20-5-24/60

The Synthesis of Polyorganoaluminum Siloxanes.Exchange
Decomposition Reaction Between Sodium Salts of Alkyl-Silantriols
and Aluminum Chloride.

organic solvents.The investigations showed that on the occasion of
the interaction of chloroaluminum with sodium salts of phenyl-silan-
troil,ethyl.silantroil andwith the disodium salt of 1,3,5-triphenyl
-1,3,5-trimethyl silanoxane,the formation of the substances mentio-
ned in the title proceeds according to pattern:$C_6H_5Si(OH)_2ONa+AlCl_3$
$--->/C_6H_5Si(OH)_2O/_3Al+SNaCl,n/C_6H_5Si(OH)_3/_3Al--->/C_6H_5Si(O)O/_3Al_n+$
$+nH_2O$.The resulting polymers represent solid,brittle,glass-like sub-
stances,soluble in benzene,alcohol and acetone.On the occasion of
the evaporation of their solutions there develop transparent films
on solid surfaces.The sodium salts of alkyl-silantriols used by the
authors in the exchange decomposition reaction,were synthetized by
the influence of an equimolecular amount of caustic soda upon poly-
organosiloxanes.These sodium salts represent solid crystalline sub-
stances containing crystallization water.According to the amount of
crystallization water these substances are soluble in alcohol and
acetone.Experimental part with the usual data.(3 Slavic references.)

ASSOCIATION Institute for Elementary-Organic Compounds of the Academy of Science
of the U.S.S.R.

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Card 2/2

ZHDANOV, A. A., ANDRIANOV, K. A.,

"The Synthesis of Polyorganometalosiloxanes and the Investigation of their properties," paper submitted at the Symposium on Organic and Nonsilicate Silicon Chemistry on 12th-14th May 1958, Dresden.

1. The reaction of metals- sodium, magnesium and aluminum- with organosilanols- diethylsilanediol, 1,3-dihydroxytetraethyl- disiloxane and polyphenylsiloxane resins, is under investigation. It will be shown that the above compounds react with the metals under anhydrous conditions with the formation of metal-siloxane (metal-oxygen-silicon) linkages.
2. The reactivity of the silanols is dependent on the stability of their hydroxyl groups. Compounds which easily undergo condensation do not react with metals. Compounds which have stable hydroxyl groups react easily with metals.
3. It will be shown that by the action of aluminum chloride on the sodium salts of phenyl- and ethylsilanetriols and of 1,3,5-trimethyl-1,3,5-triphenyltrisiloxane, polymers are formed- the polyorganoaluminosiloxanes.

Abstract: B-3,108,944 (Encl.)

ZHDANOV, A. A. and ANDRIANOV, K. A.

"Organosiloxyaluminoxane"

paper submitted for the Symposium on Organic and Non-Siliceous Silicon Chemistry, Dresden, 12-14 May 1958.

ZHDANOV, A.A.
ANDRIANOV, K. A. and ZHDANOV, A. A.

"Synthese von Neuen Polymeren Met anorganischen Kettenmolekulen,"

paper presented at the Intl. Symposium on Macromolecular Chemistry, Prague, 9-15 Sep 1957.

Inst. Organic Chemistry im Zelinskiy, AS USSR

Kautschuk und Gujmi, No. 1, 1958.

SOV/62-58-6-24/37

AUTHORS: Andrianov, K. A., Zhdanov, A.A.

TITLE: The Synthesis of Tetrakis-(Triethyl-Siloxy) Titanium and Tetrakis-(Triethyl-Siloxy)-Tin (Sintez tetrakis-(trietilsiloksi) titana i tetrakis (trietilsiloksi) olova)

PERIODICAL: Izvestiya Akademii nauk SSSR, Otdeleniye khimicheskikh nauk, 1958, Nr 6, pp. 779-780 (USSR)

ABSTRACT: The synthesis of silicon-organic titanium derivatives are dealt with by several scientific papers. In the course of the present report the authors describe the synthesis of triethylsiloxy titanium and tetratriethylsiloxy tin brought about by the exchange reaction of sodium-triethyl-silanolate with tetrachlorotitanium and zinc chloride:

$$4(C_2H_5)_3SiONa + SnCl_4 \longrightarrow [(C_2H_5)_3SiO]_4Sn + 4NaCl.$$

Further data relating to the investigation of the reaction as well as to the interaction between sodium triethylsilanolate and other halides are intended to be discussed by the authors in a paper to follow. There are 5 references, 3 of which are Soviet.

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The Synthesis of Tetrakis-(Triethyl-Siloxy) Titanium and Tetrakis-(Triethyl-Siloxy)-Tin. SOV/62-58-6-24/37

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

SUBMITTED: January 21, 1958

1. Metalorganic compounds--Synthesis 2. Titanium--Chemical reactions 3. Tin--Chemical reactions 4. Silicon compounds (Organic)--Chemical reactions 5. Zinc chloride--Chemical reactions

Card 2/2

AUTHORS: Andrianov, K. A., Zhdanov, A. A. SOV/62-58-9-9/26

TITLE: The Reaction of Metals With Hydroxyl-Containing Organosilicon Compounds (O vzaimodeystvii metallov s gidroksilsoderzhashchimi kremneorganicheskimi soyedineniyami)

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1958, Nr 9, pp 1076 - 1079 (USSR)

ABSTRACT: In the previous papers the authors showed that triethylsilanol can react with aluminum to form aluminum triethylsilanolate with the liberation of hydrogen. The high reactivity of hydroxyl-containing organosilicon compounds toward metals can only be explained by the fact that the silicon atom in these compounds exhibits a high degree of polarizability. The authors were interested in investigating the reactivity of several polymers of organosilicon compounds which had hydroxyl groups at the silicon atom. It was found that in the reaction of these compounds with metallic sodium, magnesium, and aluminum that hydrogen was liberated and a metal siloxane was formed. The reactivity of the siloxy-con-

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taining organosilicon compounds depends upon the resistivity at these hydroxyl groups. Compounds which enter into intermolecular condensation reactions easily do not react with metals. On the other hand, hydroxyl groups which are resistive to condensation reactions react relatively easily with metals. There are 6 tables and 4 references, 2 of which are Soviet.

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

SUBMITTED: February 5, 1957

20-118-6-21/43

AUTHORS: Andrianov, K. A., Corresponding Member of the AS USSR, Zhdanov, A. A., Asnovich, E. Z.

TITLE: On the Synthesis of Infusible but Soluble Polymers (O sinteze neplavkikh, no rastvorimykh polimerov)

PERIODICAL: Doklady Akademii Nauk SSSR, 1958, Vol. 118, Nr 6, pp. 1124-1127 (USSR).

[illegible]

ABSTRACT: The fusibility and solubility of polymers in organic solvents are considered to be dependent on the molecular structure of the chains. Polymers with a linear structure are soluble and meltable by heating, regardless of their molecular weight. The branching of the chain, viz. the formation of laced (sshitye .) structures and spatial structures makes the polymer lose these properties. This dependence concerns all polymers. The authors tested the synthesis of polymers which were readily soluble in non- or slightly-polar solvents but which did not melt when heated. The results obtained by thourough investigations show that no polymers with the aforesaid properties can be obtained with the production of cyclic poly-organo-siloxanes. A general composition of the polymers $(C_6H_5SiO_{1,5})$ x which cor-

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responds to a cyclic structure of the molecules, was proved during the hydrolysis of phenyltrichlorosilane. Such polymers, however, are soluble in organic solvents and melt when heated. A long lasting heating of the polyphenyl-siloxanes at 25o°C and above causes an increase of the melting temperatures, but the polymer loses its solubility at the same time. The polymeric molecule grows apparently in first line due to bursting of the rings and their polymerization under the formation of structures which are laced. For increasing the melting-temperature of the complicated cyclic polyphenyl-siloxanes, aluminum was introduced into the molecule of the polymer. Aluminum-siloxane reacts with phenyl-trihydroxy-silane by precipitating water. A further condensation at the cost of the hydroxyl-groups under formation a polymer with a molecular weight of 599o, a content of hydroxyl-groups of 5,5°/o and a ratio Si: Al = 4,1. The obtained aluminum-phenyl-siloxaneeis a colorless, brittle, vitreous substance which does not melt with heating up to 5oo°C and does not sinter either (figure 1). It is readily soluble in: benzene, toluene, acetone, ethanol, chlorobenzene and carbon tetrachloride, yet insoluble in petroleum ether and white spirit. Though the content of OH-groups in the polymer decreases from 5,53 to 2,7°/o with a heating at 15o°C for 1o hours (reference 1), its solubility remains un-

changed. The solubility in acetone is preserved also with heating at 2oo°C for 4 hours. With an action of heat of 3oo°C for 15 minutes, it is soluble in 85°/o. In the case of a longer lasting heating at 2oo°C and with a 15 minutes lasting heating at 4oo and 5oo°C, the solubility gets completely lost. The constants and the chemical analysis (table 1) are given. An empirical formula for a term of the concerned polymer is given. A spatial structure of the polymeric molecule seems impossible, whereas such a term is a constituent of a complex cyclic or volumetric-polymeric molecule. Polyaluminum-ethylsiloxane was synthesized analogously. With equal properties as polyaluminum-phenylsiloxane it does not melt with heating (figure 1). The solubility of the former in various solvents at various temperatures is shown in table 1. Polyaluminum-ethylsiloxane loses its solubility more rapidly. An experimental part with usual data follows.
There are 1 figure, 1 table, and 2 references.

On the Synthesis of Infusible but Soluble Polymers 20-118-6-21/43

ASSOCIATION: Institute for Elementary Organic Compounds, AS USSR
(Institut elementoorganicheskikh soyedineniy Akademii nauk SSSR)
All-Union Electrotechnical Institute imeni V. I. Lenin
(Vsesoyuznyy elektrotekhnicheskiy institut im. V. I. Lenina)

SUBMITTED: November 10, 1957.

[illegible]

Card 4/4

ZHDANOV, A. A.

