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# Surface modification of highly dispersed rubber fillers and pigments by titanate proadhesive and hydrophobic compounds

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*Abstract*: A method of modifying silicate and carbonate fillers with titanate coupling agents and proadhesive agents was worked out. The modification aimed at hydrophobization of filler surface by introduction to the surface of functional groups with chemical affinity to polymers. Optimum amounts of modifying substances and appropriate conditions for performing the modification process were established. The obtained fillers showed a high degree of hydrophobicity.

The modified fillers were applied in rubber mixtures based on butadiene-styrene or natural rubber, in polyurethanes, in PVC, and as pigments in oil dyes of high corossive resistance.

*Key words*: Precipitated calcium carbonate – kaolin – sodium-aluminum silicate – aluminum silicate – titanate coupling agents

## Introduction

Powdered mineral fillers are added to plastics in order to reduce their production costs and provide them with required properties (i.e., increase in the physico-mechanical parameters and in plastics resistance to the effect of aggresive factors.)

Inorganic substances, such as fillers, pigments, or strengthening fibers (e.g., glass and silicate fibers) are applied in processing polymers, in dye and laqcuer production, and in cosmetic, food, and pharmaceutical industries. Generally speaking, they are inorganic hydrophilic substances which are easily wetted by water, or they easily adsorb water on their surface, but are wetted by organic polymers only to a restricted degree.

Application of adhesive promoters or proadhesive factors in modification of inorganic materials may contribute to a considerable improvement of mechanical strengthening and chemical resistance of filled plasto- and elastomers. Inorganic pigments modified by these factors will remarkedly increase the covering power of dye and lacquer.

Among proadhesive compounds, silane coupling agents [1] deserve particular attention. The compounds were successfully used to a large scale in multiple technologies, particularly in processing of plasto- and elastomers. On a lower scale, titanate coupling agents [2], borate coupling agents [3], zirconium coupling agents [4], zirconium-aluminum adhesion promoters [5], metalorganic compounds from the group of metal alcoxy-oxides [6] and metalocens [7] were used.

In this study attention was focused on application of titanate coupling agents and proadhesive compounds for modification and hydrophobization of filler surface.

## Experimental

### 1. *Materials*

*a) fillers*: – Precipitated calcium carbonate was obtained by saturating the solution of $Ca(OH)_2$ with carbon dioxide at temperature below 10 °C for 60 min. To the solution of calcium hydroxide – as an activator – 0.02 weight parts of $Mg^{++}$

(from $MgCl_2$) with respect to calcium carbonate was introduced [8]

– KOG kaolin from the bed near Bolesławiec (Poland).

Kaolin used for the studies showed an average grain size ranging between 2.5–8.0 μm. Such fillers show no reinforcing properties and, therefore, they were subjected to additional grinding in a stream-circulatory-horizontal mill of JET-D-Mizer (model 0202, USA) [9]. The grinding medium involved air pressurized at 6 atm.

– Sodium-aluminum silicate ANS-15 [10] was obtained by precipitating from the sodium metasilicate solution by aluminum sulfate. Precipitation conditions: temperature – 80C; initial concentration of the solution of sodium metasilicate – 5% $SiO_2$; modulus of sodium metasilicate $\left(M_k = \frac{SiO_2}{Na_2O}\right)$ – 2.7; concentration of the solution of aluminum sulfate – 5%; dosing rate of sodium silicate – 10 $cm^3$/min per 1 $dm^3$ of the reaction mixture; content of coagulant-$Ca(NO_3)_2$ – 3 wt per 100 weight parts of $SiO_2$ in reaction system; final pH–10

– Aluminum silicate AS-2 [10] was obtained in analogous conditions as aluminum-sodium silicate ANS-15, yet the difference was that solution of sodium silicate was added until pH = 8.

b) titanate coupling agents-made by Kenrich Petrochemicals

I) trimethyl, isostearoyl titanate
$(CH_3O)_3{-}Ti(C_{17}H_{35}COO)$

II) triethyl, isostearoyl titanate
$(C_2H_5O)_3{-}Ti(C_{17}H_{35}COO)$

III) triisopropyl, isostearoyl titanate
$(i\text{-}C_3H_7O)_3{-}Ti(C_{17}H_{35}COO)$

isopropyl, triisostearoyl titanate KR TTS
$(i\text{-}C_3H_7O){-}Ti(C_{17}H_{35}COO)_3$

isopropyl, trimethacryl titanate KR 33 CS
$(i\text{-}C_3H_7O){-}Ti[OCOC(CH_3)=CH_2]_3$

For the purpose of comparison, silane pro-adhesive agent was also applied: γ-methacryloxypropyltrimethoxysilane A-174

$CH_2{=}(CH_3)COCO(CH_2)_3Si(OCH_3)_3$

## 2. *Procedures and methods*

Specific surface area was determined by the chromotographic method [11]. The amount of adsorbed nitrogen was measured from a desorptive peak due to its higher symmetry.

