Polydiethyl-siloxane Liquids. 4. Effect of Aldehydes and Acetone on Diethyl-diethoxy-siloxane

SOV/79-29-5-24/75

siloxanes and corresponding acetals. In the investigation of the reaction of diethyl-diethoxy-silane with formaldehyde (paraform) a prolonged time of heating was found to cause the formation of a polydiethyl-siloxane mixture with a higher content of ethoxyl groups. By the influence of diethyl formal and alcohol upon polycyclic polydiethyl-siloxanes treated with sulfuric acid a polydiethyl-siloxane mixture with 5-4 % ethoxyl groups was obtained. Acetone and diethyl-diethoxy-silane reacted in the presence of sulfuric acid traces and a polydiethyl-siloxane mixture was formed. Ketal, however, was not found in the reaction products. In addition to polydiethyl-siloxanes the reaction product contained alcohol and a considerable quantity of soluble resins which were formed owing to the condensation of acetone and probably also of ketal. Since these resins are dissolved by solvents such as polydiethyl-siloxane they could not be isolated. The distillation in vacuum accompanied by decomposition. Table 1 - interaction of diethyl-ethoxy-silane with paraform, table 2 - the same with paraldehyde. There are 2 tables

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Polydiethyl-siloxane Liquids. 4. Effect of Aldehydes and Acetone on Diethyl-diethoxy-siloxane SOV/79-29-5-24/75

and 3 Soviet references.

SUBMITTED: March 10, 1958

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5 (3) SOV/79-29-5-25/75

AUTHORS: Leznov, N. S., Sabun, L. A., Andrianov, K. A.

TITLE: Polydiethyl-siloxane Liquids (Polidietilsiloksanovyye zhidkosti). 5. On the Reaction Mechanism of Diethyl-diethoxy-silane With Acetic Acid (K voprosu o mekhanizme reaktsii dietildietoksisilana s uksusnoy kislotoy)

PERIODICAL: Zhurnal obshchey khimii, 1959, Vol 29, Nr 5, pp 1518-1522 (USSR)

ABSTRACT: On investigation of the reaction of diethyl-diethoxy-silane with acetic acid it was found that the elimination of the ethyl acetate being formed from the reaction mixture considerably reduces the rate of the reaction in which connection the reaction product is enriched by polydiethyl-siloxanes with linear polymers having ethoxy groups on the ends of the molecular chain. In order to define the chemism of the initial state of the reaction, experiments in toluene medium on continuous distillation of volatile reaction products were carried out. Polydiethyl-siloxanes and ethyl acetate were not found to be formed. Diethyl-diacetoxy-silane and the unchanged diethyl-diethoxy-silane were found in the

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Polydiethyl-siloxane Liquids. 5. On the Reaction Mechanism of Diethyl-diethoxy-silane With Acetic Acid

SOV/79-29-5-25/75

reaction products. The free alcohol was detected in the condensate. Further reactions of anhydrous alcohols with diethyl-diacetoxy-silanes were investigated. It was found that by heating of methyl, ethyl and n-butyl alcohol with diethyl-diacetoxy-silane the corresponding acetates and polydiethyl-siloxane mixtures were formed. In the presence of traces of sulfuric acid the latter are formed at room temperature. The chemical composition of these polydiethyl-siloxanes exhibits in addition to cyclic polymers also linear polymers with alkoxyl groups up to the end atoms of silicon. Heating of diethyl-dioxy-silane in xylene results in a complete elimination of water with polydiethyl-siloxanes being formed. The chemical analysis and the physical constants of the latter are indicative of their cyclic structure. Heating of diethyl-dioxy-silane in anhydrous alcohol yields a polymeric mixture in which linear polymers with ethoxyl groups were detected. The amount of these groups is determined by the acidity of the medium. On dehydration of diethyl-dioxy-silane in alcohol with traces of sulfuric and acetic acid 3.58 and 5.47 % ethoxyl groups were

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Polydiethyl-siloxane Liquids. 5. On the Reaction Mechanism of Diethyl-diethoxy-silane With Acetic Acid SOV/79-2[illegible]-3-25/75

found. In the absence of these acids their quantity was not more than 2 %. It was proved experimentally that on reaction of diethyl-diethoxy-silane with diethyl-diacetoxy-silane in the presence of ethyl-sulfuric or sulfuric acid cyclic polydiethyl siloxanes and ethyl acetate are formed. Table 1 - content of diacetoxy-diethyl-silane in the reaction products of diethyl-diethoxy-silane with acetic acid. Table 2 - reaction of alcohols with diethyl-acetoxy-silane. There are 2 tables.

SUBMITTED: March 10, 1958

Card 3/3

5(3) SOV/79-29-8-56/81

AUTHORS: Andrianov, K. A., Astakhin, V. V.

TITLE: On the Reaction of Organosilico Urethanes and Monohydroxysilanes With Alcohols

PERIODICAL: Zhurnal obshchey khimii, 1959, Vol 29, Nr 8, pp 2698 - 2701 (USSR)

ABSTRACT: As the authors have already shown (Ref 1) the reaction of the trialkylhydroxysilanes with diisocyanates takes place without any by-products. In this process the hydrogen atom of the hydroxyl group of trialkylhydroxysilane migrates to the nitrogen atom of the isocyano group while organosilico urethanes are formed:

$$R\begin{matrix}NCO\\NCO\end{matrix} + 2HOSiR_3 \longrightarrow R\begin{matrix}NHCOOSiR_3\\NHCOOSiR_3\end{matrix}$$

These urethanes are very sensitive to hydrolysis with water:

$$R\begin{matrix}NHCOOSiR_3\\NHCOOSiR_3\end{matrix} + 2H_2O \longrightarrow R\begin{matrix}NH_2\\NH_2\end{matrix} + 2CO_2 + 2HOSiR_3 .$$

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On the Reaction of Organosilico Urethanes and Mono- SOV/79-29-8-56/81
hydroxysilanes With Alcohols

The present paper shows that these urethanes do not only react with water but also with alcohols while forming a diamine, a trialkyl-substituted ester of orthosilicic acid and of carbon dioxide. The formation of these products may take place as follows: organosilico urethane reacts with very small quantities of water in the alcohol and forms dicarbamic acid and trialkyl hydroxysilane. The unstable dicarbamic acid decomposes into CO_2 and diamine while silane reacts with alcohol and forms the trialkyl-substituted ester of orthosilicic acid (Scheme 3). In order to prove this mechanism it has to be found out whether the trialkylhydroxysilanes can react with alcohols (without catalysts as well). The experiments showed that these silanes react with alcohols in the presence of diamine, but also without diamine, according to the scheme $R_3SiOH + HOR'' \longrightarrow R_3SiOR'' + H_2O$. The reaction was carried out with methyl-, propyl-, butyl-, and isoamyl alcohol. The properties of the new compounds are given in the table. Ex-

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On the Reaction of Organosilico Urethanes and Monohydroxysilanes With Alcohols SOV/79-29-8-56/81

perimental data prove the above-mentioned reaction mechanism of urethanes with alcohols. There are 1 table and 1 Soviet reference.

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

SUBMITTED: May 27, 1958

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SOV/79-29-8-57/81

5(3)
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 2702 - 2706 (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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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

ANDRIANOV, K.A.; GOLUBTSOV, S.A.; TISHINA, N.N.; TROFIMOVA, I.V.

Direct synthesis of phenyltrichlorosilane in a fluidized bed.
Zhur.prikl.khim. 32 no.1:201-207 Ja '59. (MIRA 12:4)
(Silane)

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

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SOV/80-32-4-32/47

5(3)

AUTHORS: Andrianov, K.A., Zubkov, I.A., Semenova, V.A. and Mikhaylov, S.I.

TITLE: The Arylation of Methyldichlorosilane by Aromatic Hydrocarbons (Arilirovaniye metildikhlorsilana aromaticheskimi uglevodorodami)

PERIODICAL: Zhurnal prikladnoy khimii, 1959, Vol 32, Nr 4, pp 883-888 (USSR)

ABSTRACT: As the reaction of arylation of alkylhalidesilanes is of extreme technological importance, the authors investigated the arylation of methyldichlorosilane by benzene, toluol, diphenyl and naphthalene, in the presence of boric acid. The interaction of tuluol, diphenyl and naphthalene with methyldichlorosilane in the presence of boric acid resulted in the formation of tolylmethyldichlorosilane, diphenylmethyldichlorosilane and naphthylmethyldichlorosilane. Some physical constants, such as boiling points, densities and refraction indices, were determined for these synthesized compounds.

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75687
SOV/80-32-10-36/51

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

TITLE: Direct Synthesis of Methylchlorosilanes in a Fluidized Bed

PERIODICAL: Zhurnal prikladnoy khimii, 1959, Vol 32, Nr 10, pp 2332-2335 (USSR)

ABSTRACT: The present work was done in 1954-1955. The effectiveness of the fluidized bed application was checked by the synthesis of methylchlorosilanes. The reaction between methyl chloride and silicon was carried out in the presence of a silicon-copper alloy (20% Cu), at 4-5 atmospheres pressure. The reaction is exothermic and needs to be cooled. Special apparatus was constructed which included a cooling system. Dimethyldichlorosilane content was between 42 and 47% in the reaction mixture. A schematic diagram of the apparatus is given, where 1 is methyl chloride cylinder; 2 is water bath;

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Direct Synthesis of Methylchlorosilanes in a Fluidized Bed

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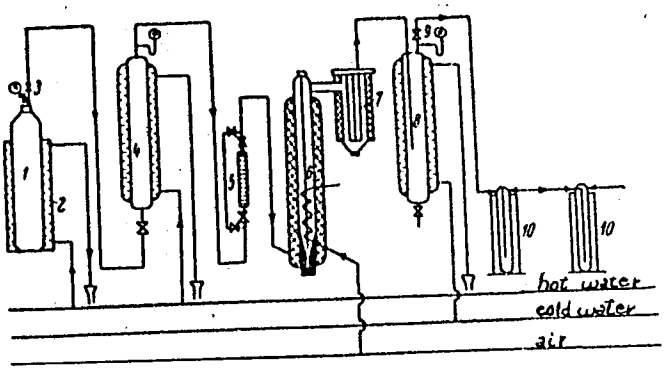

3 is valve; 4 is evaporator, heated with hot water; 5 is rotameter, 6 is reactor, 7 is filter; 8 is water-cooled trap; 9 is valve; 10 is traps cooled with dry ice and acetone. There are 2 figures; 2 tables; and 4 Soviet references.

