Reaction of bivalent ... 25259 S/190/61/003/007/003/021
B101/B208

was also reduced with increasing distance between the urethane groups, and the temperature range of the elastic state was increased: n = 0, $T_v = +20^\circ C$; n = 10, $T_v = -40^\circ C$. There are 1 figure, 1 table, and 2 Soviet-bloc references.

ASSOCIATION: Institut elementoorganicheskikh soyedineniy AN SSSR (Institute of Elemental-organic Compounds, AS USSR)

SUBMITTED: August 5, 1960

Card 4/4

15.8170

27568
S/190/61/003/009/003/016
B110/B101

AUTHORS: Andrianov, K. A., Pichkhadze, Sh. V., Bochkareva, I. V.

TITLE: Polyorganotitanosiloxanes. . I. Synthesis of poly-bis-(acetylacetonate) organotitanosiloxanes

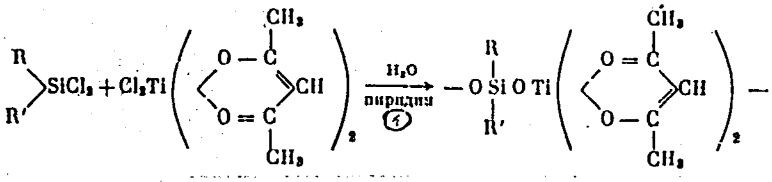
PERIODICAL: Vysokomolekulyarnyye soyedineniya, v. 3, no. 9, 1961, 1321-1325

TEXT: As the formation of polymers with linear chains is rendered difficult owing to the hydrolytic instability of the Ti-O-C bond of the alkoxy derivatives of orthotitanic acid, the authors tried to use intracomplex titanium derivatives. The present paper deals with the cohydrolysis of alkyl-(aryl-) chlorosilanes with bis-(acetylacetonate) dichlorotitanium (BADT). In the cohydrolysis of dimethyl dichlorosilane (DMDS), diethyl dichlorosilane (DEDS), methyl-phenyl dichlorosilane (MPDS), and methylvinyl dichlorosilane (MVDS) with BADT, the yield of polymers with Ti-O-Si chains is only 35% in the absence of acceptors, since 60% BADT does not react. It hydrolyzes with separation of acetylacetonate groups and formation of TiO_2. The polymers which are well soluble in conventional solvents

Card 1/5

have low melting points. The organic radicals at the Si atoms have little effect on cohydrolysis. The ratio Ti : Si is smaller in the polymers than in the initial substances. Pyridine increases the yield of cohydrolysis of DMDS + BADT to 57.6% of DEDS + BADT to 70.5%, of MVDS + BADT to 62%, and of MPDS + BADT to 63.8%. Ultimate analysis and infrared spectra indicate the following reaction:

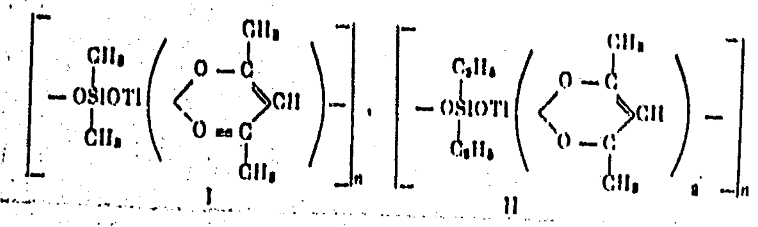
1 = pyridine.



(A)

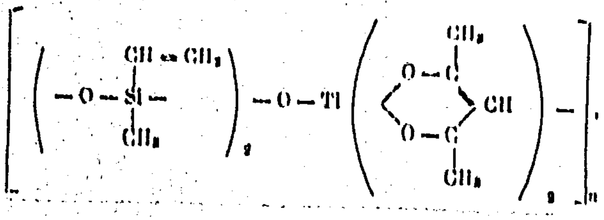
In the cohydrolysis of DMDS + BADT and DEDS + BADT the atomic Si/Ti ratio of polymers was 1 : 1 with the following composition of the repeating unit of the chain:

Polyorganotitanosiloxanes. ...



(B)

On cohydrolysis of MVDS + BADT, and of MPDS + BADT, the atomic Si/Ti ratio is 2 : 1 with the following repeating units



(III),

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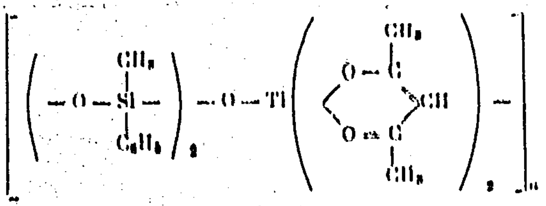

(IV).

The glass transition temperatures T_g for the polymers I, II, III, and IV were found to be ~-50, -25, -20, and +45°C, respectively. After heating to 200°C for 30 min, the polymers II, III, and IV do not flow even at 500°C, only the polymer I flows at about 100°C. Toluene and ten times the calculated amount of water were filled into a four-necked flask. A solution of alkyl-(aryl-) chlorosilane in toluene was added from the dropping funnel by stirring. Temperature rose on addition of BADT. The toluene layer was separated from the water, washed out until neutral (litmus), and distilled in vacuo. The yellow polymers dissolved readily in alcohol,

27568
S/190/61/003/009/003/016
Polyorganotitanosiloxanes. ... B110/B101

benzene, toluene, acetone, and carbon tetrachloride. The yield was 30% for poly-bis-(acetylacetonate) titanodimethylsiloxane, 40% for poly-bis-(acetylacetonate) titanodiethylsiloxane, and 38% for poly-bis-(acetylacetonate) titanomethylphenylsiloxane. Cohydrolysis of alkyl-(aryl-) chlorosilanes with BADT in the presence of pyridine gave: 57.6% for poly-bis-(acetylacetonate) titaniumdimethylsiloxane; 70.5% for poly-bis-(acetylacetonate) titanodiethylsiloxane; 62% for poly-bis-(acetylacetonate) titanomethylvinylsiloxane; and 63.8% for poly-bis-(acetylacetonate) titanomethylphenylsiloxane. The authors thank N. A. Chumayevskiy for taking the infrared spectra, and G. L. Slonimskiy, Head of the Laboratoriya issledovaniya polimerov (Laboratory for Polymer Research), for thermomechanical measurements. There are 2 figures, 3 tables, and 2 references: 1 Soviet and 1 non-Soviet.

ASSOCIATION: Institute elementoorganicheskikh soyedineniy AN SSSR (Institute of Elemental Organic Compounds AS USSR)

SUBMITTED: October 20, 1960

Card 5/5

28186

15.8170

S/190/61/003/010/016/019
B124/B110

AUTHORS: Andrianov, K. A., Yakushkina, S. Ye.

TITLE: Polymerization of mixed cyclotetrasiloxanes

PERIODICAL: Vysokomolekulyarnyye soyedineniya, v. 3, no. 10, 1961, 1554-1560

TEXT: The authors synthesized cyclic compounds in which three oxygen atoms are bound to a silicon atom, and studied their polymerization in the presence of acid and basic catalysts. For this purpose, they synthesized bis(hexamethyl-diphenyl-tetracyclosiloxane) oxide (I) and heptamethyl(trimethyl-siloxy)cyclotetrasiloxane (II), namely (I) by cohydrolysis of dimethyl dichloro silane and phenyl trichloro silane by water in acid medium at 25-30°C, 2 hr, and (II) by cohydrolysis of methyl(trimethyl-siloxy)dichloro silane and dimethyl dichloro silane under the same conditions. The compounds were isolated by fractional distillation, and identified by their elementary composition, infrared spectra, and molecular weights. The infrared spectra of (I) showed absorption bands for Si-C_6H_5

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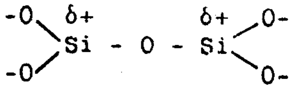
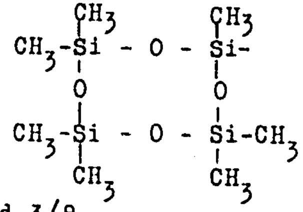
Polymerization of mixed ...

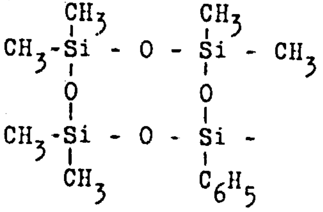


. This group increases the electropositive character of Si. In the polymerization of (II) (and the analogous triethyl-siloxy compound), there is a trimethyl-silyl (or triethyl-silyl) group (respresenting a steric hindrance) on the silicon atom to which three oxygen atoms are bound; the stoichiometric factor is of importance for the polymerizability. In conclusion, it may be stated that the rate of polymerization in the presence of KOH decreases in the order $A - O - A > R^{C_6H_4Cl}$ and $R^{C_6H_5} > R^{-O-Si(CH_3)_3}$, in the presence of H_2SO_4 in the order R and $R^{C_6H_4Cl} > A - O - A > R$, where

R =



and A =



28186

Polymerization of mixed ... S/190/61/003/010/016/019
B124/B110

There are 2 figures, 2 tables, and 6 Soviet references

ASSOCIATION: Institut elementoorganicheskikh soyedineniy AN SSSR (Institute of Elemental Organic Compounds AS USSR)

SUBMITTED: December 1, 1960

Table 1. Polymerization in the presence of a base (duration 3 hr, temperature 130°C, 0.5% KOH).
Legend: (A) Compound, (B) formula, (C) conversion, %, (D) shrinkage, %. (E) III, (F) VI, (G) II, (H) I, (J) a gel forms after 30 min heating.

28188

15.8170

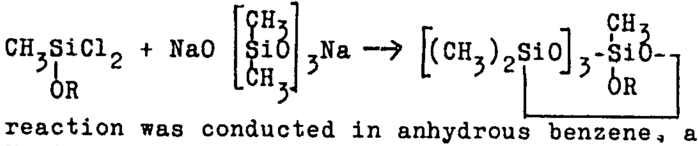
S/190/61/003/010/018/019
B124/B110

AUTHORS: Andrianov, K. A., Volkova, Lora, M.

TITLE: Synthesis and polymerization of heptamethyl alkoxy cyclotetrasiloxanes

PERIODICAL: Vysokomolekulyarnyye soyedineniya, v. 3, no. 10, 1961, 1580-1583

TEXT: The authors studied synthesis and polymerization of organosiloxanes containing methyl alkoxy siloxane groups besides dimethyl siloxane groups. The heptamethyl alkoxy cyclosiloxanes were synthesized by double decomposition of disodium-1,5-dioxy-hexamethyl trisiloxane (I) and methyl alkoxy dichloro silanes:



$$CH_3\underset{OR}{\underset{|}{Si}}Cl_2 + NaO\left[\begin{matrix}CH_3\\ SiO\\ CH_3\end{matrix}\right]_3Na \rightarrow \left[(CH_3)_2SiO\right]_3\text{-}\overset{CH_3}{\underset{OR}{SiO}}\text{-} + NaCl;\ R = C_2H_5,\ C_4H_9.$$

The reaction was conducted in anhydrous benzene, and was strongly exothermic. Heptamethyl ethoxy cyclotetrasiloxane (II) was obtained in the reaction of

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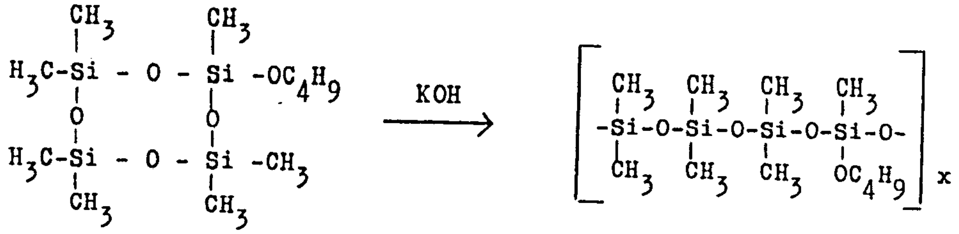
(I) with methyl ethoxy dichloro silane, and heptamethyl butoxy cyclotetrasiloxane (III) was obtained with methyl butoxy dichloro silane. The resulting alkoxy organocyclotetrasiloxanes are transparent liquids; their properties are given in Table 1. Their structure was determined on the basis of results of the ultimate analysis, the infrared spectra, and the quantitative reactions for alkoxy groups. The ring opening of the heptamethyl alkoxy cyclotetrasiloxanes in the presence of KOH as a catalyst was dilatometrically studied at 130°C; it was found that the composition of the organosiloxane groups on the eight-membered ring strongly affected the course of polymerization. When determining the degree of polymerization from the change in volume of the polymer (Table 2), the authors found that polymerization was strongly delayed by introducing alkoxy (mainly butoxy) groups. III polymerizes slowly (Curve 1, Fig. 2) but with high yield (84.28%) to a polymer with a molecular weight of 2140 whereas II polymerizes faster (Curve 2, Fig. 2) with a yield of 81.82% to a polymer with a molecular weight of 2200. The polymerization rate drops in the order: octamethyl cyclotetrasiloxane > II > III. An analysis of polyheptamethyl butoxy cyclotetrasiloxane shows that its composition corresponds to that of the chain link in the formula:

28188

S/190/61/003/010/018/019
B124/B110

Synthesis and polymerization ...



In the experimental part, the authors describe the synthesis of II and III, and the polymerization of heptamethyl alkoxy cyclotetrasiloxanes generally, and that of III in detail. There are 2 figures, 2 tables, and 5 Soviet references.

ASSOCIATION: Moskovskiy institut tonkoy khimicheskoy tekhnologii im. M. V. Lomonosova (Moscow Institute of Fine Chemical Technology imeni M. V. Lomonosov)

SUBMITTED: December 17, 1960

Card 3/6

29739

15 8121 2209, 1407

S/190/61/003/011/010/016
B110/B101

AUTHORS: Andrianov, K. A., Fromberg, M. B., Zabyrina, K. I., Sorokina, L. I.