The bulk and packing densities were established using an electromagnetic volumeter WE-5.

Absorption of water, dibuthyl phthalate, and paraffin oil were determined by commonly employed methods. The end point of water absorption was established to correspond to that moment when an excess of one drop of water brings about a marked flowing junction of the formed paste, while in the case of phthalate and oil absorption, when an excess of one drop of these compounds causes a rapid change in the consistency of the paste which sticks to the glass plate. In the case of a precipitated calcium carbonate the flow-off point was determined.

Surface modification of the studied fillers was carried out in a mixing chamber of our own design [12] and according to our methodology [13]. For modification, titanate coupling agents were used, whereas for comparative purposes, a silane coupling agent-γ-methacryloxypropyltrimethoxysilane A-174. For the above purposes, titanate solutions in carbon tetrachloride were prepared, and methacryloxysilane in methanol-(5:1) solution. Then, solutions containing 0.5–3.0 weight parts of these compounds dissolved in appropriate solvents per 100 weight parts of the modified filler were made. The amount of the solution containing modifying compounds in appropriate solvents was selected in such a way as to secure a uniform immersion of the filler surface. After one cycle of mixing, the solvent was removed by evaporation, and the appropriate filler was dried at the temperature of 110 °C in a drier.

The heat of immersion of the surface of the fillers under study (both unmodified and modified) in water ($H_i^W$) and benzene ($H_i^B$) were determined by a calorimetric method.

According to this method, ampoules were filled with an appropriate filler, then outgassed under vacuum for 6 h at 110 °C and only then was the heat of immersion measured [14]

The KRM-type calorimeter permits determining the heat effect via a dynamic method under conditions similar to the adiabatic ones. In the first phase, the heat capacity of the calorimeter was established, and only then was the heat of immersion of a given filler measured using the liquid already used in the measurements (water or benzene.) To this effect, an ampoule containing a precisely measured amount of the filler was placed between the squeezer jaws. After breaking of the ampoule, the filler drops down to a water or benzene containing vessel. The observed increase in temperature will be caused by the heat of immersion.

Moreover, relative heat of immersion of the surface ($h_i^W$ and $h_i^B$) against the size of the specific surface area of the filler was calculated

Hydrophobization degree of the surface was measured from the formula:

$$N_H = \frac{(H_i^B)_m - (H_i^B)_n}{(H_i^B)_m} * 100\% ,$$

where $(H_i^B)_m$ – heat of immersion in benzene of the surface of the modified filler $(H_i^B)_n$ – heat of immersion in benzene of the surface of the unmodified filler.

At the subsequent stage, sedimentation volume of pigments was examined as well as their resistance to light and aggressive gases ($SO_2$, $H_2S$, $NH_3$). Sedimentation volume of a given pigment was established by estimation of its volume of settling in water suspension.

For the measurements a 10 cm$^3$ measuring cylinder, with a ground cork marked every 0.10 cm$^3$ was employed. In this cylinder 1 g of a substance was shaken in 10 cm$^3$ of distilled water. The sedimentation volume was read after 6 h.

The resistance of painted pigments (sedimentation in a bleached linen oil placed on glass plates) to the effect of light, hydrogen sulfide, sulphur dioxide and gaseous ammonia was studied. Light re-emission was established by a leukometer. As a standard, a non-radiated painted plate or a plate not exposed to any aggressive agents was used.

Modified and unmodified fillers were applied as components of rubber mixtures. The mixtures were prepared according to standard recipes based on a butadiene-styrene and natural rubber. Compositions of the mixtures are compiled in Table 1.

A series of mixtures was prepared, employing a pre-determined technological regime [15]. Vulcanization was run for 10–30 min in a hydraulic press with steam heating at 143 °C and under 15.2 MPa pressure.

For polyurethane synthesis, we used toluelene diizocyanate (Izocyn T-80, containing 42% isocyanate groups), polyoxypropylene glycol (Rokopol 2002, average molecular weight 2000), polyoxypropylene triol (Rokopol 330, average molecular weight 3600) and suitable filler. Phenyl mercuric oleate (Bayer, FRG) served as a synthesis catalyzer. Synthesis was conducted at 90 °C for 2 h from the moment of adding diisocyanate. The reactive system was mixed continuously.

