Translated from *Uspekhi Khimii*, **45**, 478-509 (1976) U. D. C. 547.317 : 547.441

Silicon-containing Derivatives of Carbamic Acid—Silylurethanes

V.D.Sheludyakov, V.P.Kozyukov, and V.F.Mironov

Methods of synthesis, properties, and likely applications of silicon-containing derivatives of carbamic acid—silylurethanes—are discussed for the first time. Together with monomeric compounds, oligomeric and polymeric products as well as various compositions based on them, containing silicon and urethane groups, are considered. The review includes studies which have been published up to the middle of 1975.
The bibliography consists of 527 references.

CONTENTS

I. Introduction 227
II. Compounds with the urethane group at the silicon atom 227
III. Organosilicon urethanes containing carbon-based functional groups 230
IV. Other types of silylurethanes 234
V. Applications 235

I. INTRODUCTION

The chemistry of silyl derivatives of carbonic acid, i.e. of organosilicon carbonates, chloroformates, isocyanates, ureas, urethanes, carbodiimides, etc. began to develop only in the last decade in connection with the suggested applications of such compounds.

The present review completes a series of surveys of new organosilicon materials [1-10] and is closely related to the previous surveys devoted to silyl derivatives of carbonic acid-organosilicon isocyanates [11] and ureas [12].

In terms of structural features, silyl derivatives of carbamic acid can be divided into three main types. In the first type of silylurethanes, the so called *O*-silylurethanes, we include compounds with the structural element $\equiv Si-O-C(O)-N=$. The second type incorporates *N*-silylurethanes, characterised by the fragment $\equiv Si-\underset{|}{N}-C(O)-O-$. Finally, we have silicon-containing urethanes with a carbon-based functional group in which the carbamic acid group is linked to the silicon atom via a hydrocarbon bridge. In the last case it is useful to introduce a subdivision of the silylurethanes into independent groups containing the bond sequences $\equiv Si-R-O-C(O)-N=$ and $\equiv Si-R-\underset{|}{N}-C(O)-$. Very many examples of each of these groups are now known.

II. COMPOUNDS WITH THE URETHANE GROUP AT THE SILICON ATOM

There are 12 theoretically possible structures of this type:

$R_3SiOC(O)NH_2$ (I);	$R_3SiOC(O)NHSiR_3$ (II);	$R_3SiOC(O)N(SiR_3)_2$	(III);
$R_3SiOC(O)NHR$ (IV);	$R_3SiOC(O)N(R)SiR_3$ (V)	$R_3SiOC(O)NR_2$	(VI)
$R_3SiNHC(O)OH$ (VII)	$R_3SiN(R)C(O)OH$ (VIII)	$(R_3Si)_2NC(O)OH$	(IX)
$R_3SiNHC(O)OR$ (X)	$R_3SiN(R)C(O)OR$ (XI)	$(R_2Si)_2NC(O)OR$	(XII)

but only nine are actually known: (I)-(VI) and (X)-(XII). Incidentally, the carbamic acids (VII)-(IX) can hardly exist in a free state, since, owing to the ease of the silyl-proton exchange, they must be immediately converted into the *O*-silyl derivatives (I)-(VII).

1. METHOD OF SYNTHESIS

N-Silylurethanes

N-Monosilyl-substituted carbamic acid esters were obtained for the first time in 1959 [13,14] by the silylation reaction

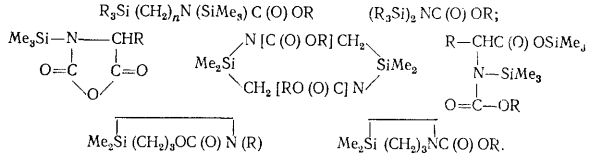
$$Q-NHSiMe_3 + ROC(O)NH_2 \rightarrow ROC(O)NHSiMe_3 + Q-NH_2;$$
$$Q=Alk,\ Ar,\ AlkC(O),\ ArC(O).$$

The silylation of the urethane $EtOC(O)NH_2$ by chlorotriorganylsilanes in the absence of acceptors for the HCl released apparently does not occur and the authors claim concerning the possibility of the conversion of the resulting *N*-silylurethanes with boiling water or alkali into the water-soluble acids $R_3SiNHC(O)OH$ is clearly erroneous, since no account is taken of the susceptibility of the N-Si bond to hydrolysis and the instability of free carbamic acid [15].

The interaction of urethane with $SiCl_4$ leads to the formation of the complex $SiCl_4.6CO(NH_2)_2$ (Wannagat et al. [16]), tentatively via the following mechanism:

$$2\,EtOC(O)NH_2 \rightarrow NH_2C(O)NH_2 + CO(OEt)_2;$$
$$SiCl_4 + 6CO(NH_2)_2 \rightarrow SiCl_4 \cdot 6\,CO(NH_2)_2;$$
$$SiCl_4 + 4CO(OEt)_2 \rightarrow Si(OEt)_4 + 4\,EtCl + CO_2.$$

Subsequently, when Me_3SiCl or $Me_3SiCl/HN(SiMe_3)_2$ were used as the silylating systems in the presence of organic bases and the reaction was carried out in aprotic organic solvents, *N*-silylurethanes became readily available. Numerous *N*-silyl derivatives of both linear and cyclic urethanes were obtained by this procedure [17-34]:



The expected urethane could not be isolated after the reaction between Ph_3SiCl and $NaNHC(O)OEt$, since its β-decomposition resulted in the formation of Ph_3SiNCO in 48% yield [35]:

$$Ph_3SiNHC(O)OEt \rightarrow Ph_3SiNCO + EtOH.$$

N-Silylurethanes have been synthesised in high yields by the reactions of alkylbis(trimethylsilyl)amines and alkyl chloroformates[27]:

$$RN(SiMe_3)_2 + ROC(O)Cl \rightarrow RN(SiMe_3)C(O)OR.$$

The reaction of chloroformates with hexamethyldisilazane (HMDS) and $R'NHSiR_3$, which proceeds preferentially via the Si–N bond rather than N–H, is of limited importance[36,37]:

$$(Me_3Si)_2NH + ROC(O)Cl \rightarrow Me_3SiNHC(O)OR + Me_3SiCl$$
$$R'NHSiMe_3 + ROC(O)Cl \rightarrow R'NHC(O)OR + Me_3SiCl.$$

The attempt to synthesise *N*-silylurethanes via the reactions of isocyanatosilanes with alcohols[11,26,35-44] and silanols[45-51] was unsuccessful owing to the ease of the alcoholysis of the N–Si bond and the inertness of silanols. The reaction with alcohols can be represented by the following mechanisms of which the second is to be preferred:

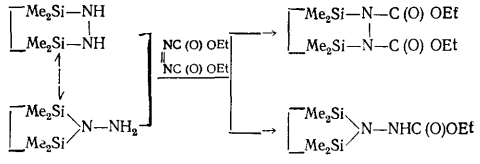
$$R_3SiNCO + R'OH \begin{cases} \rightarrow R_3SiOR' + HNCO \xrightarrow{R'OH} R'OC(O)NH_2 \\ \rightarrow R_3SiNHC(O)OR' \xrightarrow{R'OH} R_3SiOR' + R'OC(O)NH_2. \end{cases}$$

An increase in the size and branching of the groups in both the silane and the alcohol leads to a fall of the rate of alcoholysis[35,39] and Ph_3SiNCO does not change at all in boiling benzene in the presence of alcohol[35].

N-silyl-substituted esters of carbazic acids, which have been obtained from mercury-containing reagents[52-54], constitute a group of *N*-silylurethanes having the same structure:

$$EtOC(O)-N=N-C(O)OEt + Me_3Si-Hg-SiMe_3 \xrightarrow[M=Si,Ge]{-10^\circ} EtO-C(O)-N(SiMe_3)-N=N-C(O)-N(MMe_3)-OEt \quad (95\%).$$

They have also been obtained on the basis of equilibrium mixtures of tautomeric froms of disilyl-substituted hydrazines[55], for example:



Silylurethanes of the type $ROC(O)N(SiR'_3)_2$ are not formed by the above reactions. They have been synthesised by the reaction of $NaN(SiMe_3)_2$ with alkyl chloroformates[56] and, by analogy with bis(trimethylsilyl)amides of carboxylic acid, the imide structure (XIII) has been attributed to them:

$$ROC(O)Cl \xrightarrow[-NaCl]{NaN(SiMe_3)_2} ROC(O)N(SiMe_3)_2 \longleftrightarrow ROC(=NSiMe_3)OSiMe_3 . \quad (XIII)$$

When these compounds were hydrolysed with an equimolar amount of water, *N*-monosilylurethanes were obtained:

$$2ROC(=NSiMe_3)OSiMe_3 \xrightarrow{H_2O} 2ROC(O)NHSiMe_3 + Me_3SiOSiMe_3 .$$

O-Silylurethanes

The principal method for the synthesis of these compounds is carboxylation of aminosilanes[57-75]:

$$(R'R''N)_nSiR'''_{4-n} \xrightarrow[n=1\div4]{n\,CO_2} [R'R''NC(O)O-]_nSiR'''_{4-n};$$
$$R', R''=H, Alk, AlkO, Ar;\ R'''=Alk, Ar ,$$

which proceeds via an ionic-chain mechanism[62,63,70-73] and as a rule leads to the formation of the desired product in quantitative yield.

Compounds with a reduced basicity constitute exceptions to the general series of aminosilanes[60,61,69,73,76,77]: $MeN(SiH_3)_2$, $HN(SiMe_3)_2$†, $AlkN(SiMe_3)_2$, $AlkN(SiMe_2H)_2$, $PhNHSiMe_3$, $MeC(O)NHSiMe_3$, and $MeC(O)N(SiMe_3)_2$. Incidentally under severe conditions the following reaction takes place[69]:

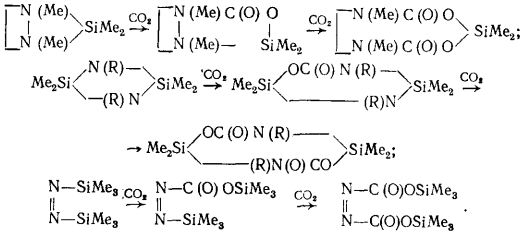
$$RN(SiMe_3)_2 \xrightarrow[500^\circ]{CO_2} [R-N(SiMe_3)C(O)OSiMe_3] \rightarrow RNCO + (Me_3Si)_2O.$$

However, when a mixture of a weakly basic amine and the silylating agent is carboxylated, it is nevertheless possible to obtain the corresponding *O*-silylurethanes, since in this case the species silylated is the intermediate carbamic acid in which the hydrogen atom is dissociated to an incomparably greater extent[73]. For example:

$$PhNH_2 + CO_2 \rightarrow PhNHC(O)OH \xrightarrow{H-N(SiMe_3)_2} PhNHC(O)OSiMe_3.$$

Urethanes are then formed rapidly and in high yields.

In many instances carboxylation of compounds with several Si–N bonds proceeds in steps and leads to adducts with both one and two CO_2 molecules[66,74,78-80]:



Aminoacids containing silicon-substituted carbamic acid groups are obtained with the aid of a wide variety of silylating agents[20,81-87]: Me_3SiCl/NEt_3, $HN(SiMe_3)_2$, organosilylcarbonates, etc. For example:

$$\text{L-tyrosine} + Me_3SiOC(O)OSiEt_3 \xrightarrow{\sim100^\circ} 4\text{-}Me_3SiOC_6H_4CH_2CH(COOSiMe_3)NC(SiMe_3)(O)OSiMe_3.$$

O-Silylurethanes can also be obtained by the silylation of carbamic acids or their salts by the usual procedures[34,64,66,85,87]:

$$R_2NC(O)OH + Me_3SiCl + R_3N \rightarrow R_2NC(O)OSiMe_3 + R_3N \cdot HCl;$$
$$H_2NC(O)ONH_4 + Me_3SiCl \rightarrow H_2NC(O)OSiMe_3 + Me_3SiNHC(O)OSiMe_3.$$

We believe that the reaction of silylated alkali metal amides with CO_2 followed by the reaction of the intermediate sodium salts, for example of *NO*-disilylated carbamic acids, with chlorosilanes[88-93] may become a convenient method for the synthesis of such compounds:

$$(Me_3Si)_2NNa \xrightarrow{CO_2} (Me_3Si)_2NC(O)ONa \xrightarrow{Me_3SiCl} (Me_3Si)_2NC(O)OSiMe_3 .$$

This view is supported by the successful reaction with the lithium salt of carbazic acid[66]:

$$(Me_3Si)_2N-N(SiMe_3)Li \xrightarrow{CO_2} (Me_3Si)_2N-N(SiMe_3)C(O)OLi \xrightarrow{Me_3SiCl} (Me_3Si)_2N-N(SiMe_3)-C(O)OSiMe_3$$

In order to obtain *O*silylurethanes, the interaction of silanols with organic and organosilicon isocyanates has been investigated and it has been shown that Ph_3SiOH and $Ph_2Si(OH)_2$ do not interact with Me_3SiNCO owing to steric hindrance and the reduced nucleophilic properties of the nitrogen atom in isocyanatosilane[49,94]. On the other hand, it has been established that $Me_3Si(NCO)_2$ acts on $Ph_2Si(OH)_2$ as a dehydrating agent. The reaction of monofunctional

† It has been stated[64] that $Me_3SiNHC(O)OSiMe_3$ is formed in a negligible yield on carboxylation of HMDS in tetrahydrofuran.

organic isocyanates with silanediols and oligosiloxanes containing terminal hydroxyls proceeds similarly [49,94-98].

Even if organosilicon polyurethanes $[-OSiR_2OC(O).NHR'NHC(O)-]_n$ (OSPU) are formed in the polycondensation of dialkylsilanediols and polyalkylsiloxanediols with hexamethylene and tolylene diisocyanates, oligourethanes with terminal isocyanato-groups, and other similar prepolymers, their yields are insignificant[51,99-106] and the reaction results mainly in the evolution of CO_2 and water and the formation of organic polyureas and polysiloxanes‡:

$$HOSiR_2OH + OCN-R'-NCO \rightarrow [-NHC(O)NHR'-]_n + -[-SiR_2O]_n + CO_2.$$

It has been suggested that the reaction of ≡SiOH groups with PhNCO be used for the quantitative determination of OH groups in polyorganylsiloxanes [105]. Subsequently it proved possible to find conditions in which *O*-silylurethanes can be obtained from aromatic diisocyanates and trialkylsilanols [107-109]:

$$R_3SiOH + Q(NCO)_2 \rightarrow Q[NHC(O)OSiR_3]_2.$$

In this connection one should note that, since the reaction of silanols with isocyanates was carried out in most cases at high temperatures or in the presence of aluminium chloride [46,47,51,97,98,104-106,111-128], this may have been the reason why the reactions did not yield the corresponding polyurethanes, their decomposition products being formed instead: CO_2, H_2O, and mixtures of organic and organosilicon high-molecular-weight compounds. However, since such materials possess properties of practical value, some of them will be considered in Section V.

In conclusion we may note that the study of the sorption of BuNCO [129,130] and PhNCO [131] vapours by aerosil showed that two processes occur: physical sorption and chemisorption. The former is due to the hydrogen bonds formed between the isocyanate and the free silanol groups of the adsorbent, which probably creates conditions for the occurrence of a chemical reaction between the isocyanates and the hydroxy-groups with formation of urethane groups.

2. PHYSICAL PROPERTIES OF *N*- AND *O*-SILYL URETHANES

O-Silylurethanes

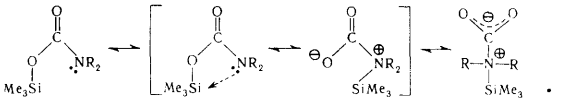
Urethanes of this type are high-boiling liquids or white crystalline, sometimes wax-like, substances which are more readily soluble in aprotic organic solvents [26,32,52,63-66,69,76,77,107-109,114]. Thixotropic properties are characteristic of organosilyltriscarbamates [58].

The combination of infrared, ultraviolet, and ^1H, ^{15}N, and ^{29}Si NMR data has shown that the N–Me groups in $Me_2NC(O)OSiH_3$ are equivalent, which is caused either by the rapid migration of the silyl group between the neighbouring oxygen atoms or by the ease of rotation about the C–N bond in consequence of its weak double bond character [60-62,76].

