Hydrolytic stability and protective properties of polyurethane oligomers based on polyester/ether/polyols

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The present study deals with effect of the type and chemical character of incorporated polyester/polyether blocks on the hydrolytic stability of crosslinked polyurethane oligomers. Diffusion parameters of the investigated polyurethane oligomers, giving information concerning chemical changes taking place in neutral, basic and acidic aqueous environments, have also been determined.

(Keywords: polyurethane oligomers; polyesterpolyols; polyetherpolyols; hydrolytic resistance; diffusion parameters; protective properties)

INTRODUCTION

Polyurethanes contain a number of different chemical groups, formed as a result of isocyanate polyaddition, and in turn these groups show different resistances to hydrolysis.

Investigation of the hydrolytic stability of polyurethanes, based on polyesters or polyethers having a variety of structures, is of great scientific and practical importance particularly in respect to the manufacture of polyurethane protective coatings.

There are a number of publications[1-7] on the hydrolytic stability of polyurethanes based on polyesters, mainly of linear structure or with a low degree of crosslinking, which are mostly used as elastomers.

Data concerning the hydrolytic stability of polyetherpolyols and polyurethanes based on them, is scarce[8,9].

The present study deals with effect of the type, and chemical character of the incorporated polyester and polyether blocks, respectively, on the hydrolytic stability of crosslinked polyurethane oligomers. Diffusion parameters of the investigated polyurethane oligomers, which give information about the chemical changes, taking place during exploitation, have been determined.

EXPERIMENTAL

The investigated polyurethane oligomers were obtained from an adduct of trimethylolpropane and toluene diisocyanate with NCO content of 13.5%.

Polyetherpolyols (PE) and polyesterpolyols (PEs) were used as the hydroxyl-containing components. Some of their properties are given in *Table 1*.

The properties of the produced polyurethane oligomers have been explained in more detail in our previous publications[10-12].

The films, obtained by pouring out solutions of the polyurethane oligomers onto a solid surface, harden in air under normal conditions. Tertiary amines have been used as crosslinking agents to accelerate the hardening.

The alkaline hydrolysis of the polyols, containing ester groups, has been carried out according to a previously discussed method[13].

The diffusion index has been determined by a method, analogous to the sorption method[14], consisting of the following: specimens of polyurethane oligomers of diameter 0.85 mm and thickness of about 0.15 mm are carefully weighed and placed in a flask, equipped with a reflux condenser. The appropriate medium is added afterwards. The flask was placed in a thermostatically controlled bath, where the temperature is maintained at a constant level with an accuracy of ±0.5°C. After a given time, the specimens are removed, washed with an equal volume of distilled water, dried with filter paper and weighed in a closed vessel.

Permeability of the polyurethane oligomers in acidic media has been determined with films, 2.5–5.0 mm thick, obtained from 25% solutions of the polyurethane oligomers in dimethylformamide.

RESULTS AND DISCUSSION

The polyester- and polyether-blocks introduced in the polyurethane oligomers are attacked mainly during hydrolysis. This is expected and simple to explain having in mind that the energy of the –C–O–C– group is 1.0 kcal mol^{-1}, and that of the –COO– group is 2.90 kcal mol^{-1}, while that of the NHCOO group is 8.75 kcal mol^{-1}.[15] That is why the present work deals especially with the hydrolysis of incorporated polyester- and polyether-blocks in polyurethane oligomers.