TITLE: Graft copolymers from polyorganosiloxanes and epoxy resin

PERIODICAL: Vysokomolekulyarnyye soyedineniya, v. 3, no. 11, 1961, 1692 - 1697

TEXT: Polar groups bound to Si are introduced to increase the mechanical strength and the adhesion of polyorganosiloxanes (POS). Since the stability of the Si-radical bond is often reduced by such introduction, graft or block copolymerization with polymers containing polar groups is recommended. The functional groups contained in the copolymer also permit reactions with bifunctional groups for POS hardening at room temperature. Epoxy resins (I) catalyze polycondensations of POS: $-\text{Si}-\text{OH} + \text{HO}-\text{Si}- \longrightarrow -\text{Si}-\text{O}-\text{Si}- + H_2O$ to solid, unmeltable substances, particularly if POS contain OCH_3 or OC_2H_5 groups. It is assumed that the alkoxy groups of POS react with the hydroxyl groups of I according to

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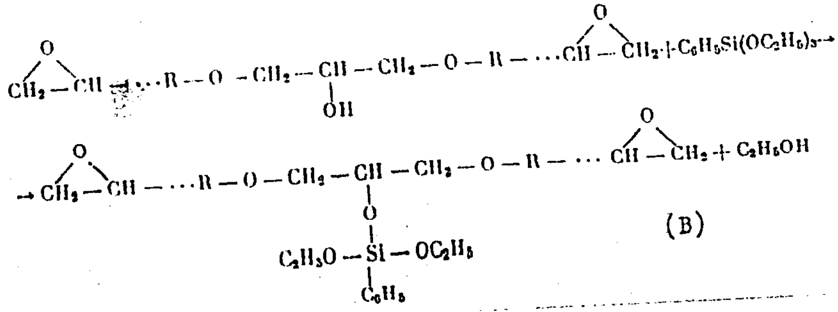
S/190/61/003/011/010/016
Graft polymers from polyorganosiloxanes... B110/B101



(B)

For producing graft copolymers the authors used polydimethyl phenyl siloxanes (II) or polydimethyl phenyl methyl siloxanes (molecular weights: 1000 - 1500, OH content 1.0 - 2.0%) with 3 - 6% methoxyl or ethoxyl groups. They obtained these polymers by hydrolysis of a mixture of $(CH_3)_2SiCl_2$ and $C_6H_5SiCl_3$ or $(CH_3)_2SiCl_2$, CH_3SiCl_3, and $C_6H_5SiCl_3$ in water-alcohol medium. Since the dimension of the alkoxy group considerably affects the thermal decomposition, polymers with OCH_3 groups react at

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S/190/61/003/011/010/016
Graft polymers from polyorganosiloxanes... B110/B101

200 - 230°C, those with OC_2H_5 groups at 280°C. No copolymer is formed at an alkoxy group content < 3%. The copolymerization is accompanied by separation of C_2H_5OH and decrease of epoxy groups, especially at increasing temperature. Investigations of the infrared spectra of polydimethyl phenyl methoxy siloxanes (III) and graft copolymers based on them confirm the reaction mechanism described. Turbidimetric analyses showed the homogeneity of III and its graft copolymers. The presence of epoxy groups in the copolymers permits hardening by means of diamines (polyethylene polyamine (IV), hexamethylene diamine (V), m-phenylene diamine, m-toluylene diamine) to nonthermoplastic varnish films which are highly thermoelastic at 200°C. The chemical nature of the hardener considerably affects the film properties. The high thermoelasticity of films hardened with IV and V is probably due to their evaporation at 200°C. Hardening is also performed at 130 - 150°C by means of polyphenyl alumosiloxanes (VI). III heated at 200°C for 4 hr and at 250°C for 10 hr has T_v = 0°C, an indistinctly marked range of highly elastic deformation, and it flows at 20°C. In graft copolymers based on III and hardened for 72 hr at 20°C by means of IV, the value of highly elastic deformation grows, and flowing

Card 4/5

starts at 150°C. Structuration at 20°C is slow. After 120 hr, the temperature range of highly elastic deformation was much wider, and the flow temperature T_f was 330°C. Graft copolymer hardened with IV for 2 hr at 200°C has a steric structure, an insignificant highly elastic deformation, and a flow temperature of 450°C. Structurated polymer with a flow temperature of 425°C is formed by hardening with VI at 140°C within 2 hr. Varnish films from solutions of copolymers hardened at 130 - 150°C by means of VI form nonthermoelastic coats with higher mechanical strength and adhesion as coats from POS There are 2 figures, 2 tables, and 2 Soviet references.

ASSOCIATION: Vsesoyuznyy elektrotekhnicheskiy institut im. V. I. Lenina (All-Union Electrotechnical Institute imeni V. I. Lenin)

X

SUBMITTED: December 25, 1960

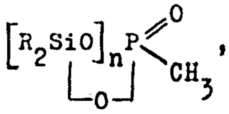
S/075/61/016/006/006/006
B106/B147

AUTHORS: Andrianov, K. A., Khananashvili, L. M., and Vasil'yeva, T. V.

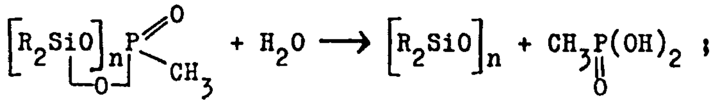
TITLE: Methods for determining phosphorus in phosphorus silicon-compounds

PERIODICAL: Zhurnal analiticheskoy khimii, v. 16, no. 6, 1961, 738-739

TEXT: The authors suggest a simple method for determining phosphorus in phospho-organosilicon compounds with the structure



$\underbrace{[R_2SiO]_n P}_{O}\begin{smallmatrix}{=}O\\ CH_3\end{smallmatrix}$, which is based on their hydrolysis:



$\underbrace{[R_2SiO]_n P}_{O}\begin{smallmatrix}{=}O\\ CH_3\end{smallmatrix} + H_2O \longrightarrow [R_2SiO]_n + CH_3\underset{\overset{\|}{O}}{P}(OH)_2$;

Card 1/2

88484

S/079/61/031/001/018/025
B001/B066

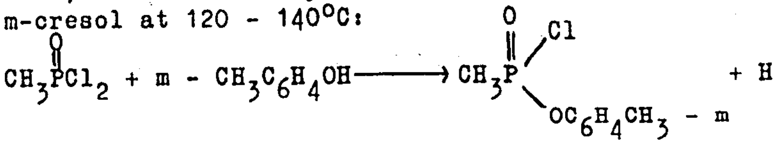
15.8114 2209

AUTHORS: Andrianov, K. A., Zhdanov, A. A., Khananashvili, L. M., and Shapatin, A. S.

TITLE: Reactions of Aluminum Isopropylate With Some Organophosphorus Compounds

PERIODICAL: Zhurnal obshchey khimii, 1961, Vol. 31, No. 1, pp. 224 - 228

TEXT: The authors studied the reaction of aluminum isopropylate with the acid chlorides of methyl-m-cresoxy phosphinic acid and dimethyl phosphinic acid, in order to use them as initial products for the synthesis of polymers with inorganic molecular chains. One of the initial organophosphorus compounds, the acid chloride of methyl-m-cresoxy phosphinic acid, was obtained by reaction of methyl phosphinic acid dichloride with m-cresol at 120 - 140°C:



$$CH_3\overset{O}{\overset{\|}{P}}Cl_2 + m - CH_3C_6H_4OH \longrightarrow CH_3\overset{O}{\overset{\|}{P}}\begin{matrix}Cl\\OC_6H_4CH_3 - m\end{matrix} + HCl \quad (1)$$

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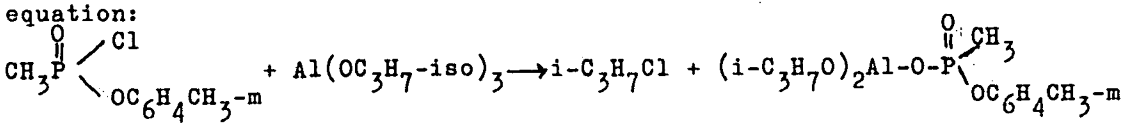
88484

Reactions of Aluminum Isopropylate With Some Organophosphorus Compounds

S/079/61/031/001/018/025
B001/B066

As by-product, considerable quantities of di-m-cresyl ester of methyl phosphinic acid are formed. Higher excess of the dichloride of methyl phosphinic acid gives a large yield of the chloride of methyl-m-cresoxy phosphinic acid and a low yield of the afore-mentioned by-product. The reaction of the chloride of methyl-m-cresoxy-phosphinic acid with aluminum isopropylate was expected to proceed according to the following equation:



$$CH_3\overset{O}{\overset{\|}{P}}\left\langle{}^{Cl}_{OC_6H_4CH_3\text{-}m}\right. + Al(OC_3H_7\text{-}iso)_3 \longrightarrow i\text{-}C_3H_7Cl + (i\text{-}C_3H_7O)_2Al\text{-}O\text{-}\overset{O}{\overset{\|}{P}}\left\langle{}^{CH_3}_{OC_6H_4CH_3\text{-}m}\right.$$

However, in addition to isopropyl chloride, also the isopropyl-m-cresyl ester was separated which is indicative of side reactions. At an elevated reaction temperature (140 - 200°C) still more complicated compounds resulted, which renders the separation of individual reaction products very difficult. To confirm the assumption on the course of reaction, tris(methyl-m-cresoxy-phosphinoxy)aluminum was synthesized. The reaction was carried out at 90 - 100°C to avoid separation of the cresoxy group. Under these conditions, tris(methyl-m-cresoxy-phosphinoxy)aluminum resulted in a yield of 59 %, isopropylchloride in a yield of 67 %, which

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Reactions of Aluminum Isopropylate With Some Organophosphorus Compounds

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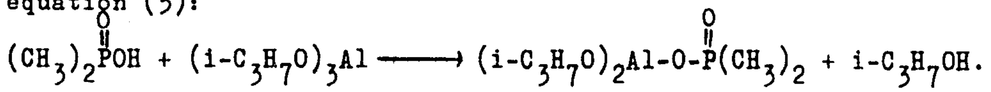
B001/B066

confirmed the predicted course of reaction. The reaction of dimethyl phosphinic acid with aluminum isopropylate takes place according to equation (5):



$$(CH_3)_2\overset{O}{\overset{\|}{P}}OH + (i\text{-}C_3H_7O)_3Al \longrightarrow (i\text{-}C_3H_7O)_2Al\text{-}O\text{-}\overset{O}{\overset{\|}{P}}(CH_3)_2 + i\text{-}C_3H_7OH.$$

This is confirmed by a nearly quantitative separation of isopropyl alcohol (99 %). According to ultimate analysis, the product distilling from the reaction mass at 164°C corresponds to dimethyl-phosphinoxy-(diisopropyl) aluminum which is contaminated. The vitreous, colorless product is soluble in common aromatic solvents. G. B. Ravich and I. F. Manucharova are thanked for their cooperation. There are 1 figure and 10 references: 4 Soviet, 2 British, 2 German, and 1 Czechoslovakian.

ASSOCIATION: Moskovskiy institut tonkoy khimicheskoy tekhnologii (Moscow Institute of Fine Chemical Technology)

SUBMITTED: February 20, 1960

Card 3/3

88485

15.8114 2205

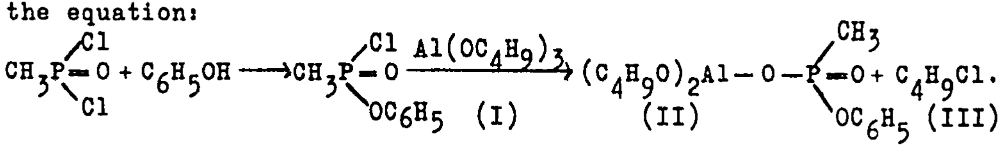
S/079/61/031/001/019/025
B001/B066

AUTHORS: Andrianov, K. A., Khananashvili, L. M., Kazakova, A. A., and Ivanov, A. A.

TITLE: Synthesis of Poly(phenoxy-methyl-phosphinoxy) Aluminum Oxanes

PERIODICAL: Zhurnal obshchey khimii, 1961, Vol. 31, No. 1, pp. 228 - 231

TEXT: Following their papers of Refs. 1 and 2, and in view of Ref. 3, the authors now studied the syntheses of some organophosphorus-aluminum compounds and tried to convert them to polymers with a principal chain of aluminum oxanes. The synthesis of these organophosphorus-aluminum compounds was made by esterification of the acid chloride of methyl phosphinic acid with phenol, combined with a reaction of the resultant methylphenoxy phosphinic acid chloride with aluminum-n-butylate, according to the equation:



$$CH_3P\begin{matrix}\diagup Cl\\ =O\\ \diagdown Cl\end{matrix} + C_6H_5OH \longrightarrow \underset{(I)}{CH_3P\begin{matrix}\diagup Cl\\ =O\\ \diagdown OC_6H_5\end{matrix}} \xrightarrow{Al(OC_4H_9)_3} \underset{(II)}{(C_4H_9O)_2Al}-O-P\begin{matrix}\diagup CH_3\\ =O\\ \diagdown OC_6H_5\ (III)\end{matrix} + C_4H_9Cl.$$

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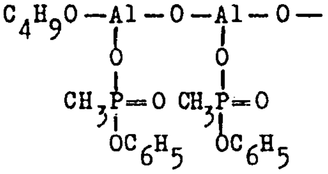
88485

Synthesis of Poly(phenoxy-methyl-phosphinoxy) Aluminum Oxanes

S/079/61/031/001/019/025
B001/B066

Compound (I), hitherto not yet described, was separated in pure condition by distillation of the reaction products (26.2 %). The low yield is due to the formation of compound $CH_3PO(OC_6H_5)_2$ and, presumably, of a mixture of condensation products of the organophosphorus compounds present. The yield of butyl chloride was 58 %. The reaction carried out at 80 - 90°C yields phenoxymethyl-phosphinoxy-dibutoxy aluminum (II). Elevated temperatures give compounds insoluble in organic solvents. The viscosity of the product of the hydrolysis of compound (II) rapidly increases. This hydrolysis probably gives:



The increase in viscosity depends on the water quantity applied, it is most pronounced at the beginning reaction. The hydrolysis products separated from the solution are solid compounds soluble in butyl alcohol. A study of the thermo-mechanical properties of the hydrolysis products reveals that an increase on the water quantity in the above hydrolysis does not affect the flow temperature of the polymer considerably, but somewhat decreases the interval between the temperatures of vitrification

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88486
S/079/61/031/001/020/025
B001/B066

5.3700

AUTHORS: Andrianov, K. A., Astakhin, V. V., and Sukhanova, I. V.