However, it was subsequently shown that trimethylsilyl esters of carbamic, thiocarbamic, and dithiocarbamic acids are characterised by different amounts of double bond character of the C–N linkage. For example, the study of the effect of the hindered internal rotation about the C–N bond in compounds described by the general formula $Me_3Si-Y-C(=X)-NR_2$, where X, Y = O, O, or S, S and R = Me or Et showed that it depends on temperature [132,133]. The experimental effective lifetimes of the rotational isomers made it possible to determine the activation energy and the free energy for the intramolecular rotation process and to compare them with the types of substituents surrounding the carbamic acid groups.

The infrared spectra of *O*-silylurethanes with an exocyclic carbamic acid group are characterised by absorption bands at 1020–1080, 1665–1690, and 3340–3350 cm^{-1}, which are due to the stretching vibrations of the Si–O–C, C=O, and N–H linkages [26,56,60-62,64,73,76,77]. One must note that the intensity of the Si–OC absorption band is very low.

We believe that the moderate solubility of *O*-silylurethanes, their high boiling and melting points despite their comparatively low molecular weights, the degenerate nature of the Si–O–C absorption band, and the specific features of the ^1H NMR spectra discussed above can be accounted for by their existence in equilibrium with the ylid form (XIVd):



(XIVa) (XIVb) (XIVc) (XIVd)

Under electron impact conditions, the molecules of the *O*-silylurethanes $Me_3SiOC(O)NH_2$ and $Me_3SiOC(O)NHSiMe_3$ each lose an electron and their mass spectra are characterised by molecular ion peaks [64].

N-Silylurethanes

Compounds of the type $R'N(SiR''_3)C(O)OR'''$, where $R' = Me$, Bz§, α-naphthyl, or $N(SiMe_3)_2$, $R'' = Me$ or Et, and $R''' = Me$, Et, or Ph are mobile liquids or low-melting crystalline solids, readily soluble in the majority of the usual aprotic organic solvents [23,26,36,66], with the exception of n-hexane, petroleum ether, and carbon tetrachloride [26,36]. Their infrared spectra agree well with the amide structure [26,36]. The molar refractions of *N*-silylurethanes correspond rigorously to the theoretical values [26].

NO-Disilylurethanes

Disilyl-substituted urethanes and carboxylic acid amides are very close analogues. The non-equivalence of the Me_3Si protons in the ^1H NMR spectra at low temperatures is characteristic of the latter compounds, disappearing when the temperature is raised to a particular value in each specific case. On this basis and also on the basis of infrared spectroscopic data and certain chemical reactions, the structure of *N*-trimethylsilyl-*O*-trimethylsilyliminoesters (XVb) with rapid intramolecular two-centre exchange of the partially ionically bound Me_3Si groups between the N and O atoms in (XVb) at elevated temperatures, rather than the structure of *NN*-bis(trimethylsilyl)-acylamides (XVa), was attributed to these compounds [56,134-138].

$$\underset{\text{(XVa)}}{R-C(O)N(SiMe_3)_2} \rightleftarrows \underset{\text{(XVb)}}{R-C(=NSiMe_3)OSiMe_3}.$$

Depending on the nature of the substituents linked to the silylamide group, the rate of migration of the Me_3Si group varies, which many investigators [134,138] believe to be a manifestation of the different degrees of hindrance of the

‡ Aniline, $Ph_3SiOSiPh_3$, symmetrical diphenylurea, and unidentified silicon-containing polyurethanes have been isolated after the reaction of Ph_3SiOOH and PhNCO. [110]

§ Bz = benzyl.

intramolecular rotation about the C–N bond. On passing from the disilyl amides $RC(=NSiMe_3)OSiMe_3$ to the disilylurethanes $ROC(=NSiMe_3)OSiMe_3$, the rate of exchange of the silyl groups increases and remains high even at low temperatures[56], while the $SiMe_3$ group is revealed by a singlet in the ^1H NMR spectrum.

3. CHEMICAL PROPERTIES OF *N*- AND *O*-SILYLURETHANES

O-Silylurethanes

O-Silylurethanes monoalkyl(aryl)-substituted at the nitrogen atom are extremely sensitive to hydrolysis, which proceeds via the formation of unstable carbamic acids, decomposing into CO_2 and amines[57-59,65,70,72,106-109].

The reactions with alcohols lead to the formation of CO_2, amines, and orthosilicate esters[108]. The authors suggest that hydrolysis (initially by traces of water in the alcohol), leading to the formation of trialkylsilanols, amines, and CO_2, takes place in the first stage. The trialkylsilanols then react with alcohols to form the corresponding orthosilicate esters and water[108]. However, we believe that a more convincing hypothesis is, for example, that the first stage involves the familiar decarboxylation reaction of urethanes[63,65,69,77] with subsequent alcoholysis of the resulting aminosilane:

$$R'(NHCOSiMe_3)_2 \xrightarrow[-CO_2]{t^\circ} R'(NHSiMe_3)_2 \xrightarrow{R''OH} R'(NH_2)_2 + Me_3SiOR''.$$

This conclusion is also confirmed by the finding that urethanes of the type $R_2NC(O)OSiR'_3$, which are no less susceptible to hydrolysis than those discussed above but which do not undergo decarboxylation, fail altogether to react with alcohols.

When the urethanes $RNHC(O)OSiMe_3$ are heated to 100–130°C, they undergo complete and irreversible decomposition to the corresponding disiloxanes and symmetrical ureas[69,77]. Pyrolysis in the presence of reactive chlorosilanes, for example $SiCl_4$ or $RSiCl_3$, alters the nature of the side reactions and the final products are an organic isocyanate, HCl, Me_3SiCl, and chlorosiloxanes[69,77]:

$$RNHC(O)OSiMe_3 + SiCl_4 \rightarrow RNHC(O)OSiCl_3 + Me_3SiCl;$$

$$RNHC(O)OSiCl_3 \rightarrow RNCO + [HOSiCl_3] \text{ etc.}$$

It has been noted that the use of other chlorosilanes (Me_2SiCl_2, Ph_2SiCl_2) is less effective, since decarboxylation of *O*-silylurethanes is observed in this case.

The formation of isocyanates proceeds satisfactorily in the presence of $SOCl_2$ and PCl_5.

When urethanes of the type $RR'NC(O)OSiMe_3$ were treated with $COCl_2$, $SOCl_2$, PBr_3,[66,139] and PCl_5,[140] the corresponding carbamoyl chlorides were obtained. It is noteworthy that, when the molecule contains both *N*- and *C*-siloxycarbonyl groups, the carbamic acid group reacts first[66,83,139], for example:

$$Me_3SiOC(O)N(R)(CHR')_nC(O)OSiMe_3 \xrightarrow[-Me_3SiX]{+YX_2} \rightarrow XC(O)N(R)(CHR')_nC(O)OSiMe_3;$$

R=H, Alk, $SiMe_3$; R'=H, Alk; X=Cl, Br;

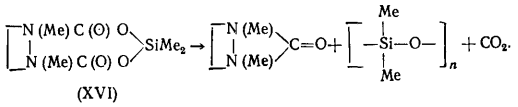
Y=>SO, >CO, >PBr, >PCl_3; n=1,2.

Apart from the thermally initiated decarboxylation noted above[63,65,69], the possibility of the disproportionation reaction has been demonstrated[64] for $Me_3SiOC(O)NH_2$:

$$2\,Me_3SiOC(O)NH_2 \rightarrow Me_3SiOC(O)NHSiMe_3 + [H_2NC(O)OH];$$

$$[H_2NC(O)OH] \rightarrow NH_2 + CO_2.$$

The cyclic *O*-silylurethane (XVI) is formed most readily when 1,1,2,5-tetramethyl-1-silaimidazolidine is treated with CO_2, being subsequently converted into polydimethylsiloxane, CO_2, and the corresponding imidazolidinone, probably via the following mechanism:



(XVI)

N-Silylurethanes

Urethanes of the type $MeN(SiMe_3)C(O)OR$, where R = Me or Et, are known not to interact with keten, but they do react with triethylsilylacetyl chloride to form $Et_3SiCH_2C(O).N(Me)C(O)OR$ in moderate yields[141].

N-Monosilyl-substituted amidals, which are at the same *N*-silylurethanes, undergo a symmetrisation reaction on heating and are then converted via β-decomposition into methylene diisocyanate[27,142]:

$$2\,CH_2[NHC(O)OR]N(SiMe_3)C(O)OR \rightarrow CH_2[N(SiMe_3)C(O)OR]_2 \rightarrow OCN{-}CH_2{-}NCO.$$

Other reactions of *N*-silylurethanes, for example *trans*-silylation and β-decomposition, are discussed in Section III (Subsections 3 and 4 respectively).

III. ORGANOSILICON URETHANES CONTAINING CARBON-BASED FUNCTIONAL GROUPS

1. METHODS OF SYNTHESIS

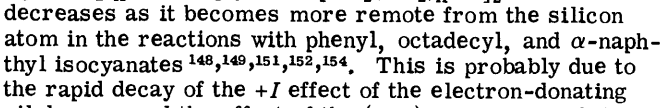
O-Silylorganyl Derivatives of Carbamic Acid

The reactions of organosilicon alcohols, glycols, and phenols (in which the functional groups are linked to carbon atoms) with isocyanates constitute a general method for the synthesis of *O*-silylorganylurethanes. For example, monohydric organosilicon alcohols[143-152] and phenols[153] readily give rise to the corresponding urethanes on reaction with both aliphatic and aromatic isocyanates:

$$R_3Si{-}Q{-}OH + R'NCO \rightarrow R_3Si{-}Q{-}OC(O)NHR' \quad (Q = \text{alkylene or arylene}).$$

It has been established that the reactivity of the hydroxy-group in homologous series of the alcohols $R_3Si(CH_2)_nOH$ and glycols $O[SiR_2(CH_2)_nOH]_2$ with n = 1–3 decreases as it becomes more remote from the silicon atom in the reactions with phenyl, octadecyl, and α-naphthyl isocyanates[148,149,151,152,154]. This is probably due to the rapid decay of the +*I* effect of the electron-donating silyl group and the effect of the (σ–*p*) conjugation of the Si–C bonds with the lone electron pair of the oxygen atom.

Polymeric urethanes have been obtained from the above glycols and organic diisocyanates, for example, hexamethylene (HMDI), *p*-phenylene (*p*-PDI), 1,5-naphthylene (1.5-NDI), tolylene (TDI), *pp'*-diphenylcyclohexyl, and *pp'*-diphenylmethylene diisocyanates[154-176]:



Polyurethanes with a high silicon content (compounds (XVII) and XVIII)] are formed from oligosiloxanes containing hydroxyalkyl groups at the ends of the siloxane chain[158, 160,165,167,169,171,173,177-181] or in the side groups surrounding the chain[159,161-165,182]:

$$\underset{\text{(XVII)}}{HO(CH_2)_nSi(R_2)[OSiR_2-]_m-(CH_2)_nOH} \quad \underset{\text{(XVIII)}}{-[-OSi(R_2)(CH_2)_nOH-]_k-}.$$

Treatment of the products (XVII) and (XVIII) with monoisocyanates leads to oligosiloxanes modified by urethane groups[182]. Oligourethanes with terminal OH or OCN groups have been obtained by combining the glycols (XVII) with silicon-containing diisocyanates having carbon-based functional groups[175,183].

Apart from polyurethanes with an oxygen atom between silicon atoms, products with methylene, polysilamethylene, and ferrocenyl bridges or altogether without any bridges are also known[160,169,171,179].

More complex compositions are produced when the above glycols are initially converted by standard procedures into oligoesters and are then cross-linked by diisocyanates or the structures are modified by a polyisocyanate adduct containing biuret groups[157,168,174].

The synthesis of *O*-silylorganylurethanes by the aminolysis of organosilicon chloroformates[2,26,31,184-187] is also a general procedure. Condensation of bischloroformates of the disiloxane series with organic di- and poly-amines leads to the corresponding polyurethanes[2,151,188-191]:

$$k\mathrm{O}\left[\begin{array}{c}R\\|\\-Si-R'-OC(O)Cl-\\|\\R\end{array}\right]_2 + kQ(NHR'')_2 \rightarrow$$

$$\rightarrow \left[-OC(O)R'\overset{R\ R}{\underset{R\ R}{Si}}OSiR'OC(O)N(R'')QN(R'')C(O)-\right]_k.$$

Instead if diamines, hydrazines, dihydrazines, piperazine, and polyamines of the general type $H(R)N[-(CH_2)_n.N(R)-]_mH$, where R = M, $n = 2$ or 3, and $m = 1$ or 2, have also been used.

When the above starting compounds are replaced by their $\alpha\omega$-bis(trimethylsilyl) derivatives, the polycondensation is significantly simplified, since Me_3SiCl formed in the reaction is inert and can be readily removed[2,190,192]:

$$k\mathrm{Me_3Si}-\underset{R}{N}-[-(CH_2)_n\underset{R}{N}-]_m-SiMe_3+k\mathrm{O}\left[\begin{array}{c}Me\\|\\-Si-R'OC(O)Cl\\|\\Me\end{array}\right]_2 \rightarrow$$

$$\rightarrow \left[\begin{array}{c}O\quad Me\ Me\quad O\qquad\qquad O\\ \|\quad\ |\ \ |\quad\ \|\qquad\qquad \|\\ OCR'-SiOSi-R'OCN-[-(CH_2)_nN-]_m-C-\\ |\quad\ |\quad\ |\qquad\qquad |\end{array}\right]_k -.$$

The reactions involving the aminolysis of organosilicon carbonates with carbon-based functional groups are of preparative value for the synthesis of *O*-silylorganylurethanes[193-198]:

$$\mathrm{RMe}_n\mathrm{Si}-[-(CH_2)_mOC(O)OPh]_{3-n}\xrightarrow{NH_3}\mathrm{RMe}_n\mathrm{Si}-[-(CH_2)_mOC(O)NH_2]_{3-n},$$

as well as the reactions of silicon-containing alcohols with alkali metal cyanates in CF_3COOH [26,198,199]:

$$\equiv Si(CH_2)_nOH + KOCN \xrightarrow[n=1\div3]{CF_3COOH} \equiv Si(CH_2)_nOC(O)NH_2.$$

The hydrosilylation of *O*-alkenylurethanes, whereby it is possible to obtain urethanes with different numbers of functional substituents at the silicon atom[26,31,200-202], constitutes an interesting addition to the above procedures, for example:

$$RR'NC(O)OCH_2CH=CH_2+HSiR''_nX_{3-n}\xrightarrow[n=1\div3]{X=Cl,OR} RR'NC(O)O(CH_2)_3SiR''_nX_{3-n}.$$

N-Silylorganylcarbamic Acid Derivatives

The reaction of organosilicon isocyanates containing carbon-based functional groups with alcohols¶ leads to urethanes with the silicon atom in the imide component of the molecule[26,178,183,203-211]:

$$R_3Si(CH_2)_nNCO + R'OH \xrightarrow{n\geqslant1} R_3Si(CH_2)_nNHC(O)OR'.$$

A modification of this method involves the interaction of halogenoalkylsilanes with alkali metal cyanates and the alcohol in molar aprotic solvents in the presence of $[(Alk)_4N]I$ as the catalyst[26,184,198,202,212,214], since organosilicon isocyanates are intermediates in this reaction:

$$(RO)_kR'_{3-k}Si(C_6H_4)_l(CH_2)_mX \xrightarrow[\text{solvent catalyst}]{MOCN,\ R''OH} \rightarrow$$

$$\rightarrow (RO)_kR'_{3-k}Si(C_6H_4)(CH_2)_mNHC(O)R'';$$

R, R' = Alk, Ar; M = K, Na; X = Cl, Br; $k = 1 \div 3$; $l = 0, 1$; $m = 1 \div 3$.

The reactivity of bromoalkylsilanes is higher than that of the chloro-derivatives and among the latter α-chloroalkylsilanes are the most reactive. On the other hand, the reactivity of the corresponding silyl isocyanates falls as the silyl and isocyanato-groups approach one another. Indeed, it has been shown in a number of investigations[26,178,183,203,205,207-210,213,215-217] that the reactivities of $(EtO)_3Si(CH_2)_3NCO$, $Et_3Si(CH_2)_3NCO$, and organic aliphatic isocyanates are comparable and approximately 20 times higher than that of Et_3SiCH_2NCO. The side products in the above reaction are organosilicon ureas and dimers (uretidinediones) and trimers (isocyanourates) of organosilicon isocyanates[26,212,213].