Hydrolytic stability of the polyesterpolyols, used in the synthesis of polyurethane oligomers, depends on the resistance of the ester group to saponification. Hydrolysis of polyurethanes, containing ester groups[2] can be represented by the following scheme:

$$\sim\mathrm{OCO(R)_nCOO(R')OCONH(R'')NHCOO}\sim + \mathrm{H_2O}\rightarrow$$
$$\sim\mathrm{OCO(R)_nCOOH} + \mathrm{HO(R')OCONH(R'')NHCOO}\sim$$

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Table 1 Properties of the initial materials

Type of the hydroxyl-containing component: Name	Type	Acid value (KOH/g)	Hydroxyl group content (%)	Water content by Fischer (%)
Desmophen 1670	PEs	<4	1.5	0.12
Desmophen 1700	PEs	<3	1.2	<0.15
Voranol 3322	PE	<0.1	1.4	0.10
Voranol P 400	PE	<0.1	8.0–9.0	0.10
Voranol P 450	PE	<0.1	10.9–12.1	0.10
Desmophen 7135	PE	<0.1	1.3	0.08
Desmophen 7116	PE	<0.1	1.2–1.3	0.14

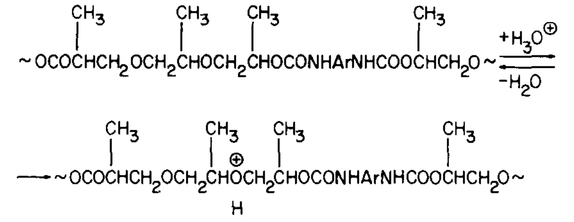
Initially the hydrolysis affects the ester groups of the oligoesterpolyol block. The newly formed carboxyl group is a catalyst for the further hydrolysis, i.e. this is an autocatalytic process[1,2].

According to the alkaline hydrolysis mechanism of the oligoesterpolyols, proposed by Ingold[16], the decomposition takes place in the ester group, concerning especially the acyl–oxygen bond. Therefore, hydrolytic resistance will depend on the chemical nature of the acyl fragment. Polarity and the three-dimensional structure of the acyl fragment determine the electro-negative nature of the formed intermediate complex and its stabilization, respectively.

The differences in the hydrolytic stabilities of polyurethane oligomers based on polyesterpolyols is conditioned by the chemical nature of the oligoester blocks introduced into them.

Hydrolysis of the polyurethane oligomers, containing ether blocks, under acidic action, takes place according to the accepted mechanism of an acidic hydrolysis of polyethers[9].

The hydrolysis of polyethers affects the C–O–C bonds as follows:



$$\sim\mathrm{OCO\overset{CH_3}{C}HCH_2OCH_2\overset{CH_3}{C}HOCH_2\overset{CH_3}{C}HOCONHArNHCOO\overset{CH_3}{C}HCH_2O}\sim \underset{-\mathrm{H_2O}}{\overset{+\mathrm{H_3O}^{\oplus}}{\rightleftarrows}}$$

$$\longrightarrow\sim\mathrm{OCO\overset{CH_3}{C}HCH_2OCH_2\overset{CH_3}{C}H\underset{H}{\overset{\oplus}{O}}CH_2\overset{CH_3}{C}HOCONHArNHCOO\overset{CH_3}{C}HCH_2O}\sim$$

Reversible formation of the conjugate acid followed by heterolytic cleavage and formation of a hydroxyl group and a carbonium ion, which is immediately transferred into the conjugate acid, takes place in this case.

It has been established[9] that hydrolysis of polyethers often proceeds similarly in a neutral medium also.

Figure 1 shows the results of the alkaline hydrolysis of the polyurethane oligomers, based on polyester–polyols, according to a previously described procedure[13]. The difference in the hydrolytic resistance of the polyurethane oligomers obtained on the basis of the tested polyesters can be explained by the different nature of the acyl fragments. It can be seen from *Figure 1* that Desmophen 1670 is hydrolysed to a lower degree than Desmophen 1700.

With Desmophen 1670 the full destruction of the ester groups takes place after 540 min at 20°C, whilst with Desmophen 1700 the alkaline hydrolysis to complete destruction is carried out after 390 min.

Protective properties of polymers and their destruction in corrosive media do not depend only on hydrolytic stability of the bonds, but also on the diffusion parameters of the polymeric materials, i.e. diffusion index (D), sorption index (C) and permeability (P) of the polymeric films.