A. A. Zhdanov and K. A. Andrianov, "The Synthesis of Polymers with Inorganic Chains."

Report presented at the Second All-Union Conference on the Chemistry and Practical Application of Silicon-Organic Compoundsheld in Leningrad from 25-27 September 1958.
Zhurnal prikladnoy khimii, 1959, Nr 1 pp 238-240 (USSR)

5(3) SOV/30-59-1-29/57

AUTHOR: Zhdanov, A. A., Candidate of Chemical Sciences

TITLE: News in Brief (Kratkiye soobshcheniya) Scientific Conference on Organosilicon Compounds (Nauchnaya konferentsiya po kremniyorganicheskim soyedineniyam)

PERIODICAL: Vestnik Akademii nauk SSSR, 1959, Nr 1, pp 115 - 117 (USSR)

ABSTRACT: The conference was organized by the Association of German Chemists in Dresden (German Democratic Republic), May 12-14, 1958. Scientists from the following countries participated: the German Democratic Republic, the German Federal Republic, the USSR and Czechoslovakia. R. Müller (R. Myuller), (Dresden), director of the Institute for Organosilicon and Organofluorine Compounds reported in his opening address on the increasing scientific and technical importance of the investigated class of chemical compounds. F.Henglein (Karlsruhe) spoke about the synthesis of polymers containing groups the type of which is shown. G. Kolschütter (Darmstadt) dealt in his report with the investigation of the surfaces

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News in Brief. Scientific Conference on Organosilicon Compounds SOV/30-59-1-29/57

of compositions which form in the case of processing hydrated silicagel by the effect of trimethyl chlorosilane. The delegates of the Soviet Union D. N. Andreyev, M. G. Voronkov, A. A. Zhdanov, D. Ya. Zhinkin, N. S. Leznov, N. S. Nametkin, V. A. Ponomarenko reported on papers which had been published in Soviet periodicals already at an earlier time. After the conclusion of the conference R. Müller received the Soviet delegates and showed them the laboratories and equipment of the institute under his direction. They also undertook an excursion to Leipzig, Berlin and Potsdam which was organized by the Association of German Chemists.

Card 2/2

ANDRIANOV, K.A.; ZHDANOV, A.A.; ODINETS, V.A.

Condensation of silicon organic dicarboxylic keto acids with glycol. Vysokom.soed. 1 no.5:704-710 My '59. (MIRA 12:10)

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

ANDRIANOV, K.A.; ZHDANOV, A.A.

Resistance of titanium, tin and aluminum triethylsiloxane derivatives to hydrolysis in the process of polymer formation. Vysokom. soed. 1 no.6:894-899 Je '59. (MIRA 12:10)

1. Institut elementoorganicheskikh soyedineniy AN SSSR.
(Siloxanes) (Polymerization)

5(3)

AUTHORS: Andrianov, K. A., Zhdanov, A. A., Kazakova, A. A. SOV/62-59-3-13/37

TITLE: Synthesis of New Polymers With Inorganic Chains of Molecules (Sintez novykh polimerov s neorganicheskimi tsepyami molekul)

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1959, Nr 3, pp 466-471 (USSR)

ABSTRACT: In the present paper some reactions of the formation of new polymers with mineral chains of molecules containing aluminum, titanium, phosphorus, and oxygen atoms were investigated. By means of double decomposition of sodium ethyl silanolate with titanium-tetrachloride as well as of sodium trimethyl silanolate with titanium tetrachloride and aluminum chloride dodecamethyl-titanoxy-tetrasiloxane, dodecaethyl-titanoxy-tetrasiloxane and nonamethyl alumoxy-trisiloxane were synthesized. In the investigation of the hydrolytic stability of nonaethyl-alumoxy-trisiloxane it was found that during hydrolysis a simultaneous formation of polyorganosilylalumoxanes - polymers with the elementary group of the formula

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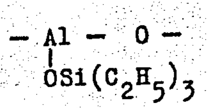
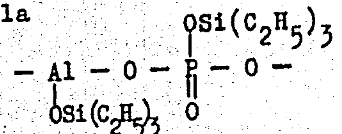
Synthesis of New Polymers With Inorganic Chains of Molecules SOV/62-59-3-13/37



$$-\underset{\substack{|\\ OSi(C_2H_5)_3}}{Al}-O-$$

takes place. On the interaction of nonaethyl-alumoxy-trisiloxane with tris-triethyl-silylphosphate polyorganosilylphosphoralumoxanes with the elementary group of the formula



$$-\underset{\substack{|\\ OSi(C_2H_5)_3}}{Al}-O-\overset{\substack{OSi(C_2H_5)_3\\ |}}{\underset{\substack{\|\\ O}}{P}}-O-$$

are formed. Similar polymers are also formed in the reaction of nonaethyl-alumoxy-trisiloxane with triethyl-silylphosphoric acid. There are 3 figures, 3 tables, and 5 Soviet references.

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

SUBMITTED: June 25, 1957

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SOV/62-59-9-12/40

5(3)

AUTHORS: Andrianov, K. A., Zhdanov, A. A.

TITLE: Polyorgano-metallic Siloxanes. Communication 2. Synthesis of the Polyorgano-alumino-cobalt Siloxane and the Polyorgano-alumino Nickel Siloxane

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1959, Nr 9, pp 1590-1594 (USSR)

ABSTRACT: The present article describes the development of a method for the synthesis of the metallic silicon-organic polymers, which is based on the composition of the initial substances. The synthesis could be made according to the scheme $2RSi(OH)_2ONa + MeCl_2 \longrightarrow [RSi(OH)_2O]_2Me + 2NaCl$ (1), at which attention has to be paid to the ratio $CoCl_2/AlCl_3$ in the reacting products in the case of aluminum - cobalt-organic compounds; here in addition to (1) the following secondary reactions occur: $RSi(OH)_2ONa + H_2O \rightleftharpoons RSi(OH)_3 + NaOH$ (2), $CoCl_2 + 2NaOH \longrightarrow$

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SOV/62-59-9-12/40

Polyorgano-metallic Siloxanes. Communication 2. Synthesis of the Polyorgano-alumino-cobalt Siloxane and the Polyorgano-alumino Nickel Siloxane

$\longrightarrow \underset{\substack{\downarrow \\ \mathrm{CoO} + \mathrm{H_2O}}}{\mathrm{Co(OH)_2}} + \mathrm{2NaCl}$ (3), and $\mathrm{RSi(OH)_3} + \mathrm{Al(OH)_3} \longrightarrow$

$\longrightarrow \mathrm{[RSi(OH)_2O]_3Al} + \mathrm{3H_2O}$. Only if this ratio is below unity can Co satisfactorily enter the reaction. Figures 1 and 2 illustrate this dependence. The experimental part of the article describes the synthesis. Tables 1-3 list the analysis data of the products obtained. There are 2 figures, 3 tables, and 3 Soviet references.

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

SUBMITTED: January 3, 1958

Card 2/2

ZHDANOV, A.A., kand.khim.nauk

Scientific conference on silicon organic compounds. Vest.AN SSSR 29 no.1:115-117 Ja '59. (MIRA 12:2)
(Silicon organic compounds)

5 (3)

AUTHORS: Andrianov, K. A., Zhdanov, A. A. SOV/79-29-4-53/77
Kazakova, A. A.

TITLE: Synthesis of the Polymers With Inorganic Molecule Chains (Sintez polimerov s neorganicheskimi tsepyami molekul). I.Polyorganosiloxyphosphoaluminumoxans (I.Poliorganosiloksifosforalyumoksany)

PERIODICAL: Zhurnal obshchey khimii, 1959, Vol 29, Nr 4, pp 1281 - 1284 (USSR)

ABSTRACT: In continuation of the preceding report (Ref 1) the investigations under review show that the polyalkylsiloxyaluminum phosphates are obtained by the polycondensation of the tris-(trialkylsiloxy)-aluminum with organo-phosphosilicon compounds according to schemes 1) and 2). The nature of the resulting polymers depends on the nature of the organic radical in the surrounding trialkylsiloxane groups. By the condensation of tris-(triethylsiloxy)-aluminum with triethylsiloxyphosphinic acid or tris-(triethylsilyl)-phosphate at 200-220° polymers were obtained which changed to an unsoluble, not meltable, and solid state above the afore-mentioned temperature. Under the same conditions solid, not meltable, and unsoluble products were

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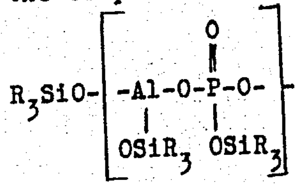
Synthesis of the Polymers With Inorganic Molecule Chains. I.Polyorganosiloxyphosphoaluminumoxans SOV/79-29-4-53/77

also obtained by the use of trimethylsiloxyphosphinic acid. In order to confirm the scheme mentioned 2 mols of tris-(triethylsiloxy)-aluminum were condensed with 1 mol of triethylsiloxyphosphinic acid. In this way the condensation product (III) of low molecular weight was obtained; hexaethyldisiloxane and water were eliminated in quantities corresponding to scheme 2. The analysis of the product corresponds to the formula given in scheme 2. By the same condensation, which was, in this case, carried out with equimolecular quantities, solid polymers of the composition



$$R_3SiO-\left[-\underset{OSiR_3}{\underset{|}{Al}}-O-\underset{OSiR_3}{\underset{|}{\overset{\overset{O}{\|}}{P}}}-O-\right]_n-R'$$

R' denoting H or SiR_3, were obtained.

Powder, not meltable products which were, at the same time, insoluble in organic solutions resulted from the condensation of tris-(trimethylsiloxy)-aluminum with trimethylsiloxyphosphinic

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Synthesis of the Polymers With Inorganic Molecule Chains. I.Polyorganosiloxyphosphoaluminumoxans SOV/79-29-4-53/77

acid or with tris-(trimethylsilyl)-phosphate. There are 2 figures and 5 references, 4 of which are Soviet.

SUBMITTED: March 15, 1958

Card 3/3

5 (3)

AUTHORS: Andrianov, K. A., Odinets, V. A., Zhdanov, A. A., SOV/79-29-5-21/75

TITLE: On the Reaction of Acylation of Arylaliphatic Disiloxanes (O reaktsii atsilirovaniya arilalifaticheskikh disiloksanov). Synthesis of Bis-(4,4'-Acetobenzyl)-tetramethyl-disiloxane (Sintez bis-(4,4'-atsetobenzil)-tetrametildisiloksana)

PERIODICAL: Zhurnal obshchey khimii, 1959, Vol 29, Nr 5, pp 1499-1503 (USSR)

ABSTRACT: The authors concluded from the formation of benzyl methyl chloro-silanes and acylation of benzyl-trimethyl silane that the Friedel-Crafts reaction may be successfully applied to the synthesis of various benzyl siloxane derivatives in which the aromatic nucleus is separated from the silicon atom by the methylene group. Experiments indicated that benzyl-dimethyl-chloro-silane is not destroyed in the presence of aluminum chloride and can be used as initial product for the synthesis of bis-(acetobenzyl)-tetramethyl-disiloxane. The benzyl-dimethyl-chloro silane was prepared according to the Grignard reaction from dimethyl-dichloro-silane and benzyl magnesium chloride. The synthetic bis-(acetobenzyl)-tetramethyl-

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SOV/79-29-5-21/75

On the Reaction of Acylation of Arylaliphatic Disiloxanes. Synthesis of Bis-(4,4'-Acetobenzyl)-tetramethyl-disiloxane

disiloxane has the properties of aliphatic-aromatic ketones and forms the dinitro-phenyl hydrazone in which case the reaction proseeds via both carbonyl groups. On oxidation of the bis-(acetobenzyl)-tetramethyl-disiloxane with sodium hypobromide in alkali the toluic acid is formed which was identified in the form of its mothyl ester. A comparatively easy separation of the benzyl carboxy-group is connected with the displacement of the reactivity in the system of the conjugated nuclear bonds. In consequence of it a decrease of the electron density on the silicon nucleus and subsequent rupture of the Si-C-bond takes place under the influence of nucleophilic agents. When using alkaline potassium solution, the oxidation is complete and terephthalic acid is formed. The formation of the p-toluic and terephthalic acid indicates that the aceto-group comes into para-position with respect to the methylene group during the Friedel-Crafts reaction. Properties of the compounds synthesized are given in the table. There are 1 table and 6 references, 4 of which are Soviet.