TITLE: Synthesis of Halogen Esters of Orthotitanic Acid

PERIODICAL: Zhurnal obshchey khimii, 1961, Vol. 31, No. 1, pp. 232 - 233

TEXT: In view of data indicating the possibility of a cleavage of the SiOSi bond by $TiCl_4$, the authors intended to synthesize alkoxy titanium chlorides, proceeding from trialkyl-alkoxy silanes and titanium tetrachloride. Trimethyl-alkoxy silanes were found to react vigorously with titanium tetrachloride according to the following equations:
$(CH_3)_3SiOR + TiCl_4 \longrightarrow (CH_3)_3SiCl + ROTiCl_3$,
$2(CH_3)_3SiOR + TiCl_4 \longrightarrow 2(CH_3)_3SiCl + (RO)_2TiCl_2$. The authors were not able to substitute the alkoxy group for more than two chlorine atoms in $TiCl_4$, at a molar ratio of $TiCl_4 : (CH_3)_3SiOR = 1 : 3$, irrespective of a prolonged heating of the reaction mass. The constants of the resultant alkoxy titanium chlorides are tabulated. The method described is of

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Synthesis of Halogen Esters of
Orthotitanic Acid

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B001/B066

preparative importance. The experiments were carried out under exclusion of atmospheric moisture and with carefully dried reagents. The following compounds were synthesized: ethoxy titanium trichloride, diethoxy titanium dichloride, butoxy titanium trichloride, and isopropoxy titanium trichloride. There are 1 table and 7 references: 7 Soviet, 3 British, 1 US, and 1 Indian.

ASSOCIATION: Vsesoyuznyy elektrotekhnicheskiy institut imeni V. I. Lenina (All-Union Electrotechnical Institute imeni V. I. Lenin)

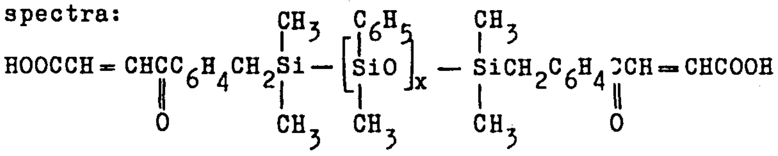
SUBMITTED: February 15, 1960

88487

Some Organosilicon Diketodicarboxylic Acids

S/079/61/031/001/021/025
B001/B066

the number of these groups. Composition and structure of the resultant acids were confirmed by chemical and spectroscopic analysis. Diagram 1 gives the infrared absorption spectrum of diketodicarboxylic acids with X = 10 in the molecule. The vibration frequencies correspond to the groups  —Si(450 cm^{-1}) and  (500 cm^{-1}), Si-CH_3(815 cm^{-1}), Si($CH_3)_2$(855 cm^{-1}), OH(936 cm^{-1}), Si-O(1036, 1072, 1088 cm^{-1}), COOH(1285, 1306 cm^{-1}), C=O(1678, 1700 cm^{-1}). In the cohydrolysis of compound (III) with methyl-phenyl-dichlorosilane, acids were formed with X methyl-phenyl-siloxane groups in the molecule (X = 1, 2, 3, 4, 5, or 10). They are viscous liquid products well soluble in the above solvents. The following structure is confirmed by ultimate analysis and their infrared spectra:



$$\mathrm{HOOCCH{=}CH\underset{\underset{O}{\|}}{C}C_6H_4CH_2\overset{CH_3}{\underset{CH_3}{Si}}-\left[\overset{C_6H_5}{\underset{CH_3}{SiO}}\right]_x-\overset{CH_3}{\underset{CH_3}{Si}}CH_2C_6H_4\underset{\underset{O}{\|}}{C}CH{=}CHCOOH}$$

Card 2/3

20951
S/079/61/031/004/005/006
B118/B209

5.3700 2209, 1274, 1282

AUTHORS: Andrianov, K.A., and Yermakova, M.N.

TITLE: Formation reactions of triethyl-siloxy-borosiloxanes

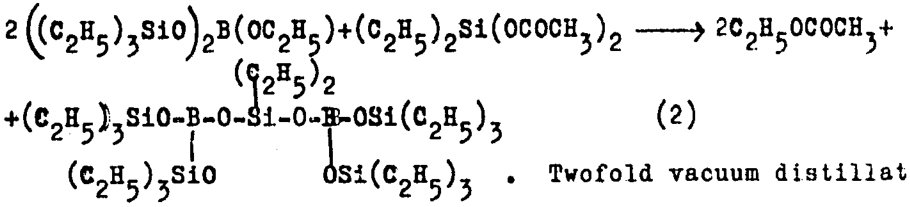
PERIODICAL: Zhurnal obshchey khimii, v. 31, no. 4, 1961, 1310 - 1312

TEXT: For the purpose of synthesizing triethyl-siloxy-diethoxy-boron, the authors of the present paper studied the reaction of triethyl-hydroxy-silane with boric acid ethyl ester. Experiments disclosed that tris-triethyl-siloxy-boron is formed even by reacting boric acid ethyl ester with triethyl-hydroxy-silane in a molar ratio; triethyl-siloxy-diethoxy-boron could not be separated. The latter is probably subjected to disproportionation during distillation, forming a stable compound, namely tris-triethyl-siloxy-boron. In subsequent experiments, boric ester was first condensed with triethyl-hydroxy-silane, combined with a distillation of the alcohol separated during the reaction:

$$2(C_2H_5)_3SiOH + B(OC_2H_5)_3 \longrightarrow \left((C_2H_5)_3SiO\right)_2B(OC_2H_5) + 2C_2H_5OH \qquad (1).$$

Card 1/3

Then, diethyl-diacetoxy-silane was added, and the reaction mixture heated again to expel the ethyl acetate:



$$2\left((C_2H_5)_3SiO\right)_2B(OC_2H_5)+(C_2H_5)_2Si(OCOCH_3)_2 \longrightarrow 2C_2H_5OCOCH_3+ (C_2H_5)_3SiO-\underset{\underset{(C_2H_5)_3SiO}{|}}{B}-O-\overset{\overset{(C_2H_5)_2}{|}}{Si}-O-\underset{\underset{OSi(C_2H_5)_3}{|}}{B}-OSi(C_2H_5)_3 \tag{2}$$

. Twofold vacuum distillation gave 1.5-bis(triethyl-siloxy-boro)-3-diethyl-diborosiloxane in a yield of 24.7% 1.5-bis(triethyl-siloxy-boro)-3-dimethyl-diborosiloxane is easily obtained according to reaction (2), if dimethyl-diacetoxy-silane is used instead of diethyl-diacetoxy-silane. Reaction of the condensation product of triethyl-hydroxy-silane with the boric ester of diethyl-silanediol gives also easily 1.5-bis(triethyl-siloxy-boro)-3-diethyl-diborosiloxane:

27909
S/079/61/031/010/009/010
D228/D302

5 3700

AUTHORS: Andrianov, K.A., Astakhin, V.V., Kochkin, D.A., and Sukhanova, I.V.

TITLE: Reaction of hexamethyldisilazane with the halides of aluminum and titanium

PERIODICAL: Zhurnal obshchey khimii, v. 31, no. 10, 1961, 3410-3411

TEXT: Previous work has shown the possibility of obtaining chlorosilane from aminosilane and HCl, so the authors studied and devised a method of synthesizing trimethylchloro-, trimethylbromo- and trimethyliodosilane in accordance with the scheme:

$$[(CH_3)_3Si]_2NH + AlX_3 \rightarrow 2(CH_3)_3SiX + NHAlX$$

$$[(CH_3)_3Si]_2NH + TiCl_4 \rightarrow 2(CH_3)_3SiCl + NHTiCl_2$$

Card 1/2

31193
S/079/61/031/012/007/011
D258/D301

5.3700

AUTHORS: Andrianov, K. A., Zhdanov, A.A., and Odinets, V. A.

TITLE: The addition of aromatic derivatives to vinyl methyl dichlorosilane

PERIODICAL: Zhurnal obshchey khimii, v. 31, no. 12, 1961, 4033-4038

TEXT: The authors showed that the addition of either benzene, toluene, chlorobenzene or diphenyl to vinyl methyl dichlorosilane yields the corresponding (ß-aryl ethyl)-methyldichlorosilanes and also a higher boiling by-product: $ArH + CH_2 = CHSi(CH_3)Cl_2 \xrightarrow{AlCl_3} ArCH_2CH_2Si(CH_3)Cl_2$ ... (1). The by-product was isolated in the case of benzene and identified as bis-(2-dichloromethyl silyl ethyl)-benzene, formed on further reaction of the primary product with a second molecule of the silane:

Card 1/3

31193

S/079/61/031/012/007/011

The addition of aromatic ... D258/D301

Pines, M. L. Dunham, Ind. Eng. Ch., no. 2, 368, (1953); R. E. Richard, H. W. Thompson, J. Chem. Soc., (1949), 124.

SUBMITTED: November 29, 1960

X

Card 3/3

31194

S/079/61/031/012/008/011
D258/D301

5.3700

AUTHORS: Andrianov, K. A., and Rumba, G. Ya.

TITLE: The hydrolysis of cyclic polymethyl silazanes

PERIODICAL: Zhurnal obshchey khimii, v. 31, no. 12, 1961, 4038-4042

TEXT: The authors investigated the hydrolysis of octamethyl cyclotetrasilazane (A) and hexamethyl cyclotrisilazane (B) in the presence of acids, alkalis and NH_4^+ - salts, in homogeneous and heterogeneous media. Specifically, a mixture consisting of one of the silazanes (3.65 gr), a solvent (45 ml), and water (5 ml) was boiled to reflux for up to 48 hours. The evolved NH_3 was trapped in water and titrated in situ every 30 mins. The tabulated results can be summarized as follows: Compound A (in toluene) is wholly hydrolyzed after 48 hours in the presence of KOH (0.5% and 10%). In the presence of HCl (0.5 N), H_2SO_4 (0.1 N and 0.5 N), and NH_4HSO_4, the

X

Card 1/4

and continues by the alternating additions of water and H^+. First, H^+ is added to one of the N atoms in the ring, forming a $Si-(NH_2)^+-Si$ group; next the N^+-Si bond is hydrolyzed and the ring opens, with a NH_2 group on one end of the chain and a silanol group on the other; the third step consists in the addition of H^+ to this NH_2 group which is converted into NH_3^+; another molecule of water breaks the N^+-Si bond, giving rise to NH_3 and a silane diol. The reaction then continues to the ultimate breakdown of the molecule. Attempts to hydrolyze both compounds by exposing them to moistened air failed because of their high volatility. Therefore, these substances are unsuitable for the hydrophobization of paper and building materials. There are 9 figures and 24 references: 4 Soviet-bloc and 20 non-Soviet-bloc. The 4 most recent references to the English-language publications read as follows: S. H. Langer, S. Connell, J. Wender, J. Org. Ch., 23, 50 (1958); E. Larsson, L. Bjellrup, J. Am. Chem. Soc., 75, 995 (1953); M. V. George, D. Wittenberg, H. Gilman, J. Am. Chem. Soc., 81, 361 (1959); D. Witten-

31194

The hydrolysis of cyclic ...

S/079/61/031/012/008/011
D258/D301

berg, M. G. George, T. C. Wu, D. H. Miles, H. Gilman, J. Am. Chem. Soc., 80, 4532 (1958).

SUBMITTED: January 2, 1961

Card 4/4

ANDRIANOV, K.A.; GOLUBENKO, M.A., inzh.

Cast insulators made of epoxide resins and polyorganosiloxanes. Vest. elektroprom. 32 no.1:1-3 Ja '61. (MIRA 14:3)

1. Chlen-korrespondent AN SSSR (for Andrianov).
(Electric insulators and insulation)

23837

15.8114 2209

S/020/61/138/002/020/024
B103/B220

AUTHORS: Andrianov, K. A., Corresponding Member AS USSR, and Zhdanov, A. A.

TITLE: Polycondensation as a method of producing polydialkyl siloxane and polyaluminum dialkyl siloxane elastomers

PERIODICAL: Akademiya nauk SSSR. Doklady, v. 138, no. 2, 1961, 361-362

TEXT: A new method of synthetizing polydialkyl siloxane elastomers having straight molecular chains is discussed. It is based on the polycondensation of bi-functional oligomers with bi-functional silicoorganic monomers. This process takes place in 2 stages: 1) production of oligomers by the known methods (see diagram no. 1); 2) polycondensation or heterofunctional polycondensation of the monomers produced, whereby elastomers of high molecular weight are formed. Of the elastomers having inorganic principal chains and framing organic radicals only polydimethyl siloxane elastomers including modifications are known. Up to the present, it has not been possible to produce elastomers by hydrolysis and polycondensation or by heterofunctional polycondensation of different bi-functional monomers; the

Card 1/6

Polycondensation as a method of producing... S/020/61/138/002/020/024
B103/B220

side reactions caused the formation of linear as well as cyclic products. The characteristic of the method described by the authors is based on the fact that in the two-stage process mentioned the formation of cycles of low molecular weight in the final stage is impossible. The oligomers subject to polycondensation have such a degree of polymerization that ring formation becomes impossible. From elastomers produced by this method, types of rubber can be produced by vulcanization, which have properties analogous to those of standard polydimethyl siloxane rubber. Furthermore, the authors stated that differently high polycondensated α,ω-dihydroxy polydimethyl siloxanes undergo the following reactions, whereby linear polymers are formed with atoms of aluminum, titanium, or boron in the inorganic polymer chain: aluminum butylate gives $[(CH_3)_2SiO]_{28}[Al\,(OC_4H_9)\,O]$ with a molecular weight of 30000; tributoxy boron gives $[(CH_3)_2SiO]_{35}[B\,(OC_4H_9)\,O]$, molecular weight 34000; tetrabutoxy titanate gives $[(CH_3)_2SiO]_{35}[Ti\,(OC_4H_9)\,O]$. Dependent on the functional end groups of the oligomers, the polycondensation can proceed with formation of various products of low molecular weight (see diagram no. 2). The

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23837
S/020/61/138/002/020/024
Polycondensation as a method of producing... B103/B220

polymers produced by the authors are elastic soluble substances with a molecular weight of 100000 to 200000. Those having a metal atom in the chain are highly reactive due to the retaining of the functional group at the metal atom. The rubber materials, thus obtained, are similar to those produced from polydimethyl siloxanes, but have still better properties. α,ω-dichloro polydimethyl siloxanes were produced by the abovementioned methods: K. A. Andrianov, V. V. Severnyy, B. G. Zavin (Ref. 4: Izv. AN SSSR, OKhN, being printed): $Cl[(CH_3)_2SiO]_{41}Si(CH_3)_2Cl$. Therefrom, oligomers were produced with siloxane chains of various lengths from which α,ω-dihydro polydimethyl siloxanes were obtained by hydrolysis. These siloxanes were produced equally from dimethyl diacetoxy siloxane. Mention is made of white soot У-333 40 (U-333 40) and of the method of determining the molecular weights by Terent'yev, which is, however, not explained in detail. The polymer $[(C_6H_5)(CH_3)SiOAl(OC_4H_9)O]_n$ was produced from phenylmethyl diacetoxy silane with aluminum butylate. There are 1 table and 5 references: 3 Soviet-bloc and 2 non-Soviet-bloc. The two references to English-language publications read as follows: Ref. 2: J. F. Hyde, J. Am. Chem. Soc., 75, 2166 (1953); Ref. 3: T. Takiguchi,

Card 3/6

Bull. Chem. Soc. Japan, 32, 556 (1959).