SUBMITTED: May 15, 1958

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5(3) SOV/20-126-5-23/69

AUTHORS: Andrianov, K. A., Corresponding Member AS USSR, Kurashova, N. A.

TITLE: Synthesis of Cyclic Dimethyl Siloxanes, Containing Triethyl Siloxane Groups (Sintez tsiklicheskikh dimetilsiloksanov, soderzhashchikh trietilsiloksanovyye gruppy)

PERIODICAL: Doklady Akademii nauk SSSR, 1959, Vol 126, Nr 5, pp 997 - 1000 (USSR)

ABSTRACT: The compounds, mentioned above, though containing other than triethyl siloxane groups, have been synthesized and described in various reports (Refs 1-7). In this report the synthesis of such compounds having a structure of $(C_2H_5)_3 SiOSiCl_2$, and their transformation into cyclic-compounds by means of the co-hydrolysis - reaction with dimethyl-dichloro silane, is described. The synthesis of the compounds, mentioned last in the title, was carried out according to reference 8. There were ethyl-(triethyloxy)-dichloro silane; methyl-(triethyl-siloxy)-dichloro silane, and phenyl-(triethyl-siloxy)-dichloro silane. The structure of these compounds was not only confirmed by analytical data, but also by their transformation into acetoxy-

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-derivates (see schedule). Table 1 puts forth the properties of the newly-produced compounds. The cyclic dimethyl siloxane containing triethyl siloxane groups were obtained by means of a co-hydrolysis reaction (see schedule). It was found that in the co-hydrolysis of methyl-(triethyl siloxy)-dichloro silane with dimethyl dichloro silane, chiefly tetramer triethyl-siloxy--hepta-methyl-tetra-siloxane is formed. A co-hydrolysis of the ethyl-(triethyl-siloxy)-dichloro-silane and phenyl-(triethyl--siloxy) dichloro silane with dimethyl-dichloro silane leads chiefly to the formation of trimers (Table2). The cyclic structure was not only confirmed by analysis but also by the infrared spectrum. There are 2 tables and 8 references, 2 of which are Soviet.

SUBMITTED: April 3, 1959

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.

Inst. Elementar. Organo Compounds AS USSR

5(3) SOV/2o-127-5-22/58

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

TITLE: Synthesis of Some Triethyl Siloxy Alkoxy Titanes

PERIODICAL: Doklady Akademii nauk SSSR, 1959, Vol 127, Nr 5, pp 1o14 - 1o15 (USSR)

ABSTRACT: The compounds mentioned in the title have hitherto remained uninvestigated. The trialkyl (aryl) siloxy groups have considerable hydrolytic stability in the tetrakis-[trialkyl(aryl)siloxy]titanes which is much higher than that of the alkoxy groups bound to titanium. It is therefore of interest to investigate the properties of compounds containing simultaneously trialkyl siloxy- and alkoxy groups. Since the method described by the first author (Ref 1) is difficultly accessible the authors investigated the possibility of the synthesis mentioned in the title by a direct interaction of triethyl silanol with butyl orthotitanate or propyl orthotitanates. In contrast to the data from publications (Ref 3) according to which the reaction between butyl orthotitanate and triphenyl silanol is said to lead to a complete substitution of all butoxy groups by triphenyl siloxy groups the authors proved that in the case of the here applied substances,

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in the presence of metallic sodium as catalyst, the reaction does not only proceed in the direction of the formation of tetrakis (triethyl-siloxy) titanium. Also products of different degrees of substitution are formed in this connection. This depends on the ratio of the reacting components. In the course of the investigation of the mentioned reaction (see Scheme) tri-(triethyl-siloxy)-butoxy-titanium (46% of the theoretically computed value), di(triethyl-siloxy)-dibutoxy titanium (34%), di-(triethyl-siloxy)-dipropoxy-titanium (21%) were isolated. Table 1 shows their physical constants, yields, and analysis results. Their hydrolytic stability is being investigated. There are 1 table, and 4 references, 2 of which are Soviet.

SUBMITTED: April 16, 1959

5 (3)

AUTHORS: Andrianov, K. A., Corresponding Member, AS USSR, Makarova, L. I.

SOV/20-127-6-19/51

TITLE: On the Synthesis of Bivalent Alcohols of the Siloxane Series. I. Interaction of Chloromethyl Dimethyl Chlorosilane and Bis(chloromethyl)tetramethyl Disiloxane With Sodium Glycolate

PERIODICAL: Doklady Akademii nauk SSSR, 1959, Vol 127, Nr 6, pp 1213-1216 (USSR)

ABSTRACT: For the synthesis mentioned in the title, the reaction mentioned in the subtitle was investigated, the reaction product being subsequently transformed into bis-(β-oxy-ethoxy-methyl)-tetramethyl disiloxane. Although the reaction course described in scheme (I) was to be expected, it still proved to be much more complicated. The two chlorine atoms: the one bound to silicon, and the one belonging to the chloromethyl group, can both be easily substituted by a glycol residue. But no β-oxy-ethoxy-methyl-dimethyl-β-oxy-ethoxy-silane was formed; neither was it formed in the reaction last mentioned in the subtitle (II). In both cases mentioned, a relatively low-boiling heterocyclic derivative was formed (see Scheme). The substitution of the two halogen atoms occurred, in both cases, with 95% at 100° within 2 h.

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On the Synthesis of Bivalent Alcohols of the Siloxane Series. I. Interaction of Chloromethyl Dimethyl Chlorosilane and Bis(chloromethyl)tetramethyl Disiloxane With Sodium Glycolate

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The formation of the heterocyclic derivative mentioned can apparently be explained by an intermediate formation of β-oxy-ethoxy-methyl-dimethyl-β-oxy-ethoxy-silane which is then cyclized to the derivative mentioned, with separation of a glycol molecule (see Scheme). The intermediate product mentioned, however, could not be isolated. In an interaction of sodium glycolate with bis(chloromethyl)tetramethyl-disiloxane, the formation reaction of the heterocyclic derivative is likely to proceed in a still more complicated way (see Scheme). Such a reaction course (via a silanol formation), conditioned by present humidity traces, is also possible in the case of chloromethyl-dimethyl-chlorosilane. The obtained cyclic product under consideration (boiling point 138°) hydrolizes rather easily to bis-(β-oxy-ethoxy-methyl)-tetra-methyl-disiloxane, and polymerizes while standing under normal conditions with its viscosity and molecular weight increasing at the same time. The kinetics of this polymerization is being investigated at present. Besides, it was proved that the said product can be easily hydrolized by a 1% HCl-solution at 60°, and is transformed into bis-(β-oxy-ethoxy-methyl)-

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On the Synthesis of Bivalent Alcohols of the Siloxane Series. I. Interaction of Chloromethyl Dimethyl Chlorosilane and Bis(chloromethyl)tetramethyl Disiloxane With Sodium Glycolate

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tetra-methyl-disiloxane with a quantitative yield (see Scheme). There are 5 references.

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

SUBMITTED: May 26, 1959

Card 3/3

ANDRIANOV, Kuz'ma A.
(Corres. Mbr., Acad. Sci. USSR)

"Thermal degradation of polymers with main inorganic molecular chains."

report to be submitted for the Symposium on High Temperature Resistance and Thermal Degradation of Polymers, British Society of Chemical Industry, London, England, 21-23 Sep 60.

ANDRIANOV, K. A.

SOV/4984

PHASE I BOOK EXPLOITATION

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., 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.

ANDRIANOV, K.A.

Research in the field of heterorganic and inorganic polymers in the U.S.A. Plast.massy no.1:31-36 '60. (MIRA 13:6)
(United States--Polymers)

KARINA, T.L.; ANDRIANOV, K.A.; SOKOLOV, N.N.

Polyurethan lacquers for the production of lacquer glass fibers. (MIRA 14:4)
Lakokras.mat. i ikh prim. no.2:1-5 '60.
(Glass fibers) (Urethans)
(Lacquers and lacquering)

87654
S/191/60/000/003/005/013
B016/B054

15.8116

AUTHORS: Andrianov, K. A., Dzhenchel'skaya, S. I., Petrashko, Yu.K.

TITLE: New Polymers of Catalytic Polymerization of Organosiloxanes

PERIODICAL: Plasticheskiye massy, 1960, No. 3, pp. 20 - 23

TEXT: The authors report on a study of catalytic polymerization of cyclic products of the cohydrolysis of phenyl trichlorosilane (PTCS) with phenyl-methyl dichlorosilane (PMDCS), as well as of PTCS with dimethyl dichlorosilane (DMDCS). Besides, they discuss cyclic products with methyl siloxane groups in their rings. Ethyl sulfuric acid was used as catalyst. The ratios of components, and the properties of cohydrolysis products of organosiloxanes are given. Polymerization was conducted at 120°, in some cases at 90°C. From the change in viscosity of 10% solutions of the resulting polymers, the authors conclude that an increasing amount of phenyl-methyl siloxane groups in the cohydrolysis products of PTCS, PMDCS, and DMDCS leads to a slight retardation in ring polymerization. It is shown that the viscosity of solutions

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New Polymers of Catalytic Polymerization of Organosiloxanes

S/191/60/000/003/005/013
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of this polymer group (PTCS with PMDCS) at the time of gel formation is lower than that of polymers obtained from cyclic cohydrolysis products. Hence, the authors conclude that, in the cohydrolysis mentioned, rings are formed which partly polymerize under the experimental conditions only on an acid catalyst at increased temperature. On the basis of the infrared spectra (studies by N. P. Gashnikova), the authors conclude that during catalytic polymerization the siloxane chains of the polymer are transformed, and phenyl radicals are partly separated from the silicon atom at the same time. This leads not only to a ramification of the polymer molecules but also to a re-grouping of rings. Polymers with ramified structure have a rather low molecular weight. The thermo-mechanical properties of polymers as observed by G. Ye. Golubkov are given. A comparison of the data obtained clearly showed that an inter-relationship exists between the vitrification temperature and the content of bifunctional components in polymers. Polymers obtained by cohydrolysis of PTCS with PMDCS at all quantitative ratios form, from solutions, brittle films which dry at 20°C. Polymers containing di-methyl siloxane groups form films drying at 200-300°C. The losses in weight during aging at 350 and 400°C for up to 10 days are given.