Moreover, some mixtures from polyvinyl chloride of the following composition were prepared:

PVC S68 – 280 g
Dioctyl phthalate – 120 g
SBK11 Ergotherm (stabilizer) – 2.8 g
Filler – 120 g

Table 1. Composition of rubber mixtures filled with unmodified and modified silicate and carbonate fillers.

| Composition of elements [wt/wt] | | | |
|---|---|---|---|
| Mixture I | | Mixture II | |
| Butadiene-styrene rubber | | Natural rubber RSS-I | 100 |
| Ker 1500 | 100 | Filler | 50 |
| Filler | 50 | Zinc oxide | 5 |
| Zinc oxide | 3 | Antioxidant Polnox R (polymerizable 2,2,4-trimethyl 1,2-dihydro quinoline) | 1 |
| Stearic acid | 2 | Accelerator DM | 0.8 |
| Accelerator DM (mercaptobenzothiazolyl disulphide) | 2.2 | Accelerator D (triphenylquanidine) | 1.2 |
| Accelerator M (2-mercaptobenzothiazole) | 1.4 | | |
| Sulphur | 2 | Stearic acid | 3 |
| | | Sulphur | 2.5 |

The weighed mixture was rolled on a laboratory rolling mill under the following conditions:

- rollers temperature – 165 C
- split – ca. 0.5 mm
- friction – 1:1.4
- rate of a slow roller – 25 turns/min
- rolling time – ca. 10 min

Gelation time and the plasticity of PVC mixtures containing the fillers under study were determined by Plastic-Corder PLV341 type Brabender. In order to soften the PVC, a crusher with volume 65 cm was employed.

## Results and discussion

Chemical composition of the studied silica and carbonate fillers is listed in Table 2.

Table 3 shows physico-chemical properties of these fillers prior to their surface modification.

A fully efficient adhesion promoter for the filler-polymer system should bind both the filler surface and the filled polymer.

Behavior of different mineral fillers in the polymer systems with respect to titanate and silane coupling agents varies. The silane coupling agents prove very effective in the case of acid or neutral fillers – sodium-aluminum silicate, or aluminum silicate, as well as kaolin, and almost ineffective with respect to basic fillers (e.g., precipitated calcium carbonate). On the surface hydroxyl group (silanol –Si–OH and aluminol –Al–OH) of the fillers water molecules may be adsorbed as a result of contact with air moisture. Surface modification with silane A-174 may bring about formation of various groups on the surface of silica and kaolin, yet the efficiency of the modification will be determined by the presence of an isolated group, e.g., methacryloxy – capable of interacting with functional groups of polymer. On the grounds of measurements of heat of immersion of filler surface in water and benzene, the degree of filler surface modification, i.e., increase or decrease in surface hydrophobicity could be established. Hydrophobization of fillers was associated with appearance on their surface of functional groups with increased chemical affinity to functional groups of polymer containing the fillers.

Contrary to the silane agents, the titanate proadhesive agents may interact both with active fillers containing bonded hydroxyl groups on the surface, and inactive fillers (e.g. precipitated calcium carbonate). As a result of the reaction, an organic monomolecular layer of titanate is formed on the inorganic surface. Table 4 shows results of the studies on the heat of immersion in water and benzene of the filler surfaces.

In the process of modification we tried to obtain fillers of a surface featuring the possibly highest hydrophobicity, and at the same time an increased chemical affinity to polymer (e.g., rubber, polyurethane, or PVC.)

Increase in hydrophobicity of the filler surface is indicated by a decrease in the heat of surface immersion in water, and by an increase in the heat of surface immersion in benzene. The effect of increasing hydrophobicity was obtained by

Table 2. Chemical composition of the filler samples [%]

| Precipitated calcium carbonate | | |
|---|---|---|
| $CaCO_3$ | 97.4 | |
| Alkalicity | 0.19 | |
| $Fe_2O_3$ | 0.03 | |
| Mn | 0.001 | |
| Cu | 0.001 | |
| Moisture (105 C) | 0.34 | |
| pH of water suspension*) | 8.7 | |
| Kaolin KOG, sludged | | |
| $SiO_2$ | 48.52 | |
| $Al_2O_3$ | 34.31 | |
| $Fe_2O_3$ | 1.50 | |
| $TiO_2$ | 0.68 | |
| CaO | 0.33 | |
| MgO | 0.20 | |
| Ignition loss (1000 C) | 12.53 | |
| Moisture (105 C) | 3.25 | |
| | Sodium-aluminum silicate ANS-15 | Aluminum Silicate AS-2 |
| $Na_2O$ | 7.2 | 0.3 |
| $Al_2O_3$ | 8.5 | 16.8 |
| $SiO_2$ | 74.5 | 75.2 |
| $Fe_2O_3$ | 0.05 | 0.03 |
| $SO_3$ | 0.2 | 0.2 |
| Moisture (105 C) | 5.0 | 5.4 |
| Ignition loss (1000 C) | 6.6 | 6.2 |
| pH of water suspension*) | 9.8 | 7.6 |

*) 4–5 g filler suspended in 100 $cm^3$ water or methanol-water (1:1) mixture.