ASSOCIATION: Institut elementoorganicheskikh soyedineniy Akademii nauk SSSR (Institute of Elemental-organic Compounds, Academy of Sciences USSR)

SUBMITTED: February 6, 1961

15.8170

25480
S/020/61/139/001/012/018
B103/B226

AUTHORS: Andrianov, K. A., Corresponding Member AS USSR, Savushkina, V. I., Golubtsov, S. A., and Charskaya, B. A.

TITLE: Thermal condensation of dichloro silane with chlorobenzene

PERIODICAL: Akademiya nauk SSSR. Doklady, v. 139, no. 1, 1961, 95 - 98

TEXT: The authors studied the thermal condensation of dichloro silane with chlorobenzene $H_2SiCl_2 + C_6H_5Cl \rightarrow C_6H_5SiHCl_2 + HCl$ (1). 30 % phenyl dichloro silane resulting in the process. In addition to reaction (1), they determined the substitution of the second hydrogen atom at silicon by the phenyl group. In the presence of the high temperatures used here, (640 - 700°C), substitution of the hydrogen atom at silicon by a chlorine atom was furthermore to be expected. As a result of this complicated process, the following compounds are present among the reaction products: Diphenyl dichloro silane and phenyl-trichloro silane (optimum total yield together with phenyl dichloro silane: 74.6 %); furthermore, benzene (5), (4), and trichloro silane (3). The present study proves that the yield of individual

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25480
S/020/61/139/001/012/018
B103/B226

Thermal condensation of dichloro...

reaction products is, above all, dependent upon temperature. Up to about 640 - 660°C (optimum temperature of reaction (1)) the yield of phenyl dichloro silane increases up to 41.7 %, and, with a further temperature rise up to 700°C, it decreases to 12 %. The yield of phenyl trichloro silane increases at 640 - 660°C to 18.3 %, and up to 700°C continues increasing up to 26 %. The yield of diphenyl dichloro silane first increases (up to 12.4% at 660°C), at 700°C, however, decreases to 2.5 %. These facts speak in favor of a continuously increasing rate of the reaction mentioned at the beginning. For these reasons, silane and chlorosilane are practically entirely absent in the reaction products, and in the decomposition of dichloro silane neither hydrogen (2) nor side reactions of the chlorination of chlorosilane hydrides (3), (4) have been proved to develop. The authors consider it quite probable that part of phenyl trichloro silane forms according to the scheme $HSiCl_3 + C_6H_5Cl \longrightarrow C_6H_5SiCl_3 + HCl$ (5). The rate of reactions (3), (4), and (5): $C_6H_5SiHCl_2 + C_6H_5Cl \longrightarrow (C_6H_5)_2SiCl_2 + HCl$ (2;

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Thermal condensation of dichloro...

25480
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B103/B226

$H_2SiCl_2 + C_6H_5Cl \longrightarrow HSiCl_3 + C_6H_6$ (3); $C_6H_5SiHCl_2 + C_6H_5Cl \longrightarrow C_6H_5SiCl_3 + C_6H_6$ (4) increases more considerably than that of (2). At 680°C the formation rates of phenyl trichloro silane tend toward similar values. Formation of trichloro silane and phenyl trichloro silane can hardly be explained other than by (3) and (4); i.e., neither by disproportionation: $2H_2SiCl_2 \rightarrow HSiCl_3 + H_3SiCl$ (6) nor by decomposition of dichloro silane: $3H_2SiCl_2 \rightarrow Si + 2HSiCl_3 + 2H_2$ (7). Also, the formation of benzene can be explained only by reactions (3) and (4), and not by pyrolysis of chlorobenzene in a reducing medium. In special experiments conducted on this pyrolysis, the authors found that the benzene yield did not exceed 9% (in hydrogen medium) and 2.2 % (in silane medium). On the other hand, in the production of phenyl dichloro silane 55 - 60 % benzene formed. Also the small yield of highly boiling products in the production of phenyl dichloro silane points to the unimportant part played by pyrolysis. S. A. Platonova and T. A. Klochkova participated in the experimental part of the study. There are 3 figures, 3 tables, and 2 Soviet-bloc references.

X

SUBMITTED: March 22, 1961
Card 3/3

15.8170

28670
S/020/61/140/002/015/023
B103/B101

AUTHORS: Andrianov, K. A., Corresponding Member AS USSR, Kurasheva, N. A., Kuznetsova, I. K., and Gerkhardt, E. I.

TITLE: Synthesis of polymers of regular structure of the polydimethylsiloxane series

PERIODICAL: Akademiya nauk SSSR. Doklady, v. 140, no. 2, 1961, 365-367

TEXT: The polycondensation of the methyl-diethoxy silyl-methyl ester of dimethyl phosphinic acid (I) with various α,ω-dihydroxy-dimethyl siloxanes (II) was studied. The distance between the dimethyl phosphine groups (DMP) could be varied by using II with different numbers of dimethylsiloxane links between the OH groups. The DMP groups were evenly distributed along the molecule chain. II was synthesized by the reaction applied for diphenyl silanediol (Ref. 3, see below). Its data are presented in Table 1. II react with I at 170°C without a catalyst in the following way:

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Synthesis of polymers of regular ... S/020/61/140/002/015/023
B103/B101

temperature was obtained by reducing the distance between the DMP groups. The low vitrification temperatures of polymers with polar DMP groups in their chains are explained by the fact that the DMP groups which are large as compared with the CH_3 groups, reduce the packing density of the molecule chain. There are 1 table and 3 references: 2 Soviet and 1 non-Soviet. The reference to English-language publication reads as follows: Ref. 3: Foshio Takiguchu, Bull. Chem. Soc. Japan, 32, no. 6, 665 (1959).

ASSOCIATION: Institut elementoorganicheskikh soyedineniy Akademii nauk SSSR (Institute of Elemental Organic Compounds of the Academy of Sciences USSR)

SUBMITTED: May 17, 1961

Table 1.
Legend: (1) substance; (2) yield; (3) molecular weight; (4) calculated; (5) found.

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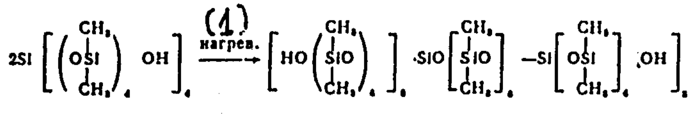
1) Polysiloxy-dimethyl siloxane (mol wt 1252 to 1258); 2) polyphenyl siloxy-dimethyl siloxane (mol wt 2146); and 3) polytitano-dimethyl siloxane (mol wt 3920). To 1): the oligomer is a readily mobile liquid at room temperature, which above 230°C condenses easily to a polymer according to the stage mechanism by separating water.



$$2Si\Big[\Big(O\overset{CH_3}{\underset{CH_3}{Si}}\Big)_4 OH\Big]_4 \xrightarrow[\text{нагрев.}]{(1)} \Big[HO\Big(\overset{CH_3}{\underset{CH_3}{Si}}O\Big)_4\Big]_4 \cdot SiO\Big[\overset{CH_3}{\underset{CH_3}{Si}}O\Big]_4 - Si\Big[O\overset{CH_3}{\underset{CH_3}{Si}}\Big]_4 \cdot OH\Big]_4$$

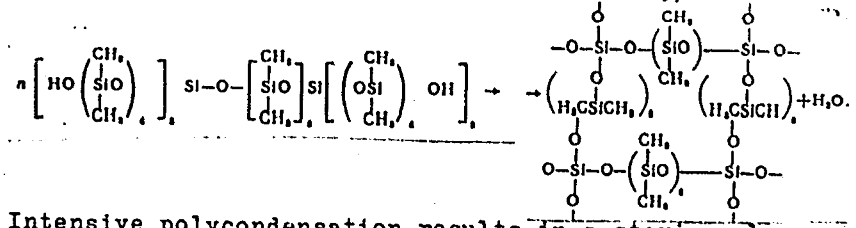
(B)

(1) = heating

Since the polymers 1) - 3) remain soluble in organic solvents in the initial stages of condensation and become insoluble only on further heating, it is concluded that further condensation results in the formation of higher molecular products owing to interaction of the hydroxyl end groups:

29819
S/020/61/140/006/016/030
B103/B101

Methods of synthesizing regular ...



(C)

Intensive polycondensation results in a steric polymer with regular ordering of side chains and cross links between the principal chains. Also the distances between the Si atoms bound to 4 O atoms are identical. To 2): A polyorgano-siloxane of regular structure was equally obtained by condensation of a trifunctional oligomer which condenses to a polymer of elastic structure at room temperature. To 3) An oligomer with monofunctional groups at the side chain ends is formed by polycondensation of α,ω-dihydroxy-dimethyl siloxane (I) with $TiCl_4$ in the presence of NH_3. It corresponds to a tetrafunctional titanium dimethyl siloxane oligomer and is liquid at room temperature. A tetrafunctional oligomer was obtained by a similar reaction from I containing 13 dimethyl groups. This

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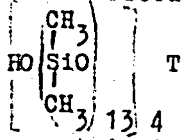
is a viscous liquid readily soluble in organic solvents  $\left[HO\left(\overset{CH_3}{\underset{CH_3}{Si}}O\right)_{13}\right]_4$ Ti. Also when I or α,ω-sodium oxy-dimethyl siloxanes are reacted with $SiCl_4$ or $TiCl_4$, polyfunctional oligomers are formed. Double excess of functional groups in one of the components and mild reaction conditions effect that only polymers are formed in the reaction. Thus, the reactions between di-, tri-, and tetrafunctional compounds may be used to synthesize polyfunctional oligomers containing monofunctional groups at the side chain ends. The tetrafunctional titanium oligomers condense equally at 150 - 200°C by separating water. Two elastic compounds (3) were obtained: a polymer with 18 dimethyl siloxane groups and a polymer with 26 such groups between the Ti atoms. It has been found that the structure of large molecules of network or steric structure can be controlled by varying the number of atoms and groups in the side chains of polyfunctional oligomers. The

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ANDRIANOV~~, K.A.;~~ TIKHONOV, V.S.; KHANANASHVILI, L.M.; KHAN' EN'-TSZE
[Han En-tsê]; KHAN' SHU-YUY [Han Shu-yü]

Hydrolytic stability of polyorganoborosiloxanes. Plast. massy
no.12:25-27 '62. (MIRA 16:1)
(Siloxanes) (Boron organic compounds) (Hydrolysis)

S/062/62/000/012/002/007
B117/B101

AUTHORS: Andrianov, K. A., and Severnyy, V. V.

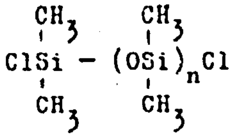
TITLE: Catalytic cleavage of dimethyl cyclosiloxanes in the presence of dimethyl-dichloro silane

PERIODICAL: Akademiya nauk SSSR. Izvestiya. Otdeleniye khimicheskikh nauk, no. 12, 1962, 2133-2138

TEXT: The effect of catalytic amounts of iron chloride on the reaction of dimethylcyclosiloxanes with dimethyl-dichloro silane was studied. Experiments with 1% by weight of iron chloride, and without any, were conducted under equal conditions: sealed glass ampuls, kept at 250°C for 5 hrs, rectification of the mixture first at atmospheric pressure, then at 4 mm Hg. Results: Without iron chloride, only α,ω-dichloro-dimethyl siloxanes containing 4, 7, and 10 silicon atoms formed. When using iron chloride, telomerization takes place with the Si-O-Si bonds being ruptured and all homologs of the formula

✓

Card 1/4



$$\mathrm{Cl}\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}} - (\mathrm{O}\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}})_n\mathrm{Cl}$$

being formed with 2 to 7 silicon atoms. The following mechanism of cleavage was suggested: The reaction begins by a coordination of the iron atom with an oxygen atom in the siloxane chain either of the telomer or dimethyl cyclosiloxane. An active complex forms which then decomposes. The assumption that this reaction takes place in equilibrium was confirmed by experiments with octamethyl cyclotetrasiloxane and dimethyl-dichloro silane at different component ratios (Fig. 2; Table 1) and also by the fact that the composition of the reaction products is determined by the quantitative ratio of the Si-O- and Si-Cl- bonds in the system, not by the type of compound used. The reaction examined was suggested as an easy method of synthesizing low-molecular and high-molecular α,ω-dichloro-methyl siloxanes. There are 2 figures and 4 tables.

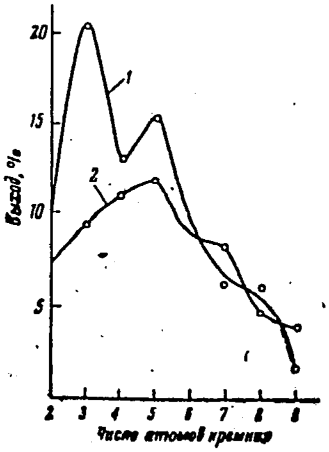
Catalytic cleavage of dimethyl...

S/062/62/000/012/002/007
B117/B101

Table 1

①	② Вычислено		③ Найдено			⑤
				M		
Соотношение	Si_n	M	Si_n	по Cl	④ по вязкости	Выход, %
10:1	40	2960	35—38	2750	2900	75—85
20:1	80	5920	71—76	5250—5630	5300	70—80
25:1	100	7400	89—93	6560—6870	64200	70—80
50:1	200	14800	150—170	11200—12600	13850	65—70
100:1	400	29600	220—250	16700—18500	18700	55—65

Fig. 2



Card 4/4

S/062/62/000/012/003/007
B117/B101

AUTHORS: Andrianov, K. A., Pichkhadze, Sh. V., Novikov, V. M., and Lavygin, I. A.