Polyurethanes with a silicon atom in the ester and amide components of the macromolecule simultaneously have been obtained by the condensation of silicon-containing diisocyanates and organosilicon glycols[178,183,208].

The interaction of alkyl(aryl)aminoalkylsilanes with organic chloroformates also leads to *N*-silylorganourethanes[201,218-220]:

$$\equiv Si(RNHR')_m \xrightarrow[m\geqslant1]{R''OC(O)Cl} \equiv Si[RN(R')C(O)OR'']_m,$$

but this method of synthesis holds out little promise, since half of the aminosilanes is consumed in binding HCl.

A modification of this reaction involving the treatment of *N*-silyl-substituted alkyl(aryl)aminoalkylsilanes with chloroformates is more important[2,27,67]:

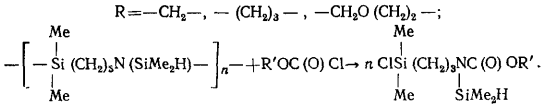
$$R_3SiCH_2N(SiMe_3)_2 + R'OC(O)Cl \rightarrow R_3SiCH_2NC(O)OR' + Me_3SiCl;$$

$$k\mathrm{O}\left[\begin{array}{c}Me\\|\\-Si-R-OC(O)Cl\\|\\Me\end{array}\right]_2 + kR'N-[-(CH_2)_nN-]_mSiMe_3 \xrightarrow[n=2,3]{m=1,2;}$$

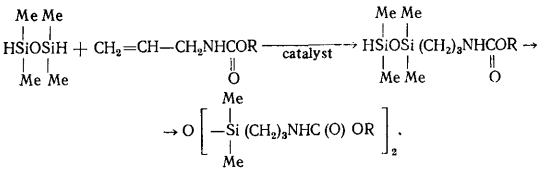
$$\rightarrow -\left\{\begin{array}{c}O\quad Me\ Me\quad O\\ \|\quad\ |\ \ |\quad\ \|\\ -CO-R-SiOSi-R-O-C-N-[-(CH_2)_nN-]_m-\\ |\quad\ |\qquad |\qquad\ |\end{array}\right\}_k -;$$

¶ Organic peroxides react with isocyanatoalkylsilanes similarly to alcohols[217]

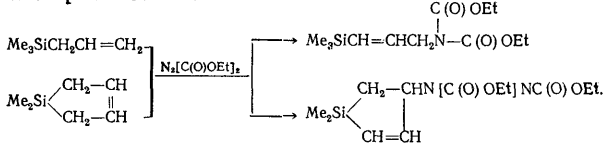
$$(MeO)_3Si(CH_2)_3NCO + HOOCMe_2Ph \xrightarrow[\text{catalyst}]{80^\circ} (MeO)_3Si(CH_2)_3NHCOOCMe_2Ph.$$



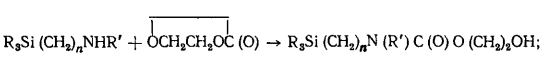
The hydrosilylation reaction, the use of which in the synthesis of *N*-silylorganylurethanes makes it possible to obtain monomeric, oligomeric, and polymeric products with partial or complete blocking of the Si–H bonds by *N*-alkenylurethanes [26,202,221], is of independent importance, for example:



The interaction of alkenylsilanes with azodiformic acid ester is accompanied by the migration of the double bond of the silane and leads to the formation of a mixture of addition products [222]:

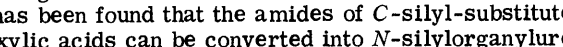


Silicon-containing glycol carbamates are obtained by the aminolysis of alkylene carbonates by alkyl(aryl)amino-alkylsilanes [223,224]:



The reactivity of γ-amines ($n = 3$) is higher in this reaction than that of α-amines ($n = 1$) and $(Me_3Si)_2NH$ does not undergo this reaction at all.

It has been found that the amides of *C*-silyl-substituted carboxylic acids can be converted into *N*-silylorganylurethanes with retention of the Si–C bonds [225-227]:



2. PHYSICAL PROPERTIES OF SYLYLORGANYLURETHANES

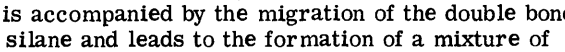
Organosilicon urethanes with carbon-based functional groups are colourless, transparent, mobile, and readily distilled liquids, which have been as a rule characterised by distinct melting points, refractive indices n_D^{20}, densities d_4^{20}, molar refractions MR_D, and infrared and ^1H NMR spectra [2,26,27].

The first amide band in the infrared spectra is in the range 1695–1733 cm^{-1}, as for other organic urethanes [25,26,228], while the second amide band is located in the wider range 1500–1625 cm^{-1}. The stretching vibrations of the free N–H group are manifested by shoulders of low and moderate intensity (3410–3450 cm^{-1}) on the more intense absorption band at 3328–3350 cm^{-1} corresponding to associated groups [25,26]. It is noteworthy that vibrations of the first type due to this group are characteristic of α-substituted urethanes alone. On passing from urethanes with an N–H group to N–$SiMe_3$ derivatives, the second amide band vanishes, but an intense absorption appears in the form of two bands at 1348 and 1321 cm^{-1} and there is a simultaneous increase in absorption intensity at 1400–1410 and 1440–1450 cm^{-1}. [25,26]

The ^1H NMR spectra of the urethanes $Me_n(RO)_{3-n}\cdot Si(CH_2)_mNHC(O)OR$, where R = Alk, $n = 0$ or 3, show the signal of the N–CH_2 groups split into two independent doublets, which can be explained (by analogy with dimethylformamide) by the double bond character of the linkage between the N and –C(=O)– atoms and the existence of these compounds in the *cis*- and *trans*-forms [26].

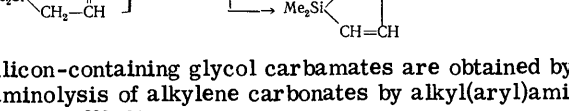
3. CHEMICAL PROPERTIES OF SILYLORGANYLURETHANES

Both *N*- and *O*-silylorganylurethanes with halogeno- or alkoxy-groups at the silicon atom are readily hydrolysed to the corresponding siloxanes [26,31,202]:

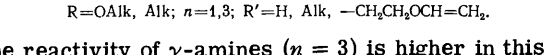


When acted upon by high-boiling alcohols, they undergo the transesterification reaction [223,224]:

Depending on the conditions and the structure of the initial silylorganylurethane, the hydrolysis may involve either the carbamic acid group or the Si–C bond with formation of aminoalkyl(aryl)silanes or desilylation products [209,225,227]:



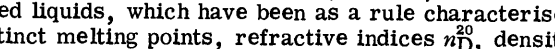
The reactions of α- or γ-silylurethanes containing N–H and Si–OAlk groups with $SOCl_2$ proceed only via the Si–O bond [26-28,31,184,228]:



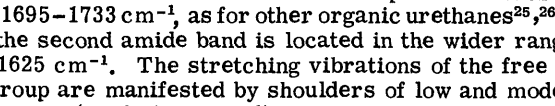
Disiloxanes with two and four urethane groups have been obtained by the Sommer reaction [196]:

N-Silylorganylurethanes are nitrosated in accordance with the classical mechanism [220,229]:

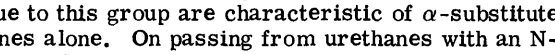
On silylation with the Me_3SiCl/NEt_3 mixture, they are converted into disilylurethanes [26,27]:



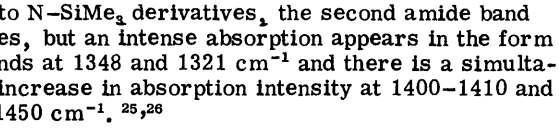
In many instances the silylation is intramolecular [11,26-28,31,67,184,230,231]:



The formation of 2,5-disilylpiperazine derivatives is an exception [27]:



N-Silylated organosilicon urethanes with carbon-based functional groups can undergo *trans*-silylation reactions [22,26-28,67,232,233]:



Since the thermolysis of *N*-silylurethanes, like that of other organosilicon urethanes, constitutes a new method for the synthesis of a wide variety of isocyanates and illustrates the theoretically important mechanism of β-decomposition in the ≡Si–N–C–X system of conjugated double bonds, data on this problem are reviewed in the next section.

4. THERMAL DECOMPOSITION OF ORGANOSILICON URETHANES

Sufficient data have now accumulated to reach definite conclusions concerning the factors controlling the β-decomposition in the ≡Si–N–C–X (X is an electronegative group) system of σ,σ conjugated bonds[11,12,26,28,31,151,184,230,234,235].

Like their purely organic analogues RNHC(O)OR, *N*-silylorganylurethanes decompose into isocyanates and alcohols on heating to 150–300°C, the decomposition taking place more readily the higher the acidity of the alcohol produced[26,145,186,194,201,218,219,234–238]:

$$R_3Si{-}Q{-}NHC(O)OR' \rightleftharpoons R_3Si{-}Q{-}NCO + R'OH.$$

The reaction is reversible and alcohol is removed from the reaction zone in order to drive it to the right. The reaction then obeys first-order kinetics[194,237].

N-Silylurethanes containing the Si–N–C(O)–OR system of conjugated bonds decompose irreversibly on heating into an isocyanate and an alkoxysilane[11,12,20–22,24–28,31,32,36,56,68,142,145,151,184,228,230,232,234–249]:

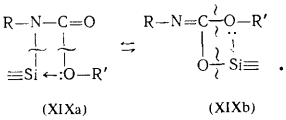
$$\equiv Si{-}\underset{\displaystyle R}{\underset{|}{N}}{-}C(O){-}OR' \rightarrow \equiv Si{-}OR' + R{-}N{=}C{=}O.$$

With the exception of the special instances discussed below[22,28,31,32,239,241–248], the reaction is irreversible, obeys first-order kinetics, and has $E_{act} = 22–30$ kcal mole^{-1}.

The pyrolysis is intramolecular, which follows from the analysis of the product obtained as a result of the pyrolysis of a mixture of different urethanes[25,27,28,31,240]:

$$\begin{array}{l} HMe_2SiN(All)C(O)OAll \\ + \\ Me_3SiN(CH_2SiMe_3)C(O)OMe \end{array} \xrightarrow{t} \begin{array}{l} \rightarrow HMe_2SiOAll + All{-}N{=}C{=}O \\ \rightarrow Me_3SiOMe + Me_3SiCH_2N{=}C{=}O. \end{array}$$

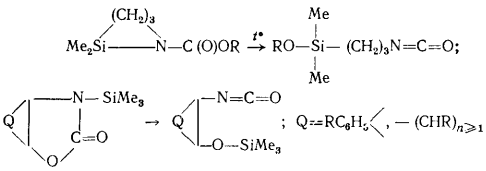
This finding suggests the intermediate formation of the following four-membered transition states involving the amide (XIXa) or imide (XIXb) forms of the *N*-silylurethane[25,26,28,31,230]:



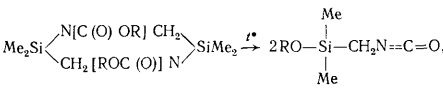
(XIXa) (XIXb)

However, according to the infrared spectra of *N*-silacyclourethanes[22] (the absence of the absorption due to the >C=N bonds at 1540–1640 cm^{-1}) and ^{1}H NMR (the singlet due to the Si–CH_3 protons), preference must be given to the amide form (XIXa). The strain in the four-membered transition complex does not rule out this mechanism, bearing in mind the possibility of the intense polarisation of the bonds involved in the electron redistribution[22,28,31,240]. This assumption is confirmed, for example, by the higher reactivity of the Si–N bond in the thermally less stable *N*-silylurethanes in relation to electrophilic agents of the type RC(O)Cl, RC(O)OC(O)R, PhNCO, [22,144], etc.

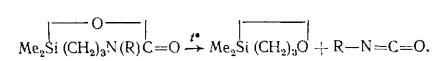
Depending on the *exo*- or *endo*-location of the ≡Si–N–C(O)–OR atomic group, silacyclourethanes form various β-decomposition products. For example, ring opening takes place in one instance[22,28,29,31,32,184,230,234,239]:



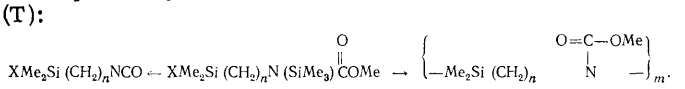
in an other the urethane decomposes into two isocyanate molecules[25,27,28,31,68,142,234]:



and in the third case, the ring contraction reaction takes place[26,28,31,184,230,234]:



The β-decomposition (D) of the urethanes (XX) is accompanied by the simultaneous *trans*-silylation reaction (T):



	m	*n*	X	Reaction, % D	T
a	2	1	Cl	0	100
b	2	1	EtO	13	87
c	1	3	EtO	70	30

Evidently the D/T ratio is influenced not only the nature of the substituents at the silicon atom but also by the relative positions of the silyl groups in the urethane molecule[27,28,31,184,232,247]. This is why the study of the kinetics of the β-decomposition of the urethanes $Me_n(MeO)_{3-n}Si(CH_2)_mN(SiMe_3)C(O)OR$ does not yield a direct answer to the question of the *C*-silyl group on the β-decomposition proper when *n* varies from 0 to 3.[24–26,184]

The influence of the substituents in the urethanes having the general formula $RN(SiMe_3)C(O)OR'$ on the temperature of the onset of appreciable decomposition is clearly illustrated by the Table below[21,22,25,26,28,29,31,56,68,184,230,250–254].

The influence of the substituents R and R′ in the urethanes $RN(SiMe_3)C(O)OR'$ on the temperature of the onset of appreciable decomposition (T_{decomp}).

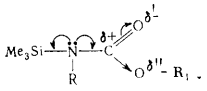
R	R′	T_{decomp}, °C	R	R′	T_{decomp}, °C
Alk	C_2H_5	170	Ph	C_6H_5	100
Alk	C_6H_5	110	Ph	$N=C(CH_3)_2$	60
Alk	C_6H_4Cl-*p*	60	Ph	C_6H_5	20
Alk	$C_6H_4NO_2$-*p*	0	Ph	$C(O)C_6H_5$	0
Alk	Cl	≪0	$SiMe_3$	$SiMe_3$	<20

The aliphatic oxa(thia)zolidinones $Me_3SiNC(X)OCH(R')C(R'')H$ (XXI) [a) R′ = R″ = H, X = O; b) R′ = R″ = H, X = S] are converted into isocyanates under more severe

conditions (>180°C) than the analogous oxa(thia)azolidine-2,5-diones $Me_3SiN-C(=X)O-C(=O)CHR$ (XXII) and the benzo-derivatives (XXIII) [c) R′ + R″ = C_6H_4; d) R′ + R″ = 5-MeC_6H_3; e) R′ + R″ = 5-ClC_6H_3; X = O throughout], corresponding to the oxa(thia)azolidinones (XXI). The latter compounds form isocyanates at 125–130°C, and the content of the β-decomposition product in the equilibrium mixture decreases in the sequence (XXIIIe) > (XXIIIc) > (XXIIId) and increases with rising temperature and also when it is removed from the reaction sphere[22]. On the other hand, compounds (XXIII) with X = O and R′ + R″ = 4-$NO_2C_6H_3$ (f) or 5-$NO_2C_6H_3$ (g) do not form isocyanates even at 165°C.[22,28,31,32] For comparison, we may note that *N*-(trimethylsilyl)benzothiazolidin-2-one is stable on heating to 260°C, while its very close analogues *N*-(trimethylsilyl)benzoxalidine-2-thione and 5-nitro-*N*-(trimethylsilyl)-benzoxazolidine-2-thione undergo β-decomposition even in the course of the introduction of silyl protecting groups into the heterocycles[22,239,242,244-246,255]. Furthermore, it is striking that in all cases thiazolidine derivatives show a small tendency towards isomerisation, while silylated oxazolidine-2-thiones rearrange irreversibly and quantitatively and *N*-(trimethylsilyl)oxazolidinones rearrange reversibly[22,239,242,244-246,255].