Table 3. Physico-chemical properties of the unmodified silicate and carbonate fillers under study

| Sample | $D_n$ [g/dm$^3$] | $D_u$ [g/dm$^3$] | $D_u/D_n$ | $H_W$ [g/100 g] | $H_F$ [g/100 g] | $S$ [m$^2$/g] | $P$ [cm$^3$/10 g] |
|---|---|---|---|---|---|---|---|
| calcium carbonate | 276 | 445 | 1.61 | – | – | 16.6 | 11.5 |
| KOG | 280 | 572 | 2.04 | 60 | 72 | 12.6 | – |
| ANS-15 | 150 | 180 | 1.20 | 250 | 600 | 92.5 | – |
| AS-2 | 110 | 140 | 1.27 | 400 | 750 | 102.5 | – |

Legend:
$D_n$ – bulk density
$D_u$ – packing density
$D_u/D_n$ – shaking coefficient
$H_W$ – water absorption
$H_F$ – dibutylphtalate absorption
$S$ – specific surface
$P$ – flow-off point

employing in the modification process fillers consisting of triisostearoyl titanate and isopropyl, trimethacryl titanate. It was observed that all fillers, both silicate and carbonate, show marked hydrophobicity under the influence of these titanates. Monoisostearoyl titanates increase the degree of hydrophobicity of the studied fillers only to a slightly lesser degree than triisostearoyl titanates.

Moreover, silane A-174 also increases the degree of hydrophobization of the surfaces of silicate fillers, though it actually has no effect on calcium carbonate for which only a minimum hydrophobization is observed. The latter observation is probably due to a lack of silanol (or aluminol) groups on the surface of carbonate which are capable of interacting with alkoxyl groups of silane. Figure 1 presents interaction of monoalkoxyl titanate or silane with a surface of mineral filler containing active hydroxyl groups on the surface (aluminum silacates, kaolin.)

Figure 2 [2] shows models of interactions between titanate coupling agents with fillers containing silanol groups on their surface (Fig. 2a) or with fillers without those groups (Fig. 2b.) As can be seen in this picture, modification of calcium carbonate involves coating of its surface with uniform titanate monolayer.

The modified fillers were used in rubber mixtures. Two kinds of those mixtures were prepared, one based on butadiene-styrene rubber, and the other based on natural rubber.

Physico-mechanical properties of vulcanizates containing the studied fillers are listed in Table 5.

Figure 3 depicts the dependence of the main physico-mechanical parameters ($R_r$ and M-100) of vulcanizates based on butadiene-styrene rubber containing different modified fillers, on the amount of coupling agents.

As follows from the presented data, the addition of modified fillers significantly improves strength parameters of vulcanizates, and, in particular, the tensile strength and modulus. In general, we can state that titanates used for modification, in particular, those containing three functional groups (isostearoyl or methacryl), bring about a marked increase in the strengthening parameters of vulcanizates filled with silicates and carbonates.

Studies conducted for different amounts of coupling agents indicated that the optimum values of tensile strength parameters and moduli in vulcanizates are obtained when 2–3 weight parts of these agents per 100 weight parts of the filler are applied, and the best effect is reported for titanate KR TTS.

Properties of urethane elastomers may also be improved by filler introduction. To account for the mechanism reinforcing the effect of fillers in urethane polymers, we have to take into account many factors causing a change in polymer properties, such as the chemical character of polymer and filler, type of a filler, the type of polymer-filler system, polymer adhesion to filler surface, conditions of polymer formation in the presence of filler, etc.

Table 4. Effect of the coupling agents on the heat of immersion of filler's surfaces and on the hydrophobization degree