TITLE: Synthesis and some reactions of 8-oxy-quinoline butoxy-titanium

PERIODICAL: Akademiya nauk SSSR. Izvestiya. Otdeleniye khimicheskikh nauk, no. 12, 1962, 2138-2141

TEXT: 8-oxy-quinoline tributoxy titanium was synthesized by the action of 8-hydroxy-quinoline on tetrabutoxy titanium at ~ 140°C; $C_{21}H_{33}O_4NTi$, light-green crystals which hydrolyze easily, m.p. 55-56°C. At a 1:1 ratio of the two components, approximately equal amounts of 8-oxy-quinoline tributoxy titanium and bis-(8-oxy-quinoline)dibutoxy titanium are formed: $C_{26}H_{30}O_4N_2Ti$, yellow crystals, m.p. 148-150°C. The latter hydrolyzed in a neutral medium with the cleavage of butoxy groups only, yielding a product identified as bis-(8-oxy-quinoline)-dihydroxy titanium: $C_{18}H_{14}O_4N_2Ti$, orange, nonfusible crystals, which disintegrate at 400°C. The condensation

Card 1/2

of bis-(8-oxy-quinoline)-dihydroxy titanium showed that water (69%) was separated by heating (250°C, 4 hrs). The structure of bis-(8-oxy-quinoline)-dihydroxy titanium was confirmed by its condensation with bis-(8-oxy-quinoline)-dibutoxy titanium. Butyl alcohol was thus separated by heating to 200°C. The reaction of bis-(8-oxy-quinoline)-dibutoxy titanium with organosilicon compounds was smooth; the reaction with trimethyl silanol took place at 50°C yielding bis-(trimethyl siloxy)-bis-(8-oxy-quinoline)-titanium $C_{24}H_{30}O_4N_2Si_2Ti$, light-yellow crystals, m.p. 143-144°C, yield 78%. The reaction with triethyl silanol at 150°C yielded bis-(triethyl siloxy)-bis-(8-oxy-quinoline)-titanium, $C_{30}H_{42}Si_2O_4N_2Ti$, yellow crystals, m.p. 162-164°C, yield 83%. The reaction with triphenyl silanol at 150-170°C yielded bis-(triphenyl siloxy)-bis-(8-oxy-quinoline)-titanium, $C_{54}H_{42}Si_2TiO_4N_2$, a crystalline substance, m.p. 188°C, yield 68%.

ASSOCIATION: Institut elementoorganicheskikh soyedineniy Akademii nauk SSSR (Institute of Elemental Organic Compounds of the Academy of Sciences USSR)

SUBMITTED: April 11, 1962

Card 2/2

S/062/62/000/012/006/007
B117/B101

Synthesis and properties of...

α,ω-dihydroxy-dimethyl siloxanes were synthesized:

Compound	b.p., °C (p mm Hg)	d_4^{20}	n_D^{20}	MR	yield %
$HO[Si(CH_3)_2O]_3H$	79-82 (2)	0.9999	1.4089	59.42	79.2
$HO[Si(CH_3)_2O]_4H$	97-100 (2)	0.9886	1.4054	78.38	77
$HO[Si(CH_3)_2O]_5H$	104-106 (1.5)	0.9914	1.4089	96.90	80.5
$HO[Si(CH_3)_2O]_6H$	119-120 (2)	0.9916	0.4099	115.1	82.2
$HO[Si(CH_3)_2O]_7H$	130-135 (1)	0.9891	1.4067	133.52	80.5
$HO[Si(CH_3)_2O]_8H$	143-145 (2)	0.9912	1.4090	152.4	79.5
$HO[Si(CH_3)_2O]_9H$	158-161 (2)	0.9921	1.4088	170.66	83

ASSOCIATION: Elektrotekhnicheskiy institut im. V. I. Lenina (Electrotechnical Institute imeni V. I. Lenin); Institut elementoorganicheskikh soyedineniy Akademii nauk SSSR (Institute of Elemental Organic Compounds of the Academy of Sciences USSR); Institut khimii Sovnarkhoza Arm.SSSR (Institute of Chemistry of the Sovnarkhoz of ArSSR)

Card 2/3

33380

S/190/62/004/002/009/021
B110/B101

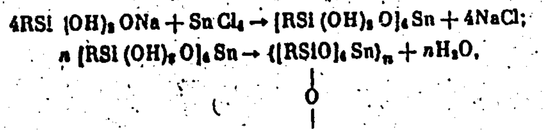
15.8150 1372

AUTHORS: Asnovich, E. Z., Andrianov, K. A.

TITLE: Polyorganotin siloxanes

PERIODICAL: Vysokomolekulyarnyye soyedineniya, v. 4, no. 2, 1962, 216 - 220

TEXT: Polyorgano siloxanes with principal chains of Si, O, and Sn atoms have been investigated. The Si atoms are surrounded by methyl, ethyl, and phenyl groups



$$4RSi(OH)_2ONa + SnCl_4 \rightarrow [RSi(OH)_2O]_4Sn + 4NaCl;$$

$$n[RSi(OH)_2O]_4Sn \rightarrow \{[RSiO]_4Sn\}_n + nH_2O,$$

where R = CH_3, C_2H_5, C_6H_5.

By changing the ratio of reagents one obtains polymers with different ratios of Si to Sn atoms: polytinmethyl siloxanes (I) from 4:1 to 17:1, polytinethyl siloxanes (II) from 1.25:1 to 19.5:1, and polytinphenyl siloxanes (III) from 1.17:1 to 17.4:1. I, II, and III with the ratios Si:Sn = 1.25

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33380
S/190/62/004/002/009/021
B110/B101

Polyorganotin siloxanes..

and 3.98 are glassy, colorless, transparent, solid, and brittle, those with the ratios 7.75, 15.5, and 19.5 are viscous, bright-yellow resins at room temperature. I are stable in solution, are no longer soluble when separated at 20 - 22°C from the solution, and do not melt. II and III keep their solubility in organics even after separation. With ratios Si:Sn > 4, I and II are well soluble in organic solvents, with Si:Sn ~1 only in acetone. After 2 hr heating (200°C), II (Si:Sn = 4) loses its solubility. III (Si:Sn = 4) becomes unsoluble (benzene, acetone) after heating at 200°C, III (Si:Sn = 17) loses its solubility much more slowly. II and III become unsoluble with increasing Sn content. The kinematic viscosities of 5, 10, and 30% solutions of II and III in toluene with different Si:Sn ratios were rather similar. The time of polymerization increases with increasing Sn content (Si:Sn = 4 ⟶ 8, time 1 ⟶ 30). The polymerization time of III is much shorter than that of II. For III, it grows strongly for polymers with Si:Sn > 13.7 (Si:Sn = 8.5: 35 sec; Si:Sn = 17.4: 10 min). The thermomechanical properties of II and III depend on the Sn content. III (Si:Sn = 4) did not flow at 400°C after plasticizing with 20% pentachloro diphenyl: at 80 - 90°C. III (Si:Sn = 14) showed flowing at 130 - 140°C. The stiffness of the polymer molecule increases with rising Sn content of III. II (Si:Sn = 4) has a flowing point of ~80°C, with Si:Sn = 7.75:

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Polyorganotin siloxanes

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B110/B101

30°C. II (Si:Sn = 4) melts at 80°C, II did not flow at 400°C. II (Si:Sn = 15.5) melts at 30°C, II (Si:Sn = 14) at 135°C. This suggests a stiffer structure of III. There are 1 figure, 5 tables, and 5 Soviet references.

ASSOCIATION: Institut elementoorganicheskikh soyedineniy AN SSSR (Institute of Elemental Organic Compounds AS USSR). Vsesoyuznyy elektrotekhnicheskiy institut im V. I. Lenina (All-Union Electrotechnical Institute imeni V. I. Lenin)

SUBMITTED: February 8, 1961

X

Card 3/3

33381

15.8170 15.81

S/190/62/004/002/010/021
B101/B110

AUTHORS: Petrashko, A. I., Andrianov, K. A.

TITLE: Physical and thermal properties of polyorganosiloxanes obtained by double decomposition reaction

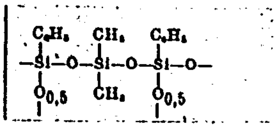
PERIODICAL: Vysokomolekulyarnyye soyedineniya, v. 4, no. 2, 1962, 221-229

TEXT: The authors studied the thermomechanical properties of polymers obtained by interaction between alkyl(aryl) sodium oxydihydroxysilanes and alkyl(aryl)dichlorosilanes according to the equation

$$2RSi(OH)_2ONa + R'R''SiCl_2 \longrightarrow 2NaCl + 2H_2O + \left[-\underset{O_{0.5}}{Si}(R)O-\underset{R''}{Si}(R')O-\underset{O_{0.5}}{Si}(R)O-\right]_n$$

New polymers were obtained from phenyl sodium oxy dihydroxysilane (A): polymer

X

I 

$$\left[-\overset{C_6H_5}{\underset{O_{0,5}}{Si}}-O-\overset{CH_3}{\underset{CH_3}{Si}}-O-\overset{C_6H_5}{\underset{O_{0,5}}{Si}}-O-\right]$$

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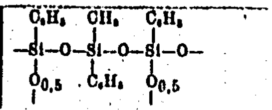
33381

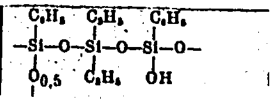
S/190/62/004/002/010/021
B101/B110

Physical and thermal properties...

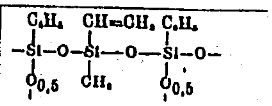
by reaction with $(CH_3)_2SiCl_2$, vitrification temperature $T_v = 52^\circ C$, yield 98%; polymer

II

$$-\overset{C_6H_5}{\underset{O_{0,5}}{Si}}-O-\overset{CH_3}{\underset{C_6H_5}{Si}}-O-\overset{C_6H_5}{\underset{O_{0,5}}{Si}}-O-$$

with $(CH_3)(C_6H_5)SiCl_2$, $T_v = 34^\circ C$, yield 96.4%; polymer

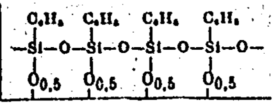
III

$$-\overset{C_6H_5}{\underset{O_{0,5}}{Si}}-O-\overset{C_2H_5}{\underset{C_2H_5}{Si}}-O-\overset{C_6H_5}{\underset{OH}{Si}}-O-$$

was obtained by reaction with $(C_2H_5)_2SiCl_2$, $T_v = 28^\circ C$, yield 89.3%, and polymer

IV

$$-\overset{C_6H_5}{\underset{O_{0,5}}{Si}}-O-\overset{CH=CH_2}{\underset{CH_3}{Si}}-O-\overset{C_6H_5}{\underset{O_{0,5}}{Si}}-O-$$

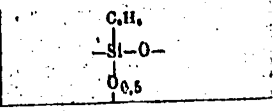
Card 2/6

by reaction with $(CH_3)(CH_2=CH)SiCl_2$, T_v = 40°C, yield 78.3%. Reaction of A with $C_2H_5SiCl_3$ gave

V


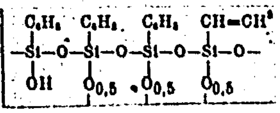
$$\begin{matrix} C_6H_5 & & C_6H_5 & & C_6H_5 & & C_6H_5 & \\ | & & | & & | & & | & \\ -Si- & O- & Si- & O- & Si- & O- & Si- & O- \\ | & & | & & | & & | & \\ O_{0,5} & & O_{0,5} & & O_{0,5} & & O_{0,5} & \end{matrix}$$

yield 55.6% and with $C_6H_5SiCl_3$

VI


$$\begin{matrix} C_6H_5 & \\ | & \\ -Si- & O- \\ | & \\ O_{0,5} & \end{matrix}$$

was obtained, T_v = 200°C, yield 73.4%, with $(CH_2=CH)SiCl_3$

VII


$$\begin{matrix} C_6H_5 & & C_6H_5 & & C_6H_5 & & CH=CH_2 & \\ | & & | & & | & & | & \\ -Si- & O- & Si- & O- & Si- & O- & Si- & O- \\ | & & | & & | & & | & \\ OH & & O_{0,5} & & O_{0,5} & & O_{0,5} & \end{matrix}$$

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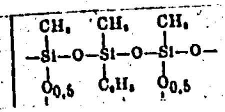
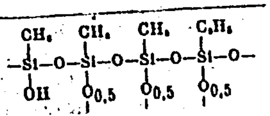
was obtained, $T_v > 400^\circ C$, yield 58.6%. . By a method already described (Vysokomolek. soyed., 2, 136, 1960) methyl sodium oxy dihydroxysilane yielded polymer

VIII 

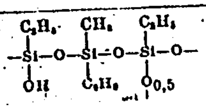
$$-\underset{O_{0,5}}{\overset{CH_3}{Si}}-O-\underset{C_6H_5}{\overset{CH_3}{Si}}-O-\underset{O_{0,5}}{\overset{CH_3}{Si}}-O-$$

yield 63.8%, a viscous liquid.