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New Polymers of Catalytic Polymerization of Organosiloxanes

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Losses slightly increase with an increasing content of phenyl-methyl siloxane groups. Absolute losses, however, are small. The authors mention a paper by K. A. Andrianov and N. N. Sokolov (Ref.7). There are 4 figures, 6 tables, and 7 references: 3 Soviet and 4 US.

X

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ANDRIANOV, K.A.; GRIBANOVA, O.I.; SOKOLOV, N.N.; TIKHONOV, V.S.

Means for increasing the mechanical strength of organosilicon enamels. (MIRA 13:10)
Lakokras.mat. i ikh prim. no.4:10-13 '60.
(Silicon organic compounds) (Enamel and enameling)

87881

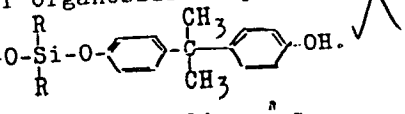
S/191/60/000/005/007/020
B004/B064

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

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81555

S/062/60/000/05/04/008
B004/B066

5.3700C

AUTHORS: Andrianov, K. A., Gashnikova, N. P., Asnovich, E. Z.

TITLE: Investigation of the Infrared Absorption Spectra of Polyaluminum Organosiloxanes and Polytitanium Organosiloxanes

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1960, No. 5, pp. 857-862

TEXT: After a short survey of the data in publications dealing with the infrared spectra of various organic and inorganic silicon and aluminum compounds (Refs. 1-13) the authors report on their own investigations. The vibration spectra of the following compounds were investigated: 1) tris-(trimethyl-siloxy)-aluminum $Al[OSi(CH_3)_3]_3$, melting point 98°-100°C, soluble in benzene, toluene and CCl_4, prepared according to Ref. 14; 2) tris-(triethyl-siloxy)-aluminum, melting point 327°C, solubility like 1), prepared like 1); 3) tetrakis-(triethyl-siloxy)-titanium $Ti[OSi(C_2H_5)_3]_4$, data in Ref. 14; 4) Polymethyl siloxane

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Investigation of the Infrared Absorption Spectra of Polyaluminum Organosiloxanes and Polytitanium Organosiloxanes

$(CH_3SiO_{1.5})_n$, prepared according to Ref. 15 by hydrolysis of methyl trichloro silane; 5) polyethyl siloxane $(C_2H_5SiO_{1.5})_n$, prepared like 4); 6) polyphenyl siloxane $(C_6H_5SiO_{1.5})_n$, prepared according to Ref. 16 by hydrolysis of phenyl trichloro silane. 7) polyaluminum-methyl siloxane, synthesized by reaction of methyl-sodium-oxy-dihydroxy-silane with $AlCl_3$, ratio of Si : Al = 1 : 4; 8) polyaluminum-ethyl siloxane, obtained according to Ref. 16, ratio of Si : Al = 1 : 4.75, average molecular weight 40,000; 9) polyaluminum-phenyl siloxane (Ref. 16), Si : Al = 1 : 4, average molecular weight 7,230; 10) polytitanium-methyl siloxane (Ref. 15), Si : Ti = 1 : 3.8; 11) polytitanium-ethyl siloxane (Ref. 15), Si : Ti = 1 : 4, average molecular weight 9,300; 12) polytitanium-phenyl siloxane (Ref. 15), Si : Ti = 1 : 4, average molecular weight 1,500. The infrared absorption spectra were photorecorded on an ИКС-11 (IKS-11) spectrometer. An ИКР-1 (IKR-1) pin was used as radiation source. The frequencies of the absorption bands observable in the range 1200-800 cm^{-1} are presented in a table, the spectra are shown in the diagrams of

81555

Investigation of the Infrared Absorption Spectra of Polyaluminum Organosiloxanes and Polytitanium Organosiloxanes

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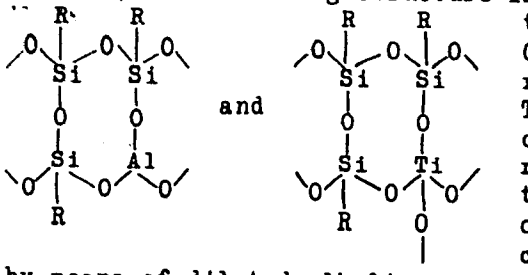
B004/B066

SUBMITTED: November 10, 1958 (initially) and February 2, 1960 (after revision)

Card 4/4

structure. Owing to the low content in functional groups and from infrared spectra, the following structure is assumed: The high thermal stability of the cycles, which contain Si, Al, Ti or Co atoms connected by means of oxygen, render thermal polymerization difficult. The data of the differential thermochemical analysis (Fig. 4) show that the ring cleavage occurs only at temperatures that are above the stability of the organic groups. On the other hand, ring cleavage and polymerization occur easily by means of diluted alkalis or acids. As an example, Fig. 3 mentions the relative viscosity of polytitanomethyl siloxane and polyaluminophenyl siloxane during heating to 80°C in 0.3% NaOH as a function of the duration of the reaction. Thus, polydimethyl siloxanes with a molecular weight of up to 3,000,000 may be obtained from octamethyl cyclotetrasiloxane and hexamethyl cyclotrisiloxane. Ring cleavage is made difficult in the following order: $CH_3 > C_2H_5 > C_6H_5 > ClC_6H_3 > R_3SiO$ in the case of organo-



Card 2/3

S/191/60/000/008/010/014
B004/B056

AUTHORS: Sokolov, N. N., Astakhin, V. V., Andrianov, K. A.

TITLE: Industrial Use of Benzoyl Peroxide

PERIODICAL: Plasticheskiye massy, 1960, No. 8, pp. 48-49

TEXT: The technical regulations ТУМХП1897-49 (TU MKhP 1897-49) require that, because of the explosiveness of benzoyl peroxide, the proximity of fire and high temperatures as well as such dangers as might be caused by percussions or impact be avoided. For the production of СКТ(SKT) rubber, the production of МПБ(MPB) paste by mixing benzoyl peroxide dried to 2 - 4% moisture with diethylsiloxane liquid No. 2 in a ball mill was suggested in a previous paper (Ref. 6). At the zavod "Elektroprovod" (Plant "Elektroprovod") РКГМ(RKGM) wires insulated with SKT rubber were produced by means of MPB paste. In view of the fact that chemical factories pointed out the danger of working with dried benzoyl peroxide, the authors produced a paste direotly from commercial benzoyl peroxide containing 35% of water. The organosilicon liquid displaces the water, so

that the latter may easily be removed. The new paste MPB-1 contains 45.7 - 48.7% benzoyl peroxide and 2.1 - 3.5% water. A comparison between the hardening of КГМС-1 (KGMS-1) sealing compound with that of benzoyl peroxide and MPB-1 led to almost the same results. Also vulcanization of SKT rubber with MPB and MPB-1 gave rubber having the same properties. Positive results were obtained from MPB-1 also in the hardening of МБК-1 (MBK-1) and МБК-3 (MBK-3). Mention is made of the use of benzoyl peroxide for hardening sealing compounds of the types КГМС-2 (KGMS-2), К-30 (K-30), К-31 (K-31), and К-33 (K-33) containing styrene or butylmethacrylate. There are 6 references: 5 Soviet and 1 British.

82850
S/105/60/000/009/002/003
B019/B054

24.2310

AUTHORS: Andrianov, K. A., Corresponding Member of the AS USSR, Volkov, V. A., Engineer, Khval'kovskiy, A. V., Candidate of Technical Sciences

TITLE: The Character of the Electric Strength of Insulations Made of Micaceous Materials

PERIODICAL: Elektrichestvo, 1960, No. 9, pp. 73-80

TEXT: The authors report on experiments to investigate the character of the electric strength of mica paper and the electric field within the paper. The experiments were made on 100% mica paper 0.045 - 0.050 mm thick, manufactured by the "Izolit" Works. The very extensive report states that the mica lamellas in the paper have equal shape and dimensions, and thus the paper represents a typical nonhomogeneous dielectric. Nonimpregnated mica paper has to be considered as a multilayered condenser; its electric strength is determined by the strength of the internal air cavities. Therefore, the high electric strength of nonimpregnated mica paper is explained by the effect of the thin air layers. The spark-over of nonimpregnated

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mica paper has a successive character, it starts from the electrically weakest air cavity, and extends successively over the whole paper thickness. The electric strength of impregnated mica paper depends on the agreement of the continuous anisotropy of the structure and the electrical properties of the impregnating compounds. The electric strength of mica paper is the higher, the more closely the electric strength and the dielectric constant of the impregnating substance lie to the corresponding values of mica. The electric strength can be increased by reducing the thickness and increasing the "linear dimensions" of the mica lamellas. In the development of insulations it is necessary to aim at an agreement with the continuous anisotropic structure of mica paper. There are 5 figures, 4 tables, and 5 Soviet references.

4

ASSOCIATION: Vsesoyuznyy elektrotekhnicheskiy institut im. Lenina (All-Union Institute of Electrical Engineering imeni Lenin)

SUBMITTED: January 7, 1960

Card 2/2

87126

S/062/60/000/009/019/021
B023/B064

2209, 1236, 1273

53700

AUTHORS: Andrianov, K. A. and Delazari, N. V.

TITLE: The Reactions of Trimethyl Siloxytrichloro Titanium With Alcohols

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1960, No. 9, pp. 1712-1713

TEXT: In continuation of previous published data and investigations, the authors report on studies of the reaction of trimethyl siloxy trichloro titanium with butyl alcohol and diphenyl methyl hydroxysilane. In this connection they found that the reaction of the chlorine substitution by butoxy- or diphenyl methyl siloxane groups on titanium is accompanied by byprocesses. The experiments showed that trimethyl siloxy trichloro titanium and butyl alcohol (in equimolar amounts with 20% butanol excess and neutralization of the hydrogen chloride by ammonia) react under the formation of tetrabutoxy titanium. Its formation shows that simultaneously with the replacement of chlorine by the butoxy group, the trimethyl siloxy group bound with titanium is also replaced by the butoxy group.