One may therefore conclude that the thermal stability of *N*-silylurethanes decreases when (a) the electronegativity of the RO group increases, (b) the *N*-alkyl group is replaced by an aromatic group, in particular by a group containing electronegative substituents, (c) on passing from aliphatic *N*-silacyclourethanes to benzo-derivatives, and finally (d) following the introduction of the thiocarbonyl group in place of the carbonyl group[21,22,24-29,31,32,56,68,77,91,142,184,230-234,239,242-256].

Indeed the introduction of an electronegative substituent lowers the basicity of the nitrogen atom as a result of which the amount of double bond character of its linkage with neighbouring Si and C atoms falls:

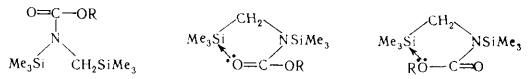


Therefore the β-decomposition reaction involves preferentially compounds containing σ,σ conjugated bond systems ≡Si–N–C(O)–OR′, i.e. in the amide form of the transition complex (XIXa) mentioned above and not in the corresponding imide form ≡Si–N=C–OR′ (XIXb).[26] Experiment confirmed this conclusion: the model compound MeC(=N–$SiMe_3$)OEt decomposes into MeCN and ethoxytrimethylsilane only above 250°C.[26]

In the light of the foregoing, the instability of $(Me_3Si)_2NC(O)OR$ (decomposition temperature of about 20°C) becomes understandable, since the degree of degeneracy of the basic properties of the nitrogen atom owing to the $(p-d)\pi$ interaction via two Si–N bonds is in this case still greater[56].

The analogous effect of two silyl groups in combination with the high electro-negativity of the NaO^- substituent is the cause of the easy β-decomposition of compounds of the type $(Me_3Si)_2NC(O)ONa$ even in the synthesis of bistrimethylsilylcarbodiimide[88-92].

Furthermore, since the Me_3Si group enhances the nucleophilic properties of the nitrogen atom in the α-position[87], it was to be expected that the thermal stability of the compounds $Me_3SiN(CH_2SiMe_3)C(O)OR$ will be higher than that of $Me_3SiN(Me)C(O)OR$, which, however, conflicts with experiment. The apparent inconsistency is probably a consequence of the superposition of the σ,σ conjugation effects in the ≡Si–C–N–C≡, ≡Si–C–N–Si≡, and ≡Si–N–C–OR bond systems or is a result of the transannular interaction of the C–$SiMe_3$ group with one of the oxygen atoms:



An appreciable decrease of the thermal stability of *N*-silylurethanes is observed not only after the interaction of aryl or silyl substituents at the nitrogen atom but also after the introduction of acyl groups. For example, the acylurethanes MeC(O)N($SiMe_3$)C(O)OMe and PhC(O)N.($SiMe_3$)C(O)OMe decompose readily at 85–100°C.[257]

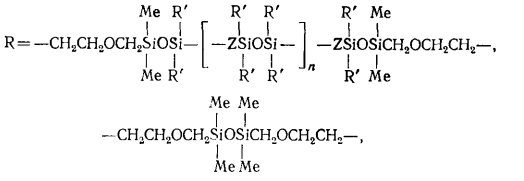
IV. OTHER TYPES OF SILYLURETHANES

This section surveys mainly the available information about systems in which the silicon atom and the carbamic acid fragment are separated by a bridge which does not consist of carbon atoms alone. We have divided the methods for the introduction of silicon into the polyurethane macromolecule into six independent groups†.

1. The polycondensation reactions of a wide variety of monoisocyanates with silicon-containing glycols lead to the synthesis of adducts with terminal urethane groups, for example[260-266]:

$$HO-R-OH + 2R'''NCO \rightarrow R'''NHC(O)O-R-OC(O)NHR''',$$

where



R′, R″, R‴ = Alk, Ar; Z = arylene or hydroxyarylene; *n* = 0 or 1.

The replacement of monoisocyanates by di- and polyisocyanates leads to polyurethanes with terminal isocyanato-groups capable of further structure formation[263,267-281]. Polyurethanes with a cross-linked structure are obtained when the structure-forming agent is a polyisocyanate having the biuret structure[275,282-286], as already noted above for organosilicon diols with purely carbon-based functional groups. In practice adducts of 2,4-TDI or 2,6-hexamethylene diisocyanate (2,6-HMDI) with tri-(hydroxymethyl)propane are most frequently used as the polyisocyanates and the glycol components consist of ester-alcohols of the series[263,274,275,287-289,302].

Similar products have been obtained from glycols with Si–OC bonds of the general type $R_nSi(OZOH)_{4-n}$ (XXIV) and $Q(SiMe_2OZOH)_2$ (XXV), where R = alkyl or aryl, Z = alkylene, arylene, hydroxyalkylene, or oligohydroxyalkylene, Q = arylene, hydroxyarylene, or oligosiloxane,

---

†Since studies on the utilisation of organosilicon compounds in industry and in the processing of polyurethanes (for example as surfactants, stabilisers, pore regulators, etc., i.e. in processes without the obligatory formation of chemical bonds with the polyurethane) are of great practical importance, they merit independent consideration. Certain data on this problem have been reviewed by Adamowski et al.[258] and Zwolinski et al.[259]

and $n = 1-4$.[66,67,113,261-265,274,282,286,290-307] By varying the reactant ratio, the polycondensation process can be arrested in many cases, at the stage involving the formation of the oligomer with terminal hydroxy- or isocyanato-groups, which are responsible for the hardening of prepolymers when suitable reagents are chosen.

2. The condensation reactions of polyethers, which do or do not contain urethane fragments but always have hydroxy-groups in side substituents or at the ends of the chain, with silanes or polysiloxanes containing hydroxy-, alkoxy-, acyloxy-, or amino-groups at the silicon atoms and subsequent condensation of the products with polyisocyanates make it possible to synthesise copolymers with a wide variety of compositions and structures[115,166,180,267,275,290,308-350].

The silicon content in polyurethanes is then regulated by the type and size of the siloxane blocks and their amount in the reaction mixture. In a typical instance of this method, the polysiloxane containing ≡SiOEt groups undergoes transesterification with poly(ethyleneglycol adipate) having terminal hydroxy-groups and is treated with TDI in the presence of a special plastisol composition. Structure formation in the copolymer is completed by heating the mixture at 150°C for 5 min.[322]

Sulphur-containing organosilicon glycols, for example $\alpha\omega$-bis-(β-hydroxyethylthiomethyl)polydimethylsiloxanes, behave in the polycondensation reactions like their oxygen analogues[272,351-353] and in the case of glycols based on diethanolamine, particularly bis-(β-hydroxyethylaminoethyl)dimethylsilane, both N–H and H–O bonds are involved in the reaction[354,355].

3. The hydrosilylation or catalytic dehydrocondensation reactions[222,223,348,356-373] involving polysiloxanes with ≡Si–H bonds and oligourethanes containing C=C and OH groups make it possible to obtain various block-copolymers. For this purpose, oligomers containing free OH or OCN groups are usually treated with the corresponding alkenyl isocyanate or an unsaturated alcohol with subsequent addition of the prepolymer to polysiloxanes with ≡Si–H bonds. Copolymers obtained from silicon-containing glycols or diisocyanates with carbon-based functional groups have similar structures. However, the first version of the synthesis is based on a more readily available starting material[2,26,99-103,368-370,374,375].

The method of synthesising oligourethanes by the reaction of alkyl(aryl)aminoalkylsilanes with chlorocarbonate esters is still less suitable owing to the difficulty of removing the HCl evolved, which causes side reactions[376,377].

Another variety of block-copolymers is obtained by the reaction of $\alpha\omega$-dihydroxy-derivatives of polyesters, polyester-amides, and poly(alkylene glycols) with di- and poly-isocyanates having different ratios of the functional groups ≡Si–H, OH, and OCN to form adducts. The synthesis can involve any of the above groups, for example the isocyanato- or silamethylidyne groups in the polysiloxane[352,355,378,379]:

$$Me_3SiO-[-SiHMeO-]_m-[-SiMeO-]_p-[-SiMe_2O-]_q-OSiMe_3$$
$$\qquad\qquad\qquad

other materials in order to make them hydrophobic, reduce their brittleness, impart to them crease resistance, make them electrically insulating, and improve other technical characteristics [13-15]. Organylsilyl tricarbamates $RSi[OC(O)NR'_2]_3$ have been suggested for the low-temperature hardening of organosilicon oligomers with terminal silanol groups [57-59,72].

Although the mode of the reactions of organic diisocyanates with silanediols and oligosiloxanes having terminal OH groups is not always clear, the polymeric products formed are capable of hardening on heating and of giving rise to a film which hardens spontaneously in air [120]; such compounds have a fairly high thermal stability and elasticity [121]. They have therefore been recommended for the preparation of fibres, plastics [104], and for other purposes [97,111,115,128]. In those cases where the principal mode of reaction involves the dehydrocondensation of silanediols [118,122,408], the polysiloxanes formed act as plasticisers on the polymeric ureas produced.

The products of the condensation of $\alpha\omega$-diisocyanatopolyurethanes and polysiloxanes with terminal hydroxy-groups impart to textiles antipilling properties and resistance to shrinking, improve physicomechanical properties, give rise to a pleasant feel, etc., and withstand frequent washing and dry-cleaning as well as prolonged action of light; they also make textiles elastic [117].

Powdered polyurethanes can be pressed into articles with satisfactory electrical insulating properties and high mechanical strength [51,106]. Silyl esters of *N*-alkyl(aryl)-carbamic acids are important intermediates in the synthesis of isocyanates by phosgene-free methods [69,73,77]. The products of the condensation of alcohols with $R_2Si(NCO)_2$ are used to stabilise poly(vinyl chloride). [41] Certain *N*-silylcarbamates exhibit anticholinesterase and insecticidal activities [86,409]. They are isolated in a pure form by a chromatographic procedure [18,19,30].

2. Compounds with Silyl and Urethane Groups Separated by a Bivalent Group

These are extremely numerous and have a wide variety of practical applications. We shall mention some of the most important of these.

Polyurethane film-forming compositions obtained by both cold and hot drying adhere to glass, wood, metals, plastics, and other constructional materials [158,159,162,163,166,183,217,273,287,288,290,292,294,306,307,311,313,316,334,344,352,356,363,373,390,405]. They have a very attractive outward appearance (smooth, transparent, and elastic or solid and lustrous films), are resistant to water, oil, petrol, corrosion, wear, and the atmosphere, their colours are fast, and their useful characteristics are retained under the conditions of high temperatures and humidities. These remarkable qualities have been used in the manufacture of decorative finishing materials [113,168,174,264,265,275,277-282,287-289,298-307,347,409-413].

Various polyurethane compositions are used to treat textile and leather articles in order to make them wear resistant and impart to them dirt-, water-, and oil-repellent properties [161,177,182,212,268,309,310,363,405]. It is important to note that, after treatment, fabrics, paper, and leather articles remain permeable to vapours and gases, are elastic, and are not sticky.

One-component oligopolyurethanes which undergo self-vulcanisation in air are used as cements, fillers, hermetically sealing compounds, gaskets, and shock absorbers in building, automobile, and avaiation industries, and as potting compounds which adhere to glass, wood, porcelain, metals, and plastics. The advantage of coatings based on them (apart from the unique combinations of different types of stability to external influences already mentioned in connection with fancy leather goods and decorative articles) consists also in their capacity to form remarkable gas-filtering and vapour permeable films which are used for encapsulation for the purpose of conservation and storage of specific materials [292,334,352,361,363,367,382-284,405].

In certain cases urethane–siloxane adducts are used as primers which improve the adhesion of polyurethanes to the support [260,271,362,376,377,414], as binders for glass and textile fibres [362], as surface-plasticising coatings [269,270], as electrically insulating articles [222,272,292,315,320-322,325-327,333,334,337,351,358,368,371,372], as sensitisers for heat-sensitive latexes [222,272,315,321,322,327-329,332,333,343,351,358,371,372,403,404,407], as antioxidant additives to anti-detonators [403,404], and as catalysts of the combustion of rocket fuels [348]. Silicon-containing stabilised liquid, semi-liquid, and elastic resins, rubbers, plastics, and other materials with prolonged resistance to water, heat, and fire with retention of geometrical dimensions are manufactured on their basis [59,115,165,183,323,330,331,335,336,342,344,354,355,360,362,378,379,396,415].

The wide variety of the physicochemical characteristics of polysiloxane–polyurethane materials gives rise to the possibility of using them as liquids with very low glass temperatures (down to −125 °C) [180,183,190,287,294,296,306,356] and in the form of corundum-filled and mould-hardened grinding discs or other types of abrasive devices [388,416].

Polyurethanes with a siloxane–hydroxyalkylene base can be used as liquid heat exchangers, emulsifiers, wetting agents, lubricants facilitating the removal of articles from moulds, for the formation of completely smooth surfaces of polymers, as well as other purposes [267,269,270,292,334,352,362]. Laminated products used as splinter-proof glass [317], in which the linking element is polyurethane based on an organic oligoisocyanate and an organosilicon polyfunctional alcohol, have been reported.

Compositions comprising silicon-containing products with organic polyurethane materials in which the individual components are not necessarily chemically combined but the formation of chemical linkages via residual functional groups is quite likely and even inevitable under certain conditions, have assumed considerable practical importance [150,161-134,237,259,269,290,308,311,323-327,329-333,338-340,342,345,346,358,364,365,371,372,396,401,406,407,412,416-517].

The siloxane component has become particularly important in the manufacture of polyurethane foam plastics [237,308,326,327,329,331,332,338,340,342,346,358,365,366,371,372,407,419,440-479]. It plays a versatile role which involves a decrease of the surface tension of the system, the emulsification of the reaction mixture (isocyanate–polyester–catalyst), the stabilisation of the foam before its hardening, and the regulation of the structure and size of the cells; at the same time it abolishes the inevitable imbalance between the functional groups of the starting materials without impairing the quality of the polyurethane foam plastic.

However, mechanical mixtures exhibit only a weak stabilising effect, probably owing to the insufficiency and random nature of the chemical linkages between the components of the reaction mixture, which in certain cases complicates the technology owing to the poor compatibility of the individual components and leads to polyurethane foam plastics having inhomogeneous compositions and variable quality [237,338,486,488,489].

Polyester–polysiloxane block-copolymers [237,308,326,327,329,331,332,338,340,342,346,358,365,366,371,372,407], which exhibit a

more pronounced stabilising effect, are more compatible. The overall favourable effect is greater the greater the uniformity of the alternation of polyester and polysiloxane blocks in the copolymer [340,485,489]. Under these conditions, the presence of ≡Si–OC groups in the macromolecule is less preferable compared to Si–C bonds [329,331,340,407,464,468,485]. Because of this and the difficulty of synthesising such copolymers, they have been replaced by polysiloxane compounds with free hydroxy-groups attached to carbon atoms [355,485-489], particularly those in which the hydroxyl-containing group is joined to silicon via the ≡Si–C linkage [355,487].

Nevertheless the degree of order among the component macromolecular units and the concentration of OH groups relative to the total number of functional groups of the polyester proved to be insufficient. The preparation of polysiloxane–polyurethane copolymers with rigorously alternating functional groups by the successive introduction into the reaction zone of the diisocyanate, the organic polyester, and the polysiloxane with OH (SH) groups attached to carbon atoms did not solve the problem completely either, since the resulting surface-active substances contained only random chemical linkages with the main polymeric mass.

The optimal version of this synthesis now provides for the use of organosilicon oligoisocyanates with carbon-based functional groups in a pure form or in combination with organic di- or poly-isocyanates. After such a substance is brought into contact with an organic polyester, a homogeneous, high-quality, self-stabilising system is produced. The use in the synthesis of organosilicon alcohols, glycols, isocyanates, etc. with carbon-based functional groups as part of the glycol or isocyanate components of the reaction mixture made it possible to obtain, as already described above to some extent, polyurethanes with an exceptionally favourable combination of technically useful characteristics [159,162,309,355,409,412,518-523].

Monomeric derivatives of carbamic acid are used as additives which improve the properties of polysiloxane lubricants for high-temperature high-speed bearings [492], as dispersing additives improving the thickening capacity of silica gel in the manufacture of greases [493], for the vulcanisation of silicone rubbers [27,494-496], and for other purposes [26,497-499].

The widely variable physiological activity of organosilicon urethanes is striking [81,86,153,166,178,193,195-198,204,362,386,399,402,409,524-527].