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On the Reaction of Acylation of Arylaliphatic Disiloxanes. Synthesis of Bis-(4,4'-Acetobenzyl)-tetramethyl-disiloxane SOV/79-29-5-21/75

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

SUBMITTED: April 3, 1958

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5(3) SOV/79-29-8-57/81

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

TITLE: On the Acylation Reaction of the Aryl Aliphatic Disiloxanes. II. Synthesis of Silicon-organic Aromatic Ketones and Difunctional Ketocarboxylic Acids

PERIODICAL: Zhurnal obshchey khimii, 1959, Vol 29, Nr 8, pp 27o2 - 27o6 (USSR)

ABSTRACT: As the authors showed in a previous paper (Ref 1), benzyldimethylchlorosilane easily reacts with acetic anhydride in the presence of $AlCl_3$ while bis-(4-acetobenzyl)-tetramethyldisiloxane is formed with a yield of 50%. In the present paper this reaction was used in the synthesis of silicon dicarboxylic acid and aromatic ketones. Benzyldimethylchlorosilane and the acylating compounds (succinic acid - phthalic anhydride and benzoylchloride) were used as a basis (Scheme 1). By means of the reaction the best yield was achieved in a benzene medium (50-60%). The acylation of benzyldimethylchlorosilane with benzoylchloride leads to the aromatic diketone according to scheme 2. Bis-(benzoylbenzyl)-tetramethyl-

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On the Acylation Reaction of the Aryl Aliphatic Disiloxanes.SOV/79-29-8-57/81
II. Synthesis of Silicon-organic Aromatic Ketones and Difunctional Keto-carboxylic Acids

disiloxane was precipitated (40%). It forms easily the dinitrophenylhydrazone which contains 11.44 % nitrogen, and thus indicates the presence of two ketone groups in the molecule of the synthesized compound. The molecular refraction of this siloxane was found to be 4 units higher than that of E. Warrick (Ref 6).(A. D. Petrov (Ref 5) found it to be higher by two units in 4-substituted silanes with one group). The data obtained show that the acylation of benzyldimethylchlorosilane is also possible with the anhydrides of the dicarboxylic acids and the acid chlorides of the monocarboxylic acids without a noticeable destruction of the compounds taking part in the reaction under the influence of hydrogen chloride. The properties of the compounds obtained are given in the table. There are 1 table and 7 references, 4 of which are Soviet.

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

SUBMITTED: July 11, 1958

Card 2/2

SOV/80-32-2-52/56

AUTHORS:	Andrianov, K.A., Zhdanov, A.A., Kashutina, E.A.
TITLE:	Synthesis of Derived Molecular Di(triethylsiloxy)-Lead With Lead Hydroxide and Its Interaction With Titanium Tetrachloride (Sintez molekulyarnogo proizvodnogo di(trietilsiloksi)svintsa s gidrookis'yu svintsa i yego vzaimodeystviye s chetyrekhkhloristym titanom)
PERIODICAL:	Zhurnal prikladnoy khimii, 1959, Vol XXXII, Nr 2, pp 463-464 (USSR)
ABSTRACT:	During the development of new methods for the synthesis of trialkylsiloxymetals of the general formula (R_3SiO) a synthesis for tetra(triethylsiloxy)titanium from di(triethylsiloxy)-lead and titanium tetrachloride was found. The various steps of the experiment are described. There are 3 references, 2 of which are Soviet and 1 American.
SUBMITTED:	April 24, 1958

Card 1/1

5 (2,3)

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

SOV/20-126-6-32/67

TITLE: Synthesis of Triethyl Siloxy Derivatives of Vanadium and Antimony (Sintez trietilsiloksiproizvodnykh vanadiya i sur'my)

PERIODICAL: Doklady Akademii nauk SSSR, 1959, Vol 126, Nr 6, pp 1261 - 1263 (USSR)

ABSTRACT: Among the syntheses for the production of compounds of type $(R_3SiO)_nMe)$, where n denotes the valency of the metal, which are known at present, the interaction reaction of the trialkyl silanolates of sodium and of some other metals is of special interest (see scheme). These monomers have an Si-O-Me bond and the synthesis of polymers which have alternating metal or oxygen atoms in the main chain is directly connected with their synthesis. By the method, illustrated by the above scheme, the authors synthesized for the first time the following compounds: a) tetrakis-(trimethyl-siloxy)-titanium (Ref 1); b) tetrakis-(dimethyl-phenyl-siloxy)-titanium (Ref 3); c) tetrakis-(triethyl-siloxy)-titanium (Ref 2), and d) tetrakis-(triethyl-siloxy)-tin (Ref 2). In the present paper the above mentioned

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method was further developed for the synthesis mentioned (see schemes). The experiments carried out produced yields of 60-70% of the theoretically possible yields. The lead-triethyl--silanolate (Ref 4) showed a considerable reactivity: by the action of I titanium-tetrachloride or of II vanadium oxychloride on its complex compound the following was formed: I Tetrakis--(triethyl-siloxy)-titanium or II tris-(triethyl-siloxy)-vanadate (see schemes). These reactions which were investigated by the authors with respect to the titanium-tetra- or vanadium--oxychloride, are of general importance for the production of trialkyl-silyl-derivatives of various elements. The investigations of the infra-red spectra of some of the compounds synthesized (by N. Gashnikova in the Vsesoyuznyy elektrotekhnicheskiy institut im. V. I. Lenina - All-Union Electrotechnical Institute imeni V. I. Lenin) proved the characteristic oscillation frequences of $VO[OSi(C_2H_5)_3]_3$ which are mentioned in the paper. Table 1 shows properties of the materials synthesized among others also of tris-(triethyl-siloxy)-stibine. There are 1 table and 4 Soviet references.

Synthesis of Triethyl Siloxy Derivatives of Vanadium and Antimony SOV/20-126-6-32/67

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

SUBMITTED: April 10, 1959

Card 3/3

ZHDANOV, A. A.

PHASE I BOOK EXPLOITATION

SOV/4984

International symposium on macromolecular chemistry. Moscow, 1960.

Mezhdunarodnyy simpozium po makromolekulyarnoy khimii SSSR, Moskva, 14-18 iyunya 1960 g.; doklady i avtoreferaty. Sektsiya III. (International Symposium on Macromolecular Chemistry Held in Moscow, June 14-18, 1960; Papers and Summaries) Section III. [Moscow, Izd-vo AN SSSR, 1960] 469 p. 55,000 copies printed.

Tech. Ed.: P. S. Kashina.

Sponsoring Agency: The International Union of Pure and Applied Chemistry. Commission on Macromolecular Chemistry.

PURPOSE: This book is intended for chemists interested in polymerization reactions and the synthesis of high molecular compounds.

COVERAGE: This is Section III of a multivolume work containing papers on macromolecular chemistry. The articles in general deal with the kinetics of polymerization reactions, the synthesis of special-purpose polymers, e.g., ion exchange resins, semiconductor materials, etc., methods of catalyzing polymerization reactions, properties and chemical interactions of high molecular materials, and the effects of various factors on polymerization and the degradation of high molecular compounds. No personalities are mentioned. References given follow the articles.

Yur'yev, V. M., A. N. Pravednikov, and S. S. Medvedev (USSR). The Effect of Formic Acid and Formates on the Oxidation of Hydrocarbons and Hydrocarbon Polymers

Popova, Z. V., and D. M. Yanovskiy (USSR). Study of the Effect of Some Organic and Organoelemental Compounds on the Thermal Degradation of Polyvinyl Chloride 364

Wichterle, O., E. Šittler, and P. Čefelin (Czechoslovakia). Degradation of Poly-ε-Caprolactam as a Result of Exchange Reaction Between Amide Bonds 372

Kučera, M., J. Láníková, and M. Jelínek (Czechoslovakia). Neutralization of Residual Catalyst in Polydimethylsiloxane; Effect of Thermal Neutralization on the Thermal Stability of the Polymer 380

Gömöri, L., O. Mlejnek, and L. Střímel (Czechoslovakia). Thermooxidational Degradation of Polyesters. Study of Degradation Reactions for Different Types of Linear Polyesters 388

Neyman, M. B., B. M. Kovarskaya, L. I. Golubenkova, A. S. Strizhkova, V. V. Levantovskaya, and M. S. Akutin (USSR). On the Degradation and Stabilization of Some Polymeric Materials 405

Angert, L. G., and A. S. Kuz'minskiy (USSR). Investigation of the Efficiency of Inhibitors of Rubber Oxidation at Various Temperatures 414

Pravednikov, A. N., and Ying Wen-k'ang (USSR). Mechanism of the Protective Action of Benzene Rings During the Radiolysis of Polystyrene 423

Zhdanov, A. A., and K. A. Andrianov (USSR). On the Hydrolytic Stability of Side Groups in Polymers With Inorganic Chains of Molecules 433

Berlin, A. A., Ye. A. Penskaya, and G. I. Volkova (USSR). Mechanicochemical Transformations and Block Copolymerization During the Freezing of Starch Solutions 440 25

Usmanov, Kh. U., B. I. Aykhodzhayev, and U. Azizov (USSR). Modification of the Properties of Cellulose by Grafting 334

344 33

5.3700(B)

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67941
SOV/20-130-1-20/69

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

TITLE: Chloromethylation of Aryl-aliphatic Disiloxanes. Synthesis of Chloromethylbenzyldimethylchlorosilane and Its Derivatives

