosilanes. Stated alternatively, we prefer to use, on a weight basis, from 3 to 9 parts water per part azeotropic mixture.

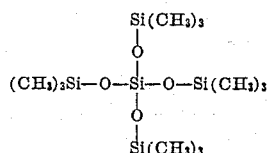
If the above-stated proportion of water to mixture of chlorosilanes is employed, two layers separate easily upon hydrolysis, one layer comprising an acid aqueous phase, and the other layer comprising a non-aqueous phase consisting essentially of a white powder which floats on the surface of the water. If too much water is employed in the hydrolysis step, a soupy gel is usually obtained which is more difficult to separate into the two aforementioned aqueous and non-aqueous phases. If too little water is employed, there is obtained a mass which is difficult to stir. We have found, in hydrolyzing the azeotrope, that the optimum weight ratio of water to azeotrope, on a weight basis, is approximately 5 to 1.

Where an excess amount of water has been employed in the hydrolysis operation so that the separation of layers is not particularly defined, the separation step may be omitted and the hydrolysis product may be contacted or mixed directly with a large excess of a concentrated aque-

ous solution of an alkali-metal hydroxide. The large excess of caustic solution is necessary to neutralize the hydrogen chloride present in the hydrolysis reaction product as well as to effect separation of the hydrolysis reaction product into an aqueous and substantially non-aqueous or oily phase. Throughout the hydrolysis step, it is especially desirable that efficient mixing and stirring of the water and mixture of chlorosilanes be accomplished in order to realize complete hydrolysis and to facilitate separation of the mass into two phases.

When separation of the hydrolysis product into an aqueous phase and a non-aqueous phase has been accomplished, the former phase is removed and the latter phase is treated with the aqueous solution of the alkali-metal hydroxide wherein the alkali-metal hydroxide is preferably present in a concentrated form, for example, in the form of from about a 5 to 20 normal solution. The amount of alkali-metal hydroxide employed is preferably equal to at least that necessary to convert the silicic acid or its condensation products obtained in the hydrolysis to an alkali-metal silicate, e. g., sodium silicate (Na_2SiO_3). From the foregoing it will be apparent that the minimum amount of alkali-metal hydroxide which may be employed comprises a molar ratio of at least 2 moles of the alkali-metal hydroxide per mol of silicon tetrachloride.

The aforementioned alkalizing step effects separation of the mass into an aqueous layer and a non-aqueous or oily layer which comprises hexamethyl disiloxane and smaller amounts of other substituted siloxanes, for example, tetra (trimethylsiloxy) silane. Fractional distillation of the non-aqueous or oily layer results in good yields of trimethylchlorosilane in the form of hexamethyl disiloxane, as well as small amounts of trimethyl silanol (which condenses easily to form hexamethyl disiloxane) and varying amounts of condensation products of trimethyl silanol and silicic acid, for example, the aforementioned tetra (trimethylsiloxy) silane of the general formula:



Because the reaction product after the addition of the solution of the alkali-metal hydroxide, under the proper conditions, separates so readily into two layers, it is more practical to remove the aqueous layer prior to isolation of the hexamethyl disiloxane. However, instead of separating the layers, the methyl-substituted siloxanes may be removed from the alkaline reaction mass by other methods, for example, by steam distillation or by solvent extraction with non-polar solvents, e. g., benzene, toluene, xylene, petroleum ether, diethyl ether, etc.

Hexamethyl disiloxane obtained in the practice of our claimed invention is useful for making liquid, oily, linear hydrocarbon-substituted (e. g., methyl-substituted) polysiloxanes of the type disclosed and claimed in Patnode application Serial No. 463,814, filed October 29, 1942 (now U. S. 2,469,888, issued May 10, 1949), and assigned to the same assignee as the present invention. These liquid polysiloxanes, which are useful for lubricating purposes, generally have from about 2.001 to 2.2 hydrocarbon groups per

silicon atom. In addition, we have found that the condensation products of trimethyl silanol and silicic acid are also useful as a source of trimethyl siloxy groups ($(\text{CH}_3)_3\text{Si}-\text{O}-$) for terminating the ends of hydrocarbon-substituted polysiloxane chains having a ratio of about 2 hydrocarbon groups per silicon atom, for example, two methyl groups per silicon atom, by effecting rearrangement by the process of cleavage and condensation between the hydrolysis product of a dihydrocarbon-substituted dihalogenosilane and the aforementioned condensation product of trimethyl silanol and silicic acid (see the aforementioned Patnode application as well as Sprung et al. application Serial No. 702,590, filed October 11, 1946 (now U. S. 2,483,158, issued September 27, 1949), and assigned to the same assignee as the instant application).