REFERENCES

1. G. Greber, J. prakt. Chem., 313, 461 (1971).
2. G. D. Khatuntsev, Candidate's Thesis, MKhP, Moscow, 1974.
3. I. Jones, Chemistry in Britain, 6, 251 (1970).
4. I. Jones, Report on Progress of Applied Chemistry, 53, 544 (1968).
5. C. L. Segak, "High-Temperature Polymers", M. Decker, Inc., New York, 1967.
6. B. K. Patnaik, J. Sci. Ind. Research, 27, 417 (1968).
7. K. E. Polmaunter, J. Elastoplastics, 2, No. 3, 165 (1970).
8. W. W. Wright and W. A. Lee, Progress in High Polymers, 2, 189 (1968).
9. G. Greber, J. prakt. Chem., 313, 461 (1971).
10. H. N. Kovacs and A. B. Dalman, Chem. Eng. News, 47, No. 37, 50 (1969).
11. V. P. Kozyukov, V. D. Sheludyakov, and V. F. Mironov, Uspekhi Khim., 42, 1451 (1973) [Russ. Chem. Rev., No. 8 (1973)].
12. V. P. Kozyukov, V. D. Sheludyakov, and V. F. Mironov, Uspekhi Khim., 44, 499 (1975) [Russ. Chem. Rev., No. 3 (1975)].
13. P. L. DeBenneville and M. J. Hurwitz, US P. 2 876 209 (1959); Chem. Abs., 53, 12 321 (1959).
14. P. L. DeBenneville and M. J. Hurwitz, US P. 2 906 756 (1959); Chem. Abs., 54, 5480 (1960).
15. G. Weissenberg, BRD P. 925 226 (1955); Chem. Abs., 52, 1645 (1958).
16. U. Wannagat, R. Schwarz, H. Voss, and K. G. Knauff, Z. anorg. Chem., 277, 73 (1954).
17. D. W. Keiser, US P. 2 697 720 (1954); Offic. Gaz., 689, No. 3 (1954).
18. L. Fishbein and W. L. Zielinski, J. Chromatog., 20, 9 (1965).
19. R. Nery, Analyst, 94, No. 1115, 130 (1969); Chem. Titles, No. 5, 114 (1969).
20. L. Birkofer, W. Knipprath, and A. Ritter, Angew. Chem., 70, 404 (1958).
21. G. Greber and H. R. Kricheldorf, Angew. Chem., Int. Ed. Engl., 7, 941 (1968).
22. H. R. Kricheldorf, Annalen, 772 (1973).
23. N. Ya. Derkach and N. P. Smetankina, Zhur. Obsch. Khim., 34, 3613 (1964).
24. V. D. Sheludyakov, F. N. Vishnevskii, E. S. Rodionov, G. D. Khatuntsev, and V. F. Mironov, Zhur. Obsch. Khim., 41, 1764 (1971).
25. F. N. Vishnevskii, Candidate's Thesis, MKhP, Moscow, 1972.
26. V. P Kozyukov, Candidate's Thesis, MKhP, Moscow, 1969.
27. E. S. Rodinov, Candidate's Thesis, MKhP, Moscow, 1973.
28. V. F. Mironov, V. D. Sheludyakov, and V. P. Kozyukov, Organometal. Chem. Syn., 1, 329 (1972).
29. G. Greber and H. R. Kricheldorf, "International Symposium on Organosilicon Chemistry, Prague", 1965, p. 83.
30. L. Fishbein and W. L. Zielinsky, J. Chromatog., 20, 19 (1965).
31. V. F. Mironov, Symposium, "Khimiya i Tekhnologiya Elementoorganicheskikh Soedinenii" (The Chemistry and Technology of Organic Derivatives of the Elements), NIITEKhIM, Moscow, 1972, p. 63.
32. V. P. Kozyukov and V. F. Mironov, Zhur. Obshch. Khim., 44, 553 (1974).
33. R. Nery and E. Boyland, J. Chem. Soc., C 346 (1966).
34. R. Bentley, C. C. Sweeley, M. Makita, and W. W. Wells, Biochem. Biophys. Res. Comm., 11, 14 (1963).
35. H. Gilman, B. Hafferth, H. W. Melvin, and G. Dunn, J. Amer. Chem. Soc., 72, 3045 (1950).
36. J. Pump and U. Wannagat, Monatsh., 93, 352 (1962); Chem. Abs., 57, 12 525 (1962).
37. E. A. V. Ebsworth and M. J. Mays, J. Chem. Soc., 4844 (1962).
38. J. F. O'Brien, "Chemical Reactions of Isocyanatosilanes", WADC Techn. Rept., 1957, p. 57–503.
39. J. Goubeau and D. Paulin, Chem. Ber., 93, 1111 (1960).
40. G. S. Forbs and H. H. Anderson, J. Amer. Chem. Soc., 69, 1241 (1947).
41. K. Thinius, Plaste u. Kautschuk, 12, 714 (1965).
42. H. H. Anderson, J. Amer. Chem. Soc., 72, 193 (1950).
43. G. S. Forbs and H. H. Anderson, J. Amer. Chem. Soc., 70, 1043 (1948).

44. H. H. Anderson, J. Amer. Chem. Soc., 72, 196 (1950).
45. J. M. Pollock, B. P. 920 517 (1963).
46. H. C. Fielding and J. M. Pollock, B. P. 923 581 (1963), 8H46.
47. H. C. Fielding and J. M. Pollock, B. P. 923 583 (1963).
48. J. Goubeau and E. Heubach, Chem. Ber., 93, 1117 (1960).
49. E. Heubach, Diss. Stutgart, 1958.
50. U. Wannagat and C. Krüger, Monatsh., 94, 63 (1963).
51. M. F. Shostakovskii, V. I. Kotrelev, D. A. Kochkin, S. P. Kalinina, and V. V. Borisenko, Zhur. Prikl. Khim., 31, 652 (1958).
52. H. P. Becker and W. P. Neumann, J. Organomet. Chem., 37, 57 (1972).
53. U. Blaukat and W. P. Neumann, J. Organomet. Chem., 49 (2), 323 (1973).
54. K. Kühlein, W. P. Neumann, and H. P. Becker, Angew. Chem., 79, 870 (1967).
55. C. G. Pitt and K. R. Skillern, Inorg. Chem., 6, 865 (1967).
56. I. Pump and E. G. Rochow, Chem. Ber., 97, 627 (1964).
57. J. C. Goosenns, US P. 3 284 485 (1966).
58. I. F. Di Paola, US P. 3 364 175 (1968); Offic. Gaz., 846, No. 3 (1968); Chem. Abs., 68, 50 842a (1968).
59. J. C. Goosenns, French P. 1 426 346 (1966); Chem. Abs., 65, 13 759 (1966).
60. E. A. V. Ebsworth, G. Rocktäschel, and J. C. Tompson, J. Chem. Soc., A362 (1967).
61. E. A. V. Ebsworth, G. Rocktäschel, and J. C. Tompson, Angew. Chem., 79, 654 (1967).
62. R. H. Cragg and M. F. Lappert, J. Chem. Soc., A82 (1967).
63. H. Breederveld, Rec. Trav. chim., 81, 276 (1962).
64. L. Birkofer and P. Sommer, J. Organomet. Chem., 35, C15 (1972).
65. G. Oertel, H. Malz, and H. Holtschmidt, Chem. Ber., 97, 891 (1964).
66. N. Wiberg and G. Schwenk, Chem. Ber., 104, 3986 (1971).
67. V. D. Sheludyakov, E. S. Rodionov, G. D. Khatuntsev, and V. F. Mironov, Zhur. Obshch. Khim., 42, 367 (1972).
68. V. D. Sheludyakov, S. N. Vishnevskii, V. S. Rodionov, and V. F. Mironov, Zhur. Obshch. Khim., 42, 879 (1972).
69. V. F. Mironov, V. P. Kozyukov, and V. P. Bulatov, Zhur. Obshch. Khim., 43, 2089 (1973).
70. V. F. Mironov, V. D. Sheludjakov, V. P. Kozjukov, and A. D. Kirilin, "The Fourth International Symposium on Organosilicon Chemistry", NIITEHIM, Moscow, 1975, Vol. 1, Part 2, p. 60.
71. G. Oertel, H. Holtschmidt, and H. Malz, BRD P1 157 226 (1963); Chem. Abs., 60, 6868 (1964).
72. B. P. 1 077 239 (1964); Chem. Abs., 68, 3546 (1968).
73. V. F. Mironov, V. D. Sheludyakov, and A. B. Kirilin, Zhur. Obshch. Khim., 45, 479 (1975).
74. H. R. Kricheldorf, Synthesis, 259 (1970).
75. R. H. Cragg and M. F. Lappert, Adv. Chem. Ser., 220 (1964).
76. G. Glidewell and D. W. H. Rankin, J. Chem. Soc., C279 (1970).
77. V. F. Mironov, V. P. Kozyukov, A. D. Kirilin, V. D. Sheludyakov, Yu. I. Dergunov, and I. A. Vostokov, Zhur. Obshch. Khim., 45, 2007 (1975).
78. C. H. Yoder and J. J. Zuckermann, J. Chem. Soc. (D), Chem. Comm., 694 (1966).
79. L. Birkofer, H. P. Rühlhau, and A. Riher, Chem. Ber., 93, 2810 (1973).
80. V. F. Mironov, V. D. Sheludyakov, and E. S. Rodionov, Zhur. Obshch. Khim., 43, 2573 (1973).
81. BRD P. 2 101 221 (1971); Chem. Abs., 75, 151 815 (1971).
82. L. Birkofer and A. Ritter, Chem. Ber., 93, 424 (1960).
83. H. R. Kricheldorf, Chem. Ber., 103, 3353 (1970).
84. Y. Yamamoto, D. S. Tarbell, J. R. Fehlner, and B. M. Pope, J. Org. Chem., 38 (14), 2521 (1973).
85. A. E. Pierce, "Silylation of Organic Compounds", Rockford, Illinois, 1968, p. 7.
86. M. G. Voronkov, G. Zelcans, and E. Lukevics, "Kremnii i Zhizn'" (Silicon and Life), Izd. Zinatne, Riga, 1971.
87. V. Bazant, V. Chvalovsky, and J. Rathousky, "Organosilicon Compounds", Prague, 1965, Vol. 1, p. 16; Vol. 4–4(4) (1973).
88. F. Kurzer and K. Douraghi-Zaden, Chem. Rev., 67, No. 2, 107 (1967).
89. J. Pump and U. Wannagat, Angew. Chem., 74, 117 (1962).
90. U. Wannagat and H. Seyffert, Angew. Chem., 77, 457 (1964).
91. J. Pump and U. Wannagat, Annalen, 652, 21 (1962).
92. U. Wannagat and H. Kuckertz, anorg. Chem., 333, No. 1/3, 54 (1964).
93. H. Breederveld, Rec. Trav. chim., 79, 1126 (1960).
94. E. Heubach, Diplomarb., Tech. Hockschule Stuttgart (1955).
95. J. C. Wilson, M. A. Nadler, J. Katz, and A. Walti, US P. 2 932 586 (1960).
96. T. Goubeau and E. Heubach, Chem. Ber., 93, 1111 (1960).
97. E. Windemuth and G. Braun, BRD P. 1 085 333 (1960); Chem. Abs., 55, 18 180 (1961).
98. B. N. Dolgov and Yu. N. Vol'nov, Zhur. Obshch. Khim., 1, 91 (1931).
99. B. P. 1 153 169 (1967); Brit. Pat. Abstr., 9, No. 025 (1), 1 (1969).
100. B. P. 1 179 310 (1967); Brit. Pat. Rep., R. N. 4 (2), 2 (1970).
101. French P. 2 030 242 (1970); Bull. Offic. Propr. Ind., No. 050, 23 524 (1970).
102. J. Dunoulin, BRD P. 1 694 841 (1966); Auszüge Offenlegungsschr., 3, 1668 (1970).
103. Japanese P. 640 (1968); Derw. Jap. Pat. Rep., 7, No. 1 (1), 5 (1968).
104. R. W. Upson, US P. 2 511 310 (1949); Chem. Abs., 44, 9730e (1950).
105. W. Noll and K. Damm, Angew. Chem., 70, 512 (1958).
106. V. V. Astakhin, Candidate's Thesis, Mendeleev Moscow Institute of Chemical Engineering, Moscow, 1958.
107. V. V. Astakhin, I. P. Losev, and K. A. Andrianov, Dokl. Akad. Nauk SSSR, 113, 581 (1957).
108. K. A. Andrianov and V. V. Astakhin, Zhur. Obshch. Khim., 29, 2698 (1959).
109. V. V. Astakhin, I. P. Losev, and K. A. Andrianov, Zhur. Obshch. Khim., 29, 904 (1959).
110. N. E. Tsyganash, N. M. Lapshin, and O. S. D'yankovskaya, Izv. Akad. Nauk SSSR, Ser. Khim., 2330 (1973).
111. J. M. Pollock, B. P. 888 938 (1962); Chem. Abs., 57, 7310 (1962).
112. H. F. Mark and S. M. Atlas, French P. 1 392 118 (1965); Chem. Abs., 63, 16 522 (1965).
113. V. P. Kuznetsova, K. V. Zapunnaya, S. I. Omel'chenko, and N. I. Shchepetkina, Lakokras. Mater., No. 6, 36 (1971).