PERIODICAL: Doklady Akademii nauk SSSR, 1960, Vol 130, Nr 1, pp 75-78 (USSR)

ABSTRACT: The authors proved that the chloromethylation of the benzyl group bound to silicon can be successfully used for the synthesis mentioned in the subtitle (see Scheme). This reaction proceeds well in fuming hydrochloric acid. Paraform is used as an agent of chloromethylation. The chloromethylation in the presence of zinc chloride is accompanied by secondary processes. They form viscous, nondistillable products containing diphenyl-methane groups (see Scheme). The isolation of pure chloromethylbenzyldimethylchlorosilane from the reaction mixture was attained by hydrolysis with excess water while the disiloxane mixture was split by strong sulfuric acid in the presence of ammonium chloride (see Scheme). The total yield in chloromethylbenzyldimethylchlorosilane was 60% of the benzyldimethylchlorosilane reacted, and 30% of the quantity used respectively. Direct fractionation of the chloromethylation products purified with water in the vacuum delivered smaller

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57047

Chloromethylation of Aryl-aliphatic Disiloxanes. SOV/20-130-1-20/69
Synthesis of Chloromethylbenzyldimethylchlorosilane and Its Derivatives

yields. The end product obtained had all properties of the alkylchlorosilane halides. By hydrolysis with water, it readily forms the disiloxane. Bis-(chloromethylbenzyl)-tetramethyldisiloxane was isolated as a consequence of this reaction (see Scheme). By the action of potassium acetate on this latter substance in acetic medium, bis-(acetoxymethylbenzyl)-tetramethyldisiloxane was formed. On hydrolysis of the latter compound, the acetate group is split off. In the first stage, bis-(oxymethylbenzyl)-tetramethyldisiloxane develops which afterwards decomposes by the catalytic action of the alkali during distillation. Toluyl methanol and polydimethylsiloxanes with functional end groups as shown in the scheme are probably formed. Table 1 shows the properties of the substances synthesized. A. V. Topchiyev and N. S. Nametkin are mentioned in the paper. There are 1 table and 8 references, 5 of which are Soviet.

SUBMITTED: September 30, 1959

Card 2/2

87881

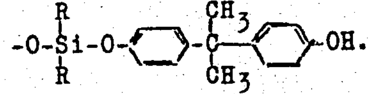
S/191/60/000/005/007/020
B004/B064

15.8116

AUTHORS: Andrianov, K. A., Zhdanov, A. A., Baksheyeva, T. S.

TITLE: Synthesis of Organosilicon Oligomers Containing Oxyphenyl Groups

PERIODICAL: Plasticheskiye massy, 1960, No. 5, pp. 18 - 21

TEXT: Aim of the present study was the synthesis of organosilicon polymers with end groups of the following structure: 

Synthesis was carried out in two stages. First, organosilicon oligomers with butoxy end groups were produced. They were reacted with dihydroxyl-diphenyl propane. Phenyl-tributoxy silane, phenyl-methyl dibutoxy silane, and dimethyl-dibutoxy silane were the initial compounds used. They resulted from esterification of the respective chloro silanes. The oligomers with different degree of polymerization were produced by partial hydrolysis. Hydrolysis of 1 mole of dimethyl-dibutoxy silane with 0.5 moles

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Synthesis of Organosilicon Oligomers
Containing Oxyphenyl Groups

S/191/60/000/005/007/020
B004/B064

of water yielded, in the presence of HCl, the dimer in a 73 % yield. 4 moles of dimethyl-dibutoxy silane yielded, with 3 moles of water, 41 % tetramer. 50 % hexamer was obtained from 6 moles of dimethyl-dibutoxy silane and 5 moles of water. Partial hydrolysis of 1 mole of phenyl-tributoxy silane with 1 mole of water gave an 86 % yield in polyphenyl-butoxy siloxane on heating in the presence of HCl. Phenyl-methyl dibutoxy silane was polymerized in the same way, but, in the presence of NaOH. The composition determined by equation $A = n/(n - m)$ was confirmed by elementary analysis (A = number of silicon atoms in the polymer chain, n = number of moles of the substance subjected to hydrolysis, m = number of moles of water used for hydrolysis). The oligomers with butoxy end groups were reacted, in the presence of Na- or Al butylate, with dihydroxydiphenyl propane. The ratio of components was 1:1. 1-n-butoxy-polydimethyl siloxane yielded a polymer with the degree of polymerization 246; 1-n-butoxy-polyphenyl-methyl siloxane gave a polymer whose degree of polymerization was 2468. Determination of the butanol set free during the reaction showed that the reaction proceeds up to a yield of 80 %. The resulting organosilicon compounds which contained the end group

87881

Synthesis of Organosilicon Oligomers Containing Oxyphenyl Groups

S/191/60/000/005/007/020
B004/B064

$SiOC_6H_5C(CH_3)_2C_6H_4OH$ were highly reactive to aldehydes. Urotropine or furfurole caused rapid polymerization under the formation of insoluble, non-melting, three-dimensional polymers. There are 3 tables and 3 references: 2 Soviet and 1 US.

Card 3/3

S/190/60/002/007/011/017
B020/B052

AUTHORS: Andrianov, K. A., Zhdanov, A. A.

TITLE: Investigation of the Polymerization of Polyorganosiloxanes Under the Influence of Polyaluminum Ethyl Siloxanes

PERIODICAL: Vysokomolekulyarnyye soyedineniya, 1960, Vol. 2, No. 7, pp. 1071-1076

TEXT: The authors found that polyaluminum organosiloxanes reduce the reaction time of the polymerization of polyorganosiloxanes obtained from trifunctional, and bi- and trifunctional monomers. The reaction time of the polyorganosiloxane polymerization in dependence on the amount of the polyaluminum organosiloxane introduced, was investigated to explain the rules governing the above polymerization. Polymers produced by cohydrolysis of methylchloro silane and phenyl trichloro silane, methyl triacetoxy silane, and phenyl acetoxy silane (polymer 1-A) were used for this investigation. Polyaluminum siloxane A-16 (Ref. 1) was used as catalyst. Table 1 gives the characteristics of the polymers used. Fig. 1 shows the dependence of the polymerization time on the amount of the

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Investigation of the Polymerization of Polyorganosiloxanes Under the Influence of Polyaluminum Ethyl Siloxanes

S/190/60/002/007/011/017
B020/B052

added polymer A-16. Already with 0.5% of the polymer A-16, a considerable reduction of the polymerization time was found. Fig. 2 shows the dependence of the polymerization time of a 99% mixture of 1- X (1-Kh) and 1% of A-16 on the amount of dimethyl aniline and pyridine, respectively. The amount of the tertiary amine addition also reduces the polymerization time of the polymers 1-Kh and 1-A (Figs. 4,5). For the evaluation of the maxima of the curves shown in Figs. 2 and 3, the molar ratio between tertiary amine and aluminum in the mixtures investigated, was calculated for points corresponding to the maximum value of the polymerization time (Table 2). The maximum polymerization time in all cases approximately corresponds to the equimolar ratio between the amount of the amine addition and the aluminum in the polymer molecule. The mechanism of the interaction between polyaluminum ethyl siloxane and the organosilicon polymer was explained by the data obtained. Finally, the syntheses of polymers 1-Kh, 1-A, and A-16 are described. Their elementary composition is given in Table 1. The determination of the polymerization time is also described, respective results being graphically presented in Figs. 1 to 5. There are 5 figures, 2 tables, and 1 Soviet reference.

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Investigation of the Polymerization of Polyorganosiloxanes Under the Influence of Polyaluminum Ethyl Siloxanes

S/190/60/002/007/011/017
B020/B052

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

SUBMITTED: March 16, 1960

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Card 3/3

ANDRIANOV, K.A.; ZHDANOV, A.A.

Process of the polymerization of polyorganosiloxanes, induced by polyaluminoethyl siloxanes. Vysokom.soed. 2 no.7:1071-1076 Jl '60. (MIRA 13:8)

1. Institut elementoorganicheskikh soyedineniy AN SSSR.
(Polymerization) (Siloxanes)

S/661/61/000/006/051/081
D235/D302

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

TITLE: Polyorgano-metallo-siloxanes and polyorgano-siloxy-metalloxanes

SOURCE: Khimiy i prakticheskoye primeneniye kremneorganicheskikh soyedineniy; trudy konferentsii, no. 6: Doklady, diskussii, resheniye. II Vses. konfer. po khimii i prakt. prim. kremneorg. soyed., Len. 1958. Leningrad, Izd-vo AN SSSR, 1961, 220-224

TEXT: A discussion of the above paper (this publication, no. 2, p. 100) between the authors and N. F. Orlov (IKhS AN SSSR, Leningrad), S. N. Borisov, (VNIISK, Leningrad) and M. G. Voronkov (IKhS AN SSSR, Leningrad). The following points are discussed: Thermal and hydrolytic stability of the bonds silicon-oxygen-metal; introduction of the elements magnesium and zinc into the siloxane structure; the formation of poly-diethyl-alumina-siloxane; reasons for the increase in thermal stability obtained by the authors; thermal

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S/661/61/000/006/051/081
Polyorgano-metallo-siloxanes ... D235/D302

and hydrolytic stability of poly-organo-titanium siloxanes. The thermal stability of the bonds Si-O-M is fairly high and a compound such as $(R_3SiO_4)Ti$ is hydrolized only very slowly by water. Magnesium reacts like aluminum with hydroxyl containing silicon compounds to give hydrogen and the siloxane polymer containing magnesium. Reference is made to a patent by Viberg and Katnslev where poly-diethyl-alumina-siloxane is obtained by reacting the metal with diethyl siloxane at $310^{\circ}C$; the authors only obtained a 1.5 - 2% yield by such a reaction. Alkaline hydrolysis of dimethyl-siloxane with aluminum chloride in the ratio Si-Al of 3:1 to 45:1 leads to the formation of gel-like polymers and in the ratio Si:Al of 60:1 to 100:1 to co-polymers similar to poly-dimethyl-siloxane rubbers, but the exterior is frequently gummy. Thermal stability of poly-organo-titanium-siloxanes is considerably higher than for the aluminum compounds. The bond Si-O-Ti has higher thermal stability than the compounds with a siloxane bond due to the effect of oxygen on Si-C under the action of titanium. The hydrolytic stability depends on the nature of the radical connected to silicon and the molecular structure. Derivatives from elements of group V possess the greatest

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Polyorgano-metallo-siloxanes ... S/661/61/000/006/051/031
D235/D302

stability, as compared with derivatives from groups III and IV, but there is no quantitative information concerning this.