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87126

The Reactions of Trimethyl Siloxytrichloro Titanium With Alcohols

S/062/60/000/009/019/021
B023/B064

The chemical process may be illustrated by following reactions:

a) $(CH_3)_3SiOTiCl_3 + 3C_4H_9OH \xrightarrow{NH_3} [(CH_3)_3SiOTi(OC_4H_9)_3] + 3NH_4Cl$

b) $[(CH_3)_3SiOTi(OC_4H_9)_3] + C_4H_9OH \longrightarrow$

$(CH_3)_3SiOH + Ti(OC_4H_9)_4$

$\downarrow$

$(CH_3)_3SiOSi(CH_3)_3$

The exchange of the trimethyl siloxy groups on titanium by the butoxy group due to the action of butyl alcohol upon trimethyl siloxy trichloro titanium proceeds at a maximum temperature of 70°C. The reactivity of the trimethyl siloxy group in trimethyl siloxy trichloro titanium proved to be considerable, i.e., not only under the action of butyl alcohol, but also in the reaction of trimethyl siloxy trichloro titanium with diphenyl methyl hydroxysilane. Heating of the solution of the last two substances to 40°C and passing through of ammonia leads to the formation of tetrakis-(diphenyl methyl siloxy) titanium. The absence of absorption in the range of 916 - 920 cm^{-1} was found when determining the infrared

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87434

S/191/60/000/010/006/017
B004/B060

15.8116

AUTHORS: Kuznetsova, A. G., Andrianov, K. A., Zhinkin, D. Ya.

TITLE: Production and Properties of Some Organohydroxy Silanes

PERIODICAL: Plasticheskiye massy, 1960, No. 10, pp. 16-19

TEXT: The authors wanted to define the conditions relative to the production of dimethyl dihydroxy silane and to determine the solubility of dimethyl dihydroxy silane, diethyl dihydroxy silane, and phenyl trihydroxy silane in different solvents. Moreover, they wanted to study their condensation in the presence of HCl. The reactions took place in vessels rendered water-repellent by means of the ГКЖ-94 (GKZh-94) organosilicon liquid. The synthesis of dihydroxy silanes proceeded from dimethyl dimethoxy-, dimethyl diethoxy-, and phenyl trimethoxy silane, respectively, which were obtained by reaction of the corresponding chloro compounds with the corresponding alcohol in the presence of pyridine. The following processes are described. 1) 40 g $(CH_3)_2Si(OCH_3)_2$ were allowed to react at room temperature with 24 g of distilled water, the

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Production and Properties of Some Organohydroxy Silanes

solvents (alcohol and water) were distilled off at 3-10 mm Hg, and the crystals were washed with benzene, heptane, or petroleum ether. Yield 70-75%. 2) 44 g of $(C_2H_5)_2Si(OC_2H_5)_2$ were allowed to react with 18 g of 0.5% acetic acid. The liquid turned homogeneous after 5-7 days, and was then treated as desoribed under 1). 3) 99 g of $C_6H_5Si(OCH_3)_3$ were allowed to react with 50 g of 0.5% acetic acid, temperature being kept at 5-10°C. The product was cooled down to -20°C after 3-5 hours and filtered off in vacuum. Condensation took place in dioxan in the presence of 0.0012, 0.012, or 0.046 N HCl. The dimethyl compound condensed in 0.5N HCl to 80-85% within 15 min. The diethyl compound reacted more slowly, but its condensation rose with an increase of the HCl concentration. The same holds for the phenyl compound. Up to a yield of 40% the condensation proceeded at a constant rate which depended on the concentration of HCl only. It is believed that dimers are formed at this stage. The gradual condensation was particularly well observable in the phenyl compound. Cyclization takes place above the 35% yield. Cyclic and linear polymers with considerable OH group contents resulted. They were determined by titration with Fischer's reagent. The following data for the solubility

S/191/60/000/011/009/016
B013/B054

AUTHORS: Antipina, G. N., Andrianov, K. A., Zhinkin, D. Ya.

TITLE: Method of Producing Anhydrous Ethylene Chlorohydrin

PERIODICAL: Plasticheskiye massy, 1960, No. 11, pp. 39-41

TEXT: The authors suggest a new method of producing pure, anhydrous ethylene chlorohydrin which is based on the reaction of silicon tetrachloride with ethylene oxide, and subsequent hydrolysis of the resulting tetra-β-chloro-ethoxy silane:

(I) $SiCl_4 + 4CH_2\text{—}CH_2 \longrightarrow Si(OCH_2CH_2Cl)_4$ (O)

(II) $Si(OCH_2CH_2Cl)_4 + 3H_2O \longrightarrow 4ClCH_2CH_2OH + SiO_2$

Reaction (I) proceeds smoothly with gradual heating of the reaction mixture to 30° - 35°C. Optimum reaction temperature was 60 - 80°C, reaction time was about 20 hours. The reaction was conducted in a laboratory plant. Other experiments were made in a pilot plant. The reaction time was longer with a larger volume. Reaction (II) proceeds quickly and smooth-

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S/191/60/000/012/008/016
B020/B066

158500 2209

AUTHOR: Andrianov, K. A.

TITLE: Thermooxidative and Hydrolytic Stability of Polymers With Inorganic Chain Molecules

PERIODICAL: Plasticheskiye massy, 1960, No. 12, pp. 23 - 29

TEXT: In the present paper, an attempt is made to compare the thermo-oxidative destruction of some types of organic polymers and of polymers with inorganic chain molecules, and to study the effect of structure and chemical composition of polymers with inorganic chain molecules on their stability. The thermooxidative stability of polymers (in some cases in the presence of fillers) was determined by the loss of weight at different temperatures in the air, by the thermoplasticity of polymer films on metallic bases, and the change in chemical composition. Data were obtained for organosilicon, organofluorine compounds, polyamides, epoxy resins, terephthalates, phenol formaldehyde resins, and rubbers. As may be seen from Table 1 and also from Fig. 1, the loss of weight of organic polymers is much higher than that of polymers with inorganic chain molecules. The

Thermooxidative and Hydrolytic Stability of Polymers With Inorganic Chain Molecules

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autooxidative reactions proceed very intensely in organic polymers, not only in the side groups but also in the principal chain. Polymers with inorganic chain molecules contain carbon which forms oxygen-containing high-volatility compounds in the side groups only. From among the organic polymers studied in this paper, only polytetrafluoro ethylene showed exceptional thermooxidative stability which is explained by the strong screening effect of the fluorine atom surrounding the principal carbon chain of the molecule, and by the dense packing of chain molecules. Substitution of one chlorine atom for one fluorine atom effects a considerable reduction of thermooxidative stability. Similar results are obtained when studying the thermoelasticity of films (Table 3). All films of organic polymers exhibited a much more rapid loss of elasticity on heating than the films of polymers with inorganic principal chains. Fig. 2 shows the heating time at different temperatures at which polymer films attain an elongation of less than 4 %. The effect of organic groups and of the structure of chain molecules in polymers with inorganic chain molecules on the loss of weight is illustrated in Table 4. Table 5 gives the half-life period of decomposition of organic groups on heating, which strongly differs for

Thermooxidative and Hydrolytic Stability of Polymers With Inorganic Chain Molecules

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individual polymers. The change in thermooxidative stability of polymers with inorganic chain molecules in the presence of two elements (Ti or Al and Si) in addition to oxygen in the principal chain is shown in Tables 6 and 7. It may be seen from these tables that the losses of weight in this case are lower than in other polymers, but the thermal elasticity of polymers which contain aluminum drops most rapidly. The hydrolytic stability of polymers was studied on compounds of the general composition $(R_2SiO)_xM$ (where M denotes aluminum, titanium, tin), on a polytitano-phenyl siloxane, and a polyalumino-phenyl siloxane. The rate of hydrolysis depends on the nature of the metal in the molecule. When studying the stability of polytitano siloxane to hydrolysis in acid aqueous solutions, the Si - O - Ti bond was found to hydrolyze difficultly. Fig. 3 shows the hydrolytic cleavage of polytitano-phenyl siloxane, polyalumino-phenyl siloxane, and polyalumino-ethyl siloxane with 10 - 30 % HCl. The analysis of hydrolysis products is presented in Tables 8 and 9. There are 3 figures, 9 tables, and 6 references: 4 Soviet, 1 US, and 1 German.

Card 3/3

5.3700

S/190/60/002/01/17/021
B004/B061

AUTHORS: Andrianov, K. A., Asnovich, E. Z. 82085

TITLE: Polytitanomethylsiloxanes and Polytitanoethylsiloxanes

PERIODICAL: Vysokomolekulyarnyye soyedineniya, 1960, Vol. 2, No. 1, pp. 136-140

TEXT: For the production of polytitanoalkylsiloxanes, the authors used the following reactions: $RSiCl_3 + 3\ H_2O \longrightarrow RSi(OH)_3 + HCl$;

$RSi(OH)_3 \xrightarrow{-1.5H_2O} RSiO_{1.5}$; $4RSiO_{1.5} + 4NaOH + TiCl_4 \xrightarrow{2\ H_2O} 4NaCl +$ $+ [RSi(OH)_2O]_4Ti$; $n[RSi(OH)_2O]_4Ti \longrightarrow nH_2O + \{[RSi(O)O]_4Ti\}_n$. R = CH_3 (I), C_2H_5 (II). The polymers were bright yellow, hard, brittle, glass-like substances, easily soluble in organic solvents. They did not melt when heated to 500°C. The average degree of polymerization was 22. The substances lost their solubility by heating (Table). They had no

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Polytitanomethylsiloxanes and Polytitanoethylsiloxanes

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82085

elasticity- or plastic ranges (Fig.), but plasticizing of (I) with pentachlorodiphenyl (50%) at 20°C, and plasticizing of (II) with a hydrocarbon (50%) boiling at 320°C led to a flow at 25°C. Fig. 2 shows the infrared spectra of I and II and of polytitanophenylsiloxane, taken by N. P. Gashnikova. A linear-cyclic structure of the polymers was assumed from these data. The synthesis took place from methyltrichlorosilane (70.9% Cl), ethyltrichlorosilane (65% Cl), caustic soda "pro analysi" ГОСТ 4328-48 (GOST 4328-48), and $TiCl_4$ "pure" ТУ 2553-31 (TU 2553-31). The content of hydroxyl groups was determined according to Tserevitinov-Terent'yev. The authors thanked I. I. Tverdokhlebova for the determinations of molecular weight carried out in S. R. Rafikov's laboratory. There are 2 figures, 1 table, and 7 references: 5 Soviet and 2 US.

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

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82085
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B004/B061

Polytitanomethylsiloxanes and
Polytitanoethylsiloxanes

SUBMITTED: October 19, 1959

Card 3/3

S/190/60/002/01/19/021
B004/B063

5.3700 82086

AUTHORS: Andrianov, K. A., Nikitenkov, V. Ye., Sokolov, N. N.