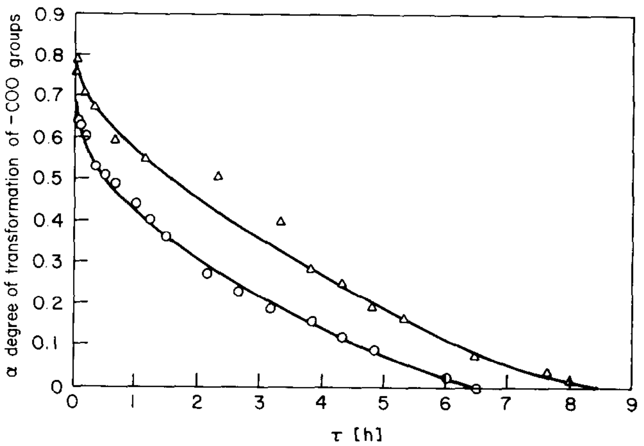


Figure 1 Alkaline hydrolysis of polyesterpolyols at 20°C: (△) Desmophen 1670; (○) Desmophen 1700

Diffusion properties exert substantial influence on the chemical changes, occurring in the polymeric material during the process of its exploitation.

The diffusion parameters of the polyurethane specimens in various media (20% solution of NaOH, 20% solution of HNO_3 and distilled water) have been determined by the already mentioned method of swelling[14]. Experimental data are represented in form of a relation between the substance quantity (Q) and the time (τ) necessary for its adsorption by the specimen. The experimental data are shown in *Figures 2, 3* and *4*.

The sorption index (C, g cm^{-3}), characterized by the quantity of the substance, having diffused, which is absorbed by the polymer under equilibrium conditions, is determined by the equilibrium sorption isotherm.

The diffusion index (D) of the polyurethane films formed in the corresponding aggressive media has been determined on the basis of the equation, proposed by Kanavtsev[14]*:

$$-\frac{4\pi^2 D}{l^2}\tau = \ln\frac{Q_{\max} - Q_\tau}{Q_{\max}}$$

where l is the thickness of the film.

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*This equation is derived from the equation of Fick for unstatic flow

$$\frac{\partial C}{\partial \tau} = D\frac{\partial^2 C}{\partial x^2} \tag{1}$$

At the first moment when $\tau = 0$, for chemically resistant materials the distribution of concentration of aggressive media in the specimen will depend on its thickness $C = f(X)$. The concentration in the specimen will be at a minimum (it is taken as equal to zero), but on the surface of the specimen it will be at a maximum. Kanavtsev, taking into account the chosen initial and extreme conditions, after integration of equation (1), has obtained the following equation:

$$Q_\tau = Q_{\max}[1 - \exp(-4\pi^2 D\tau/l^2)] \tag{2}$$

where $Q_{\max}$ is the quantity absorbed by the specimen in equilibrium condition, and Q_τ is the quantity absorbed by the specimen for the time it was immersed in the aggressive media. In half logarithmic coordinates, equation (2) achieves the form shown in the text.

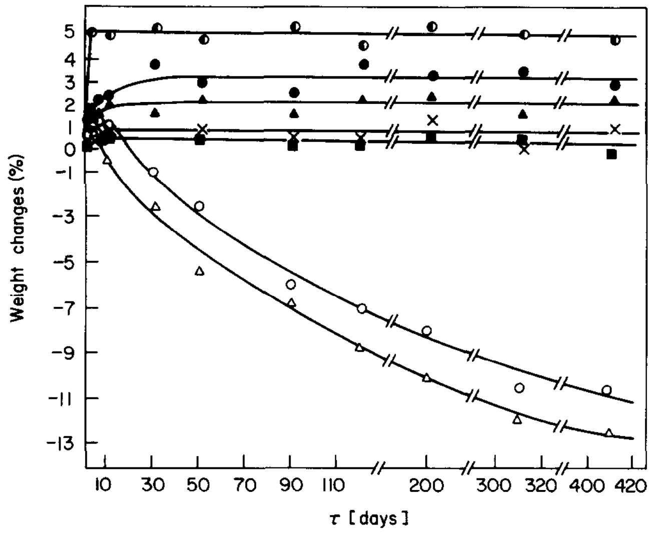

Figure 2 Hydrolytic stability of polyurethane oligomers based on polyester (ether) polyols at 20°C in 20% solution of NaOH: (◐) Voranol 3322; (●) Voranol P400; (▲) Voranol CP450; (×) Desmophen 7135; (■) Desmophen 7116E; (○) Desmophen 1670; (△) Desmophen 1700