ASSOCIATION: Institut elementoorganicheskikh soedineniy Akademii nauk SSSR, Moskva (Institute of Elemental Organic Compounds, Academy of Sciences, USSSR, Moscow)

Card 3/3 ✓

88484

15.8114 2209

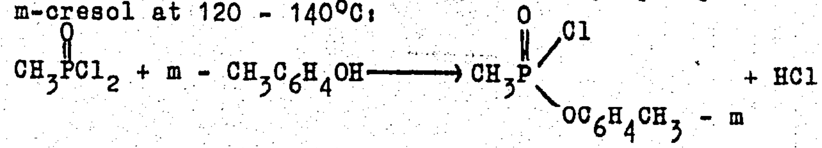
S/079/61/031/001/018/025
B001/B066

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:



$$CH_3P(O)Cl_2 + m-CH_3C_6H_4OH \longrightarrow CH_3P(O)(Cl)(OC_6H_4CH_3-m) + HCl \quad (1)$$

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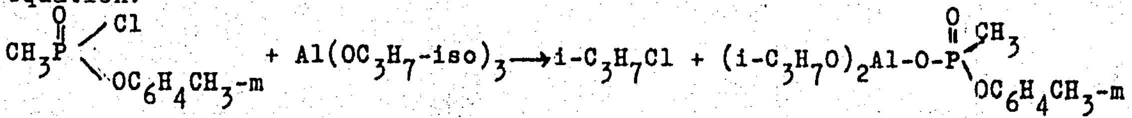
88484

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:



$$CH_3\overset{O}{\overset{\|}{P}}\begin{smallmatrix}\diagup Cl\\ \diagdown OC_6H_4CH_3\text{-m}\end{smallmatrix} + Al(OC_3H_7\text{-iso})_3 \longrightarrow i\text{-}C_3H_7Cl + (i\text{-}C_3H_7O)_2Al\text{-}O\text{-}\overset{O}{\overset{\|}{P}}\begin{smallmatrix}\diagup CH_3\\ \diagdown OC_6H_4CH_3\text{-m}\end{smallmatrix}$$

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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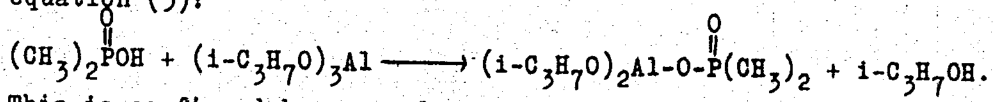
Reactions of Aluminum Isopropylate With Some Organophosphorus Compounds

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

31193

5.3700

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

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:

X

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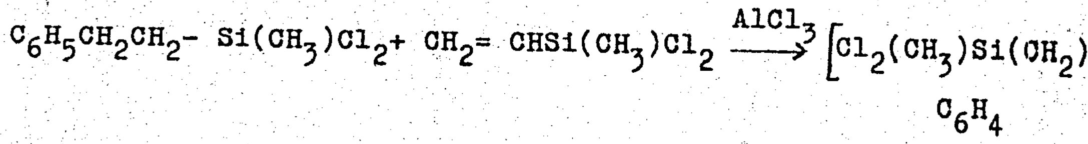

$$C_6H_5CH_2CH_2-Si(CH_3)Cl_2 + CH_2=CHSi(CH_3)Cl_2 \xrightarrow{AlCl_3} [Cl_2(CH_3)Si(CH_2)_2]_2C_6H_4 \qquad (2)$$

The primary addition products were converted to the corresponding silane diols by acetylation with CH_3COOK and subsequent hydrolysis. The infrared-spectra of all these diols confirm the presence of $Si-CH_3$ groups (1258 cm^{-1}), of an aromatic nucleus and of SiOH groups (830 - 880 cm^{-1}). The authors conclude that the phenyl compound adds on in the ß-position (with respect to Si). The syntheses of the primary addition products are then described: The melting points of the benzene, toluene, chlorobenzene, and diphenyl derivatives were 80-81, 70, 89-91, and 132-134°C respectively. There are 4 figures, 1 table and 3 references: 1 Soviet-bloc and 2 non-Soviet-bloc. The references to the English-language publications read as follows: G. H. Wagner, D. L. Bailey, A. H.

31193

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

The addition of aromatic ...

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

37775

15,8170

S/661/61/000/006/068/081
D247/D302

AUTHORS: Konstantinova, N. G., Zhdanov, A. A., Andrianov, K. A., Sharov, M. Ya., Kyutner, M. A. and Zakharov, A. A.

TITLE: Thermostable lacquer coatings based on silico-organic polymers

SOURCE: Khimiya i prakticheskoye primeneniye kremneorganicheskikh soyedineniy; trudy konferentsii, no. 6: Doklady, diskussii, resheniye. II Vses. konfer. po khimii i prakt. prim. kremneorg. soyed., Len. 1958. Leningrad, Izd-vo AN SSSR, 1961, 296-299

TEXT: A study was made of the thermostability of several lacquer-painted materials on the basis of different film-forming substances. The silico-organic resin K-47 was modified by the use of organic polymers to give a hard, cold-drying coat of increased thermostability. The metallic surface and its preparation was found to have a great influence on the adhesion, the protective properties and the thermostability of the coatings. In the discussion, the

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Thermostable lacquer coatings ...

S/661/61/000/006/068/081
D247/D302

registration and technical specifications of some of the silico-organic varnishes are given. Elasticity and hardness data are also given. Coatings withstanding radioactive irradiation are mentioned. Comparison of the properties of silico-organic and other enamels are made, and methods of preparing surfaces before application of the enamels are mentioned. The best thermostability recorded was for a duration of 150 hours at 500°C. A discussion followed in which P. A. Filippov (Leningrad) took part.

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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

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

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23837

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

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

Card 4/6

S/062/61/000/007/004/009
B117/B215

25214

15.8170

AUTHOR: Zhdanov, A. A., Andrianov, K. A., and Bogdanova, A. A.

TITLE: Reaction of aluminum chloride with dialkyl cyclosiloxanes

PERIODICAL: Akademiya nauk SSSR. Izvestiya. Otdeleniye khimicheskikh nauk, no. 7, 1961, 1261 - 1266

TEXT: The interaction of aluminum chloride with dimethyl- and diethyl cyclosiloxanes was investigated in a study of the methods of producing polyalumo-organosiloxanes. A flask with mixer, thermometer, recooler, and cooling vessels for collecting the reaction products were used for the experiments. It was found that aluminum chloride reacts easily with dimethyl- and diethyl cyclosiloxanes at equimolecular ratios. Crystalline reaction products are formed which are quantitatively sublimated in vacuo. In the examination of the reaction mixture obtained by reaction between octamethyl cyclotetrasiloxane and aluminum chloride (mixing time: 10 hr at 120°C), the following reaction products were isolated: 1,3-dichloro tetramethyl disiloxane, boiling point: 32° - 36°C (10 mm); 1,5-dichloro hexamethyl trisiloxane, boiling point: 72° - 75°C (10 mm); 1,7-dichloro octamethyl tetrasiloxane, boiling point: 90° - 95°C (10 mm); a

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crystalline substance, boiling point: 152° - 153°C, of the empirical composition $C_8H_{24}O_6Cl_5Si_4Al_3$. The formation of these products in the reaction mixture followed the scheme

$$2\left[(CH_3)_2SiO\right]_4 + 3AlCl_3 \rightarrow C_8H_{24}O_6Cl_5Si_4Al_3 + 2C_4H_{12}Si_2CCl_2$$

The crystalline substance of the above empirical formula showed a constant composition in repeated sublimation. On the basis of analytical data and chemical studies it may be assumed that the respective substance contains a complex aluminum chloride molecule. The reaction between aluminum chloride and hexamethyl cyclotrisiloxane (mixing time: 6 hr at 50° - 60°C) is similar to the previous one, with the only difference that besides the crystalline substance also dimethyl dichlorosilane and highest α,ω - dichloro polysiloxanes are formed. This process may be expressed by the scheme $2\left[(CH_3)_2SiO\right]_3 + 3\,AlCl_3 - C_8H_{24}O_6Cl_5Si_4Al_3 + 2C_2H_6SiCl_2$.

Similar ethyl derivatives were isolated in the reaction between aluminum chloride and octaethyl cyclotetrasiloxane (mixing time: 11 hr at 120°C)

1,3-dichloro tetraethyl disiloxane, boiling point: 85° - 90°C (10 mm); 1,5 dichloro hexaethyl trisiloxane, boiling point: 124° - 131°C (10 mm); 1,4-dichloro octaethyl tetrasiloxane, boiling point: 131°C - 145°C (10 mm); a crystalline substance which is sublimated at 225°C - 233°C, melting point: 112°C (unstable), of the empirical composition $C_{16}H_{40}O_6Cl_5Si_4Al_3$. The structures of the crystalline substances are similar in both cases. An identical, crystalline substance of the above composition and highest polydiethyl siloxanes were obtained in the reaction between aluminum chloride and hexaethyl cyclotrisiloxane (mixing time: 5 hr at 80°C). Conclusion: Rupture of the cycle takes place in the interaction of aluminum chloride and the above cyclic dialkyl siloxanes, and α-chloro-ω-dichloro alumoxydialkyl polysiloxanes are formed. The latter then separate α,ω-dichloro polysiloxanes and form cyclic compounds: 1-chloro-3,3,5,5-tetramethyl cycloalumodisiloxane and 1-chloro-3,3,5,5-tetraethyl cycloalumodisiloxane. These compounds were isolated and characterized in the form of complexes with aluminum chloride. There is 1 non-Soviet-bloc reference.

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25214

Reaction of aluminum chloride ... S/062/61/000/007/004/009
B117/B215

X

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

SUBMITTED: September 26, 1960

Card 4/4

KORSHAK, V.V.; VINOGRADOVA, S.V.; FRUNZE, T.M.; GRIBOVA, I.A.; ZHDANOV, A.A.; MOZGOVA, K.K.; KRONGAUZ, Ye.S., red.izd-va; TIKHOMIROVA, S.G., tekhn.red.