It is desirable to acidify the non-aqueous or oily layer obtained as a result of the alkalizing step with a dilute acid, for example, a dilute aqueous hydrochloric acid solution, for instance, a 5 per cent solution, prior to fractional distillation of the mass to isolate the hexamethyl disiloxane or other substituted methyl siloxanes. This acidification step effects condensation of free silanol groups present in the mass thereby increasing the yields and simplifies the distillation of, e. g., hexamethyl disiloxane.

In order that those skilled in the art may better understand how the present invention may be practiced, the following examples are given by way of illustration and not by way of limitation.

Example

About 400 grams (containing 1.44 mols SiCl_4) of an azeotrope of tetrachlorosilane and trimethylchlorosilane (the trimethylchlorosilane being equivalent to 103 grams hexamethyl disiloxane) was added with vigorous stirring through a dropping funnel to about 2000 parts water over a period of 15 minutes. During the hydrolysis, the temperature rose spontaneously to about 50° to 70° C. If desired, the hydrolysis may be carried out with ice water to maintain a lower temperature, or other external cooling means may be employed to prevent the temperature from rising above the boiling point of the azeotrope.

After the mixture of chlorosilanes had been added, the stirring was continued for about one half hour to powder the hydrolysis product and to whip air into the slurry in order to float the powder. After allowing the lower aqueous layer to settle completely, the latter layer was drained from the powder and the powder was washed twice with water.

A solution of about 500 grams (12.5 mols sodium hydroxide) sodium hydroxide dissolved in approximately 500 grams water was then added slowly through a dropping funnel to the washed powder, the sodium hydroxide thus being present in a molar ratio of approximately 8.6 mols of the latter per mol of SiCl_4 , taking into account the amount of SiCl_4 in the azeotropic mixture. The powder dissolved with the evolution of heat and two layers separated immediately. The contents of the flask containing the reaction product was drained into a separatory funnel and the oily phase collected. The yield of this non-aqueous or oily phase which was about 117 grams, was subjected to a fractional distillation step to yield about 70 grams of an oily product which consisted essentially of hexamethyl disiloxane.

Tetra (trimethylsiloxy) silane was isolated from the residue. This compound has the following properties:

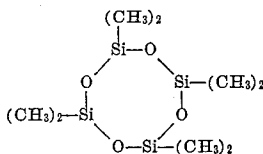
B. P.=130.8–131.0° C. at 50 mm.

$n_D^{20}=1.3894$

$d_4^{20}=0.8677$

This compound on analysis was found to contain 2.405 methyl groups per silicon atom (calculated 2.40 methyl groups per silicon atom), 37.38 per cent carbon (calculated 37.46), and 9.32 per cent hydrogen (calculated 9.43 per cent).

An oily or non-aqueous phase obtained in accordance with the process in the example immediately after the alkalizing step was found to have a methyl to silicon ratio of 2.70. Varying amounts of this oily phase and the tetra (trimethylsiloxy) silane were each shaken with octamethyl tetrasiloxane (having a methyl to silicon ratio of 2.0) in the presence of a small amount of concentrated sulfuric acid in accordance with the method disclosed in the aforementioned Patnode application. The oils obtained were washed several times with water and centrifuged to remove the last traces of water. The following table shows the properties of the oils containing varying proportions of the aforementioned two compositions intercondensed with the octamethyl tetrasiloxane. The number "2.7" in the first column of the table refers to the number of methyl groups per silicon atom of the non-aqueous or oily layer obtained as in the example after the alkalizing step. The number "2.4" in the same column refers to the number of methyl groups per silicon atom of tetra (trimethylsiloxy) silane. The term "tetramer" refers to octamethyl tetrasiloxane having the structural formula



Table

Type Oil	Me/Si ¹	Per Cent Wt. Chain Stopper ²	Per Cent Evapo- ration Loss 8 Days at 150° C.	Viscosity In Centistokes		Viscosity Temper- ature Co- efficient	Freezing Point
				100° C.	210° C.		
Tetramer +2.4	2.0038	0.989	11.3	1,320	438	0.668	-38
	2.0075	1.937	11.2	263			-43
	2.0152	3.893	12.4	8,714			-45
	2.0222	5.736	13.7	51.5	20.7	0.594	-63
	2.0351	9.073	17.7	30.8	12.5	0.594	-67
	2.0068	1.035	10.7	565	230	0.594	-38
Tetramer +2.7	2.0127	1.939	11.5	171	66.1	0.604	-43
	2.0253	3.821	13.0	57.0	23.1	0.594	-43
	2.0376	5.713	14.9	32.9	13.5	0.589	-45
	2.0605	9.168	20.4	19.5	8.2	0.580	-67
	2.0865	13.070	27.6	14.1	5.54	0.607	-70

¹ This refers to the ratio of methyl groups to silicon atoms in the complete chain-stoppered oil.

² This refers to the per cent, by weight, of the liquid oily phase or of tetra (trimethylsiloxy) silane intercondensed with the octamethyl tetrasiloxane.