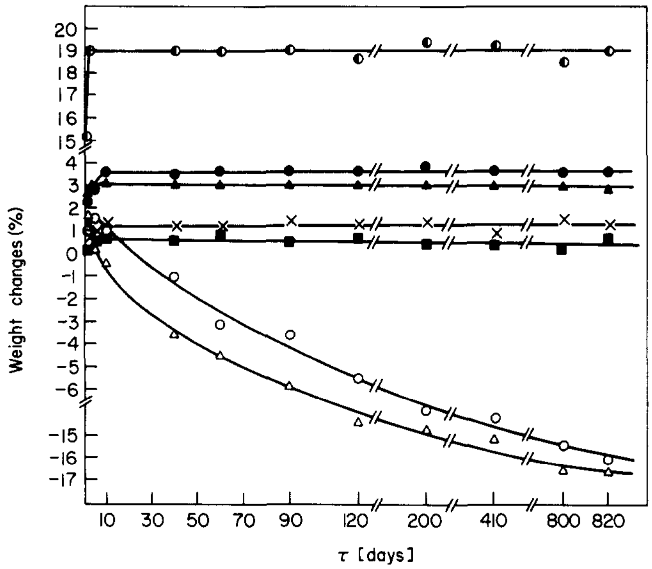

Figure 3 Hydrolytic stability of polyurethane oligomers based on polyester (ether) polyols at 20°C in distilled water: (◐) Voranol 3322; (●) Voranol P400; (▲) Voranol CP450; (×) Desmophen 7135; (■) Desmophen 7116E; (○) Desmophen 1670; (△) Desmophen 1700

Proceeding from the diffusion and sorption indices values, the permeability of the polyurethane films is calculated via the following equation[14]:

$$P = CD \ (\mathrm{g\ cm^{-1},\ s^{-1}})$$

The calculated diffusion parameters of the polyurethane oligomers based on polyester (ether) polyols in the studied media are shown in *Table 2*.

It can be seen from *Table 2* that the diffusion characteristics of the polyurethane films depend on the type and chemical nature of the oligoester/oligoether blocks incorporated in the chain.

Diffusion characteristics show that the polyurethane oligomers based on polyetherpolyols possess lower diffusion velocity and permeability in alkaline and water media. Therefore they will have better chemical stability during exploitation in those media as compared with those based on polyesterpolyols. The minimum diffusion velocity and permeability in the above mentioned media are shown by the polyurethane oligomer specimens based on Voranol 3322. The sorption and diffusion indices and the respective permeabilities of the polyurethane oligomers based on polyetherpolyols are of one and the same order, except for Voranol 3322.

Diffusion values for the polyurethane oligomers, based on polyesterpolyols, such as Desmophen 1670 and Desmophen 1700 in aqueous and alkaline media, are one order greater than those of Voranol 3322, while the acidic hydrolysis goes in inverse sequence. Polyurethane oligomers, based on Desmophen 1670, possess the best chemical stability in an acidic medium.

The difference in stability of polyurethane oligomers based on hydroxyl containing compounds, involving ester or ether groups in the chain, is clearly expressed at acidic and alkaline hydrolysis, which can be easily explained, having in mind the behaviour of the mentioned groups in acidic and alkaline media.