| Proadhesive compound | Amount [wt/wt] | $H_i^W$ [J/g] | $H_i^B$ [J/g] | $h_i^W$ [J/m$^2$] | $h_i^B$ [J/m$^2$] | $N^*$ [%] |
|---|---|---|---|---|---|---|
| Precipitated calcium carbonate | | | | | | |
| unmodified | – | 6.32 | 7.08 | 0.38 | 0.43 | – |
| A-174 | 2.0 | 6.01 | 7.25 | 0.36 | 0.44 | 2.3 |
| | 3.0 | 5.88 | 7.60 | 0.35 | 0.45 | 6.8 |
| Titanate I | 2.0 | 5.30 | 9.05 | 0.31 | 0.57 | 21.8 |
| | 3.0 | 4.90 | 9.61 | 0.29 | 0.58 | 26.3 |
| Titanate II | 2.0 | 5.25 | 9.02 | 0.32 | 0.54 | 21.5 |
| | 3.0 | 4.90 | 9.55 | 0.29 | 0.57 | 25.9 |
| Titanate III | 2.0 | 5.32 | 8.98 | 0.32 | 0.54 | 21.2 |
| | 3.0 | 4.85 | 9.39 | 0.29 | 0.56 | 24.6 |
| KR TTS | 0.5 | 5.85 | 7.95 | 0.35 | 0.48 | 10.9 |
| | 1.0 | 5.40 | 8.92 | 0.32 | 0.54 | 20.6 |
| | 2.0 | 4.90 | 9.95 | 0.30 | 0.60 | 28.8 |
| | 3.0 | 4.42 | 10.54 | 0.27 | 0.63 | 32.8 |
| KR 33 CS | 2.0 | 4.95 | 9.60 | 0.30 | 0.58 | 26.3 |
| | 3.0 | 4.50 | 10.15 | 0.27 | 0.61 | 30.2 |
| Kaolin KOG | | | | | | |
| unmodified | – | 9.80 | 10.10 | 0.78 | 0.80 | – |
| A-174 | 2.0 | 7.65 | 13.44 | 0.61 | 1.07 | 24.8 |
| Titanate I | 2.0 | 7.60 | 13.45 | 0.60 | 1.07 | 24.9 |
| Titanate II | 2.0 | 7.62 | 13.28 | 0.60 | 1.05 | 23.9 |
| Titanate III | 2.0 | 7.69 | 13.15 | 0.61 | 1.04 | 23.2 |
| KR TTS | 2.0 | 7.06 | 15.08 | 0.56 | 1.19 | 33.0 |
| KR 33 CS | 2.0 | 7.25 | 14.79 | 0.57 | 1.17 | 31.7 |
| Sodium-aluminum silicate ANS-15 | | | | | | |
| unmodified | – | 20.45 | 20.32 | 0.22 | 0.22 | – |
| A-174 | 1.0 | 18.33 | 24.78 | 0.19 | 0.27 | 18.0 |
| | 2.0 | 16.21 | 26.65 | 0.17 | 0.29 | 23.8 |
| | 3.0 | 14.15 | 28.15 | 0.15 | 0.30 | 27.8 |
| Titanate I | 1.0 | 18.15 | 25.16 | 0.19 | 0.27 | 19.2 |
| | 2.0 | 14.01 | 26.42 | 0.15 | 0.28 | 23.0 |
| | 3.0 | 10.94 | 27.85 | 0.12 | 0.30 | 27.0 |
| Titanate II | 2.0 | 14.05 | 26.50 | 0.15 | 0.28 | 23.3 |
| Titanate III | 2.0 | 14.20 | 26.38 | 0.15 | 0.28 | 23.0 |
| KR TTS | 1.0 | 17.77 | 26.12 | 0.19 | 0.28 | 22.2 |
| | 2.0 | 14.50 | 27.98 | 0.15 | 0.30 | 27.4 |
| | 3.0 | 10.11 | 29.84 | 0.11 | 0.32 | 31.9 |
| KR 33 CS | 1.0 | 17.90 | 25.95 | 0.19 | 0.28 | 21.7 |
| | 2.0 | 14.01 | 27.44 | 0.15 | 0.29 | 25.9 |
| | 3.0 | 10.94 | 29.50 | 0.12 | 0.32 | 31.1 |
| Aluminum silicate AS-2 | | | | | | |
| unmodified | – | 22.35 | 22.60 | 0.22 | 0.22 | – |
| A-174 | 2.0 | 16.07 | 28.88 | 0.16 | 0.28 | 21.7 |
| Titanate I | 2.0 | 15.95 | 28.75 | 0.15 | 0.28 | 21.4 |
| Titanate II | 2.0 | 15.70 | 28.40 | 0.15 | 0.27 | 20.4 |
| Titanate III | 2.0 | 15.85 | 28.52 | 0.15 | 0.28 | 20.8 |
| KR TTS | 2.0 | 14.90 | 30.15 | 0.14 | 0.29 | 25.0 |
| KR 33 CS | 2.0 | 15.14 | 29.81 | 0.14 | 0.29 | 24.2 |