TITLE: Comparison of the Properties of Polymers With Polysiloxane and Phenylenesiloxane Chains in the Molecule

PERIODICAL: Vysokomolekulyarnyye soyedineniya, 1960, Vol. 2, No. 1, pp. 158-161

TEXT: The authors compare the thermoelasticity at 300°C, the mechanical resistance to abrasion, and the loss of weight at 300°C of the following compounds:

$$\left[\begin{array}{cc} CH_3 & CH_3 \\ | & | \\ -Si-C_6H_4-Si-O- \\ | & | \\ C_6H_5 & C_6H_5 \end{array}\right]_{2.75} \left[\begin{array}{cc} CH_3 & CH_3 \\ | & | \\ -Si-C_6H_4-Si-O- \\ | & | \\ O_{\frac{1}{2}} & O_{\frac{1}{2}} \end{array}\right]_{1.5} \left[\begin{array}{cc} C_6H_5 & C_6H_5 \\ | & | \\ -Si-C_6H_4-Si-O- \\ | & | \\ O_{\frac{1}{2}} & O_{\frac{1}{2}} \end{array}\right]_{0.75} \quad (I);$$

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Comparison of the Properties of Polymers With Polysiloxane and Phenylenesiloxane Chains in the Molecule

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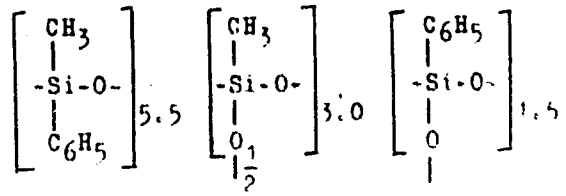

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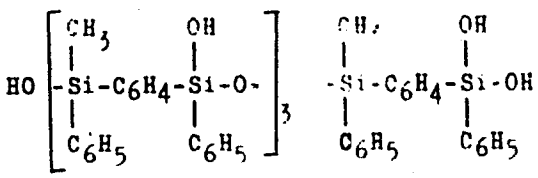

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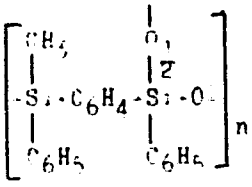

(IIIa)

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Comparison of the Properties of Polymers With Polysiloxane and Phenylenesiloxane Chains in the Molecule

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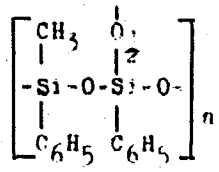
and  (IV). In polymer (I) the ratio of bifunctional to

trifunctional groups is 55 : 45, in compound (III) it is 1 : 1. Compound (III) forms bright, white crystals, melting point 84 - 85°C, soluble in acetone, benzene, chlorobenzene, carbon tetrachloride, and ether, insoluble in methanol, ethanol, and water. Under loss of water on being heated, (III) is converted into the steric polymer (IIIa). The properties of the polymers are given in a Table. Polymers (IIIa) and (IV) contain less methyl- and more phenyl radicals than (I) and (II). This small change has the following effect on the properties. The loss of weight at 300°C is considerably smaller than with (I) and (II). The thermoelasticity and resistance to abrasion of (IIIa) are very small; this polymer is brittle as a result of the large concentration of phenyl-

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81610

S/190/60/002/02/09/011
B004/B061

5.3830

AUTHORS: Andrianov, K. A., Golubkov, G. Ye.

TITLE: Polydimethylpolyphenylsiloxanes Obtained by Catalytic Condensation

PERIODICAL: Vysokomolekulyarnyye soyedineniya, 1960, Vol. 2, No. 2, pp. 279-283

TEXT: The authors synthesized polydimethylpolyphenylsiloxane (I) from phenyltrichlorosilane and dimethyldichlorosilane by catalytic condensation, and also polymer (II) whose trifunctional component is 25% larger than that of (I). As apart from (I), polymer (III) contains 5% of a trifunctional component, and polymer (IV) differs similarly from (II) (5% of tetrafunctional component). Polymer (V) contains polyaluminomethylphenylsiloxane. The following properties of the films of these polymers were examined: strength (Fig. 1), deformation and vitrification temperatures (Fig. 2), dependence of the thermomechanical properties on the preceding heat treatment (Fig. 3), absorption of benzene vapor

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28908
S/191/61/000/011/004/008
B110/B147

5.3700 2209

AUTHORS: Andrianov, K. A., Golubenko, M. A.

TITLE: Condensation of methyl-phenyl diethoxy silane with bivalent phenols

PERIODICAL: Plasticheskiye massy, no. 11, 1961, 21-22

TEXT: The authors studied the condensation of 27 g (0.127 moles) of methyl-phenyl diethoxy silane (I) (boiling point 60-62°C/2 mm Hg; $n_D^{20} = 1.4700$) with 28.5 g (0.125 moles) of 4,4'-dioxy-diphenyl propane (II) taking place at 150-180°C under separation of C_2H_5OH. At the beginning, the reaction proceeds quickly. It results in a decrease in the number of functional groups. Heating was carried out for 7 hr in an N_2 flow, and functional groups and viscosity were determined hourly by means of Pinkevich's viscosimeter (0.8 mm capillary). After final heating for 1 hr at 240-250°C, 39 g of a solid, transparent substance (%: Si = 7.15; OH = 1.11; OC_2H_5 = 2.45, MW = 1758) was obtained. ($C_{112}H_{116}O_{11}Si_5$, %:

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Si = 7.92; OH = 0.96; OC_3H_5 = 2.53; MW = 1778). The determination of Si, hydroxyl and ethoxyl groups in the polymers permits to infer the following stepwise polycondensation:

$$x\text{HOROH} + x\text{CH}_3\text{C}_6\text{H}_5\text{Si}(\text{OC}_2\text{H}_5)_3 \rightarrow [-\text{OROSi}(\text{CH}_3)(\text{C}_6\text{H}_5)-]_x + 2x\text{C}_2\text{H}_5\text{OH}$$

$$R = C_6H_4C(CH_3)_2C_6H_4,\ C_6H_4$$

In the case of equimolar amounts of the reaction products the molecular weight lies at about 1800. Condensation of 52.5 g (0.25 moles) of I with 27.5 g (0.25 moles) of hydroquinone (III) begins at 110°C and takes place during heating for 7 hr at 160-180°C and for 1 hr at 200-210°C in N_2 flow. Here, too, the initial rate with reduction of the functional groups is high. The molecular weight is 1500 at equimolecular ratio of the initial compounds, which corresponds to a polymer with six structural units, as proved by the Si, hydroxyl, and ethoxyl determination. 55 g of a dark, viscous substance (%: Si = 11.32; OH = 1.21; OC_2H_5 = 3.42; MW = 1...

Condensation of methyl-phenyl...

was obtained ($C_{80}H_{78}O_{13}Si_6$, %: Si = 11.88; OH = 1.21; OC_2H_5 = 3.18; MW = 1416). The viscosity of the condensation products increases only slowly. After heating for 10-15 min at 240-250°C, the condensation product of I + III changes into a highly viscous polymer. The polymers obtained are soluble in toluene, benzene, chlorobenzene, and amyl acetate. They are being tested as modifying substances for epoxy resins. There are 3 figures and 7 references: 2 Soviet and 5 non-Soviet. The two references to English-language publications read as follows: US Pat. 2584342, 2584344, 2584351; C. A., 46, 4851 (1952); US Pat. 2628215 (1953).

Card 3/3

15.8106 2109, 1526, 1460, 2209

84506
S/190/60/002/004/007/020
B004/B056

AUTHORS: Andrianov, K. A., Parbuzina, I. L., Sokolov, N. N.

TITLE: Polymers on the Basis of 4,4'-Dihydroxydiphenylpropane and Phthalic Acids

PERIODICAL: Vysokomolekulyarnyye soyedineniya, 1960, Vol. 2, No. 4, pp. 518-520

TEXT: In the present paper, the authors report on the condensation of 4,4'-dihydroxydiphenylpropane with phthalic acid, isophthalic acid, and the dimethyl ester of terephthalic acid. The reaction develops in nitrogen at 250°C and forms, with phthalic acid, a polymer having a melting point of 105°C and, with isophthalic acid, a polymer with a melting point of 260°C. As terephthalic acid sublimates at high temperatures, the reaction was carried out with its dimethyl ester in the presence of lead oxide at 300°C. The resulting polymer had a melting point of 280°C. As shown by the Fig., the viscosity during the polymerization increases first rises slowly and then with increasing

Card 1/2

84506
S/190/60/002/004/007/020
B004/B056

Polymers on the Basis of 4,4'-Dihydroxydiphenylpropane and Phthalic Acids

rapidity. A Table gives melting points and viscosity for dissolution in cresol. These polymers are tested for their applicability as components of block copolymerization. The authors mention papers by V. V. Korshak and S. V. Vinogradova (Refs. 4 and 6). The thermomechanical properties were investigated by means of the scale designed by V. A. Kargin (Ref. 7). There are 1 figure, 1 table, and 7 references: 3 Soviet, 1 US, 2 British, and 1 Belgian.

ASSOCIATION: Vsesoyuznyy elektrotekhnicheskiy institut (All-Union Electrotechnical Institute)

SUBMITTED: December 28, 1959

Card 2/2

15.8114 2109,2209,1436

84507
S/190/60/002/004/008/020
B004/B056

AUTHORS: Andrianov, K. A., Gribanova, O. I., Prelkova, A. G., Sokolov, N. N., Sun' Shu-men

TITLE: Investigation of the Reaction of Polycondensation of Polyethyleneterephthalate and Polyorganoethoxysiloxanes

PERIODICAL: Vysokomolekulyarnyye soyedineniya, 1960, Vol. 2, No. 4, pp. 521-525

TEXT: In order to give greater mechanical strength and better adhesion to polyorganosiloxane resins, the authors studied the modifying of polymethylphenylsiloxanes by means of polyethyleneterephthalate. As initial substances for the synthesis of the organic silicon compounds, methylphenylethoxychlorosilane and phenyltriethoxysilane in a ratio of 1 : 0.5 were used. The hydrogen chloride formed in the reaction and the acetoacetic ester were distilled off, so that, as shown by Table 1, only a slight hydrolysis occurred. The molecular weight of the polyorganosilanes was 600 - 800. As a second component for the copolymer,

Card 1/3

Investigation of the Reaction of Polycondensation of Polyethyleneterephthalate and Polyorganoethoxysiloxanes

the polycondensation product of the methyl ester of terephthalic acid with multivalent alcohols, synthetized by a method described in Ref. 2, was used. It has the following structural formula:

$HO\left[CH_2CH_2OC.C_6H_4.\underset{O}{\overset{\|}{C}}O\right]_n.CH_2CH_2OH$. The molecular weight was 450 - 510.