114. M. T. Bryk, T. I. Fil', G. V. Lantukh, and E. M. Natanson, Vysokomol. Soed., A14, 472 (1972); Ref. Zhur. Khim., 11S241 (1972).
115. D. P. Dodgson, B. P. 864 314 (1961).
116. K. Schwanev, Plaste u. Kautschuk, 7, 59 (1960).
117. K. Hosokawa and M. Ichikawa, US P. 3 705 823 (1970).
118. R. A. Falk, US P. 3 032 530 (1962); Chem. Abs., 57, 3604 (1962).
119. M. F. Lappert and H. Pyszora, Adv. Inorg. Chem. Radiochem., 9, 144 (1966).
120. K. Jost, BRD P. 802 895 (1951); Chem. Abs., 45, 5453 (1951).
121. W. Stegemann and G. Reuter, BRD P. 957 978 (1957); Chem. Abs., 53, 7650 (1959).
122. B. P. 836 954 (1960); Chem. Abs., 54, 23 423 (1960).
123. M. F. Shostakovskii, N. V. Komarov, and I. A. Shikhiev, Uspekhi. Khim., 28, 765 (1959).
124. A. Gabier-Rambaud and B. Blanc, BRD P. 2 036 873 (1970); Chem. Abs., 71, 102 694 (1969).
125. BRD P. 1 769 666 (1968); Auszüge Offlenlegungsschr., 2, No. 5, 4180 (1972).
126. BRD P. 1 570 576 (1965); Auszüge Offlenlegungsschr., 2, No. 50, 3436 (1969).
127. X. Kente, National Technical Report, 10, 226 (1964).
128. B. P. 887 905 (1962); Chem. Abs., 57, 1014 (1963).
129. N. V. Kulik, L. A. Negievich, N. P. Kurgan, and A. A. Kachan, Ukrain. Khim. Zhur., 36, 904 (1970).
130. N. V. Kulik, L. A. Negievich, N. P. Kurgan, G. F. Belitskaya, and A. A. Kachan, Teor. Eksper. Khim., 6, 55 (1970).
131. N. V. Kulik, L. A. Negievich, and A. A. Kachan, Teor. Eksper. Khim., 7, 695 (1971).
132. A. F. Lemire and J. C. Thompson, J. Amer. Chem. Soc., 93, 1163 (1971).
133. C. H. Yoder, A. Komoriya, J. E. Kochanowski, and F. H. Snydam, J. Amer. Chem. Soc., 93, 6515 (1971).
134. B. Dejak and Z. Lasocki, J. Organomet. Chem., 44, No. 2, C39 (1972).
135. A. Komoriya and C. H. Yoder, J. Amer. Chem. Soc., 94, 5285 (1972).
136. C. H. Yoder and D. Benelli, Inorg. Nuclear Chem. Letters, 8, 1027 (1972).
137. W. Kantlehner, W. Kugel, and H. Bredereck, Chem. Ber., 105, 2264 (1972).
138. M. Fukui, K. Itoh, and Y. Jshii, J. Chem. Soc. Perkin Trans. II, 1043 (1972).
139. H. R. Kricheldorf, Chem. Ber., 104, 87 (1971).
140. L. Birkofer and K. Kerbs, Tetrahedron Letters, 885 (1968).
141. A. S. Kostyuk, N. I. Savel'eva, Yu. I. Baukov, and I. F. Lutsenko, Zhur. Obshch. Khim., 44, 1753 (1974).
142. V. F. Mironov, V. D. Sheludyakov, E. S. Rodionov, and V. V. Shcherbinin, "Soveshchanie. Vliyanie Vysshikh Atomnykh Orbitalei na Fizicheskie i Khimicheskie Svoistva Soedinenii Neperekhodnykh Metallov. Tezisy Dokladov" (Conference on the Influence of the Highest Atomic Orbitals on the Physical and Chemical Properties of Non-Transition Metal Compounds. Abstracts of Reports), Izd. Zinatne, Riga, 1971, p. 110.
143. E. W. Bennett, Diss. Abs., 19, 3121 (1959).
144. J. L. Speier, B. F. Daubert, and R. R. McGregor, J. Amer. Chem. Soc., 70, 1117 (1948).
145. V. D. Sheludyakov, F. N. Vishnevskii, V. P. Kozyukov, G. D. Khatuntsev, and V. F. Mironov, Zhur. Obshch. Khim., 39, 810 (1968).
146. P. A. Konstantinov and R. Sh. Shchupik, Zhur. Obshch. Khim., 33, 1251 (1963).
147. V. F. Mironov and N. A. Pogonkina, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 1998 (1960).
148. N. A. Pogonkina, Candidate's Thesis, Institute of General Chemistry, USSR Academy of Sciences, Moscow, 1960.
149. V. F. Mironov, Doctoral Thesis, INKhS, USSR Academy of Sciences, Moscow, 1961.
150. J. L. Speier, US P. 2 527 591 (1974); Chem. Abs., 45, 2968d (1951).
151. A. D. Petrov, V. F. Mironov, V. A. Ponomarenko, and E. A. Chernychev, "Sintez Kremniiorganicheskikh Monomerov" (Synthesis of Organosilicon Monomers), Izd. Akad. Nauk SSSR, 1961.
152. Huang Chin-tang and Wang Pao-jen, Acta Chim. Sinica, 23, 291 (1957); Chem. Abs., 52, 19 911 (1958).
153. R. L. Metcalf and T. R. Fukuto, J. Econ. Entomol., 58, 1151 (1965).
154. N. P. Smetankina and L. E. Karbovskaya, Zhur. Obshch. Khim., 38, 911 (1968).
155. N. P. Smetankina, S. N. Borkovets, and L. E. Karbovskaya, "Sintez i Fiziko-Khimiya Polimerov (Poliuretany). Respublikanskoi Mezhvedevskii Sbornik" [The Synthesis and Physical Chemistry of Polymers (Polyurethanes). All-Republic Interdisciplinary Reports], Izd. Naukova Dumka, Kiev, 1968, Vol. 5, p. 44.
156. N. P. Smetankina and L. E. Karbovskaya, see Ref. 155, 1971, Vol. 8, p. 29.
157. K. A. Andrianov, V. M. Pakhomov, and N. E. Lapteva, Plast. Massy, No. 11, 17 (1961); Ref. Zhur. Khim., 19P73 (1962).
158. J. L. Speier, US P. 2 527 590 (1947); Chem. Abs., 45, 2968 (1951).
159. J. L. Speier, B. P. 810 283 (1959).
160. G. Greber and S. Jåger, Makromol. Chem., 57, 150 (1962).
161. L. M. Shorr, US P. 2 924 587 (1960).
162. J. L. Speier, US P. 2 925 402 (1960).
163. H. A. Clark and J. H. Thomas, US P. 2 931 786 (1960).
164. B. P. 840 832 (1960); Chem. Abs., 55, 5038 (1961).
165. B. P. 1 154 692 (1965); Chem. Abs., 69, 10 589 (1968).
166. B. P. 1 168 157 (1967); Brit. Pat. Abstrs., 9, No. 46, 1,7 (1969).
167. J. Speier, Canad. P. 503 091 (1954).
168. N. P. Smetankina and L. E. Karbovskaya, USSR P. 229 797 (1967); Byul. Izobret., No. 33 (1968).
169. G. Greber and M. L. Hallensleben, see Ref. 29, p. 91.
170. W. H. Knoth and R. U. Lindsey, J. Amer. Chem. Soc., 80, 4106 (1958).
171. G. Greber and M. L. Hellensleben, Makromol. Chem., 92, 137 (1966); Chem. Abs., 64, 17 634 (1966).
172. T. Tanaka, R. Tanaka, and H. Ryoke, J. Chem. Soc. Japan, Ind. Chem. Sect., 71, 2072 (1968).
173. T. Tanaka, H. Ryoke, and T. Nonaka, J. Chem. Soc. Japan, Ind. Chem. Sect., 71, 2088 (1968).
174. N. P. Smetankina and L. E. Karbovskaya, see Ref. 155, 1970, Vol. 7, p. 111.
175. N. P. Smetankina, L. E. Karbovskaya, and N. I. Miryan, see Ref. 155, 1971, Vol. 8, p. 34; Ref. Zhur. Khim., 24S589 (1971).
176. W. H. Knoth, US P. 2 983 744 (1961); Chem. Abs., 55, 22 132 (1961).
177. B. P. 1 176 490 (1966); Brit. Pat. Abstr., 10, No. 4 (1), 8 (1970).
178. V. A. Evdokimova, L. V. Mozzhukhina, A. P. Apukhtina, E. I. Sotnikova, and G. P. Orlenko, in "Geterogennye Polimernye Materialy" (Heterogeneous Polymeric Materials), Izd. Naukova Dumka, Kiev, 1973, p. 143.

179. S. Migdal, D. Gertner, and A. Zilkha, Canad. J. Chem., 46, 1125 (1968); Chem. Abs., 68, 105 572 (1968).
180. V. N. Mileshkevich, N. F. Novikova, and A. V. Karlin, Vysokomol. Soed., 14B, 682 (1972); Ref. Zhur. Khim., 1S365 (1973).
181. B. P. 1 324 942 (1971); Abridgem. Pat. Specif., No. 4400, 25/07 (1973).
182. French P. 2 017 122 (1968); Bull. Off. Propr. Ind., 1, No. 68, 11 762 (1968).
183. N. P. Smetankina and N. I. Miryan, USSR P. 262 392 (1969); Byul. Izobret., No. 6 (1970).
184. F. N. Vishnevskii, Candidate's Thesis, MKhP, Moscow, 1972.
185. V. P. Kozyukov, V. D. Sheludyakov, and V. F. Mironov, "Kremniiorganicheskie Soedineniya, Trudy Soveshchaniya" (Organosilicon Compounds. Conference Proceedings), Izd. NIITEKhIM, Moscow, 1966, Vol. 1, p. 52.
186. V. P. Kozyukov, V. D. Sheludyakov, and V. F. Mironov, Zhur. Obshch. Khim., 38, 1179 (1967).
187. V. F. Mironov, V. P. Kozyukov, and V. D. Sheludyakov, Zhur. Obshch. Khim., 36, 1860 (1966).
188. G. S. Gol'din, V. F. Mironov, V. D. Sheludyakov, G. D. Khatuntsev, and L. S. Baturina, USSR P. 374 346 (1970); Byul. Izobret., No. 15 (1973).
189. G. S. Gol'din, V. D. Sheludyakov, G. D. Khatuntsev, and L. S. Baturina, see Ref. 155, Vol. 16, 1974, p. 37.
190. G. S. Gol'din, L. S. Baturina, V. D. Sheludyakov, and G. D. Khatuntsev, see Ref. 155, 1974, Vol. 13, p. 33.
191. T. Takehide, R. Hideyasu, and N. Takehisa, J. Chem. Soc. Japan, Ind. Chem. Sect., 71, 2092 (1968) [Sic. This reference appears not to exist (Ed. of Translation)].
192. G. S. Gol'din, L. S. Baturina, V. G. Poddubnyi, and S. N. Tsiomo, see Ref. 31, p. 146.
193. R. J. Fessenden and M. D. Coon, J. Medicin. Pharmaceut. Chem., 8, 604 (1965).
194. M. S. Fedoseev, G. S. Marchenko, and L. K. Kir'yanova, see Ref. 155, 1970, Vol. 7, p. 163.
195. R. J. Fessenden and M. D. Coon, J. Medicin. Pharmaceut. Chem., 9, 262 (1966).
196. R. J. Fessenden and C. Ahlfors, J. Medicin. Pharmaceut. Chem., 10, 810 (1967).
197. E. D. Green, Master's Thesis, Dept. of Philology, San Jose State College, Aug., 1965.
198. R. J. Fessenden and M. D. Coon, Chem. Eng. News, 42, No. 37, 60 (1964).
199. V. F. Mironov, V. D. Sheludyakov, V. P. Kozyukov, and G. D. Khatuntsev, Zhur. Obshch. Khim., 39, 813 (1969).
200. B. Kanner, US P. 3 426 057 (1969).
201. Dutch P. 6 410 324 (1965); Chem. Abs., 63, 11 614 (1965).
202. V. F. Mironov, V. P. Kozyukov, and V. D. Sheludyakov, Dokl. Akad. Nauk SSSR, 178, 358 (1968).
203. E. J. Pepe, US P. 3 511 866 (1970).
204. US P. 3 515 734 (1970); Offic. Gaz., 874, No. 1 (1970).
205. J. L. Speier, French P. 1 371 405 (1964); Chem. Abs., 62, 664 (1965).
206. S. Brinolt, Acta, Chem. Scand., 10, 883 (1956).
207. N. P. Smetankina and N. I. Miryan, Zhur. Obshch. Khim., 39, 2020 (1969).
208. N. I. Miryan, Candidate's Thesis, Institute of General Chemistry, Academy of Sciences of Ukrainian SSR, Kiev, 1969.
209. Y. Sakata and T. Hashimoto, J. Pharm. Soc. Japan, 79, 875 (1959).
210. N. P. Smetankina and N. I. Miryan, "Tezisy Dokladov Predstavlennykh na IV Konferentsii po Khimii i Primeneniyu Kremniiorganicheskikh Soedinenii, Tbilisi" (Abstracts of Reports at the Fourth Conference on the Chemistry and Applications of Organosilicon Compounds, Tbilisi), Izd. NIITEKhIM, Moscow, 1968, p. 61.
211. N. P. Smetankina, N. N. Laskovenko, and V. A. Mironov, Vysokomol. Soed., 160, 196 (1974).
212. A. Berger, US P. 3 494 951 (1967).
213. A. Berger, US P. 3 598 852 (1971).
214. V. P. Kozyukov, V. F. Mironov, G. D. Khatuntsev, and V. D. Sheludyakov, USSR P. 213 875 (1968); Byul. Izobret., No. 11 (1968).
215. N. P. Smetankina and N. I. Miryan, Zhur. Obshch. Khim., 38, 2315 (1968).
216. N. P. Smetankina, N. I. Miryan, and G. F. Belitskaya, Zhur. Obshch. Khim., 41, 1148 (1971).
217. R. J. Joy, US P. 3 746 611 (1971).
218. J. L. Speier, US P. 3 170 891 (1965).
219. J. L. Speier, BRD P. 1 225 639 (1966); Chem. Abs., 62, 664 (1965).
220. D. Seyferth, H. Menzel, and T. O. Flood, J. Organomet. Chem., 44, 279 (1972).
221. R. J. Boudreau, US P. 3 541 031 (1970).
222. A. Laporterie, J. Dubac, and M. Lesbre, Compt. rend., C278, 375 (1974).
223. L. P. Vakhrusheva, E. V. Serebrennikova, and N. V. Komarov, USSR P. 295 764 (1969); Ref. Zhur. Khim., 24N143 (1971).
224. E. V. Serebrennikova, L. P. Vakhrushev, and N. V. Komarov, Zhur. Obshch. Khim., 41, 933 (1971).
225. L. H. Sommer, US P. 2 557 803 (1951); Offic. Gaz., 647, No. 3, 953 (1951).
226. R. A. Miller, Diss. Abs., 17, 2847 (1957).
227. H. Sommer and J. Rockett, J. Amer. Chem. Soc., 73, 5130 (1951).
228. N. B. Colthup, L. H. Daly, and S. E. Wiberly, "Introduction to Infrared and Raman Spectroscopy", Acad. Press, New York, 1964, p. 266.
229. V. D. Sheludyakov, G. D. Khatuntsev, and V. F. Mironov, Zhur. Obshch. Khim., 35, 2785 (1965).
230. V. F. Mironov, V. D. Sheludyakov, and V. P. Kozyukov, "Tezisy Dokladov, Predstavlennykh na II Mezhdunarodnyi Simpozium po Khimii Kremniiorganicheskikh Soedinenii, Bordo, 1968" (Abstracts of Reports Presented at the Second International Symposium on the Chemistry of Organosilicon Compounds, Bordeaux, 1968), p. 135,
231. V. D. Sheludyakov, E. S. Rodionov, G. D. Khatuntsev, and V. F. Mironov, Zhur. Obshch. Khim., 41, 2340 (1971).
232. V. F. Mironov, V. D. Sheludyakov, E. S. Rodionov, and V. V. Shcherbinin, see Ref. 142, p. 109.
233. V. F. Mironov, V. D. Sheludyakov, and A. D. Kirilin, Zhur. Obshch. Khim., 45, 707 (1975).
234. V. F. Mironov, V. D. Sheludyakov, and V. P. Kozyukov, see Ref. 210, p. 51.
235. A. W. P. Jarvie, Organometal. Chem. Rev., Sect. A, No. 6, 153 (1970).
236. V. F. Mironov, V. D. Sheludyakov, V. P. Kozyukov, A. D. Kirilin, and A. S. Tkachev, "IV Mezhdunarodnyi Simpozium po Khimii Kremniiorganicheskikh Soedinenii. Moskva, 1975" (The Fourth International Symposium on the Chemistry of Organosilicon Compounds, Moscow, 1975), p. 117.