$N^*$ – Hydrophobization degree

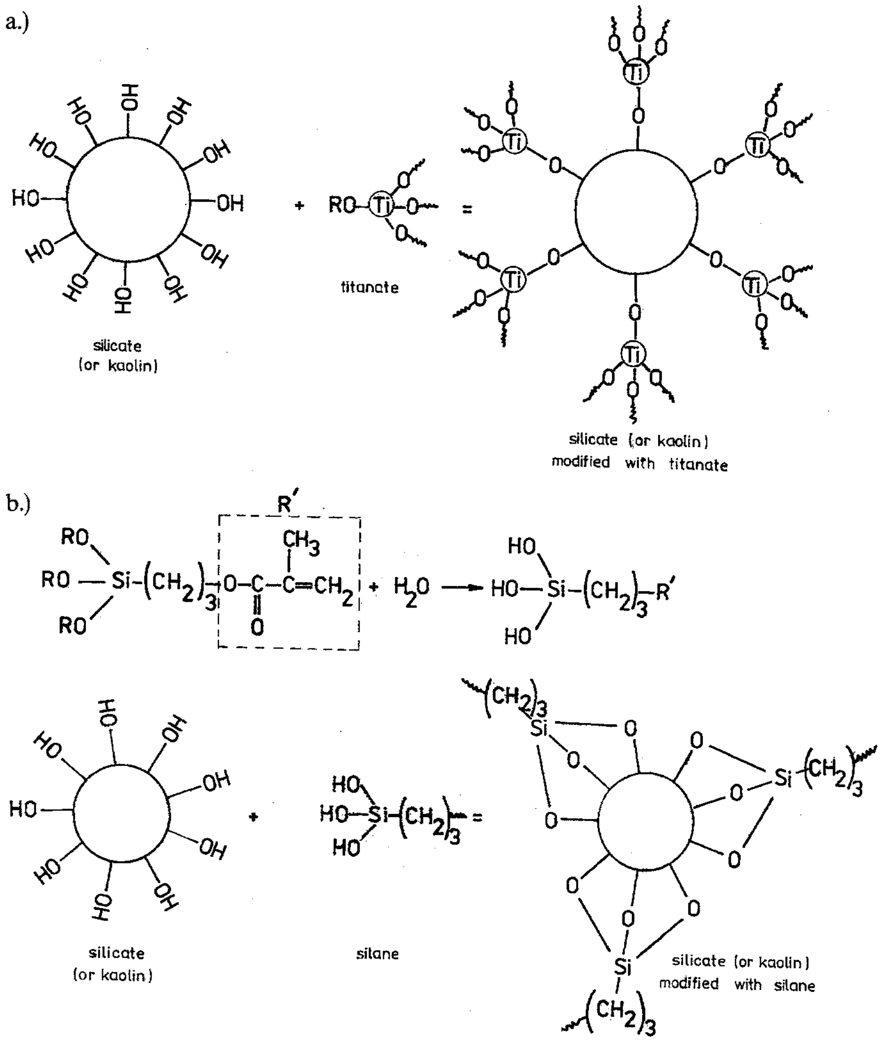
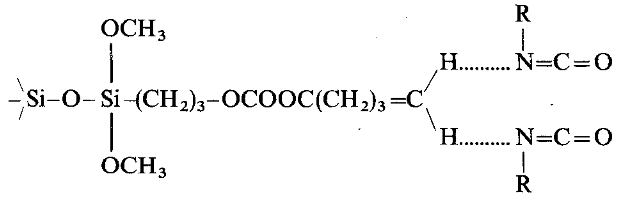


Fig. 1. Interaction of monoalkoxyl titanate (a) and trialkoxylsilane (b) with a surface of silicate or kaolin

As noticed during our studies, ANS-15 and AS-2 silicates, in particular, in the urethane composition, favor formation of additional cross-linking bonds, which leads to an increase in relaxation moduli. It follows from Table 6 that clearly higher strengthening parameters (M-100 and $R_r$) were obtained for polyurethanes filled with silicates modified with silane and titanate containing methacryl groups.

Surface modification, especially of silicates, with 2 weight parts of silane A-174 or titanate KR 33 CS clearly exerts the best reinforcing effect for polyurethanes. In particular, the influence of KR 33 CS has been reported to be very favorable, as it increases tensile strength of polyurethanes filled with ANS-15 silicate modified with this titanate up to 5.00 MPA (for 30 weight parts of filler in polymer.) Improvement of tensile strength parameters of polyurethanes filled with silicates modified by silane A-174 or titanate KR 33 CS is probably due to the fact that the methacryl group facilitates formation of cross-linking bonds between polyurethane and silica.

Silicas modified with methacryloxysilane A-174 may also interact with isocyane groups in the following way [16]:



$$\begin{array}{lr} & \overset{\displaystyle R}{|}\\ & H\ldots\ldots N{=}C{=}O\\ {-}Si{-}O{-}\underset{\displaystyle OCH_3}{\overset{\displaystyle OCH_3}{Si}}{-}(CH_2)_3{-}OCOOC(CH_2)_3{=}C & \\ & H\ldots\ldots N{=}C{=}O\\ & \underset{\displaystyle R}{|} \end{array}$$

Urethane elastomers without filler are characterized by a low ability to attenuate the mechanical