Copolymerization began at 130°C with the liberation of ethanol (Table 2), and was finished at 190°C. The copolymer obtained had good mechanical, thermal, and dielectric properties. As mentioned in Table 3, its hardness is somewhat less than that of polyethyleneterephthalate, but greater than that of polyorganosiloxanes. A Fig. shows that the loss in weight due to aging at 250°C is less than in the case of polyethylene-terephthalate, and approaches that of polyorganosiloxane films. The breakdown voltage in dry films amounted to 120-140 kv/mm at 120°C. There are 1 figure, 3 tables, and 2 references: 1 Soviet and 1 US.

84507

Investigation of the Reaction of Polycondensation of Polyethyleneterephthalate and Polyorganoethoxysiloxanes

S/190/60/002/004/008/020
B004/B056

ASSOCIATION: Vsesoyuznyy elektrotekhnicheskiy institut (All-Union Electrotechnical Institute)

SUBMITTED: December 28, 1959

X

Card 3/3

84513

15.8114 2109,2209,1460

S/190/60/002/004/014/020
B004/B056

AUTHORS: Andrianov, K. A., Sun' Shu-men

TITLE: Polydimethylpolyphenylsiloxanes

PERIODICAL: Vysokomolekulyarnyye soyedineniya, 1960, Vol. 2, No. 4, pp. 554-557

TEXT: It was the purpose of the present work to investigate the influence exerted by the structure of the main chain of a polymer molecule upon thermal stability. Polymers were produced, which differ only by the number of bifunctional (B) dimethylsiloxane groups between the number of trifunctional (T) phenylsiloxane groups. At first, compounds with the structure

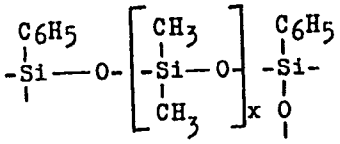
$$C_2H_5O-\left[\begin{array}{c}CH_3\\|\\-Si-O\\|\\CH_3\end{array}\right]_n-C_2H_5$$ (n = 3,4,5) were synthetized from dimethyl-

Card 1/2

Polydimethylpolyphenylsiloxanes

81513
S/190/60/002/004/014/020
B004/B056

dichlorosilane and dimethyldiethoxysilane. By condensation with phenyltrichlorosilane, compounds with the general structure



were then obtained (Table 1). The resulting polymers have the following structures: (-T-B-B-T-) (I), (-T-B-B-B-T) (II), and (T-B-B-B-B-T) (III). The polymers showed good elastic properties, which they retained also after 1000 h of heating at 200°C. As shown by Table 2, a loss of weight occurred. Thermal stability decreased with increasing distance between the trifunctional groups (T). (I) was therefore more stable than (II) and (III). There are 2 tables.

ASSOCIATION: Vsesoyuznyy elektrotekhnicheskiy institut (All-Union Electrotechnical Institute)

SUBMITTED: January 9, 1960

Card 2/2

83820

S/190/60/002/005/010/015
B004/B067

15.8116 also 2209

AUTHORS: Andrianov, K. A., Khananashvili, L. M., Konopchenko, Yu. F.

TITLE: Synthesis of Eight-membered Mixed Organocyclosiloxanes and Their Polymerization

PERIODICAL: Vysokomolekulyarnyye soyedineniya, 1960, Vol. 2, No. 5, pp. 719-727

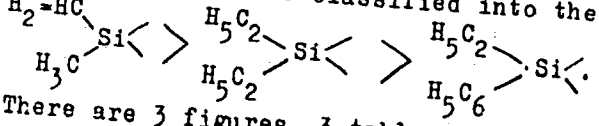
TEXT: The authors cohydrolyzed two bifunctional organosilicon compounds: $m(CH_3)_2SiCl_2+nRR'SiCl_2+(m+n)H_2O \longrightarrow [(CH_3)_2SiO]_m[RR'SiO]_n+2(m+n)HCl$. By cohydrolyzing dimethyldichlorosilane and methylvinyldichlorosilane they obtained heptamethylvinylcyclotetrasiloxane (1); hexamethyldivinylcyclotetrasiloxane (2); pentamethyltrivinylcyclotetrasiloxane, and by cohydrolyzing dimethyldichlorosilane with diethyldichlorosilane they obtained hexamethyldiethylcyclotetrasiloxane (4). Furthermore, by cohydrolyzing dimethyldichlorosilane with phenylethyldiethoxysilane, hexamethylethylphenylcyclotetrasiloxane (5) was obtained; and by hydrolyzing methylvinyldichlorosilane in an acid medium, tetramethyltetravinylcyclotetrasiloxane (6) was obtained. The yields were about 80%. The compounds were analyzed by Z. M. Kuptsova. Their molecular weight and the bromine number of the

Card 1/3

Synthesis of Eight-membered Mixed Organocyclo- siloxanes and Their Polymerization

83820
S/190/60/002/005/010/015
B004/B067

compounds containing vinyl groups were determined. N. P. Gashnikova took the infrared spectra. Fig. 1 shows the infrared spectra of (1) and (5). The physical data of the compounds are given in Table 1. The authors polymerized compounds (1) - (6) by means of potassium hydroxide at 130°C, and studied the influence exerted by the various radicals on the course of polymerization. Table 2 gives the results for (5) on variation of the KOH concentration between 0.5 and 1.5%. With 0.5% KOH the yield was 77.3%; with 1.5% KOH it was 91.5%, with decreasing viscosity. Fig. 2 shows the volume change in the polymerization of (5). The largest decrease in volume was observed with 0.5% KOH. Hence, the other compounds were polymerized by means of 0.5% KOH (Fig. 3). The experimental data are given in Table 3. According to their influence on the polymerization coefficient, the siloxane groups can be classified into the following series:



There are 3 figures, 3 tables, and 9 references: 2 Soviet, 4 US, 1 British and 1 Japanese.

Card 2/3

ANDRIANOV, K.A.; BOCHKAREVA, G.P.; FREIKOVA, A.G.; SOKOLOV, N.N.

Polyanhydrides from phthalic and mixed phthalo-adipic acids.
Vysokom.soed. 2 no.5:793-796 My '60. (MIRA 13:8)

1. Vsesoyuznyy elektrotekhnicheskiy institut im. V.I. Lenina.
(Phthalic acid) (Adipic acid) (Anhydrides)

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

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.

Investigation of the Polymerization of Poly-organosiloxanes 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

Card 3/3

87030

15.8114

S/190/60/002/007/014/017
B020/B052

AUTHORS: Andrianov, K. A., Nikitenkov, V. Ye.

TITLE: Synthesis of Cyclic Organosilicon Compounds With Phenylene Siloxane Chains in the Molecule

PERIODICAL: Vysokomolekulyarnyye soyedineniya, 1960, Vol. 2, No. 7, pp. 1099-1102

TEXT: Here, the hydrolysis and polymerization of 1,4-bis(methyl-dichlorosilane)benzene and 1-methyl-dichlorosilane-4-phenyl-dichlorosilane benzene were investigated. Hydrolysis and condensation showed that these compounds produce polymers which easily change from the fusible and soluble into the infusible and insoluble states. The fact that these processes take place at temperatures below 100°C is explained by the high functionality of the initial monomers which easily develop structurized polymers. In this paper it was attempted to explain the formation mechanism of such polymers. First, low-molecular, crystalline, cyclic compounds with many hydroxyl groups are developed which are very unstable and easily become polymers during the melting point determination. An 82.7% yield of

Card 1/2

Synthesis of Cyclic Organosilicon Compounds With Phenylene Siloxane Chains in the Molecule

87030
S/190/60/002/007/014/017
B020/B052

low-molecular, cyclic bis-[1,4-bis-(methyloxy silane)benzene]cyclodioxide was obtained by hydrolysis of 1,4-bis(methyldichloro silane)benzene in acid medium. The properties of the former compound are described. 1-Methyl-dichlorosilane-4-phenyl-dichlorosilane benzene not only gives rise to polymers; under mild conditions bis-(1-methyloxy silane-4-phenyloxy silane benzene)-cyclodioxide can be obtained with a yield of 89.3%. Properties, synthesis, and analysis results of the above compounds are given. The polymer formation mechanism was determined from the structure of the new cyclic, crystalline compounds which were isolated during the polymerization. There are 2 Soviet references.

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

SUBMITTED: March 22, 1960

Card 2/2

86391

S/190/60/002/008/015/017
B004/B054

15.8114 2209

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

TITLE: Interaction of Bis(chloro-methyl)-tetramethyl Siloxane With Hexamethylene Diamine

PERIODICAL: Vysokomolekulyarnyye soyedineniya, 1960, Vol. 2, No. 8, pp. 1261-1265

TEXT: The authors attempted to produce linear organosilicon compounds of the structure $\left[-Si(CH_3)_2-CH_2-NH-(CH_2)_6-NH-CH_2-Si(CH_3)_2O\right]_x$, making use of the high reactivity of the halogen of the methyl group bound to silicon with amines. In the present paper, they report on the reaction of bis(chloro-methyl)-tetramethyl siloxane with hexamethylene diamine. The reaction was performed by adding 0.315 moles of siloxane to 0.63 moles of molten hexamethylene diamine. It proceeded exothermically with a temperature increase up to 200°C. The low increase in viscosity, however, showed that the required linear polymers had not formed. At an equimolecular ratio of components, 60% distilled over at 170°C and 1 mm Hg, 25% could not be distilled. At a component ratio of 1:2, 80-90% distilled over at 250°C and 1 mm Hg.

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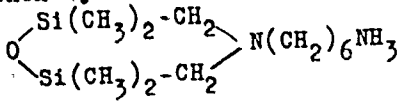
86301

Interaction of Bis(chloro-methyl)-tetramethyl Siloxane With Hexamethylene Diamine

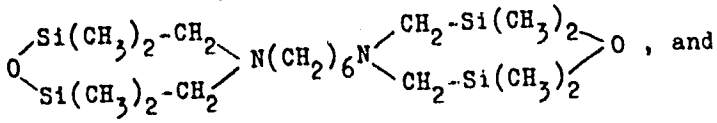
S/190/60/002/008/015/017
B004/B054

Cyclic compounds were mainly formed. A substitution of methyl radicals by phenyl radicals did not prevent cyclization. The structure of the resulting substances was determined by analyses, the molecular weight, and infrared spectra (taken by N. O. Chumayevskiy). Three hitherto unknown compounds were found: a)



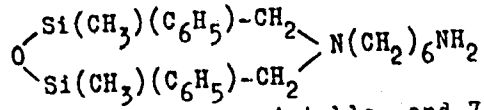
;

b)



, and

c)



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There are 2 figures, 1 table, and 7 references: 3 Soviet, 3 US, and 1 British.