237. J. H. Saunders and K. C. Frisch, "Polyurethanes–Chemistry and Technology" (Translated into Russian), Izd. Khimiya, Moscow, 1968.
238. P. Wright and A. Camming, "Polyurethane Elastomers" (Translated into Russian), Izd. Khimiya, Leningrad, 1973.
239. G. Greber and H. R. Kricheldorf, Angew. Chem., 80, 1092 (1968).
240. V. F. Mironov, V. D. Sheludyakov, E. S. Rodionov, and V. V. Shcherbinin, see Ref. 142, p. 108.
241. J. Kenji and L. Kyn, J. Chem. Soc. C, 2007 (1969).
242. G. Greber and H. R. Kricheldorf, Angew. Chem., Int. Ed. Engl., 7, 94 (1968).
243. Y. Ishi and K. Itoh, Rep. Res. Lab., Asah Glass Co. Ltd., 14, 39 (1968); Chem. Abs., 72, 43 812 (1970).
244. H. R. Kricheldorf and G. Greber, Chem. Ber., 104, 3131 (1971).
245. H. R. Kricheldorf, Chem. Ber., 104, 3146 (1971).
246. H. R. Kricheldorf, Chem. Ber., 104, 3156 (1971).
247. V. D. Sheludyakov, E. S. Rodionov, A. I. Popov, and V. F. Mironov, Zhur. Obshch. Khim., 42, 1650 (1972).
248. G. Greber and H. R. Kricheldorf, Angew. Chem., 80, 1028 (1968).
249. H. R. Kricheldorf, Synthesis, 649 (1970).
250. H. R. Kricheldorf, Annalen, 748, 101 (1971).
251. H. R. Kricheldorf, Angew. Chem., 83, 539 (1971).
252. H. R. Kricheldorf, Angew. Chem., Int. Ed. Engl., 10, 507 (1971).
253. H. R. Kricheldorf, Angew. Chem., 84, 107 (1972).
254. H. R. Kricheldorf, Angew. Chem., Int. Ed. Engl., 11, 128 (1972).
255. H. R. Kricheldorf, Synthesis, 539 (1970).
256. H. R. Kricheldorf, Annalen, 745, 81 (1971).
257. V. D. Sheludyakov, V. V. Shcherbinin, E. S. Rodionov, and V. F. Mironov, Zhur. Obshch. Khim., 42, 1870 (1972).
258. A. Adamowski, B. Nowakowski, W. Nowakowski, and J. Papinski, Polymery-tworz. wielkoelasteczk, 18, No. 9, 456 (1973).
259. L. M. Zwolinski and J. W. Frink, J. Cell. Plast., 8, 20 (1972).
260. R. L. Rellar, US P. 3 502 704 (1970).
261. A. Aleksandrov, Zhur. Obshch. Khim., 39, 141 (1969).
262. V. P. Kuznetseva and G. N. Belogolovina, Zhur. Obshch. Khim., 39, 547 (1969).
263. K. A. Andrianov, L. I. Makarova, and E. I. Sudzhashvili, "Kremniiorganicheskie Soedineniya" (Organosilicon Compounds), Izd. NIITEKhIM, Moscow, 1967, p. 139.
264. V. P. Kuznetseva, N. Ya. Kuz'menko, L. L. Chervyatsova, and A. A. Kachan, Vysokomol. Soed., **15A**, 1323 (1973).
265. N. Ya. Kuz'menko, Candidate's Thesis, Dzerzhinskii Dnepropetrovsk Institute of Chemical Engineering, Dnepropetrovsk, 1972.
266. L. A. Bokalo, V. P. Kuznetsova, N. Ya. Kuz'menko, and R. F. Gongalo, Zhur. Obshch. Khim., 42, 845 (1972).
267. BRD P. 1 241 611 (1967); Auszüge Patentanmeld., 13, 1763 (1967).
268. M. A. Brown, US P. 3 179 713 (1965); Offic. Gaz., 83, No. 3, 1020 (1965).
269. A. Reischl, W. Goebel, and H. Roehr, B. P. 1 034 702 (1966); Chem. Abs., 65, 9127 (1966).
270. French P. 1 427 660 (1966); Bull. Offic. Prop. Ind., No. 7, 2022 (1966).
271. B. P. 1 121 026 (1967); Brit. Pat. Abstr., 8, No. 033 (1), 4 (1968).
272. W. Simmler, H. Neiderprum, W. Noll, and K. Schnurrbusch, BRD P. 1 252 904 (1968).
273. Dutch P. 6 609 898 (1966); Chem. Abs., 67, 11 578 (1967).
274. V. P. Kuznetsova, M. Ya. Kuz'menko, and K. A. Korneev, Dokl. Akad. Nauk Ukrain. SSR, 2, 149 (1972).
275. K. A. Andrianov, N. P. Smetankina, V. Ya. Oprya, and N. N. Makarova, see Ref. 155, 1972, Vol. 10, p. 119; Ref. Zhur. Khim., 20S797 (1972).
276. K. A. Andrianov and L. I. Makarova, Vysokomol. Soed., 966 (1961).
277. N. P. Apukhtina, see Ref. 155, 1970, Vol. 7, p. 137.
278. T. S. Bebchuk and G. E. Golubkov, Trudy VEI, No. 74, 171 (1966).
279. T. S. Bebchuk, G. E. Golubkov, T. L. Karina, and N. N. Sokolov, Trudy VEI, No. 74, 223 (1966).
280. N. P. Apukhtina, I. B. Belov, and F. B. Noselok, "Uretanovye Elastomery" (Urethane Elastomers), Izd. Khimiya, Leningrad, 1971, p. 83.
281. K. A. Andrianov, "Metody Elementoorganicheskoi Khimii (Kremnii)" [Methods in the Chemistry of Organic Derivatives of the Elements (Silicon)], Izd. Nauka, Moscow, 1968, p. 623.
282. L. M. Sergeeva, Yu. S. Lipatov, T. T. Savchenko, N. N. Bin'kevich, V. P. Kuznetsova, and G. N. Belogolovina, see Ref. 155, 1970, Vol. 6, p. 122; Ref. Zhur. Khim., 21S869 (1970).
283. K. Wagner, Paint, Manufact., 33, 261 (1963).
284. K. Wagner, BRD P. 1 001 394 (1961).
285. K. Wagner, Angew. Chem., 74, 799 (1962).
286. Yu. S. Lipatov, Yu. Yu. Kercha, and L. M. Sergeeva, "Struktura i Svoistva Poliuretanov" (The Structure and Properties of Polyurethanes), Izd. Naukova Dumka, Kiev, 1970.
287. V. P. Kuznetsova, R. M. Sokolovskaya, and S. I. Omel'chenko, see Ref. 155, 1970, Vol. 7, p. 115.
288. V. P. Kuznetsova, R. M. Sokolovskaya, and A. P. Soboleva, see Ref. 155, 1971, Vol. 8, p. 96.
289. V. P. Kuznetsova and N. Ya. Kuz'menko, see Ref. 155, 1973, Vol. 11, p. 110.
290. B. P. 875 109 (1961); Chem. Abs., 56, 10 190 (1962).
291. BRD P. 803 079 (1951); Chem. Abs., 45, 5453.
292. F. Weigel, BRD P. 1 021 443 (1957); Chem. Abs., 55, 3878 (1961).
293. Japanese P. 36/66 (1966); Chem. Abs., 65, 20 316 (1966).
294. V. P. Kuznetsova, S. I. Omel'chenko, and G. N. Belogolovina, USSR P. 257 741 (1968); Byul. Izobret., No. 36 (1969).
295. V. P. Kuznetsova and S. I. Omel'chenko, USSR P. 262 385 (1968); Byul. Izobret., No. 6 (1970).
296. N. F. Novikova, V. P. Mileshkevich, and A. V. Karmin, USSR P. 341 816 (1970); Byul. Izobret., No. 19 (1972).
297. L. A. Bakalo, V. P. Kuznetsova, R. F. Gonchalo, and N. Ya. Kuz'menko, Zhur. Obshch. Khim., 42, 895 (1972).
298. N. P. Smetankina, V. Ya. Oprya, and V. P. Kuznetsova, Khim. Tekhnol., Nauch.-Proizv. Sbornik, 58, No. 4, 42 (1971).
299. V. P. Kuznetsova, G. N. Belogolovina, and N. N. Shchepetkina, see Ref. 155, 1970, Vol. 6, p. 162.
300. V. P. Kuznetsova, K. V. Zapunnaya, P. I. Goroshko, and A. P. Soboleva, see Ref. 155, 1971, Vol. 8, p. 92.
301. V. P. Kuznetsova and R. M. Sokolovskaya, see Ref. 155, 1972, Vol. 10, p. 123.
302. V. P. Kuznetsova and N. F. Kuz'menko, see Ref. 155, 1972, Vol. 10, p. 126.
303. K. A. Andrianov, L. M. Khananashvili, and A. S. Kochetkov, Plast. Massy, No. 8, 13 (1964).

304. V. P. Kuznetsova, S. I. Omel'chenko, G.N.Belogolovina, and V.G.Smelova, see Ref. 155, 1968, Vol. 5, p. 162.
305. V. P. Kuznetsova, S. I. Omel'chenko, and K. V. Zapunnaya, see Ref. 155, 1970, Vol. 5, p. 15.
306. N. P. Smetankina, S. I. Omel'chenko, G.N.Krivchenko, and V. Ya. Oprya, see Ref. 155, 1970, Vol. 6, p. 175.
307. M. William and J. Probst, French P. 794 284 (1960); Bull. Offic. Prop. Ind., 9, No. 33, 1167 (1960).
308. J. W. Britain, US P. 3 054 759 (1962).
309. L. A. Haluska, US P. 3 246 048 (1966).
310. L. A. Haluska, BRD P. 1 260 150 (1968); Auszüge Patentanmeld, 14, No. 5, 442 (1968).
311. M. A. Glaser and J. K. Hughers, US P. 3 257 343 (1966); Chem. Abs., 65, 10 807 (1966).
312. D. E. Green, US P. 3 288 754 (1966).
313. M. Wismer, V. G. Ammons, and G. W. Miller, US P. 3 388 101 (1968).
314. L. A. Haluska, US P. 3 398 104 (1968); Offic. Gaz., 853, No. 3 (1968).
315. K. Damm, H. Steinbach, and W. Holl, US P. 3 398 172 (1968).
316. M. Sigura and J. P. Bilisoly, US P. 3 404 130 (1968).
317. H. Wismer, US P. 3 522 142 (1970); Offic. Gaz., 876, No. 4 (1970).
318. US P. 3 539 658 (1970); Offic. Gaz., 880, No. 2 (1970).
319. R. S. Craig, US P. 3 600 414 (1971).
320. US P. 3 624 010 (1971); Offic. Gaz., 892, No. 5 (1972).
321. US P. 3 629 308 (1971); Offic. Gaz., 893, No. 3 (1972).
322. J. Winkler, US P. 3 632 533 (1972).
323. B. P. 717 408 (1954); Chem. Abs., 49, 2780 (1955).
324. G. P. Crowley, B. P. 884 153 (1961).
325. B. P. 908 608 (1962); Chem. Abs., 58, 3586 (1963).
326. M. S. Magson, B. P. 926 413 (1963).
327. A. Koebner and C. G. Pitt, B. P. 981 811 (1965); Chem. Abs., 62, 10 631 (1965).
328. A. Koebner and C. G. Pitt, B. P. 981 812 (1965); Chem. Abs., 62, 10 632 (1965).
329. N. G. Holdstock, French P. 1 358 153 (1964); Chem. Abs., 61, 7045 (1964).
330. L. A. Haluska, French P. 1 370 886 (1964); Chem. Abs., 62, 6645 (1965).
331. French P. 1 380 326 (1964); Chem. Abs., 63, 3138 (1965).
332. French P. 1 386 645 (1965); Chem. Abs., 62, 13 343 (1965).
333. K. Damm, H. H. Steinbach, and W. Noll, French P. 1 398 599 (1965); Chem. Abs., 63, 8404 (1965).
334. K. Sekmakas, French P. 1 536 758 (1968); Bull. Offic. Prop. Ind., 9, No. 33, 11 667 (1968).
335. French P. 1 588 138 (1968); Chem. Abs., 73, 121 181 (1970).
336. French P. 2 013 118 (1969); Bull. Offic. Prop. Ind., 1, No. 68, 8073 (1970).
337. F. Weigel, BRD P. 1 011 624 (1957); Chem. Abs., 54, 9356 (1960).
338. J. H. Saunders and P. G. Semeinhardt, BRD P. 1 104 690 (1959); Chem. Abs., 56, 3646 (1962).
339. A. Reischl and H. Roehr, BRD P. 1 184 080 (1964); Chem. Abs., 62, 9322 (1965).
340. W. Simmler, H. Niederpruem, M. Dahm, and H. W. Patzelt, BRD P. 1 197 616 (1965); Chem. Abs., 64, 2245 (1966).
341. R. I. Boudreau, BRD P. 1 595 783 (1966); Auszuge Offenlegungsschr., 2, 983 (1967).
342. P. Gemeinhardt and S. A. Bingham, Belg. P. 614 186 (1962); Chem. Abs., 57, 13 994 (1963).
343. Dutch P. 6 409 104 (1965); Chem. Abs., 63, 1963 (1965).
344. Dutch P. 297 031 (1965); Chem. Abs., 64, 864 (1966).
345. Dutch P. 6 409 104 (1965); Chem. Abs., 63, 1963 (1965).
346. K. Tamura, Sh. Ono, T. Wada, and H. Yamamoto, Japanese P. 10 595 (1965); Chem. Abs., 63, 16 573 (1965).
347. N. P. Smetankina, G. N. Krivenko, and V. Ya. Oprya, USSR P. 252 606 (1967); Ref. Zhur. Khim., 21S812 (1970).
348. J. M. Hammond, S. Hryhorciw, and I. E. Stutchbury, AIAA Journal, 8, 163 (1970).
349. K. A. Andrianov, L. I. Makarova, and N.M.Zharkova, Vysokomol. Soed., 2, 1378 (1960).
350. K. Sekmakas and J. E. Gaske, US P. 3 450 791 (1969); Chem. Abs., 74, 51 350 (1971).
351. B. P. 1 038 348 (1966); Brit. Pat. Abstr., 6, No. 36 (1), 4 (1966).
352. B. P. 1 161 359 (1967); Brit. Pat. Abstr., 9, No. 36 (1), 5 (1969).
353. Dutch P. 6 408 328 (1965); Chem. Abs., 63, 18 153 (1965).
354. N. V. Unilever, French P. 1 364 168 (1964); Chem. Abs., 61, 14 901 (1964).
355. A. Reischl, W. Simmler, and E. Mueller, BRD P. 1 114 632 (1960); Chem. Abs., 56, 7520 (1962).
356. L. A. Haluska, US P. 3 179 622 (1965).
357. K. I. Bourdrean, US P. 3 483 240 (1969); Offic. Gaz., 869, No. 2 (1969).
358. A. Ibbotson and E. J. Vickers, B. P. 963 437 (1964); Chem. Abs., 61, 8479 (1964).
359. B. P. 1 127 729 (1967); Chem. Abs., 70, 4270 (1969).
360. B. P. 1 151 960 (1967); Chem. Abs., 71, 71445a (1969).
361. B. P. 1 154 853 (1966); Brit. Pat. Abstr., 9, No. 27 (1), 7 (1969).
362. B. P. 1 158 670 (1967); Brit. Pat. Abstr., 9, No. 32 (2), 10 (1963).
363. L. A. Haluska, French P. 1 352 325 (1964); Chem. Abs., 62, 2890 (1965).
364. H. A. Clark and L. A. Haluska, French P. 1 385 096 (1965); Chem. Abs., 62, 10 554 (1965).
365. French P. 1 395 901 (1965); Chem. Abs., 63, 18 393 (1965).
366. French P. 1 411 757 (1965); Chem. Abs., 65, 5624 (1966).
367. F. Senge, BRD P. 1 595 654 (1969); Auszuge Offenlegungsschr., 2, 2602 (1969).
368. N. G. Holdstock, BRD P. 1 769 519 (1968); Chem. Abs., 72, 112 958 (1970).
369. D. W. Simmler, BRD P. 1 812 564 (1968); Chem. Abs., 73, 45 592 (1970).
370. D. W. Simmler, BRD P. 1 905 101 (1969); Chem. Abs., 73, 88 662 (1970).
371. L. A. Haluska, Belg. P. 620 800 (1963); Chem. Abs., 59, 13 023 (1963).
372. Belg. P. 667 046 (1966); Chem. Abs., 65, 7409 (1966).
373. T. Hashiguchi and A. Enomoto, Japanese P. 19 424 (1968); Ref. Zhur. Khim., 15S885 (1973).
374. V. P. Kuznetsova and N. F. Kuz'menko, see Ref. 155, 1974, Vol. 13, p. 157.
375. V. L. Kozlikov, Candidate's Thesis, MKhP, Moscow, 1972.
376. French P. 2 025 248 (1970); Bull. Offic. Prop. Ind., 68, No. 1, 19 805 (1968).
377. French P. 2 033 796 (1970); Bull. Offic. Prop. Ind., 68, No. 1, 25 458 (1968).
378. B. Kanner and E. J. Pepe, US P. 3 519 579 (1970).
379. B. P. 1 216 158 (1968); Chem. Abs., 72, 79 844 (1970).