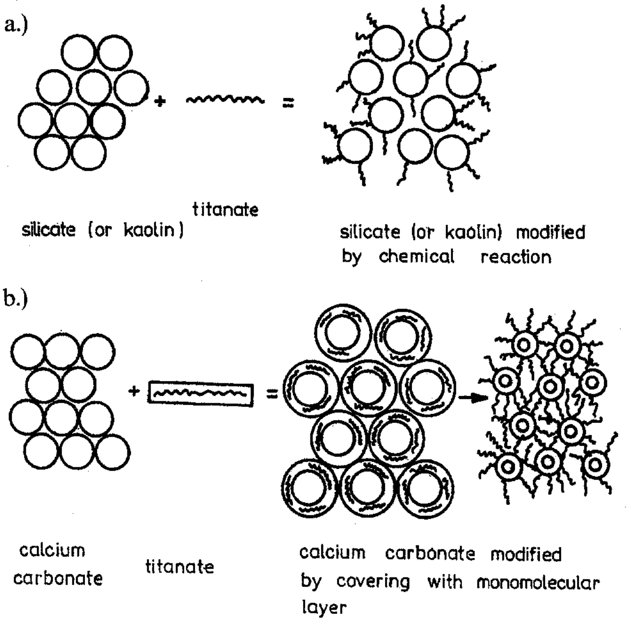


Fig. 2. Interaction of titanate coupling agents (KR TTS of KR 33 CS) and filler surface

a) sodium-aluminum silicate, aluminum silicate or kaolin
b) precipitated calcium carbonate

energy, as they have a small histeresis loop (Table 6), while polyurethanes, particularly those containing silicates, show a higher absorption of mechanical energy. With increasing amount of filler, the histeresis loop increases. The highest values of the histeresis loop are noted for polyurethanes containing silicates ANS-15 and AS-2 modified with 2 weight parts of silane A-174 or titanate KR 33 CS.

Addition of silicates to polyurethanes up to an amount of 30% brings about a regular increase in the relative elongation, but the type of silicate or of the modifying agent does not have a significant effect on changes of this parameter. The dependence of polyurethanes strengthening parameters on the amount of silicate is extreme in character, with the optimum modulus and tensile strength parameters obtained for compositions containing 20–30% of filler (silicate or carbonate.)

Neither of the studied silicates are suitable for filling plastics, e.g., polyvinyl chloride, which results from the fact that silicates surface adsorbed the mixtures' plasticizers and stabilizers. Due to a relatively low adsorption of plasticizers and

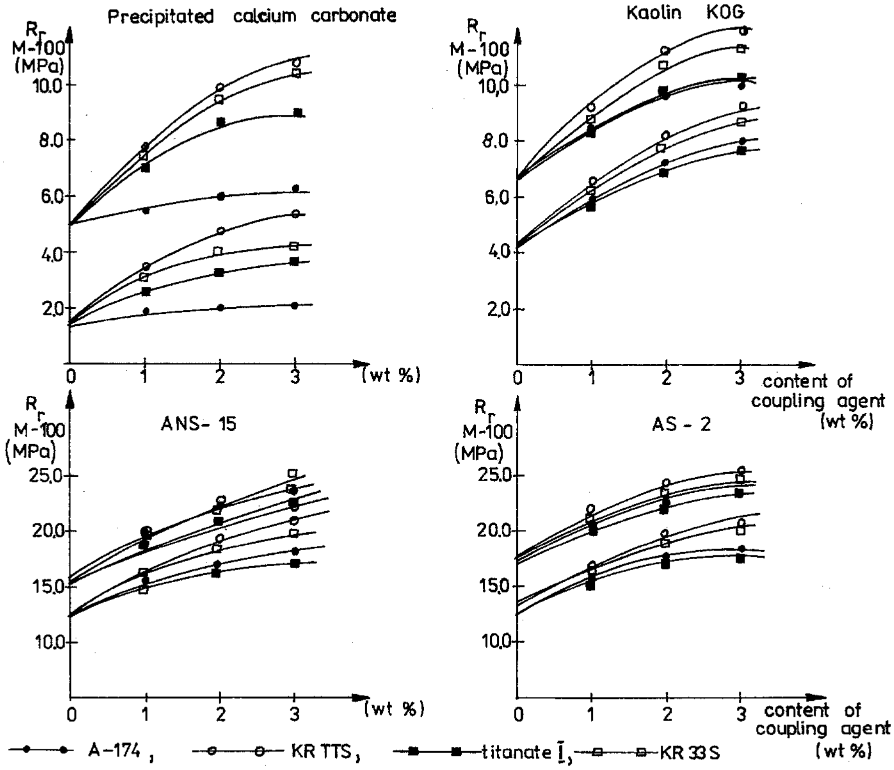


Fig. 3. Strengthening parameters of vulcanizates (mixture I) with studies fillers as a function of proadhesive agent content