The highest values of diffusion velocity and permeability in acid media have been found experimentally for the polyurethane specimens based on Desmophen 7135, while the highest values in alkaline and aqueous media have been observed with specimens based on

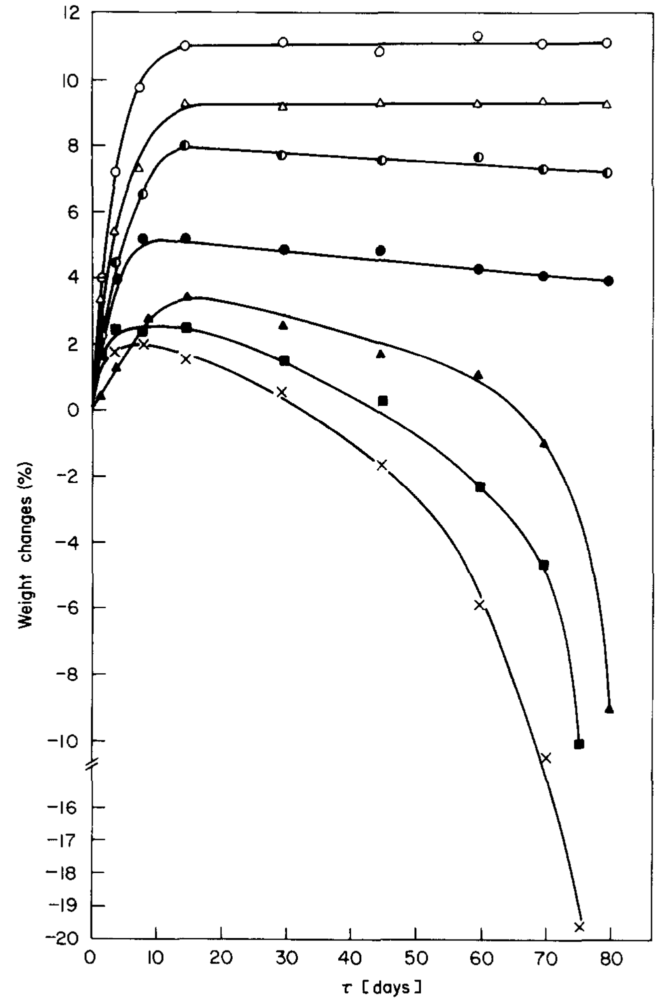

Figure 4 Hydrolytic stability of polyurethane oligomers based on polyester (ether) polyols at 20°C in 20% solution of HNO_3: (○) Desmophen 1670; (△) Desmophen 1700; (◐) Voranol 3322; (●) Voranol P400; (▲) Voranol CP450; (■) Desmophen 7116 E

Table 2 Diffusion properties of polyurethane oligomers

PU-oligomer based on:	Investigated medium	Sorption index $C \times 10^2$ ($g\ cm^{-3}$)	Diffusion index $D \times 10^{10}$ ($cm^2\ s^{-1}$)	Permeability $P \times 10^{11}$ ($g\ cm^{-1}\ s^{-1}$)
Desmophen 1670	NaOH	2.197	1.848	0.406
	H_2O	3.260	2.672	0.871
	HNO_3	0.781	0.730	0.057
Desmophen 1700	NaOH	2.776	1.909	0.530
	H_2O	3.567	2.745	0.979
	HNO_3	0.899	0.957	0.086
Voranol 3322	NaOH	1.005	0.478	0.048
	H_2O	1.201	0.766	0.093
	HNO_3	3.128	1.365	0.427
Voranol P-400	NaOH	1.334	0.922	0.123
	H_2O	1.403	1.411	0.198
	HNO_3	3.242	1.582	0.513
Voranol P-450	NaOH	1.345	0.952	0.128
	H_2O	1.421	1.443	0.205
	HNO_3	3.255	1.601	0.521
Desmophen 7116	NaOH	1.363	1.012	0.138
	H_2O	1.595	1.611	0.257
	HNO_3	3.324	1.656	0.551
Desmophen 7135	NaOH	1.398	1.138	0.159
	H_2O	1.740	1.782	0.310
	HNO_3	3.436	1.778	0.611

Desmophen 1700. This might be due to the higher segmental mobility of the polyurethane chains, obtained with these polyols.