380. H. C. Fielding and J. M. Pollock, B. P. 968 109 (1964).
381. H. R. Kricheldorf and E. Leppert, Makromol. Chem., 167, 47 (1973).
382. G. L. Brode and L. B. Conte, US P. 3 632 557 (1972).
383. B. P. 1 058 385 (1967); Brit. Pat. Abstr., 7, No. 9 (1), 9 (1967).
384. D. S. G. William, US P. 3 707 521 (1970).
385. W. F. Tousignant and W. E. Walles, US P. 3 004 950 (1961).
386. E. Nyilas, US P. 3 562 352 (1971).
387. O. B. Johnson, US P. 3 585 065 (1971).
388. I. H. Albrecht, Swiss P. 532 452 (1970).
389. E. J. Kelley, US P. 3 360 504 (1969).
390. W. Hodes, US P. 3 463 662 (1969).
391. H. D. Golitz and W. Simmler, US P. 3 658 864 (1972); Offic. Gaz., 897, No. 4, 1393 (1972).
392. US P. 3 674 891 (1972); Offic. Gaz., 900, No. 1 (1972).
393. T. I. Fil', M. T. Bryk, and E. M. Natanson, Symposium, "Fiziko-Khimiya, Mekhanika i Liofil'nost' Dispersnykh Sistem" (The Physical Chemistry, Mechanics, and Lyophilicity of Dispersed Systems), Izd. Naukova Dumka, Kiev, 1973, No. 4, p. 102.
394. M. T. Bryk and N. M. Baglei, Symposium, "Fiziko-Khimiya, Mekhanika i Liofil'nost' Dispersnykh Sistem" (The Physical Chemistry, Mechanics, and Lyophilicity of Dispersed Systems), Izd. Naukova Dumka, Kiev, 1973, No. 5, p. 60.
395. B. P. 1 281 416 (1972); Chem. Abs., 72, 101 454 (1970).
396. J. L. Speier, BRD P. 1 101 766 (1961); Chem. Abs., 56, 11 804 (1962).
397. R. L. Barnes, W. M. Block, and D. Grafstein, US P. 3 730 950 (1972), 7C396.
398. R. C. Hartlein, US P. 3 453 243 (1969); Chem. Abs., 67, 65 182 (1969).
399. French P. 2 017 527 (1970); Bull. Offic. Propr. Ind., 68, No. 1, 12 463 (1968).
400. O. B. Johnson and S. S. Labana, US P. 3 719 521 (1970).
401. H. J. Schenck, BRD P. 1 028 646 (1958); Chem. Abs., 54, 20 017 (1960).
402. B. P. 1 054 688 (1967); Brit. Pat. Abstr., 7, No. 6 (1), 7 (1967).
403. B. P. 1 075 542 (1967); Brit. Pat. Abstr., 7, No. 31 (1), 9 (1967).
404. B. P. 1 076 426 (1967); Brit. Pat. Abstr., 7, No. 32 (1), 6 (1967).
405. G. R. Hodge and A. V. Patsis, US P. 3 642 936 (1972).
406. E. D. Garnett and A. V. Mercer, B. P. 981 687 (1965); Chem. Abs., 63, 11 990 (1965).
407. L. A. Haluska, French P. 1 374 032 (1965); Chem. Abs., 63, 13 330 (1965).
408. R. Falk, BRD P. 1 101 767 (1961); Auszüge Patentanmeld, No. 19, 834 (1961).
409. M. A. H. Fahmy, R. L. Metcalf, T. R. Fukuto, and D. J. Hennessy, J. Agr. Food Chem., 14 (1), 79 (1966); Chem. Abs., 64, 13 326 (1966).
410. V. P. Kuznetsova, K. V. Zapunnaya, and S. I. Omel'chenko, See Ref. 210, p. 76.
411. N. P. Smetankina, V. P. Kuznetsova, L. E. Karbovskaya, R. M. Sokolovskaya, and S. I. Omel'chenko, see Ref. 210, p. 130.
412. Yu. S. Lipatov, see Ref. 155, 1967, p. 199; Ref. Zhur. Khim., 3S1K (1969).
413. V. P. Kuznetsova, K. V. Zapunnaya, S. I. Omel'chenko, and M. I. Shchepetkina, Farbe u. Lack, 78, No. 7, 636 (1972).
414. F. D. Swanson and S. J. Price, "Mater. 71, 16th Nat. Symp. and Exhib. Azusa, Calif.," Vol. 16, 1971, p. 45; Ref. Zhur. Khim., 1S437 (1973).
415. B. P. 1 280 750 (1970); Abridg. Pat. Specif., 5/07 (1972).
416. G. Reuter, BRD P. 1 015 597 (1957); Chem. Abs., 54, 2686 (1960).
417. French P. 2 027 391 (1970); Bull. Offic. Prop. Ind., 9, No. 33, 1168 (1970).
418. Japanese P. 17 999 (1968); Derw. Jap. Pat. rep., 7, No. 30 (1), 8 (1968).
419. M. A. Deisz and M. Ohta, PB Rept. 131 795, 87 pp; Chem. Abs., 54, 10 385 (1960).
420. H. Gibello, Offic. Matieries plast., 7, No. 71, 494 (1960).
421. R. N. Meals, Silicones, Annalen, New York Acad. Sci., 125, 137 (1965).
422. A. Berger, Paint Manufacture, 39, 29 (1969).
423. W. Fichler, "The Applications of Silicone in the German Democratic Republic" (Translated into Russian), INTI, Moscow, 1967.
424. H. Reinshussel and A. Wille, BRD P. 1 034 320 (1958); Chem. Abs., 54, 16 032 (1960).
425. L. M. Vinogradova, A. Ya. Korolev, P. V. Davydov, and R. V. Kuchenkova, Plast. Massy., No. 9, 18 (1964).
426. T. France, G. Scheibling, and A. Bandeket, French P. 1 371 970 (1964); Chem. Abs., 62, 13 400 (1965).
427. W. Kubitza, Industrie Lackier-Betrieb, 31, No. 1, 1 (1963).
428. D. R. Bartley and G. S. Irby, US P. 3 133 978 (1964); Chem. Abs., 61, 12 164 (1964).
429. P. R. McCorthy and Ch. S. Tempalski, US P. 3 153 631 (1964); Chem. Abs., 62, 501 (1965).
430. S. Witz and E. Mishuck, US P. 3 260 631 (1966); Chem. Abs., 65, 10 418 (1966).
431. G. Benier and K. Intrup, French P. 1 419 563 (1965); Chem. Abs., 65, 17 155 (1966).
432. B. P. 804 025 (1958); Chem. Abs., 53, 8684 (1959).
433. I. Wood and G. Woods, B. P. 896 901 (1962); Chem. Abs., 57, 8743 (1962).
434. F. Hostettler and E. F. Cox, B. P. 914 579 (1963); Chem. Abs., 59, 4134 (1963).
435. A. Ibbotson and E. I. Vickers, B. P. 954 041 (1964); Chem. Abs., 61, 5815 (1964).
436. K. L. Brown, US P. 3 087 900 (1963); Chem. Abs., 59, 4122 (1963).
437. E. M. Maxey, French P. 1 389 881 (1964); Chem. Abs., 63, 776 (1965).
438. C. L. Whipple, BRD P. 1 153 166 (1963); Chem. Abs., 60, 1903 (1964).
439. Belg. P. 667 176 (1966); Chem. Abs., 65, 12 378 (1966).
440. E. Gee and A. Packer, B. P. 839 184 (1960).
441. B. P. 862 361 (1961); Chem. Abs., 55, 24 076 (1961).
442. I. H. Wild, J. F. Wood, and G. Woods, B. P. 907 971 (1962); Chem. Abs., 58, 2250 (1963).
443. B. P. 908 012 (1962); Chem. Abs., 58, 3585 (1963).
444. P. Merriman and M. D. Roll, B. P. 922 860 (1963); Chem. Abs., 59, 7741 (1963).
445. I. L. Brooks and D. Williams, B. P. 981 675 (1965); Chem. Abs., 62, 12 026 (1965).
446. B. P. 1 054 041 (1967); Brit. Pat. Abstr., 7, No. 5, 1, 6 (1967).
447. W. G. Caroll, B. P. 1 077 888 (1967); Chem. Abs., 68, 3546x (1968).
448. R. F. Harris, US P. 2 901 445 (1959).
449. G. T. Gmitter and E. V. Braidich, US P. 3 050 477 (1962).
450. G. Loew and G. Hoerl, BRD P. 1 105 607 (1959).

451. E. Degener, H. Holtschmidt, and G. Braun, Belg. P. 616 865 (1962); Chem. Abs., 58, 1605 (1963).
452. W. I. Considine and M. A. Riccardi, Belg. P. 618 373 (1962); Chem. Abs., 58, 8110 (1963).
453. Belg. P. 660 101 (1965); Chem. Abs., 64, 16 574 (1965).
454. Dutch P. 6 408 400 (1965); Chem. Abs., 63, 18 392 (1965).
455. F. Scheermesser, BRD P. 1 148 379 (1963); Auszüge Patentanmeld, 9, No. 19, 1026 (1963).
456. I. H. Saunders, Rubber Chem. and Technol., 33, 1293 (1960).
457. E. A. Petrov and O. G. Tarakanov, Kolloid. Zhur., 28, 431 (1966).
458. S. Polis, US P. 3 044 971 (1962).
459. P. G. Gemeinhardt and R. L. Sanbridge, US P. 3 060 137 (1962).
460. W. I. Remington, US P. 3 145 185 (1964).
461. F. Hostettler, US P. 3 194 773 (1965); Chem. Abs., 63, 8577 (1965).
462. B. P. 942 616 (1963); Chem. Abs., 60, 13 412 (1964).
463. B. P. 944 904 (1963); Chem. Abs., 60, 891 (1964).
464. D. L. Bailey and A. S. Pater, Belg. P. 618 786 (1962); Chem. Abs., 58, 8109 (1963).
465. H. Kopnick, M. Dahm, and D. Delfs, BRD P. 1 144 475 (1963).
466. A. Ibbotson, D. B. Morgan, K. Stephenson, and E. I. Vickers, B. P. 960 240 (1964); Chem. Abs., 61, 5869 (1964).
467. A. Ibbotson and E. I. Vickers, B. P. 971 309 (1964); Chem. Abs., 61, 14 864 (1964).
468. N. G. Holdstock, French P. 1 364 214 (1964); Chem. Abs., 62, 7961 (1965).
469. P. K. Huester and D. P. Huntington, J. Cell. Plast., 1, No. 2, 301 (1965).
470. G. A. Haggis and H. I. Twitchett, B. P. 1 009 007 (1965); Chem. Abs., 65, 20 313 (1966).
471. French P. 1 391 300 (1965); Chem. Abs., 63, 10 181 (1965).
472. Belg. P. 65 576 (1965); Chem. Abs., 65, 10 762 (1966).
473. Austrian P. 241 827 (1965); Ref. Zhur. Khim., 13S496 (1966).
474. C. D. Pande, S. K. Kapoor, I. Bajaj, and B. Venkataramani, Indian J. Technol., 4 (4), 109 (1966); Chem. Abs., 65, 2422 (1966).
475. B. P. 1 074 332 (1967); Chem. Abs., 63, 13 517d (1965).
476. G. A. Hudson, K. A. Pigott, and I. H. Saunders, French P. 1 425 572 (1966); Chem. Abs., 65, 17 160 (1966).
477. T. K. Brotherton and J. W. Lynn, Belg. P. 672 010 (1966); Chem. Abs., 65, 12 361 (1966).
478. Dutch P. 6 517 009 (1966); Chem. Abs., 65, 20 316 (1966).
479. Dutch P. 6 601 245 (1966); Chem. Abs., 65, 18 723 (1966).
480. F. Hostettler, BRD P. 1 091 324 (1960); Chem. Abs., 55, 25 359 (1961).
481. H. Koepnick, G. Loew, and D. Delfs, BRD P. 1 096 033 (1960); Chem. Abs., 55, 19 331 (1961).
482. G. Loew, BRD P. 1 101 752 (1961); Chem. Abs., 56, 3664 (1962).
483. R. Merten, O. Bayer, and G. Loew, BRD P. 1 111 378 (1961); Chem. Abs., 56, 3664 (1962).
484. H. Piechota, BRD P. 1 134 196 (1962); Chem. Abs., 57, 11 403 (1962).
485. G. Rossmy, BRD P. 1 223 148 (1966); Chem. Abs., 65, 18 794 (1966).
486. R. Merten, H. Brachel, H. Holtschmidt, and G. Hauptmann, BRD P. 1 110 857 (1961); Chem. Abs., 55, 279 972 (1961).
487. M. Dahm and W. Simmler, BRD P. 1 122 698 (1962); Chem. Abs., 57, 3632 (1962).
488. P. G. Gemeinhardt, BRD P. 1 128 133 (1966); Chem. Abs., 57, 2443 (1962).
489. G. Rossmy, BRD P. 1 215 922 (1966); Chem. Abs., 65, 7409 (1966).
490. A. Reischl, H. Holtschmidt, W. Neumann, and W. Simmler, BRD P. 1 190 176 (1965); Auszüge Patentanmeld, 11, No. 13, 980 (1965).
491. N. V. Unilever, French P. 1 364 168 (1964); Chem. Abs., 61, 14 901 (1964).
492. P. R. McGarthy and T. R. Orem, US P. 3 082 170 (1963).
493. N. L. Remes, T. W. Martinek, and E. T. Fronczak, US P. 2 913 409 (1959).
494. B. P. 767 226 (1957); Chem. Abs., 51, 10 951 (1957).
495. B. P. 793 594 (1958); Chem. Abs., 52, 21 206 (1958).
496. US P. 2 713 564 (1955).
497. B. P. 826 322 (1960); Chem. Abs., 54, 13 714 (1960).
498. US P. 3 050 485 (1962); Chem. Abs., 57, 16 876 (1962).
499. US P. 2 921 900 (1960).
500. A. Yu. Korolev, P. V. Davydov, and L. N. Vinogradova, Adgeziya Polimerov, No. 3, 11 (1973).
501. A. Baigozhin, L. V. Sergeev, and G. S. Fattakhov, Vysokomol. Soed., 4, 977 (1962).
502. I. M. Fain, E. M. Donnell, and R. Blaufen, US P. 3 244 541 (1966); Chem. Abs., 64, 19 999 (1966).
503. B. P. 1 091 650 (1967); Chem. Abs., 68, 22 572 (1968).
504. B. P. 1 020 052 (1966); Chem. Abs., 64, 16 055 (1966).
505. B. P. 825 717 (1960); Chem. Abs., 58, 3586 (1963).
506. Adhesive Age, 15, No. 3, 194 (1972).
507. G. Koerner and G. Rossmy, BRD P. 2 208 149 (1972); Auszüge Patentanmeld, 8, No. 9, 916 (1973).
508. G. Rossmy and G. Koerner, US P. 3 723 491 (1971).
509. Peintures-Pigments-Vernis, 47, 422 (1971).
510. Kunstst.-Rundsch., 18, 570 (1971).
511. D. L. Bailey and A. S. Pater, Australian P. 421 262 (1967).
512. R. S. Stuart, B. P. 1 329 572 (1970).
513. US P. 3 703 489 (1969); Offic. Gaz., 904, No. 3, 713 (1972).
514. E. L. Morehouse, US P. 3 741 917 (1970).
515. M. L. Davis and I. M. McClellan, Adhesive Age, 7, No. 5, 22 (1964).
516. G. Duncan and R. I. Heridge, Talanta, 17, 766 (1970).
517. I. Aeton and M. I. Napoli, Rev. gen. cautch. et plast., 48, 715, 717, 719, 721, 821 (1971).
518. N. Ya. Kuz'menko, V. P. Kuznetsova, and L. L. Chervyatsova, "III Vsesoyuznoe Soveshchanie po Khimii i Fiziko-Khimii Poliuretanov" (The Third All-Union Conference on the Chemistry and Physical Chemistry of Polyurethanes), Izd. Naukova Dumka, Kiev, 1971, p. 39.
519. K. A. Kornev and V. G. Ostroverkhov, "II Vsesoyuznoe Soveshchanie po Khimii i Fiziko-Khimii Poliuretanov" (The Second All-Union Conference on the Chemistry and Physical Chemistry of Polyurethanes), Izd. Naukova Dumka, Kiev, 1968, p. 14.
520. V. Ya. Oprya, N. P. Smetankina, and S. P. Omel'chenko, "II Respublikanskaya Konferentsiya po Vysokomolekulyarnym Soedineniyam" (The Second All-Republic Conference on Macromolecular Compounds), Izd. Naukova Dumka, Kiev, 1970, p. 122.
521. N. N. Laskovenko, Candidate's Thesis, IKhVS [Institute of the Chemistry of Macromolecular

Compounds ?], Academy of Sciences of Ukrainian SSR, Kiev, 1974.
522. B. P. 1 253 760 (1968); Chem. Abs., 72, 101 454 (1970).
523. M. T. Bryk, T. I. Fil', and E. M. Natanson, see Ref. 520, p. 21.
524. N. Ya. Kuz'menko, R. F. Gongalo, L. A. Bakalo, and V. P. Kuznetsova, see Ref. 520, p. 21.
525. M. Frankel, D. Gerther, and A. Sheuhar, J. Chem. Soc. C, 1334 (1967).
526. R. I. Fessenden, Angew. Chem., 76, 448 (1964).
527. R. I. Fessenden and M. D. Coon, Nachr. Chem. Technik., 14, 1951 (1966).