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

SUBMITTED: April 11, 1960

Card 2/2

83479
S/190/60/002/009/010/019
B004/B060

5.3700 also 2109, 2209

AUTHORS: Andrianov, K. A., Makarova, L. I., Zharkova, N. M.

TITLE: Polycondensation of Bis-(β-hydroxy-ethoxy-methyl)-tetramethyl Disiloxane With Dicarboxylic Acids

PERIODICAL: Vysokomolekulyarnyye soyedineniya, 1960, Vol. 2, No. 9, pp. 1378-1382

TEXT: The authors studied the condensation of organosilicon diketo dicarboxylic acids $HOOCC_6H_4COC_6H_4CH_2Si(CH_3)_2O-\left[Si(CH_3)_2O\right]_n-Si(CH_3)_2CH_2C_6H_4CO-C_6H_4COOH$ with $HOCH_2CH_2OCH_2Si(CH_3)_2OSi(CH_3)_2CH_2OCH_2CH_2OH$ at 220°C. Unlike the reaction with ethylene glycol, no cyclic polydimethyl siloxanes were formed. A table shows the

Card 1/3

Polycondensation of Bis-(β-hydroxy-ethoxy-methyl)-tetramethyl Disiloxane With Dicarboxylic Acids

S/190/60/002/009/010/019
B004/B060

silicon content of the condensates. There occurred neither a cleavage of the siloxane bond in the diketo-dicarboxylic acid nor a cleavage of the Si-C bond in organosilicon glycol. As is shown in Fig. 1, the acid number drops during polycondensation while the ester number rises. The polyesters obtained are high-viscous, dark-colored substances well soluble in benzene - alcohol mixture. As is shown by Fig. 2; the viscosity of polyesters rises with the number of dimethyl siloxane groups in diketo dicarboxylic acid. On the reaction of the polyester obtained from diketo dicarboxylic acid (n=5) with hexamethylene diisocyanate, the authors obtained an elastic, rubber-like, cresol-soluble product. The change (increase) in viscosity as dependent on the reaction period is illustrated in Fig. 3. Bis-(β-hydroxy-ethoxy-methyl)-tetramethyl disiloxane also condenses with adipic acid without a cleavage of the Si-C bond to form a polyester. Fig. 4 shows the change in the acid number and ester number during the reaction. There are 4 figures, 1 table, and 3 references: 2 Soviet and 1 US.

Card 2/3

83479

Polycondensation of Bis-(β-hydroxy-ethoxy-methyl)-tetramethyl Disiloxane With Dicarboxylic Acids

S/190/60/002/009/010/019
B004/B060

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

SUBMITTED: April 11, 1960

Card 3/3

88538

S/190/60/002/010/010/026
B004/B054

5.3831

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

TITLE: Polymerization of Octamethyl Cyclotetrasiloxane in the Presence of Tin Chloride

PERIODICAL: Vysokomolekulyarnyye soyedineniya, 1960, Vol. 2, No. 10, pp. 1508-1511

TEXT: The authors studied the polymerization of octamethyl cyclotetrasiloxane in the presence of $SnCl_4$ (0.02 and 0.058 moles) as a catalyst at 120, 134, and 152°C. They found that the ring is cleft above 100°C, and rubber-like linear polymers with a molecular weight of about 350,000 are formed (Table). The polymer with a molecular weight of 350,000 had the same vitrification temperature as polydimethyl siloxane rubber with the same molecular weight. Fig. 1 shows the yields in polymers, Fig. 2 the relative viscosity as a function of the reaction time. The relative viscosity rises with increasing addition of $SnCl_4$. Fig. 3 shows that the viscosity also rises with increasing polymerization temperature. The

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88538

Polymerization of Octamethyl Cyclotetrasiloxane in the Presence of Tin Chloride

S/190/60/002/010/010/026
B004/B054

authors assume that an active intermediate complex is formed in the polymerization by means of tin tetrachloride:

$$-Si-O-Si-.$$
$$\|$$
$$SnCl_4$$

There are 3 figures, 1 table, and 10 references: 6 Soviet, 3 US, and 1 Japanese.

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

SUBMITTED: April 28, 1960

Card 2/2

ANDRIANOV, K.A.

Thermostabel polymers. Nauka i zhizn' 27 no.9:35 S '60.
(MIRA 13:9)

1. Chlen-korrespondent AN SSSR.
(Polymers--Thermal properties)

ANDRIANOV, K.A.

Work of American scientists in the field of high molecular weight compounds. Vest.AN SSSR 30 no.5:62-67 My '60. (MIRA 13:5)

1. Chlen-korrespondent AN SSSR.
(Macromolecular compounds)

S/079/60/030/06/06/009
B002/B016

53830

AUTHORS: Andrianov, K. A., Dabagova, A. K.

TITLE: Esterification of Bis(hydroxy-methyl)-tetramethyl-disiloxane by Means of Organic Acid Chlorides

PERIODICAL: Zhurnal obshchey khimii, 1960, Vol. 30, No. 6, pp. 1968-1971

TEXT: The properties of bis(hydroxy-methyl)-tetramethyl-disiloxane were investigated to find out whether the universal esterification methods may be applied to this compound. The stability of this compound was investigated by changing the conditions of synthesis. Bis(hydroxy-methyl)-tetramethyl-disiloxane was obtained from bis(acetoxy-methyl)-tetramethyl-disiloxane by treating it with methanol in the presence of HCl (for 72 hours at 20°). The methyl acetate resulting in addition to the former and the excess of methanol were distilled from the acid reaction mixture or from the mixture previously neutralized by means of sodium bicarbonate. The content of hydroxyl groups and Si in the compound remained unchanged both in the neutralized reaction mixture and in the compound distilled off; both were stable for four months (no change of viscosity, no water

Card 1/3

Esterification of Bis(hydroxy-methyl)-tetramethyl-disiloxane by Means of Organic Acid Chlorides

separation). The bis(hydroxy-methyl)-tetramethyl-disiloxane thus obtained was esterified with methacrylic acid chloride and allyl formic acid chloride. The reaction schemes are given. The starting material + allyl formic acid chloride gave bis(carboxy-allylate-methyl)-tetramethyl-disiloxane (yield: 30%), whereas the reaction: starting material + allyl formic acid chloride + methacrylic acid chloride led to 1-methacrylate-methyl-2-carboxy-allylate-methyl-tetramethyl-disiloxane (yield: 19%). The poor yield is explained by the considerable tendency of the reaction products toward further polymerization. Polymerization with peroxy initiators proceeds very smoothly. Solid, vitreous polymers are formed. The properties of the substances synthesized are tabulated. The reactions are described in detail in an experimental part. There are 1 table and 1 non-Soviet reference.

Card 2/3

Esterification of Bis(hydroxy-methyl)-tetra-methyl-disiloxane by Means of Organic Acid Chlorides

S/079/60/030/06/06/009
B002/B016

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

SUBMITTED: June 23, 1959

Card 3/3

S/079/60/030/007/016/020
B001/B067 82299

5.3700C

AUTHORS: Andrianov, K. A., Volkova, L. M.]

TITLE: Synthesis Methods of 1,n-Diethoxymethylchloromethylsiloxanes and Substitution Reactions of Chlorine in the α-Chloromethyl Group

PERIODICAL: Zhurnal obshchey khimii, 1960, Vol. 30, No. 7, pp. 2393 - 2397

TEXT: In the present paper, some low-molecular 1,n-diethoxymethylchloromethylsiloxanes which, besides ethoxy, groups also contain chloromethyl groups in the end position, were synthesized, and the reaction of chlorine in the α-chloromethyl group with aniline was studied. The above siloxanes were synthesized by two methods; 1) by hydrolyzing methylchloromethyldiethoxysilane with a small amount of water in alcohol solution (Scheme 1), and 2) by direct action of 99% alcohol on methylchloromethyldichlorosilane (Scheme 2). 1,n-diethoxymethylchloromethylsiloxanes of the general

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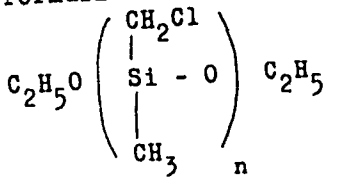
Synthesis Methods of 1,n-Diethoxymethylchloromethylsiloxanes and Substitution Reactions of Chlorine in the α-Chloromethyl Group

S/079/60/030/007/016/020
B001/B067 82299

formula



were obtained as polymerization products (n=2,3,4) (Table). The compounds obtained were examined for their viscosity at various temperatures (Diagram). The determination of the activation energy of the viscous flow shows that it is considerably higher than the activation energy of the series $(CH_3)_3SiO[Si(CH_3)_2O]_nSi(CH_3)_3$ at the same degree of polymerization (Ref.1). This shows that the chloromethyl group and the ethoxy groups in the end position intensify intermolecular reaction. In reacting aniline with bis(chloromethylmethylethoxy)disiloxane, products are formed of different molecular weight from which phenylaminomethylmethyldiethoxysilane and 1,2,3-tri(phenylaminomethylmethyl)-1,3-diethoxytrisiloxane could be isolated. Simultaneously, chlorine was substituted by the phenylamino group. These compounds are formed only by a regrouping with simultaneous cleavage of the Si-O-Si group and by a rearrangement of the ethoxy groups

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due to the action of aniline (Scheme 3). In the same way the highly viscous polymer phenylaminomethylmethyldiethoxysilane which cannot be distilled was formed by reacting 1,2,3-tri(chloromethylmethyl)-1,3-diethoxytrisiloxane with aniline (Scheme 4). There are 1 figure, 1 table, and 1 non-Soviet reference.