On the basis of the diffusion characteristics, obtained for the investigated polymers, it has been found that the polyurethane oligomers based on Voranol 3322 (in alkaline and aqueous media) and Desmophen 1670 (in acidic medium), possess the lowest diffusion velocity and permeability, and the highest hydrolytic stability, respectively. This is most probably due to the chemical nature of the mentioned polyols, which makes for diminishing mobility and flexibility of the segments of the polyurethane chain, resulting in a reduced mobility.

The values of *D*, *S* and *P* and the maxima of the curves shown in *Figures 2*, *3* and *4* are a little bit lower than the real ones, which can be explained by chemical changes, occurring in parallel to the basic physical processes.

The hydrolysis velocity of the hydroxyl containing compounds, differing in their chemical structure and diffusion characteristics to the polyurethane oligomers based on them, determines the different behaviour of the studied polymers in acidic, alkaline and aqueous media.

The difference in the oligoester block structure is strongly manifested when testing polyurethane oligomers in alkaline media (*Figure 2*). The mass of the tested specimen, based on Desmophen 1670 in 20% NaOH at 20°C, starts diminishing quickly after the fifth day, while with Desmophen 1700, diminishing of the specimen mass is observed immediately after the first day.

It has been proved experimentally that the oligomeric polyurethanes, based on polyetherpolyols, behave characteristically with very good hydrolytic stability toward 20% NaOH. No changes have been observed during a period of 14 months (*Figure 2*).

Properties of the polyurethane oligomers, based on polyether and polyester polyols in aqueous medium are completely analogous to those undergoing alkaline hydrolysis (see *Figure 3*). However, under acidic hydrolysis (*Figure 4*), the mass of the specimens of polyurethane oligomers based on polyester polyols (Desmophen 1670 and Desmophen 1700) remain constant after the 15th day for 96 and 81 days, respectively.

The polyurethane specimens, based on polyetherpolyols, change constantly their mass after swelling and the curves, reflecting that change have analogous pattern. A period of time is observed, when the mass changes are weakly expressed and afterwards the specimens become friable.

An exception in this respect are the polyurethane specimens, based on polyetherpolyol Voranol 3322 and to a certain extent the specimens, based on polyetherpolyol Voranol P-400 (see *Figure 4*). The mass of the studied polyurethane specimens, based on Voranol 3322 and Voranol P-400, changes weakly in acidic medium, as compared with the rest of the polyurethane oligomers, based on polyesterpolyols. This fact might be due to the formation of a more compact crosslinked structure of the polyurethane specimens, based on those polyethers as compared with the ether studied polyurethane oligomers, based on polyetherpolyols. That is why the polyurethane oligomers based on Voranol 3322 and Voranol P-400 are used in the synthesis of polyurethane varnishes and coatings, resistant both in alkaline and acidic media.

Analogous results for the permeability of the studied polyurethane oligomers have been obtained by means of another method, described previously[17]. It consists of measuring the concentration of H-ions from hydrochloric acid solution, having passed through the polyurethane film in water.

The results shown in *Figure 5* correspond to those results, given in *Table 2*, which is an additional confirmation of the parameters, obtained by the other method.

Protective properties of polyurethane coatings based on the investigated polyurethane oligomers, have been studied by observation of corrosion on metallic specimens, placed in aggressive media. The experimental results are given in *Table 3*. The data shown in *Table 3* are in agreement with the permeability values of polyurethane specimens, based on polyols of various chemical structure, as well as with the data for the chemical stability of those polyurethanes and coatings on their base, published in references 10–12.