IX 

$$-\underset{OH}{\overset{CH_3}{Si}}-O-\underset{O_{0,5}}{\overset{CH_3}{Si}}-O-\underset{O_{0,5}}{\overset{CH_3}{Si}}-O-\underset{O_{0,5}}{\overset{C_6H_5}{Si}}-O-$$

yield 75.3%, which melts readily was obtained from ethyl sodium oxy dihydroxysilane. The viscous liquid

X 

$$-\underset{OH}{\overset{C_2H_5}{Si}}-O-\underset{C_6H_5}{\overset{CH_3}{Si}}-O-\underset{O_{0,5}}{\overset{C_2H_5}{Si}}-O-$$

33381

S/190/62/004/002/010/021
B101/B110

Physical and thermal properties...

was obtained from ethyl sodium oxy dihydroxysilane with $(CH_3)(C_6H_5)SiCl_2$. VI has a high thermal stability compared with the polymer obtained by hydrolyzing $C_6H_5SiCl_3$ whose T_v, inspite of equal composition, was only 40 - 50°C. The thermomechanical properties of I and its copolymers with polyaluminophenylsiloxanes were compared. After a 2-hr heating at 500°C the loss in weight of I was 58.3%, the loss in Si was 38.5%. For the copolymer I-A (0.05% Al) these values were 47.2, 19.8; for I-C (0.25% Al) 47.8, 17.6; for I-D (0.5% Al) 48.0, 19.2%, respectively. The high loss in I is explained by cyclization which in the copolymers is prevented by their aluminum content. Structuralization occurs in the copolymers. At 200°C the copolymer I did not gelatinize after 6 hrs. With I-C gelation occurred after 12 min 36 sec, with I-D after 7 min 12 sec. From a comparison of the behavior of polymethylsiloxane (M) and its aluminum-containing copolymer M-D (0.5% Al) as well as of polyphenylsiloxane (P) and of the copolymer P-D at 400°C the following losses in weight were determined: M 10% after 24 hrs, no further loss in weight within 15 days; M-D 6% after 5 days; P 15% after 15 days, P-D 40% after 15 days. The C/Si ratio decreased to 0.211 after 6 hrs, with M-D it remained ~1. With

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33381

Physical and thermal properties... S/190/62/004/002/010/021
B101/B110

P it remained almost unchanged (5.97), with P-D it decreased to 2.65. The thermomechanical values were determined by G. Ye. Golubkov and N. P. Gashnikova. There are 4 figures, 4 tables, and 8 references: 6 Soviet and 2 non-Soviet. The two references to English-language publications read as follows: US Patent 2853503, 1958; L. H. Sommer, L. Q. Green, F. C. Whitmore, J. Amer. Chem. Soc., 71, 3253, 1949.

X

ASSOCIATION: Institut elementoorganicheskikh soyedineniy AN SSSR (Institute of Elemental Organic Compounds of AS USSR). Vsesoyuznyy elektrotekhnicheskiy institut im. V. I. Lenina (All-Union Electrotechnical Institute imeni V. I. Lenin)

SUBMITTED: February 8, 1961

Card 6/6

33384

S/190/62/004/002/015/021
B110/B101

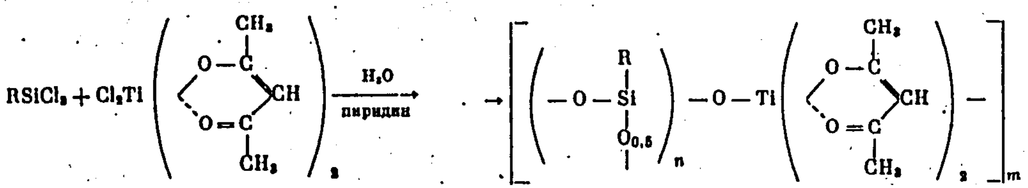
15 8150

AUTHORS: Andrianov, K. A. Pichkhadze, Sh. V., Bochkareva, I. V.

TITLE: Polyorganotitanosiloxanes. II. Cohydrolysis of bis(acetylacetonate)dichloro titanium with alkyl(aryl)trichloro silanes

PERIODICAL: Vysokomolekulyarnyye soyedineniya, v. 4, no. 2, 1962, 256-260

TEXT: The cohydrolysis of bis(acetylacetonate) dichloro titanium with methyl-ethyl and phenyl trichloro silanes in aqueous medium, with pyridine as acceptor and toluene as solvent, has been investigated. It proceeds as follows:



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33384
S/190/62/004/002/015/021
B110/B101

Polyorganotitanosiloxanes...

In the polymer, the Si:Ti ratio was always higher than that of the initial substances. Cohydrolysis of bis(acetylacetonate)dichloro titanium with methyl trichloro silane yielded maximum, poly-bis(acetylacetonate)titano phenyl siloxane (I) minimum ratio. The osmometrically determined molecular weight of I was 103,000. All polymers showed, in the infrared spectrum, absorption bands for Ti-O in the Ti-O-Si group, and complete absorption for Si-O in the Si-O-Si group. Analyses and investigations of properties of I, poly-bis(acetylacetonate)titano methyl siloxane (II), and poly-bis(acetylacetonate)titano ethyl siloxane (III) showed cyclolinear structure with oxygen-bound chains of eight- or six-membered rings. The viscosity in benzene was 0.073 for I; 0.069 for II; 0.0670 for III. The yellow, film-forming polymers were structurized at 100, 160, and 200°C; they became unsoluble except for I which was partially soluble even after 4 hr heating at 200°C. In this case, their thermomechanical properties correspond to those of structurized polymers. The structure of II and III is an intermediate stage between crystalline and amorphous structures, only I is amorphous. The OH groups were determined according to Terent'yev. The infrared spectra were taken at the opticheskaya laboratoriya INEOS (Optical Laboratory of INEOS) headed

X

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Polyorganotitanosiloxanes...

33384
S/190/62/004/002/015/021
B110/B101

by I. V. Obreimov, the X-ray patterns at the laboratoriya rentgenostrukturnogo analiza (Laboratory for X-ray Structural Analysis) headed by A. I. Kitaygorodskiy; the thermomechanical measurements were made at the laboratoriya fiziki polimerov (Laboratory for Polymer Physics) headed by G. L. Slonimskiy. Yu. S. Ksimantovskaya determined the molecular weight. There are 1 figure, 3 tables, and 4 references: 3 Soviet and 1 non-Soviet.

ASSOCIATION: Institut elementoorganicheskikh soyedineniy AN SSSR (Institute of Elemental Organic Compounds AS USSR)

SUBMITTED: February 11, 1961

X

Card 3/3

34992
S/190/62/004/003/012/023
B110/B144

15.8170

AUTHORS: Andrianov, K. A., Volkova, Lora, M., Sokolova, N. V.

TITLE: Synthesis and polymerization of α- and β-cyano dimethyl cyclosiloxanes

PERIODICAL: Vysokomolekulyarnyye soyedineniya, v. 4, no. 3, 1962, 403-408

TEXT: The cohydrolysis of bifunctional polymers was conducted in an acid medium:

$$m\,(CH_3)_2SiCl_2 + RCH_3SiCl_2 + (m+n)\,H_2O \rightarrow |(CH_3)_2SiO|_m|CH_3RSiO|_n + 2\,(m+n)\,HCl,$$

where R = $CHCNCH_3$; CH_2CH_2CN. The cohydrolysis of dimethyl dichloro silane with α-cyano-ethyl-methyl dichloro silane yielded heptamethyl-α-cyano-ethyl cyclotetrasiloxane (I), that of β-cyano-ethyl-methyl dichloro silane and dimethyl dichloro silane yielded heptamethyl-β-cyano-ethyl cyclotetrasiloxane (II) and a complicated cyclic compound (III). Hydrolysis products are transparent liquids distillable without decomposition and well

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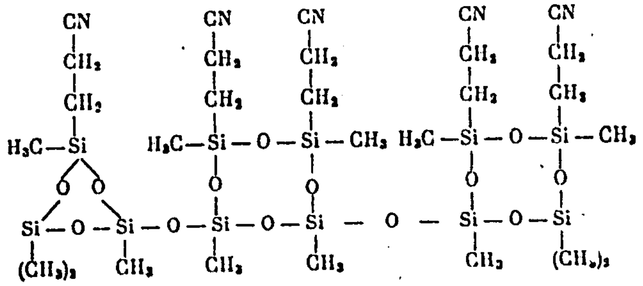
soluble in benzene, toluene, ether, and CCl_4. Their structure was determined by elementary analysis their molecular weight was determined and IR spectra were taken. Absorption bands at 1079-1088 cm^{-1} showed vibrations of the Si-O bond in the 8-membered ring, bands at 800 and 1250 cm^{-1} showed those of the Si-CH_3 bond, and bands at 2332 cm^{-1} showed those of the C≡N bond. Peaks at 1020 cm^{-1} and 1080 cm^{-1} (Si-O bonds in the 6- and 8-membered rings) and further analytical results suggest the following structure of III:



Synthesis and polymerization of... S/190/62/004/003/012/023
B110/B144

In polymerization with KOH, III behaves like bicyclic polydimethyl siloxanes owing to its easy polymerization at 20°C. At 120°C it forms a structurized product. Catalytic polymerization of II at 130°C was found to cause 2.02 % shrinkage. The polymerization rates form the sequence II > copolymer II + III > III. Higher polymerization rate of II is probably due to the positive polymerization of the Si atom bound to the β-cyanoethyl group, which easily coordinates with the OH group. There are 3 figures, 1 table, and 5 references: 1 Soviet and 4 non-Soviet. The most important reference to English-language publications reads as follows: G. Cooper, M. Prober, J. Organ. Chem., 25, 240, 1960.

ASSOCIATION: Moskovskiy institut tonkoy khimicheskoy tekhnologii im. M. V. Lomonosova (Moscow Institute of Fine Chemical Technology imeni M. V. Lomonosov)

SUBMITTED: March 1, 1961

Card 3/3

34999
S/190/62/004/003/019/023
B124/B101

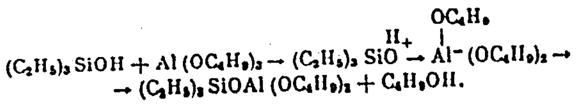
11.2219
15.9205

AUTHORS: Nudel'man, Z. N., Andrianov, K. A., Kudryavitskaya, G. B.

TITLE: Synthesis of linear polytriethylsiloxyalumino- and polytriethylsiloxytitanodimethylsiloxanes

PERIODICAL: Vysokomolekulyarnyye soyedineniya, v. 4, no. 3, 1962, 440-447

TEXT: Polymers were prepared by reacting α,ω-polydimethylsiloxanediols with triethylsiloxydibutoxyaluminum (TA) and bis-(triethylsiloxy)dibutoxytitanium (BI), respectively, resulting in the splitting off of butyl alcohol and the formation of metal-siloxane bonds. The starting monomers were prepared by reacting triethylsilanol with aluminum butylate and tetrabutoxytitanium, respectively; the first reaction yields product



$$(C_2H_5)_3SiOH + Al(OC_4H_9)_3 \rightarrow (C_2H_5)_3\overset{H_+}{SiO} \rightarrow \overset{\overset{OC_4H_9}{|}}{Al^-}(OC_4H_9)_2 \rightarrow (C_2H_5)_3SiOAl(OC_4H_9)_2 + C_4H_9OH.$$

A and the second product

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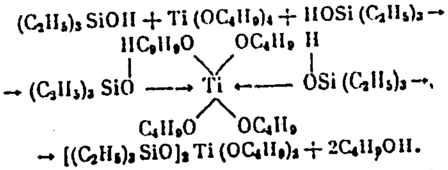
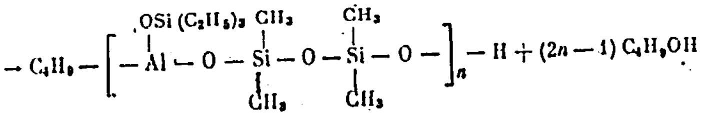
B124/B101

Synthesis of linear ...



B. This scheme is verified by the fact that no condensation of triethylsilanol yielding hexaethyldisiloxane was observed to take place which is explained to be due to its combination resulting in an intermediary donor-acceptor complex. The preparation of a polymer by reacting TA with tetramethyldisiloxanediol-1,3 (polymer I) was found to take place according to formula



$$\rightarrow C_4H_9-\left[-\overset{\overset{\displaystyle OSi(C_2H_5)_3}{|}}{Al}\leftarrow O-\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{Si}}-O-\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{Si}}-O-\right]_n-H+(2n-1)C_4H_9OH$$

(C).

The respective material had a molecular weight of about 2000, was easily soluble in benzene, and exhibited cold-flow properties. Polymer II has been prepared by heterofunctional condensation of dimethyldiacetosiloxane

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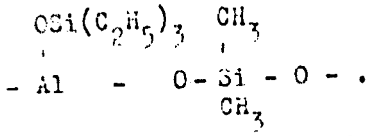
S/190/62/004/003/019/023
B124/B101

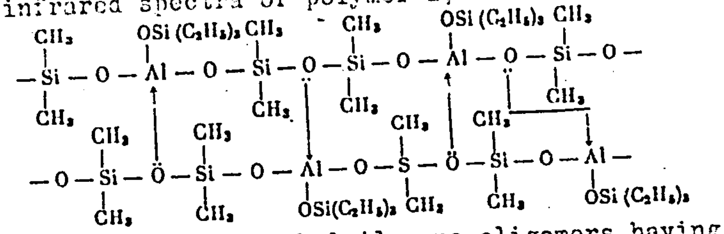
Synthesis of linear ...

with TA in the absence of a catalyst; its composition is



$$-\overset{\overset{\displaystyle OSi(C_2H_5)_3}{|}}{Al}-O-\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{Si}}-O-$$

. The existence of donor-acceptor bonds between the Al atoms of one and the O atoms of another molecule as well as of intermolecular interactions has been verified by the examination of the infrared spectra of polymer I, to which the structure



(D) has been attributed. With α,ω-dioxydimethylsiloxane oligomers having molecular weights of 1500, 2400, and 30,000, elastomers were prepared with rigidity increasing with the decreasing molecular weight of the reacted oligomer. The fact that

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S/190/62/004/003/019/023
B124/B101

Synthesis of linear ...

equimolar amounts of TA are insufficient to yield polymers of rigidity equal to those prepared with excessive TA is ascribed to hydrolytic splitting off of butoxy groups. Conclusions on the existence of intermolecular interactions are verified by the thermomechanical curves of all polymers synthesized from oligomers with molecular weights of 1500 and 2400. Aluminodimethylsiloxanes prepared from polydimethylsiloxanediols of a molecular weight of 30,000 are elastomers which can be vulcanized to rubbers with properties resembling those of polydimethylsiloxane rubber with a molecular weight of about 500,000. There are 2 figures, 1 table, and 17 references: 12 Soviet and 5 non-Soviet. The two most recent references to English-language publications read as follows: J. D. Danforth, J. Amer. Chem. Soc. 80, 2585, 1958; D. Bradly, J. M. Tomas, Chem. and Industr., 1958, 17.