[Chemistry and technology of synthetic macromolecular compounds. Heterocyclic compounds]. Khimiia i tekhnologiia sinteticheskikh vysokomolekuliarnykh soedinenii. Geterotsepnye soedineniia. Moskva, Izd-vo Akad.nauk SSSR. 1961. 721 p. (Itogi nauki: Khimicheskie nauki, no.7) (MIRA 14:11)

1. Chlen-korrespondent AN SSSR (for Korshak).
(Macromolecular compounds)
(Heterocyclic compounds)

27491
S/062/61/000/009/006/014
B117/B101

15.8170

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

TITLE: Synthesis of liquid 1,n-hexamethyl-poly(phenyl-ethyl)-methyl siloxanes and investigation of their properties

PERIODICAL: Akademiya nauk SSSR. Izvestiya. Otdeleniye khimicheskikh nauk, no. 9, 1961, 1615-1624

TEXT: The lowest-molecular members of the polymerhomologous series of 1,n-hexamethyl-poly(phenyl-ethyl)-methyl siloxanes were synthesized and their properties studied. The work was undertaken to study the dependence of the polar properties of these liquid organo-silicon polymers on various polar substituents at the benzene ring. The polar properties were studied on the basis of the activation energy of viscous flow and the temperature dependence of the viscosity. The flowing initial substances were used for the synthesis: (phenyl-ethyl)-methyl-dichloro silane ($C_6H_5C_2H_4(CH_3)SiCl_2$, b.p. 90°-92°C (5 mm Hg)), (tolyl-ethyl)-methyl-dichloro silane ($CH_3C_6H_4C_2H_4(CH_3)SiCl_2$, b.p. 103°-105°C (2 mm Hg)), (chloro-

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27491

Synthesis of liquid 1,n-hexamethyl- ...

S/062/61/000/009/006/014
B117/B101

phenyl-ethyl)-methyl-dichloro silane $(ClC_6H_4C_2H_4(CH_3)SiCl_2$, b.p. 124°-126°C (2 mm Hg). The synthesis of these compounds is described in Ref. 11 (K. A. Andrianov, et al, Zh. obshch. khimii (in print)). The liquid polymers were obtained by the joint hydrolysis of toluene solution of mixtures of these compounds with trimethyl-chloro silane (b.p. 58°-59°C) at 90-95°C. Polymers of varying degrees of polymerization, according to the reactant ratio, may be isolated from the reaction mixture (Table 1). Hydrolysis of ethereal solution of (phenyl)-methyl-dichloro silane yielded cyclic polymers also: tri(phenyl-ethyl)-trimethyl cyclotrisiloxane $[C_6H_5C_2H_4(CH_3)SiO]_3$ and tetra(phenyl-ethyl)-tetramethyl cyclotetrasiloxane $[C_6H_5C_2H_4(CH_3)SiO]_4$. Evaluation of the infrared spectra of the compounds investigated indicates that the addition of the vinyl aromatic nucleus takes place in β position, giving β-substituted derivatives. The density of the liquids was determined pycnometrically. Viscosity measurements were carried out by standard methods with an Ostwald-Pinkevich viscosimeter. Data on the activation energy of viscous flow and the temperature coefficients of the viscosity are shown in Table 2. It was found that for the lowest-molecular members of the homologous series the

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Synthesis of liquid 1,n-hexamethyl- ... S/062/61/000/009/006/014
B117/B101

activation energy of viscous flow is hardly dependent on the polar groups. Substitution of the hydrogen atom at the nucleus by methyl or chlorine, however, always increases the activation energy. The activation energy of flow depends on the number of silicon atoms in the polymers under study. The polar properties of the radicals investigated decreases in the order $-C_2H_4C_6H_4Cl > -C_2H_4C_6H_4CH_3 > -C_2H_4C_6H_5$. There are 12 figures, 2 tables, and 12 references: 7 Soviet and 5 non-Soviet. The three references to English-language publications read as follows: C. C. Currie, Industr. and Engng. Chem. 46, 2331 (1954); L. H. Sommer, R. P. Pioch, J. Amer. Chem. Soc. 75, 6337 (1953); L. H. Sommer, W. D. English, G. R. Ansul, D. N. Vivona, J. Amer. Chem. Soc. 77, 2485 (1955).

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

SUBMITTED: December 12, 1960

Card 3/6

ANDRIANOV, K.A.; ZHDANOV, A.A.; ODINETS, V.A.

Reaction of addition of aromatic derivatives to vinylmethyldichlorosilane.
Zhur.ob.khim. 31 no.12:4033-4038 D '61. (MIRA 15:2)
(Aromatic compounds)
(Silane)

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)

ANDRIANOV, Kuz'ma Andrianovich; KORSHAK, V.V., otv. red.; ZHDANOV, A.A., red.; BALLOD, A.I., tekhn. red.; DOROKHINA, I.N., tekhn. red.

[Polymers with inorganic main chains of molecules]Polimery s neorganicheskimi glavnymi tsepiami molekul. Moskva, Izd-vo Akad. nauk SSSR, 1962. 326 p. (MIRA 16:2)

1. Chlen-korrespondent Akademii nauk SSSR (for Korshak).
(Silicon organic compounds) (Polymers)
(Organometallic compounds)

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

Synthesis of polyorganosiloxane oligomers containing malonate end groups. Izv.AN SSSR.Otd.khim.nauk no.3:454-456 Mr '62.
(MIRA 15:3)

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

35592
S/062/62/000/003/008/014
B117/B144

15.8170

AUTHORS: Andrianov, K. A., Zhdanov, A. A., and Kashutina, E. A.

TITLE: Synthesis of polyorganosiloxane-oligomers with terminal malonate groups

PERIODICAL: Akademiya nauk SSSR. Izvestiya. Otdeleniye khimicheskikh nauk, no. 3, 1962, 454-456

TEXT: The joint hydrolysis of dimethyl-diethoxy silane and (diethylmalonylmethyl)dimethyl-ethoxy silane was studied. Dimethylchloromethylethoxy silane synthetized by the method described by K. A. Andrianov and M. A. Golubenko (Ref. 4: Dokl. AN SSSR 112, 257 (1957)), boiling point 131-133°C, dimethyl-diethoxy silane, boiling point 112-116°C and freshly distilled malonic ester were used. The reaction was shown to take a smooth course in slightly acid medium without cleavage of ethoxy groups in malonic ester rests. Polyorganosiloxane-oligomers with terminal malonate groups are formed here. Investigation of infrared spectra of the compounds produced showed that the malonic ester residue is not added to the oxygen atom, but to the carbon atom. The following compounds were synthetized:

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S/062/62/000/003/008/014
Synthesis of polyorganosiloxane-oligomers... B117/B144

(diethylmalonylmethyl) dimethylethoxysilane, $C_{10}H_{19}O_4Si$, yield 42 %, clear, colorless liquid, boiling point 120-123°C (5 mm Hg), n_D^{20} 1.4312, d_4^{20} 1.0058, MR 71.29; 1,3-bis-(diethylmalonylmethyl)tetramethylsiloxane, $C_{20}H_{38}O_9Si_2$, yield 78.4 %, clear, colorless liquid, boiling point 184-188°C (2 mm Hg), n_D^{20} 1.4425, d_4^{20} 1.0588, MR 119.94; 1,5-bis-(diethylmalonylmethyl) hexamethyltrisiloxane, $C_{22}H_{44}O_{10}Si_3$, heavy, colorless liquid, boiling point 232-234°C (7-8 mm Hg), n_D^{20} 1.4363, d_4^{20} 1.0425, MR 138.93; 1,7-bis-(diethylmalonylmethyl)octamethyltetrasiloxane, $C_{24}H_{50}O_{11}Si_4$, clear, colorless liquid, boiling point 242-255°C (8-10 mm Hg), n_D^{20} 1.4338, d_4^{20} 1.0375, MR 157.56; 1,17-bis-(diethylmalonylmethyl)octadecamethylnonasiloxane, $C_{34}H_{80}O_{16}Si_9$, n_D^{20} 1.4250, d_4^{20} 1.0190, MR 250.66; 1,37-bis-(diethylmalonylmethyl)octatricontamethylnonadecasiloxane, $C_{54}H_{140}O_{26}Si_{19}$, clear, viscous liquid, n_D^{20} 1.4165, d_4^{20} 1.0068, MR 434.48. N. S. Leznov and

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Synthesis of polyorganosiloxane-oligomers... S/062/62/000/003/008/014
B117/B144

Ya. I. Mindlin are mentioned. There are 2 figures and 4 references: 2 Soviet and 2 non-Soviet. The references to English-language publications read as follows: L. Sommer, G. Goldberg, G. Barnes, L. Stone, J. Amer. Chem. Soc. 76, 1609 (1954); L. Sommer, J. Masterson, O. Steward, R. Leitheiser, J. Amer. Chem. Soc. 78, 2010 (1956).

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

SUBMITTED: September 26, 1961

Card 3/3

36635
S/062/62/000/004/004/013
B110/B101

15.9205

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

TITLE: Polyboron dimethyl siloxanes

PERIODICAL: Akademiya nauk SSSR. Izvestiya. Otdeleniye khimicheskikh nauk, no. 4, 1962, 615-619

TEXT: Polyboron dimethyl siloxanes, which are of interest as elastomers (molecular weight 200,000-400,000), were produced by heterofunctional polycondensation as described by the authors (Dokl. AN SSSR 138, 361 (1961)). In the first stage, 326 g (1.1 moles) of octamethyl cyclotetrasiloxane was telomerized in the presence of 2.37 g (0.0184 moles) of dimethyl dichlorosilane in an autoclave for 4 hrs at 200°C. The resultant substance, 79 g of colorless, viscous α,ω-dichloro polydimethyl siloxane ($ClSi(CH_3)_2O[Si(CH_3)_2O]_{70}Si(CH_3)_2Cl$) was hydrolyzed in acetone and benzene by means of sodium bicarbonate, whereby 72 g of colorless, viscous α,ω-dioxy polydimethyl siloxane, $[(CH_3)_2SiO]_m$, was obtained. The molecular weight of the compound was calculated from

X

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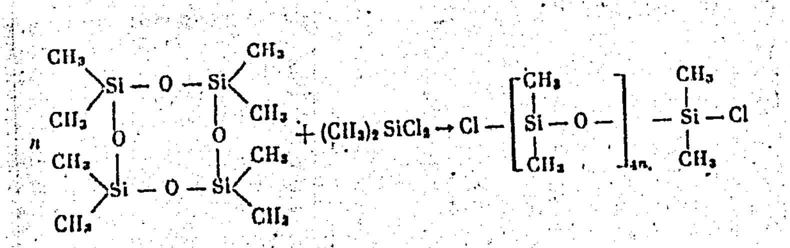
S/062/62/000/004/004/013
B110/B101

Polyboron dimethyl siloxanes

$(\eta) = 2.15\cdot10^{-4}M^{0.65}$. In the second stage, 100 g of α,ω-dioxy polydimethyl siloxane (molecular weight 3300, specific viscosity of the 8% solution: 0.413) and 6.97 g of dibutoxy boron were polycondensed to a gel-like polymer, $[Si(CH_3)_2O]_{44}B(OC_4H_9)O$. The complete synthesis can be represented as follows:



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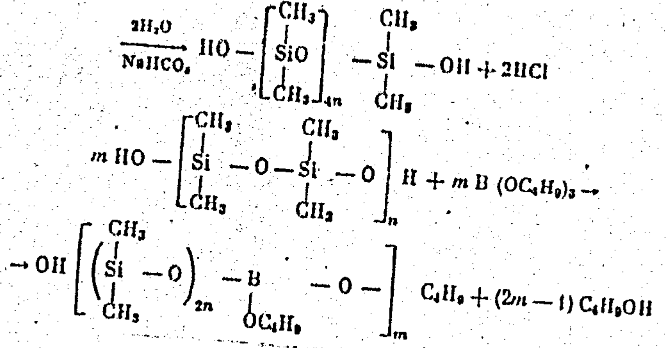
Polyboron dimethyl siloxanes

S/062/62/000/004/004/013
B110/B101



$$\xrightarrow[NaHCO_3]{2H_2O} HO-\left[\overset{CH_3}{\underset{CH_3}{SiO}}\right]_{4n}-\overset{CH_3}{\underset{CH_3}{Si}}-OH+2HCl$$

$$m\,HO-\left[\overset{CH_3}{\underset{CH_3}{Si}}-O-\overset{CH_3}{\underset{CH_3}{Si}}-O\right]_n H+m\,B\,(OC_4H_9)_3\rightarrow$$

$$\rightarrow OH\left[\left(\overset{CH_3}{\underset{CH_3}{Si}}-O\right)_{2n}-\underset{OC_4H_9}{B}-O-\right]_m C_4H_9+(2m-1)\,C_4H_9OH$$

In the two-stage process, the degree of polymerization of the oligomeric intermediate product is already so high as to render the formation of low-molecular cycles impossible. On heating, tributoxy boron reacts with the oligomer, whereas in the cold it reacts only by

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Polyboron dimethyl siloxanes

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B110/B101

association. The characteristic viscosity of the reaction mixture of α,ω-dioxy polydimethyl siloxane and tributoxy boron does not increase at 20°C at ratios of 1:1 or 1:2. Measurements of viscosity showed that the removal of the resulting butanol with carbon dioxide accelerated the reaction. After 30-min heating at 200°C, the specific viscosity of the 8% solution increased to 0.946, butanol being obtained in a quantity of 43% of the theoretical amount. The gel-like, polymeric substance, which is soluble in polar and apolar solvents, was also formed after 30-40 min heating at 150°C in vacuo. Its vitrification temperature (-125°C) and yield point (-50°C) were established by thermomechanical investigations. It is elastic on sudden deformation, capable of springbacks on shocks, but flows under slow stress as in the case of polyaluminosiloxanes, coordination bonds are assumed to exist between oxygen and boron atoms in the siloxane chains:

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X

36061
S/079/62/032/004/002/010
D204/D30.

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

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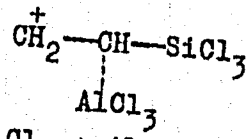
Reactivity of the vinyl group in ... S/079/62/032/004/002/010
D204/D301



A, the first stage consists of the formation of $\overset{+}{CH_2}—\underset{AlCl_3}{\underset{|}{CH}}—SiCl_3$, 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

37403

S/062/62/000/005/005/008
B110/B101

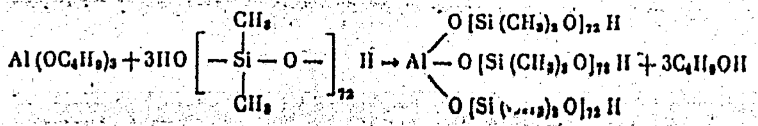
5.3700
15.9205

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

TITLE: Synthesis of polyaluminoorganosiloxanes with molecules of a periodic network structure

PERIODICAL: Akademiya nauk SSSR. Izvestiya. Otdeleniye khimicheskikh nauk, no. 5, 1962, 837 - 840

TEXT: The polycondensation of α,ω-dioxypolydimethyl siloxanes (K. A. Andrianov et al. (Dokl. AN SSSR 134, 1347 (1961)) with aluminum butylate was investigated. When the components were in a proportion 3:1, the following reaction took place at 200°C:



$$Al(OC_4H_9)_3 + 3HO\left[-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{Si}}}}-O-\right]_n H \rightarrow Al\left(-O[Si(CH_3)_2O]_n H\right)_3 + 3C_4H_9OH \qquad (A).$$

In the first stage of polycondensation, the intrinsic viscosity changed very slowly, increasing from 0.052 to 0.092 within 48 hrs. This indicates the formation of a branched oligomer with a central aluminum atom, whereby

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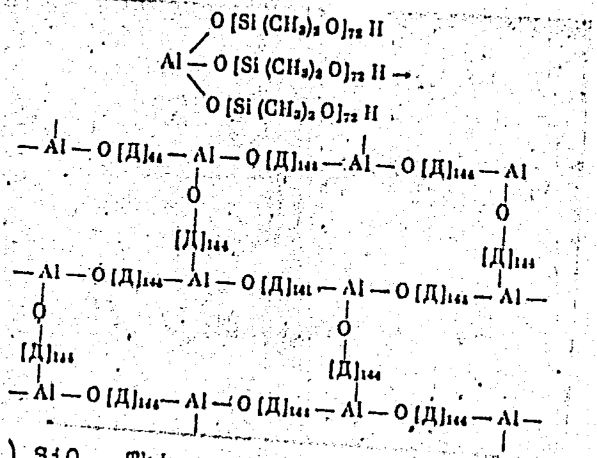
viscosity is only slightly increased. A polymer with a periodic network structure, $C_{148}H_{441}O_{74}Si_{72}Al$, is obtained by further heating:



(B),

where Д = $(CH_3)_2SiO$. This assumption is confirmed by the substantial

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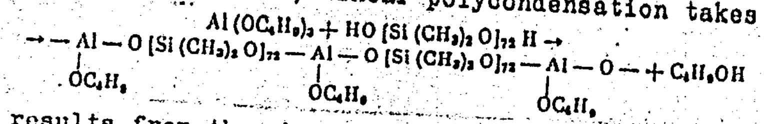
increase in viscosity from 0.092 to 0.263 during polycondensation for 32 hrs. At a ratio 1:1, linear polycondensation takes place:



$$\mathrm{Al(OC_4H_9)_3 + HO[Si(CH_3)_2O]_{72}H \rightarrow}$$
$$\mathrm{\rightarrow -\underset{\displaystyle OC_4H_9}{\underset{|}{Al}}-O[Si(CH_3)_2O]_{72}-\underset{\displaystyle OC_4H_9}{\underset{|}{Al}}-O[Si(CH_3)_2O]_{72}-\underset{\displaystyle OC_4H_9}{\underset{|}{Al}}-O- + C_4H_9OH} \quad (C).$$

This results from the change in viscosity during polycondensation at 180 and 200°C. At 200°C, viscosity rises from 0.092 to 0.164 after polycondensation for 14 hrs, but at a ratio 3:1 this value is only reached after 72 hrs. At room temperature, the 3:1 polymer with an intrinsic viscosity of 0.263 is very elastic, soluble in benzene, toluene, and ether, but becomes insoluble when kept on at a temperature of 200°C. It is elastic over a wide range and has a vitrification temperature of ~-60°C. The high elasticity of its periodic network structure is due to the large spacing of the Al atoms and the considerable flexibility of the polydimethyl siloxane chains. At room temperature, the linear molecule is elastic, readily soluble in organic solvents, and has a wider range of elasticity than the network polymer. There are 3 figures.

Synthesis of polyaluminoorganosiloxanes ... S/062/62/000/005/005/008
B110/B101

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

SUBMITTED: December 19, 1961

Card 4/4

38718

S/191/62/000/007/005/011
B124/B144

15.8170

AUTHORS: Andrianov, K. A., Zhdanov, A. A.

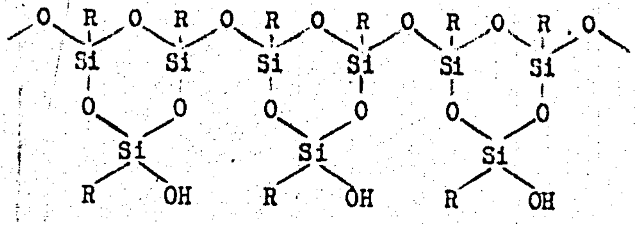
TITLE: Some peculiarities in the structure of polyorganosiloxanes and polyorganometal siloxanes

PERIODICAL: Plasticheskiye massy, no. 7, 1962, 24-27

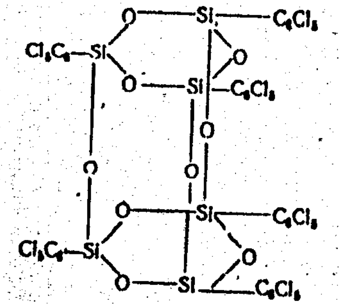
TEXT: Problems concerning the structure of polyorganosiloxanes and polyorganometal siloxanes are discussed on the basis of earlier papers by the authors and in publications from the USA. The flexibility of Si-O-Si bonds surrounded by organic groups is proved by the formation of cyclic compounds (e.g. octamethyl cyclotetrasiloxane) in the hydrolysis of aqueous dimethyl dichlorosilane solutions, the size of the resulting ring being dependent on the type of organic groups on the Si atom. Cyclic polymers of the structure

Card 1/6

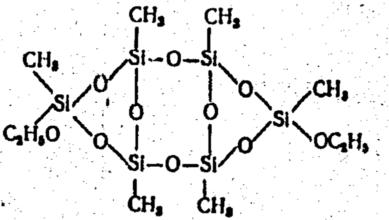
X

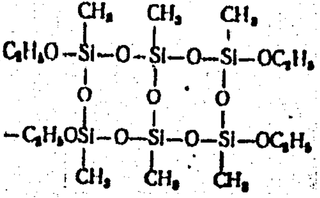


were also formed in the hydrolysis and cohydrolysis of trifunctional organosilicon monomers (phenyl trichlorosilane) in aqueous solution. A polymer having the structure

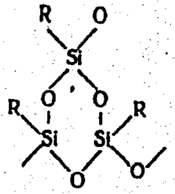


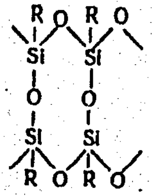
is formed in the hydrolysis of phenyl trichlorosilane, whereas compounds with the structure



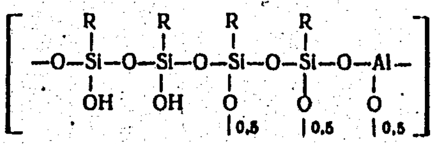


are formed in the hydrolysis of ethyl triethoxy silane and methyl triethoxy silane. Rings of the composition



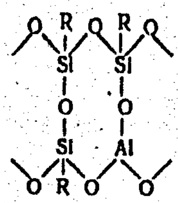


are formed in the synthesis of polymers with inorganic chain molecules by hydrolysis and condensation. Polyalumophenyl- or polyalumoethyl siloxanes:



$$\left[-O-\overset{R}{\underset{OH}{Si}}-O-\overset{R}{\underset{OH}{Si}}-O-\overset{R}{\underset{O_{0,5}}{Si}}-O-\overset{R}{\underset{O_{0,5}}{Si}}-O-\underset{O_{0,5}}{Al}-\right]$$

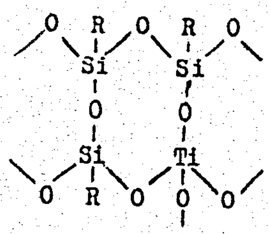
result from the cohydrolysis of phenyl trichlorosilane or ethyl trichlorosilane with $AlCl_3$, as well as from reactions of $Cl_6H_5Si(OH)_2ONa$ with $Al_2(SO_4)_3$; they are readily soluble in organic solvents and do not melt at 700°C; their structure may be stated as follows:



Some peculiarities in the structure ...