The polyurethane coatings based on polyesters possess greater corrosive stability in acidic medium than those

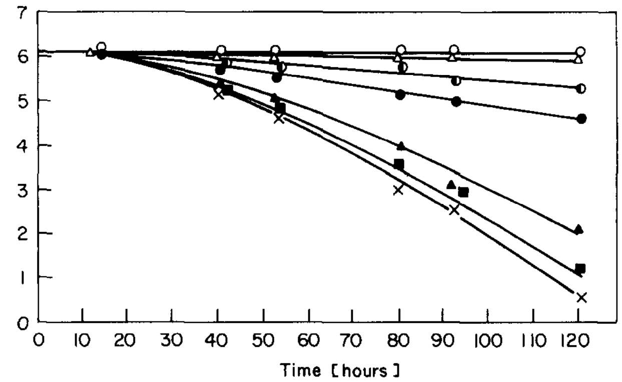

Figure 5 Permeability of polyurethane coatings on the base of studied polyester (ether) polyols at 20°C in 25% HCl solution: (○) Desmophen 1670; (△) Desmophen 1700; (◐) Voranol 3322; (●) Voranol P400; (▲) Voranol CP450; (×) Desmophen 7135; (■) Desmophen 7116E

based on polyethers, while the coatings based on polyetherpolyols are more resistant in alkaline and aqueous media. These properties of the polyurethane coatings seem quite natural, having in mind the behaviour of the ester/ether blocks, incorporated in the polymeric chain, in alkaline and acidic media.

On the basis of the results obtained, we can conclude that, when preparing chemically resistant protective coatings of polurethane oligomers, the type and chemical character of the hydroxyl containing component used should be taken into consideration.

The high protective properties of the studied polyurethane oligomers make the synthesis of chemical resistant polyurethane coatings possible, which possess good stability in the above mentioned aggressive media and high physico-mechanical parameters[11].

REFERENCES

1 Müller, E. *Angew. Makromol. Chem.* 1970, **4**, 75

2 Schollenberger, C. S. and Stewart, F. D. *J. Elastoplast.* 1971, **3**, 28

3 Pitrovskii, K. B., Rolina, M. P. and Apuhtina, N. P. Uretanovie Elastomeri, 'Chimia', 1971, s. 74–76 (in Russian)

4 Sotnikova, E. N., Panteleeva, B. N. and Korotkina, D. M. 'Kautchuk i rezina', 1972, No. 10, s. 13-15 (in Russian)

5 Schollenberger, C. S. and Stewart, F. D. *Angew. Makromol. Chem.* 1973, **25/30**, 413

6 Cohen, I. L. and Aartsen, G. *J. Polym. Sci. Polym. Symp. Edn.* 1973, **42**, 1325

7 Okupeva, A. G. *Plast. Massi* 1977, **3**, s. 46 (in Russian)

8 Omelchenko, S. I. i dr. VWS, 1972, t/A/XIV1, **91**, 1981 (in Russian)

9 Furukawa, J. and Saegusa, T. 'Polymerizatsiya Aldegidov i Okisey', izd. 'Mir', Moskva 1965, 409 (in Russian)

10 Pavlova, M. and Novakov, P. *Adhäsion* 1980, **9**, s. 278

11 Pavlova, M. and Novakov, P. i dr., 'Lakokrasochnie Materiali i ich Primenenie', 1981, s. 3 (in Russian)

12 Pavlova, M., Draganova, M. and Novakov, P. *Adhäsion* 1983, **9**, s. 7

13 Fijolka, P., Lenz, I. *Plaste Kautsch.* 1960, **7**, s. 481

14 Tihomirova, N. P., Zernova, K. I. and Kotrelev, V. N. *Plast. Massi*, 1962, **12**, s. 40 (in Russian)

15 Blagonravova, A., Vassileva, O. and Ustenko, T. 'Lakokrasochnie Materiali i ich Primenenie'. No. 2, 1977, s. 42 (in Russian)

16 Ingold, C. 'Teoretitcheskie Osnovi Organitcheskoy Chimii', M., 'Mir', 1973, s. 1054 (in Russian)

17 Kondrateva, L. N. i dr. Lakokrasochnie Materiali i ich Primenenie', No. 13, 1981, s. 25 (in Russian)