ASSOCIATION: Nauchno-issledovatel'skiy institut rezinovoy promyshlennosti (Scientific Research Institute of the Rubber Industry). Moskovskiy institut tonkoy khimicheskoy tekhnologii im. M.V. Lomonosova (Moscow Institute of Fine Chemical Technology imeni M. V. Lomonosov)

Card 4/5

S/190/62/004/004/015/019
B117/B138

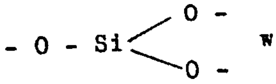
5.3700
15.8170

AUTHORS: Andrianov, K. A., Khananashvili, L. M., Belen'kaya, I. S.

TITLE: Synthesis and polymerization of dimethyl cyclosiloxanes with silsesquioxane bonds

PERIODICAL: Vysokomolekulyarnyye soyedineniya, v. 4, no. 4, 1962, 591-595

TEXT: Bi- and tricyclic compounds of the dimethyl siloxane series with silsesquioxane bonds

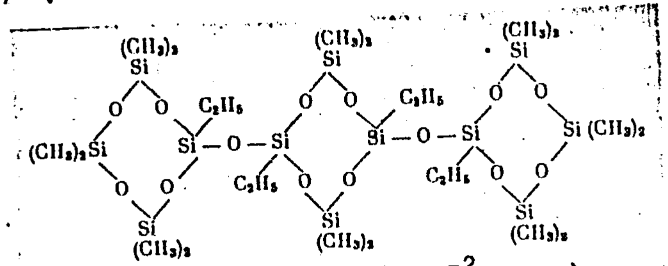


$-O-Si\langle{}^{O-}_{O-}$

were obtained by hydrolysis and condensation of hexamethyl ethyl cyclotetrasiloxane and tetramethyl diethyl cyclotetrasiloxane. The hydrolysis of the hydrogen-containing cyclotetrasiloxanes synthetized by the method described in Ref. 3 (N. N. Sokolov, Zh. obshchey khimii, 29, 248, 1959) was carried out in alkaline medium (caustic soda) at room temperature, and the condensation in acid medium (hydrochloric acid, pH 5) at 40-45°C. The following substances were obtained: bis-(hexamethyl ethyl cyclotetrasiloxanyl)oxide (I) ($Si_8C_{16}H_{46}O_9$, boiling point 135-147°C/1-2 mm HG) and a tricyclic compound (II) with the structure:

X

Card 1/3



($Si_{12}C_{24}H_{68}O_{14}$, boiling point 240-250°C/$2\cdot10^{-2}$ mm Hg). Both compounds are readily soluble in benzene, toluene and ethyl alcohol. They easily polymerize at room temperature (in toluene solution in the presence of 0.3% KOH), (I) producing an insoluble polymer after 93 hr and (II) after 20.5 hr. The reactivity increases with a higher number of silsesquioxane links in the chain. The stronger reactivity of silsesquioxane bonds as compared with siloxane bonds is probably connected with the fact that the silicon atom bonded with three oxygen atoms is more electropositive and the attack of these bonds gets more effective during the action of nucleophilic reagents. There are 2 figures and 1 table.

Synthesis and polymerization...

S/190/62/004/004/015/019
B117/B138

ASSOCIATION: Moskovskiy institut tonkoy khimicheskoy tekhnologii im. M. V. Lomonosova (Moscow Institute of Fine Chemical Technology imeni M. V. Lomonosov)

SUBMITTED: February 22, 1961

X

Card 3/3

37431
S/190/62/004/005/007/026
B110/B144

15.8170

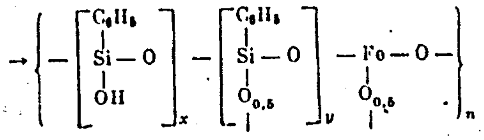
AUTHORS: Andrianov, K. A., Ganina, T. N., Sokolov, N. N.

TITLE: Synthesis of polyferro organosiloxanes and polyferroalumo organosiloxanes

PERIODICAL: Vysokomolekulyarnyye soyedineniya, v. 4, no. 5, 1962, 678-682

TEXT: Low-molecular polyferrophenyl siloxanes and polyalumoferrophenyl siloxanes were obtained by an exchange reaction of phenyl sodium oxy-dioxy silane with iron ($FeCl_3$) or aluminum salts ($AlCl_3$) (5 hrs, 100°C). Polyferrophenyl siloxanes with the molecular weight 4500:

$$C_6H_5Si(OH)_2ONa + FeCl_3 \ [\text{или} \ FeNH_4(SO_4)_2] \rightarrow$$



$$\rightarrow \left\{ - \left[\begin{array}{c} C_6H_5 \\ | \\ Si - O \\ | \\ OH \end{array} \right]_x - \left[\begin{array}{c} C_6H_5 \\ | \\ Si - O \\ | \\ O_{0,5} \\ | \end{array} \right]_y - \begin{array}{c} \\ Fe - O - \\ | \\ O_{0,5} \\ | \end{array} \right\}_n$$

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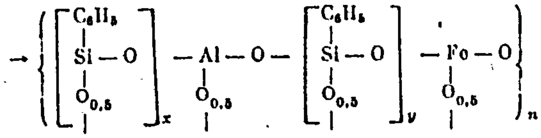
S/190/62/004/005/007/026
Synthesis of polyferro organosiloxanes ... B110/B144

are nonfusible powders soluble in benzene, toluene, xylene, chloro benzene, acetone, amyl acetate, dichloro ethane, and carbon tetrachloride, partly soluble in ethanol, insoluble in benzine and decahydronaphthalene. Nonfusible polyferrophenyl siloxanes soluble in organic substances with x and y = 2 are obtained by decomposing phenyl sodium oxy-dioxy silane with 20% ammonium ferric alum in an aqueous-alkaline medium. The decomposition of phenyl sodium oxy-dioxy silane with $AlCl_3$ and $FeCl_3$ in toluene follows the reaction

$$C_6H_5Si(OH)_2ONa + FeCl_3 + AlCl_3 \rightarrow$$



$$\rightarrow \left\{ \left[\begin{array}{c} C_6H_5 \\ | \\ Si-O \\ | \\ O_{0.5} \\ | \end{array} \right]_x - \begin{array}{c} Al-O- \\ | \\ O_{0.5} \\ | \end{array} \left[\begin{array}{c} C_6H_5 \\ | \\ Si-O \\ | \\ O_{0.5} \\ | \end{array} \right]_y - \begin{array}{c} Fe-O \\ | \\ O_{0.5} \\ | \end{array} \right\}_n$$

The resulting polyferroalumophenyl siloxanes (Si : Fe = 12.0; Si : Al = 12.0; Al : Fe = 1.0, and x and y = 6) are nonfusible; their solubility equals that of polyferrophenyl siloxanes. They remain soluble

Card 2/4

in toluene and their molecular weight increases from 3770 to 7430 when kept at 200°C for 2 hrs. The weight of polyferrophenyl siloxanes decreases by 6.7, 14.93, 53.21% after 5-hr heating at 200, 320°C, and red heat, respectively. When kept for 5.5-10 hrs at 200°C, their hydroxyl group content decreases from 4.5-5.8% to 3.2-4.1% by condensation, with unchanged solubility. Structuration of polymers thus only takes place at high temperatures which make them insoluble in organic substances. The content of OH groups in polyalumophenyl siloxanes decreases from 5.53 to 2.7% after 10 hrs at 150°C, whereas their solubility in organic substances remains unchanged. Structuration takes place at 200-500°C. Five solid, powdery fractions were separated from polyferrophenyl siloxane (Si : Fe = 10) by fractional precipitation: fraction I: 6% by weight (17.11% Fe, Si : Fe = 1.4); fraction II: 22% by weight (molecular weight: 5770, 6% Fe, Si : Fe = 5.6); fractions III, IV, and V: 50% by weight (molecular weight: 3660, 4.2-4.4% Fe, Si : Fe = 9). There are 2 tables.

37637

S/190/62/004/005/013/026
B110/B108

15.9205

AUTHORS: Andrianov, K. A., Vasil'yeva, T. V., Khananashvili, L. M.

TITLE: Polymerization of dimethyl cyclomethyl phosphinoxysiloxanes

PERIODICAL: Vysokomolekulyarnyye soyedineniya, v. 4, no. 5, 1962, 708 - 713

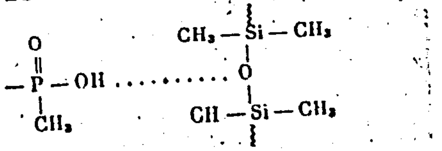
TEXT: An attempt was made to polymerize inorganic cycles containing silicon, oxygen, and phosphorus, and to copolymerize them with octamethyl cyclotetrasiloxane. Tetramethyl cyclomethyl phosphinoxydisiloxane and hexamethyl cyclomethyl phosphinoxytrisiloxane were polymerized with H_2SO_4, dichloroanhydride of methyl phosphinic acid, tin chloride, and KOH. The slight increase in viscosity indicated that polymerization was very poor. The thermal copolymerization of octamethyl cyclotetrasiloxane with tetramethyl cyclodi(methylphosphinoxy)disiloxane proceeded slowly while forming low-molecular products. In addition, the copolymerization of octamethyl cyclotetrasiloxane with tetramethyl cyclomethyl phosphinoxydisiloxane or tetramethyl cyclodi(methylphosphinoxy)disiloxane was studied at Si:P ratios of 6:1, 21:1, 42:1, 101:1, 201:1, and 301:1 in the presence of water. The amounts of water were sufficient for the hydrolysis of

Card 1/3

S/190/62/004/005/013/026
B110/B108

Polymerization of dimethyl ....

dimethyl cyclomethyl phosphinoxysiloxane. Two of the resultant polymers were liquid, and three were elastomers with [η] equal to 0.100, 0.202, 0.448 and with molecular weights of 12,590; 37,150; 125,900, respectively. At a ratio of Si to P = 21:1 and at a temperature of 100°C, polymerization takes place within the first six hours. At Si:P = 42:1, the rate of polymerization is temperature-dependent. The resulting transparent polymers, which are soluble in organic compounds, become dull, insoluble, and elastic on standing in air. The structuralization, which is irreversible after 60 min, is attributed to the formation of a hydrogen bond:



(B).

A built-up system is formed if the polymer chain contains several methyl phosphine groups. The resultant intermolecular forces cannot be removed even by boiling in polar solvents for 30 hrs. The structuralized polymer exhibits an infrared absorption band at 1600 - 1700 cm^{-1}. A study of the

Card 2/3

38262

S/190/62/004/006/008/026
B110/B138

15.8150

AUTHORS: Andrianov, K. A., Pichkhadze, Sh. V.

TITLE: Polyorgano-titanium siloxanes. III. Synthesis of poly-bis-(acetylacetonate)titanium methyl phenyl siloxane on the basis of bis-(acetylacetonate)dibutoxy titanium

PERIODICAL: Vysokomolekulyarnyye soyedineniya, v. 4, no. 6, 1962, 839-842

TEXT: The studies covered the heterofunctional condensation of methyl phenyl diacetoxy silane (I) with bis-(acetylacetonate)dibutoxy titanium (II) and the combined hydrolysis of diethoxy silane with II. Butyl acetate was separated at 165°C. The viscosity of the condensation product increased as the separation advanced. The reaction developed according to

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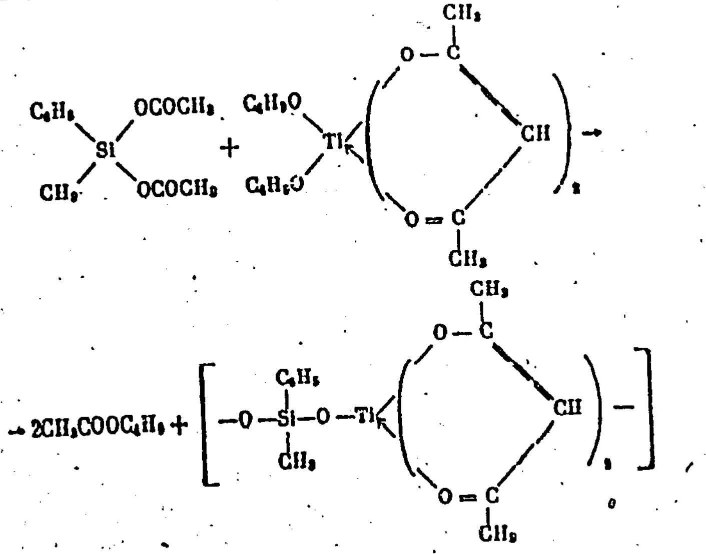
S/190/62/004/006/008/026
B110/B138

Polyorgano-titanium siloxanes. III. ...

A



A

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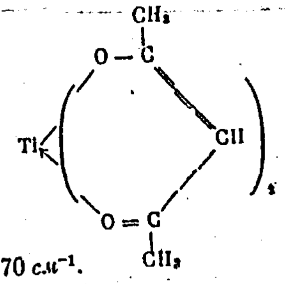
S/190/62/004/006/008/026
B110/B138

Polyorgano-titanium siloxanes. III. ...

At 917 cm^{-1} the IR spectra showed the absorption bands characteristic of Ti-O in Ti-O-Si, as well as bands at 1370, 1520 and 1570 cm^{-1} for



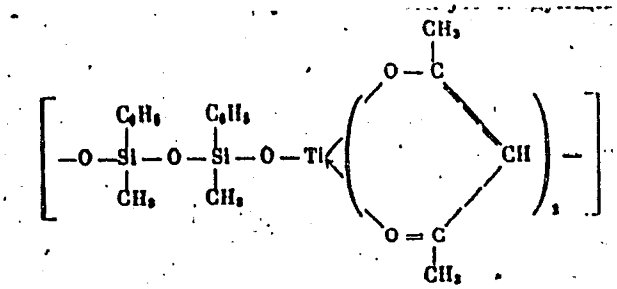
в области 1370, 1520, 1570 $см^{-1}$.

During the cohydrolysis a water-soluble polymer (10.94% C; 3.39% H; 37.79% Ti) developed and toluene-soluble bis-(acetylacetonate)titanium methyl phenyl siloxane with the elementary link

Card 3/4

S/190/62/004/006/008/026
B110/B138

Polyorgano-titanium siloxanes. III. ...



The vitrification temperature fell as the Si:Ti rose, while the solubility of poly-bis-(acetylacetonate)titanium methyl phenyl siloxanes heated at 160-200°C decreased with increasing Ti content. The molecular weight of the polymer obtained by cohydrolysis was 12,100. There are 2 figures and 1 table.