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

SUBMITTED: July 1, 1959

S/079/60/030/007/017/020
B001/B067

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

TITLE: Reactions of Bis(phenylaminomethyl)tetramethyldisiloxane With Acids

PERIODICAL: Zhurnal obshchey khimii, 1960, Vol. 30, No. 7, pp. 2397 - 2400

TEXT: The reactions of organosilicon amines with acids have hitherto been little described (Ref. 1). The authors studied the reaction of bis(phenylaminomethyl)tetramethyldisiloxane with adipic-, phthalic-, succinic-, and fumaric acid. At 150°C under normal pressure and in the vacuum the condensation with adipic acid took place very slowly. This reaction was also made with the above acids at 250° and 300° in the nitrogen current. On heating the above siloxane with adipic acid at 250° a certain amount of water was separated and on further heating a product was condensated which did not mix with water. On distillation considerable amounts of this product were obtained. The reaction products are a mixture of hexamethylcyclotrisiloxane, octamethylcyclo-

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tetrasiloxane, and methylaniline. In this case, only small amounts of water are separated. The condensation product is a viscous liquid containing 3-5% silicon, or a low-melting resin without silicon (when the reaction lasts until the volatile products are distilled off). In condensing the above siloxane with the other acids, e.g. with terephthalic-, succinic-, and fumaric acid the process takes place in similar way. The experimental data obtained show that the reaction between the secondary amine of bis(phenylaminomethyl)tetramethyldisiloxane and the dibasic organic acids is very complicated and does not lead to organosilicon polyamides; in the further course of the reaction the S-C and Si-O-Si bonds are cleft (Scheme 1). At high temperatures, the water which is separated in this case reacts with the reaction products, or with bis(phenylaminomethyl)tetramethyldisiloxane which causes the cleavage of the S-C bond (Scheme 2). Besides octamethylcyclotetrasiloxane also hexamethylcyclotrisiloxane is formed whose formation is connected with the cleavage of the Si-O-Si bond. The mixtures of viscous and solid particles which cannot be distilled are difficult to separate and are probably the reaction product of methylaniline with the acids. There is 1 non-Soviet reference.

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Reactions of Bis(phenylaminomethyl)tetramethyl-disiloxane With Acids

S/079/60/030/007/017/020
B001/B067

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

SUBMITTED: July 1, 1959

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82682

S/079/60/030/008/007/008
B004/B064

5.3700

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

TITLE: Synthesis of Low-molecular Polyorganoethoxy Siloxanes With Regular Structure

PERIODICAL: Zhurnal obshchey khimii, 1960, Vol. 30, No. 8, pp. 2777 - 2781

TEXT: The authors aimed at synthesizing polyorgano siloxanes, whose chain consists of Si and O atoms, while the different organic groups bound to the Si atom alternate in a certain order: $R_2SiCl_2 + 2R'_2Si(OR")_2 \rightarrow R"O\overset{R'}{\underset{R'}{Si}}O\overset{R}{\underset{R'}{Si}}O\overset{R'}{\underset{R'}{Si}}OR" + 2R"Cl$. Corresponding to this reaction equation the condensation was carried out of methyl-phenyl dichlorosilane with dimethyl-diethoxysilane, methyl-phenyl diethoxysilane, ethyl-phenyl diethoxysilane, phenyl-triethoxysilane as well as the condensation of methyl-phenyl diethoxysilane with methyl-phenyl chloroethoxysilane and

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82682

Synthesis of Low-molecular Polyorganoethoxy Siloxanes With Regular Structure

S/079/60/030/008/007/008
B004/B064

dichlorophenyl dichloroethoxysilane. $FeCl_3$ served as catalyst, the ethyl chloride forming in this connection was collected in a vessel cooled with liquid nitrogen. Isolating the reaction products formed met with considerable difficulties so that the yields were between 13 and 47%. 1,5-dimethyl-1,5-diphenyl-3-ethoxy-3-dichlorophenyl-diethoxytrisiloxane and 1,5-diethoxy-3-methyl-1,3,5-triphenyl-diethoxytrisiloxane were obtained. Besides, 1,1,3-trimethyl-3-phenyl diethoxydisiloxane, 1-methyl-3-ethyl-1,3-diphenyl diethoxydisiloxane and hexamethyl-3,5-diphenyl-1,7-diethoxy tetrasiloxane formed by the re-arrangement of the functional groups. The assumed course of reaction could be experimentally proven. A table lists the compounds and their physical data. There are 1 table and 5 Soviet references.

ASSOCIATION: Vsesoyuznyy elektrotekhnicheskiy institut (All-Union Electrotechnical Institute)

SUBMITTED: July 27, 1959

Card 2/2

84880

S/079/60/030/010/021/030
B001/B066

5.3700 only 1273, 2209
11.1250

AUTHORS: Andrianov, K. A., Zubkov, I. A., Grinevich, K. P., Shashkova, Z. S., and Kleynovskaya, M. A.

TITLE: Fluoroaryl Methyl Silane Chlorides

PERIODICAL: Zhurnal obshchey khimii, 1960, Vol. 30, No. 10, pp. 3380 - 3382

TEXT: The authors of the present paper synthesized some fluoroaryl silane chlorides and studied their reactions with ethyl alcohol. These fluoroaryl silane chlorides were obtained according to the following Scheme:

$FRBr + Mg \longrightarrow FRMgBr$

$FRMgBr + R'SiCl_3 \longrightarrow FRSiR'Cl_2$ (R = alkyl, R' = aryl). According to this reaction, p-fluorophenyl magnesium bromide and o- and p-fluorobenzyl magnesium bromides were obtained. Irrespective of the high yield of the organomagnesium compound (95-96%), the yields of the end products (p-fluorophenyl methyl silane dichloride, p-fluorophenyl methyl silane

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S/122/60/000/006/008/012
A161/A026

15.9210

AUTHORS: Glukhova, A. I., Andrianov, K. A., Kozlovskaya, L. N.

TITLE: Use of Heat-Resistant Rubber-Like FKS Material in Machines

PERIODICAL: Vestnik mashinostroyeniya, 1960, No. 6, pp. 46-49

TEXT: A new polymer, called ФКС (FKS), is produced in the USSR which has previously been described (Ref. 3). This polymer readily combines with anorganic fillers, and with 33-35% of filler it gives a material for sealings working at high temperatures. There are three grades: FKS-1, FKS-2, and FKS-3, with 55, 45 and 33% of filler, respectively. Compared with heat resistant rubber on silico-organic or other base it has higher mechanical strength, heat resistance, is less affected by kerosene or dichloroethane, and does not deteriorate without air access. Vulcanization for 24 hours in 150 and 200°C lowers its tensile strength and raises the elongation capacity; vulcanization in 250°C increases the tensile strength to 60 kg/cm^2 at a 280% elongation; vulcanization in 300°C has negative effect. Short treatment in 350°C without air access in a press mold under pressure also gives good result and even faster. The behavior

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Use of Heat-Resistant Rubber-Like FKS Material in Machines

after vulcanization is described and illustrated by curves (Fig. 4). The production process was developed in cooperation with the Nauchno-issledovatel'skiy institut rezinovoy promyshlennosti (Scientific Research Institute of Rubber Industry) and is now being employed by some chemical works. Three grades are being produced in bands and vulcanized to 2/10 mm plates: FKS-1, FKS-2 and ФКС-2Б (FKS-2B). The latter is not vulcanized because it does not contain any vulcanizing agent. FKS-1 is used for gaskets in long term operations at temperatures from - 70 to + 350°C, for short times (up to 5 hours) at temperatures as high as + 400°C, and as seals for operation in hydrocarbons at temperatures as high as 200°C. The design of seals is illustrated (Fig. 5). FKS-2 has good dielectric properties and may be used for electroinsulating linings, insulation for electric wires operating in 300 and 350°C over long periods and for short time (10 hours) in 400°C. FKS-2 is frequently used for sealing undetachable joints working at 400°C in 2 hour periods. Pressing technology is being developed for producing bushings reinforced with glass fabric (Fig. 7), for high temperature and high pressure work. There are 7 figures, 2 tables and 3 references: 2 English and 1 Soviet.

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85542

S/026/60/000/009/007/010
A166/A029

5.3700 2209,1273,2109

AUTHORS: Andrianov, K.A., Corresponding Member; Petrashko, A.I.; Asnovich, E.Z.

TITLE: Elementoorganic Polymers

PERIODICAL: Priroda, 1960, No. 9, pp. 27 - 32

TEXT: The authors review some of the modern elementoorganic polymers and the uses to which they can be put. The Soviet GKZh-94 (GKZh-94) silicoorganic fluid could be used to coat transporter belts in bakeries to prevent the bread from sticking to the belt during the baking process. Silicoorganic liquids can be used to impart a super-thin hydrophobic coating, making the treated material waterproof but yet permeable to air. Fabrics so treated do not stick together and the method is therefore good for artificial fur. Brick or roofing tiles treated with a 1 - 2% solution of GKZh-11 silicoorganic polymer do not absorb water. Silicoorganic polymers also give thermostable coatings for molds in precision casting and make excellent insulating material at high and low termperatures and for submarine cables and electrical equipment. Polyorganometallosiloxanes with widely varying properties have been synthesized in the USSR, including polyorganoalumosiloxanes

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S/026/60/000/009/007/010
A166/A029

Elementoorganic Polymers

capable of withstanding temperatures of up to 500°C. Some organoalumosiloxanes dissolve readily in water and are similar in structure to alkite and anorthoclase. They have good adhesion to glass, metals, asbestos and fabrics and can therefore be used as hydrophobizers for fabrics, paper, leather and building material. Polyorganotitanosiloxanes are also used as hydrophobizers. Non-friable coatings can be obtained from a 50/50 mixture of polyorganoborosiloxane and polymethylsiloxane. The introduction of boric acid, boric ethers or borium anhydride to polydimethylsiloxane rubbers gives them greater resilience to sudden stress. Polymers can now be synthesized with a basic siloxane chain containing periodic inclusions of nickel, cobalt, chromium or tin atoms. Chemists have developed high-molecular compounds with inorganic molecule chains framed by organic or organosiloxane groups. Silicon, aluminum, titanium boron, lead, tin or phosphorus are commonly used for the main chains. Alukons (polymers with chains of aluminum and oxygen) are soluble in organic solvents and soften at temperatures ranging from 50 to 170°C. Polyorganolumoxanes, used as additives for varnishes and paints, accelerate drying, improve mechanical strength and chemical stability and retard oxidation. They also have good hydrophobizing properties. Polyorganotitanoxanes are soluble in organic solvents, have good thermostable and waterproofing properties and adhere readily to metals and glass. High thermostability (up to 700°C) and

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