S/191/62/000/007/005/011
B124/B144

Polytitanophenyl siloxanes with the structure:



are also formed in the cohydrolysis of phenyl trichlorosilane or phenyl sodium oxydihydroxysilane with $TiCl_4$. A similar structure was determined for polytitanoethyl- and polytitanomethyl siloxanes. This also occurred in polyarsenophenyl siloxane of cyclolinear structure obtained by cohydrolysis of $AsCl_3$ and phenyl trichlorosilane, as well as in polyphenyl siloxane synthesized from phenyl trichlorosilane. Thus it has been proved that the synthesis of the polymers here mentioned proceeds via cyclic compounds with functional groups which react with one another to

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form cyclolinear polymers, but steric hindrances caused by organic radicals on the Si atom prevent branching of molecular chains. There is 1 table. The most important English-language references are: M. M. Sprung, F. O. Guenther, J. Am. Chem. Soc. 77, 6045 (1955); ibid. 77, 3996 (1955); B. L. Chamberland, A. G. McDiarmid, ibid., 83, 549 (1961); J. F. Brown et al., ibid. 82, 6194 (1960); K. A. Andrianov, J. Polymer Sci. 52, 257 (1961).

X

Card 6/6

ACCESSION NR: AT4033984 S/0000/63/000/000/0045/0052

AUTHOR: Zhdanov, A. A.; Andrianov, K. A.

TITLE: Mechanism of formation of Al containing silicones in the reaction of aluminum butylate with dialkyl (alkyaryl) diacetoxysilanes

SOURCE: Geterotsepny*ye vy*sokomolekulyarny*ye soyedineniya (Heterochain macromolecular compounds); sbornik statey. Moscow, Izd-vo "Nauka," 1963, 45-52

TOPIC TAGS: aluminum butylate, polymer, silicone, acetoxysilane, butyl acetate, aluminum containing silicone, dimethyldiacetoxysilane, phenylmethyldiacetoxysilane, diethyldiacetoxysilane, trimethylacetoxysilane, polycondensation, heterofunctional polycondensation, acetate group, acetoxy group, butoxy group, polyorganosiloxane

ABSTRACT: Mixtures of aluminum butylate (I; b.p. 296-297C/24 mm) with phenylmethyldiacetoxysilane (II; b.p. 127C/7 mm, acetate group (49.78%), diethyldiacetoxysilane (III; b.p. 95-97C/20 mm; ag 58.52%), dimethyldiacetoxysilane (IV; b.p. 65-67C/20 mm; ag 66.76%) or trimethylacetoxysilane (V; b.p. 102-105C/ag 45.18%) were heated in an oil bath to 200C and kept at that temperature for 30 hours to study the formation of polymers containing the Si-O-Al bond. Reaction with II, III and IV proceeded rapidly at 140-160C, with formation of a polymerproduct (Al-containing silicone) and precipitation of butyl acetate. Dimethyldibutoxysi-

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ACCESSION NR: AT4033984

lane and diethyldibutoxysilane were byproducts of the reactions with III and IV. The reaction pattern followed the mechanism of heterofunctional polycondensation, but also involved an exchange of acetoxy- groups in Si for butoxy- groups. Reaction with V served to demonstrate a dual reactive capability (i.e. the positive charge on the C atom of the carbonyl group increases or decreases). Orig. art. has: 2 tables, 3 graphs, and numerous chemical formulas.

ASSOCIATION: Institut elementoorganicheskikh soyedineniy AN SSSR (Institute of Metalloorganic Compounds AN SSSR)

SUBMITTED: 21May62 DATE ACQ: 30Apr64 ENCL: 00

SUB CODE: OC NO REF SOV: 006 OTHER: 003

Card 2/2

ZHDANOV, A.A., kahd.tekhn.nauk

New class of polymers. Priroda 52 no.8:53-55 Ag '63.
(MIRA 16:9)

1. Institut elementoorganicheskikh soyedineniy AN SSSR, Moskva.
(Polymers)

ACCESSION NR: AP4035102 S/0191/64/000/005/0023/0026

AUTHOR: Zhdanov, A. A.; Andrianov, K. A.; Baksheyeva, T. S.; Polikanin, N. A.; Levitskiy, M. M.

TITLE: Investigation of the properties of organosilicon polymers containing hydroxyphenyl groups.

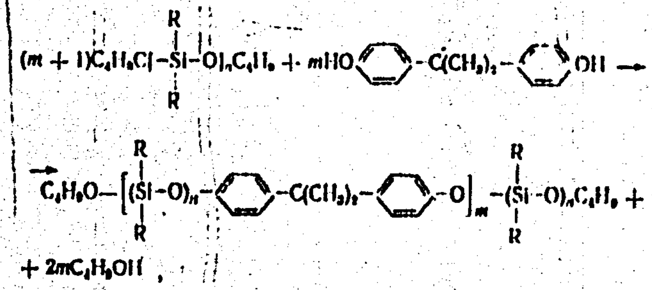
SOURCE: Plasticheskiye massy*, no. 5, 1964, 23-26

TOPIC TAGS: organosilicon polymer, hydroxyphenyl containing siloxane, ester interchange reaction, polymer chain growth, diphenylolpropane, polyphenylbutoxysiloxane, diane reaction product, molded composition, physical property, mechanical property, cross linkage, polymerization

ABSTRACT: The reaction of forming organosilicon compounds containing the hydroxyphenyl group, and the properties of the product polymers were investigated. The hydroxyphenyl group can be introduced into the siloxane chain by ester interchange of the diphenylolpropane (diane) with organosilicon polymers or oligomers containing butoxy groups on the silicon atom. If the oligomer has only terminal butoxy groups the product formed will have diane groups at the ends of the chain. If the

ACCESSION NR: AP4035102

butoxy groups are also on the side chain of the organosilicon polymer, the product will contain the diane group in each link of the polymer chain. The composition and properties of the end products are determined by the molecular ratio of the reagents. With a 1:1 ratio of diane: α, ω-dibutoxypolydimethylsiloxane a linear polymer is formed with blocks of the organosilicon molecules joined by the diane: $[-(SiR_2O)_nC_6H_4C(CH_3)_2C_6H_4O-]$



where $R = CH_3$ or C_6H_5.

With a 2:1 ratio, the oligomer formed contains terminal diane groups: $HOC_6H_4C(CH_3)_2C_6H_4O[SiR_2O]_nC_6H_4C(CH_3)_2C_6H_4OH$.

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ACCESSION NR: AP4035102

Using the product of the 2:1 reagent ratio there is no viscosity change in going from the dimer to the tetramer, but in the 1:1 product the viscosity increases indicating growth of the polymer chain. When the polymer formed by reaction of polyphenylbutoxysiloxane with diane is completely polymerized (in 8-25 minutes) the product is fusible and soluble; when the polymethylbutoxysiloxane-diane reaction product is polymerized to 60-70% it gels, indicating crosslinkage. Molded fiberglass compositions containing 32% of these polymers were formed at 250-300 kgs/cm^2 at 145-150C, 1.5-2 min/mm and cured at 160C for 6-7 hours. Their physical and mechanical properties are tabulated. Orig. art. has: 4 tables, 4 figures and 3 equations.

ASSOCIATION: None

SUBMITTED: 00 ENCL: 00

SUB CODE: OC NO REF SOV: 001 OTHER: 000

Card 3/3

WRITE BELOW THIS LINE

ACCESSION NR: AP4037291 S/0190/64/006/005/0940/0944

AUTHOR: Zhdanov, A. A.; Andrianov, K. A.; Kazakova, A. A.; Baksheyeva, T. S.

TITLE: Polymers with inorganic backbone. Synthesis of polyorganophosphoroaluminoxanes

SOURCE: Vy*sokomolekulyarny*ye soyedineniya, v. 6, no. 5, 1964, 940-944

TOPIC TAGS: polymers, inorganic backbone containing polymer, phosphorus containing polymer, aluminum containing polymer, aluminoxane, polyorganophosphoroaluminoxane, aluminum containing polymethylphosphonate, aluminum ethylate, aluminum butylate, diethyl methylphosphonate, dibutyl methylphosphonate, diphenyl methylphosphonate, polycondensation, methylphosphonyl chloride

ABSTRACT: The reaction of aluminum alcoholates with some derivatives of methylphosphonic acid, and the properties of the condensation products obtained have been studied. Aluminum ethylate or

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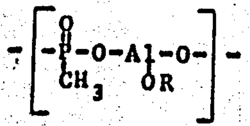
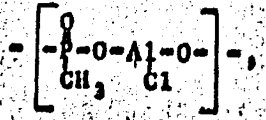
ACCESSION NR: AP4037291

aluminum butylate was condensed with either methylphosphonyl chloride or diethyl, dibutyl, or diphenyl methylphosphonate. Solid polymers obtained in the process of the progressing condensation contained the group



$$-\left[-\underset{CH_3}{\overset{O}{\overset{\|}{P}}}-O-\underset{OR}{\underset{|}{Al}}-O-\right]-$$

and, if methylphosphonate chloride was used, the group



$$-\left[-\underset{CH_3}{\overset{O}{\overset{\|}{P}}}-O-\underset{Cl}{\underset{|}{Al}}-O-\right]-,$$