ASSOCIATION: Institut elementoorganicheskikh soyedineniy AN SSSR (Institute of Elemental-organic Compounds AS USSR)

SUBMITTED: April 6, 1961

Card 4/4

ANDRIANOV, K.A.; PICHKHADZE, Sh.V.

Polyorganotitanosiloxanes. Part 4: Reactions of co hydrolysis and heterofunctional condensation of bis-(8- hydroxyquinoline) dubutoxytitanium with dimethyl- and phenylmethyldiacetoxysilanes. Vysokom.soed. 4 no.7:1011-1018 Jl '62. (MIRA 15:7)

1. Institut elementooganicheskikh soyedineniy AN SSSR.

(Titanium organic compounds)

(Silane)

ANDRIANOV, K.A.; RUMBA, G.Ya.

Catalytic polymerization of hexamethylcyclotrisilazane and octamethylcyclotetrasilazane. Vysokom.soed. 4 no.7:1060-1063 Jl '62. (MIRA 15:7)

1. Institut elementoorganicheskikh soyedineniy AN SSSR.
(Silicon organic compounds)
(Polymerization)

ANDRIANOV, K.A.; GOLUBKOV, G.Ye.

Thermomechanical and electrical properties of epoxypolysiloxane polymers of various composition. Vysokom.soed. 4 no.9:1375-1379 S '62. (MIRA 15:11)

1. Vsesoyuznyy elektrotekhnicheskiy institut im. V.I. Lenina.

(Epoxy resins)
(Silicon organic compounds)

48601

G/004/62/009/009/001/004
D029/D109

15.9205

AUTHOR: Andrianov, K.A., Professor, Doctor (Moscow)

TITLE: Possibilities of synthesizing element-organic polymers

PERIODICAL: Plaste und Kautschuk, vol 9, no. 9, 1962, 419-421/424

TEXT: The author gives a survey on the present state of synthesis of element-organic polymers. Despite the large possibilities of synthesizing such high-molecular compounds, their formation reactions remain still to be investigated. The article treats only the synthesis reactions of polymers with inorganic metal chains. By means of the synthesis method for polydialkyl siloxane elastomers with linear molecular chains - polycondensation of the difunctional oligomers with difunctional silicon-organic monomers - the author obtained polydimethyl siloxane elastomers of a molecular weight of approximately 200,000. Their vulcanization produced rubbers with properties similar to those of polydimethyl siloxane rubbers. This polycondensation method is applicable also for producing high-molecular compounds, the molecular chains of which contain also metallic atoms. Thus,

Card 1/2

ANDRIANOV, K.A.; ZHDANOV, A.A.; KASHUTINA, E.A.

Reaction of diethylmethoxychlorosilane with sodium derivatives of acetylacetone and acetoacetic ester. Zhur. ob. khim. 32 no.1:297-301 Ja '62. (MIRA 15:2)
(Silane) (Pentanedione) (Acetoacetic acid)

33921

S/079/62/032/002/006/011
D204/D303

5.3700

AUTHORS: Popeleva, G.S., Savushkina, V.I., Andrianov, K.A. and Golubtsov, S.A.

TITLE: Interaction of the halogen derivatives of aryl chlorosilanes with hydrogen chlorosilanes

PERIODICAL: Zhurnal obshchey khimii, v.32, no. 2, 1962, 557-562

TEXT: High temperature condensations of methyl dichlorosilane (I) with methyl chlorophenyl dichlorosilane (II) (reaction 1), methyl phenyl chlorosilane (III) with p-dichlorobenzene (reaction 2) and of III with methyl chlorophenyl phenyl chlorosilane (IV) (reaction 3) were investigated. Reaction 1 was carried out with 1:11 molar ratios of the reagents at 570, 600, 620, 640 and 670°C, with contact times of 40, 50, 60 and 80 sec., in stainless steel tubes and yielded a mixture of the ortho-, meta- and para-isomers of bis (methyl dichlorosilyl) benzene (A). It was found that the yield of A, under optimum conditions (640°C, 60 sec.), was 27%, calculated with respect to I. The product then consisted of 60% of the liquid meta-isomer and 40% of the crystalline ortho- and para-isomers. Reaction 2 at
Card 1/2

33921

S/079/62/032/002/006/011
D204/D303

Interaction of the halogen ...

550°C, with a contact time of 40 sec., in silica tubes, gave IV in 34.6% yield, (calculated with respect to III), when the molar ratio of III to the p-dichlorobenzene was 2:1. Reaction 3 was carried out in silica tubes, at 650°C and with 40 sec. contact time, with reagents in 1:1 molar ratio, and gave para-bis (methyl phenyl chlorosilyl) benzene (B), in ~ 30% yield (calculated with respect to III). The structure of B was confirmed by a Grignard synthesis. Physical constants of the products and full experimental details are given. There are 2 figures, 4 tables and 15 references: 9 Soviet-bloc and 6 non-Soviet-bloc. The 4 most recent references to the English-language references read as follows: British Pat. 752,700 (1956); Ch.A., 51, 7402, (1957); Ch.A. 47, 3875, (1953); Ch.A. 47, 3334, (1953).

SUBMITTED: January 30, 1961

Card 2/2

S/079/62/032/003/004/007
D204/D302

AUTHORS: Trofimova, I.V., Lobusevich, N.P., Golubtsov, S.A. and Andrianov, K.A.

TITLE: The effect of certain metallic additions to Si-Cu alloys on their activity in the reaction with methyl chloride

PERIODICAL: Zhurnal obshchey khimii, v. 32, no. 3, 1962, 841-846

TEXT: The optimum amount of Cu and the effect of adding metals usually present in Cu and Si on the synthesis of methyl chlorosilanes were investigated, at 350-370°C, under 4 atm, by a method described earlier. Purified Si (total Al+Ca+Fe+Ti $<$ 0.2%) and Kp-1(Kr-1)Si were used, with M-1 and M-0 copper. Assessment of the additions of Al, Ca, Fe, Ti, Pb, Sb and Bi was made on the basis of the yield of methyl chlorosilanes (g/kg alloy/hr) and by the selective formation of Me_2SiCl_2. The optimum Cu content proved to be 7-10%.. Using pure silicon, Al and Ti lowered the alloy activity when present to the extent of 0.2-0.3%, whilst Fe and Ca

Card 1/2 ✓

S/079/62/032/003/004/007
The effect of certain metallic ... D204/D302

did not affect the reaction in quantities of 3 and 0.6% respectively. With Kr-1 Si, the negative influence of Al was apparent only at $\sim$2%, of Fe at 5%, Ti at 1% and Ca at 1.5%. With Kr-1 Si again, Pb and Bi behaved as catalytic poisons at $\sim$0.004-0.01%. 0.002-0.005% Sb promoted the reaction but this phenomenon was reversed at percentages $>$ 0.005%. These effects were affected by the presence of other additions. The alloys were prepared by D.I. Layner, L.A. Malysheva and L.A. Sotnikova. There are 5 figures, 4 tables and 8 references: 3 Soviet-bloc and 5 non-Soviet-bloc. The 4 most recent references to the English-language publications read as follows: Brit. Pat. 637,941 (1950); US Pat. 2,464,033 (1949); Japan.Pat. 421,(1954), Ch.A. 49,1102, (1955); Brit. Pat. 609,172, 609,173 (1950).

SUBMITTED: February 2, 1961

Card 2/2

36051

S/079/62/032/004/002/010
D204/D301

15.8170

AUTHORS: Andrianov, K.A., Zhdanov, A.A., and Odinets, V.A.

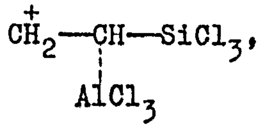
TITLE: Reactivity of the vinyl group in substituted silanes in addition reactions with benzene, in the presence of aluminum chloride

PERIODICAL: Zhurnal obshchey khimii, v. 32, no. 4, 1962, 1126-1130

TEXT: Addition reactions of C_6H_6 to $CH_2 = CHSiCl_3$ (A), $CH_2 = CH\ Si(Me)\ Cl_2$ (B), $CH_2 = CHSi(Me)_2Cl$ (C), and $CH_2 = CHSiMe_3$ (D) were studied, to determine the effect of substituents on the reactivity. All reactions were carried out over 4 1/2 hours at 75°C, in the presence of $AlCl_3$. Additions took place across the double bond to give $PhCH_2CH_2SiCl_3$, $PhCH_2CH_2Si(Me)Cl_2$ and $PhCH_2CH_2Si(Me)_2Cl$ in the cases of A, B and C respectively. The reactivity decreased from A to C and D did not react at all. The reaction mechanism is discussed in terms of displacements of π-electrons of the vinyl group by the Cl and CH_3 groups in compounds A, B, C and D. It is suggested that in

Card 1/2

Reactivity of the vinyl group in ... S/079/62/032/004/002/010
D204/D301

A, the first stage consists of the formation of  $\overset{+}{C}H_2-\underset{\substack{\vdots\\ AlCl_3}}{CH}-SiCl_3$, which then reacts with C_6H_6 to give $C_6H_5CH_2CH_2SiCl_3 + AlCl_3$. This is confirmed by the anomalous addition of the aromatic radical to the β-C. Successive replacement of Cl by CH_3 makes the formation of the carbonium ion less probable. Experimental details are fully described and physical properties of the addition products are given. There are 1 table and 5 references: 2 Soviet-bloc and 3 non-Soviet-bloc. The references to the English-language publications read as follows: G.H. Wagner, D.L. Bailey, A.N. Pines, M.L. Dunham and D.B. McIntile, Ind. Eng. Ch., 45, 367, 1953; L.H. Sommer, R.E. VanStrien F.C. Whitmore, J. Am. Chem. Soc., 71, 3056, 1949; M Kanazashi, Bull Chem. Soc. Japan, 1953, 493.

SUBMITTED: April 24, 1961

Card 2/2

S/079/62/032/005/004/009
D204/D307

AUTHORS: Andrianov, K.A., and Severnyy, V.V.

TITLE: Hydrolysis of trimethylsiloxychlorosilanes and condensation of their hydroxy derivatives

PERIODICAL: Zhurnal obshchey khimii, v. 32, no. 5, 1962, 1633-1636

TEXT: The hydrolysis reactions were studied to determine the reactivity of the above compounds with electrophilic and nucleophilic reagents. $[(CH_3)_3SiO]_2$ (I) was hydrolyzed in acid and basic media, with and without solvents. In the absence of solvent, aqueous hydrolysis at 10°C resulted in the removal of the trimethylsiloxy group, yielding $(CH_3)_3SiOSi(CH_3)_3$ (II) and a polymer $(CH_3)_3$ $SiO.SiO_{1.5}$ $(SiO_2)_n$ (III). Solvents decreased the tendency of the trimethylsiloxy group to split off; thus in ether and THF aq. hydrolysis gave an insoluble polymer and crystalline $[(CH_3)_3SiO]_2Si(OH)_2$ (IV). No polymers were obtained from the hydrolysis of I in the presence of HCl acceptors (pyridine, NH_3, $NaHCO_3$), under similar conditions, the
Card 1/2

S/079/62/032/005/004/009
Hydrolysis of trimethylsiloxy- ... D204/D307

only product being IV, in $\gtrsim$ 50 % yields. On heating at 200°C for 30 min. IV condensed to $HO\{[(CH_3)_3SiO]_2SiO\}_2H$ and $HO\{[(CH_3)_3SiO]_2SiO\}_3H$. Trimethylsiloxy group was also split off $[(CH_3)_3SiO]_3SiCl$ in an acid medium, without a solvent. In aq. $NaHCO_3$ the latter compound gave $[(CH_3)_3SiO]_3SiOH$, in 60 % yield. There are 2 tables.

SUBMITTED: April 22, 1961

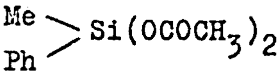
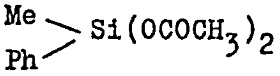
Card 2/2

S/079/62/032/005/005/009
D204/D307

AUTHORS: Andrianov, K.A., Astakhin, V.V., and Sukhanova, I.V.

TITLE: The reaction of alkyl (aryl) diacetoxysilanes with alkyl orthotitanates

PERIODICAL: Zhurnal obshchey khimii, v. 32, no. 5, 1962, 1637-1638

TEXT: The interactions of $(EtO)_4Ti$ with $Me_2Si(OCOCH_3)_3$ and with  $\begin{smallmatrix}Me\\Ph\end{smallmatrix}\!>Si(OCOCH_3)_2$ and of $(BuO)_4Ti$ with  $\begin{smallmatrix}Me\\Ph\end{smallmatrix}\!>Si(OCOCH_3)_2$ were studied, taking the reagents in molar proportions. The products consisted of alkyl acetates, alkyl (aryl) dialkoxysilanes (I) and polymers soluble in alcohol, benzene and toluene. The formation of I is ascribed to the reaction $\geqslant TiOR + \geqslant SiOCOCH_3 \rightarrow \geqq TiOCOCH_3 + \geqslant SiOR$, where R = Et or Bu.

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AUTHORS: Andrianov, K. A. and Rumba, G. Ya.

TITLE: The re-amination reactions of polymethyl-cyclosilazanes with aniline

PERIODICAL: Zhurnal obshchey khimii, v. 32, no. 6, 1962, 1993-1997

TEXT: The authors, investigating the possibility of substituting the $>$NH group by that of $C_6H_5N<$ in dimethyl-cyclosilazanes, studied the reactions of hexamethylcyclotrisilazane and octamethylcyclotetrasilazane with aniline. It was found that the re-amination with elimination of NH_3 takes place without a catalyst. From the reaction products of octamethylcyclotetrasilazane with aniline, taken in 1:1, 1:3 and 1:4 molar ratios, a crystalline tri-N-phenylhexamethylcyclotrisilazane (m.p. 247 - 248°C) was separated. The same compound was obtained from hexamethylcyclotrisilazane and aniline taken in a molar ratio of 1:3. The authors checked its com-

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position by direct synthesis from dimethyldichlorosilane and aniline. These results prove that in the reaction of octamethylcyclotetrasilazane with aniline not only is $>NH$ substituted by $C_6H_5N<$, but also the 8-membered ring is rearranged into a 6-membered one. The authors conclude that this rearrangement proceeds through the formation of dimethyl-bis-(N-phenylamino)-silane which is then condensed into a 6-membered ring. There are 1 table and 1 figure.

SUBMITTED: April 4, 1961