What we claim as new and desire to secure by Letters Patent of the United States is:

1. The process which comprises (1) hydrolyzing with water a mixture of tetrachlorosilane and trimethyl chlorosilane, (2) contacting the hydrolysis reaction product in an aqueous medium with an alkali-metal hydroxide thereby to obtain a layer comprising hexamethyl disiloxane, the alkali-metal hydroxide being present in a ratio of from 2 to 8.6 mols of the latter per mol tetrachlorosilane, and (3) isolating the hexamethyl disiloxane present in the aforesaid layer.

2. The process which comprises (1) hydrolyzing

with water a mixture of tetrachlorosilane and trimethylchlorosilane, (2) contacting the non-aqueous phase of the hydrolysis product with an aqueous solution of an alkali-metal hydroxide, thereby to obtain a layer rich in hexamethyl disiloxane, the alkali-metal hydroxide being present in a ratio of from 2 to 8.6 mols of the latter per mol tetrachlorosilane, and (3) isolating the hexamethyl disiloxane present in the aforesaid layer.

3. The process which comprises (1) hydrolyzing with water an azeotropic mixture of tetrachlorosilane and trimethylchlorosilane, (2) contacting the non-aqueous phase of the hydrolysis product with an aqueous solution of sodium hydroxide, thereby to obtain a substantially non-aqueous layer comprising hexamethyl disiloxane, the sodium hydroxide being present in a molar ratio of from 2 to 8.6 mols of the latter per mol of tetrachlorosilane, and (3) isolating the hexamethyl disiloxane present in the non-aqueous layer.

4. The process for separating the components of a mixture of tetrachlorosilane and trimethylchlorosilane thereby to obtain the latter component in the form of hexamethyl disiloxane substantially free of the former component, which process comprises (1) hydrolyzing with water the mixture of chlorosilanes, (2) removing the aqueous layer resulting from the hydrolysis mixture, (3) contacting the substantially non-aqueous portion resulting from the hydrolysis step in (1) with a concentrated aqueous solution of an alkali-metal hydroxide, the latter being present in a molar ratio of from 2 to 8.6 mols of the alkali-metal hydroxide per mol of the tetrachlorosilane, and (4) separating the resulting substantially non-aqueous layer from the reaction mass in (3) and isolating the hexamethyl disiloxane present therein.

5. The process for separating the components of an azeotropic mixture of tetrachlorosilane and trimethylchlorosilane thereby to obtain the latter component in the form of hexamethyl disiloxane substantially free of the former component, which

process comprises (1) hydrolyzing the azeotropic mixture with an amount of water in excess of that calculated as necessary for the complete hydrolysis of the two components, (2) removing the resulting aqueous layer from the hydrolysis mixture, (3) thoroughly mixing the remaining substantially non-aqueous powdery portion with a concentrated aqueous solution of sodium hydroxide, the latter being present in the molar ratio of from 2 to 8.6 mols of the sodium hydroxide per mol of the tetrachlorosilane, (4) separating the resulting substantially non-aqueous liquid layer from the aqueous layer, and (5) isolating hexamethyl di-

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siloxane from the non-aqueous layer obtained in (4).

6. The process for separating the components of an azeotropic mixture consisting substantially of about 45 to 55 mol per cent trimethylchlorosilane and 55 to 45 mol per cent tetrachlorosilane thereby to obtain the former component in the form of hexamethyl disiloxane, which process comprises (1) hydrolyzing the azeotropic mixture with water present, by weight, in an amount equal to from about 75 to 90 per cent of the total weight of water and azeotropic mixture of chlorosilanes, (2) separating the resulting substantially non-aqueous portion, (3) treating the latter non-aqueous portion with a concentrated aqueous solution of sodium hydroxide, the latter being present in a molar ratio of from 2 to 8.6 mols of the sodium hydroxide per mol of the tetrachlorosilane, and (4) isolating hexamethyl disiloxane from the non-aqueous phase resulting from the alkaline treatment in (3).

7. The process which comprises (1) hydrolyzing an azeotropic mixture of tetrachlorosilane and trimethylchlorosilane with water present, by weight, in an amount equal to from about 75 to 90 per cent of the total weight of water and azeotropic mixture of chlorosilanes, (2) separating the resulting substantially non-aqueous portion, (3) treating the latter non-aqueous portion with a concentrated aqueous solution of sodium hy-

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droxide, the latter being present in a molar ratio of from 2 to 8.6 mols of the sodium hydroxide per mol of the tetrachlorosilane, and (4) isolating hexamethyl disiloxane and tetra (trimethylsiloxy) silane from the non-aqueous phase resulting from the alkaline treatment in (3).

WINTON I. PATNODE.
JOHN R. ELLIOTT.

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