Table 5. Physico-mechanical properties of vulcanizates containing the unmodified and modified fillers under study (vulcanization time 20 min).

| Filler | $H$ [° Sh] | M-300 [MPa] | $R_r$ [MPa] | $E_r$ [%] | $E_t$ [%] | $R_{rd}$ [kN/m] |
|---|---|---|---|---|---|---|
| Mixture I | | | | | | |
| Precipitated calcium carbonate | | | | | | |
| unmodified | 50 | 1.6 | 5.3 | 750 | 18 | – |
| + 2 wt/wt A-174 | 50 | 2.0 | 6.0 | 750 | 18 | – |
| + 2 wt/wt Titanate I | 52 | 3.3 | 8.5 | 680 | 16 | – |
| + 2 wt/wt KR TTS | 54 | 4.5 | 10.0 | 640 | 14 | – |
| + 2 wt/wt KR 33 CS | 52 | 4.0 | 9.6 | 660 | 16 | – |
| Kaolin KOG | | | | | | |
| unmodified | 60 | 4.3 | 6.6 | 500 | 24 | – |
| + 2 wt/wt A-174 | 64 | 7.1 | 9.8 | 370 | 20 | – |
| + 2 wt/wt Titanate I | 62 | 7.4 | 9.9 | 360 | 20 | – |
| + 2 wt/wt KR TTS | 64 | 8.1 | 11.4 | 400 | 18 | – |
| + 2 wt/wt KR 33 CS | 63 | 7.9 | 10.7 | 420 | 18 | – |
| ANS-15 | | | | | | |
| unmodified | 75 | 12.6 | 15.9 | 380 | 10 | 78.5 |
| + 2 wt/wt A-174 | 75 | 16.8 | 20.4 | 360 | 8 | 80.4 |
| + 2 wt/wt Titanate I | 75 | 16.2 | 20.3 | 340 | 8 | 79.9 |
| + 2 wt/wt KR TTS | 77 | 18.0 | 21.1 | 340 | 6 | 87.7 |
| + 2 wt/wt KR 33 CS | 76 | 17.5 | 20.9 | 360 | 8 | 87.0 |
| AS-2 unmodified | 75 | 12.9 | 17.2 | 380 | 10 | 78.0 |
| + 2 wt/wt A-174 | 77 | 17.7 | 22.1 | 360 | 10 | 82.3 |
| + 2 wt/wt Titanate I | 76 | 17.4 | 22.0 | 360 | 10 | 83.3 |
| + 2 wt/wt KR TTS | 77 | 19.1 | 23.6 | 360 | 8 | 88.1 |
| + 2 wt/wt KR 33 CS | 77 | 18.8 | 22.9 | 360 | 10 | 87.5 |
| Mixture II | | | | | | |
| Precipitated calcium carbonate | | | | | | |
| unmodified | 50 | 1.5 | 5.0 | 750 | 18 | – |
| + 2 wt/wt A-174 | 50 | 2.0 | 5.2 | 700 | 18 | – |
| + 2 wt/wt Titanate I | 50 | 2.8 | 8.1 | 680 | 16 | – |
| + 2 wt/wt KR TTS | 51 | 4.1 | 9.9 | 600 | 16 | – |
| + 2 wt/wt KR 33 CS | 50 | 3.7 | 9.1 | 620 | 16 | – |
| Kaolin KOG | | | | | | |
| unmodified | 62 | 4.4 | 7.2 | 480 | 20 | – |
| + 2 wt/wt A-174 | 64 | 7.3 | 9.9 | 360 | 18 | – |

Table 5. (*continued*)

| Filler | $H$ [° Sh] | M-300 [MPa] | $R_r$ [MPa] | $E_r$ [%] | $E_t$ [%] | $R_{rd}$ [kN/m] |
|---|---|---|---|---|---|---|
| + 2 wt/wt Titanate I | 65 | 7.3 | 10.2 | 400 | 16 | – |
| + 2 wt/wt KR TTS | 65 | 8.0 | 12.1 | 360 | 16 | – |
| + 2 wt/wt KR 33 CS | 65 | 7.5 | 11.3 | 400 | 18 | – |
| ANS-15 unmodified | 69 | 16.2 | 18.1 | 360 | 12 | 77.2 |
| + 2 wt/wt A-174 | 70 | 19.5 | 21.2 | 360 | 12 | 79.2 |
| + 2 wt/wt Titanate I | 71 | 19.1 | 20.8 | 340 | 12 | 79.8 |
| + 2 wt/wt KR TTS | 72 | 19.7 | 22.7 | 340 | 10 | 84.5 |
| + 2 wt/wt KR 33 CS | 71 | 19.5 | 22.4 | 340 | 12 | 83.9 |
| AS-2 unmodified | 72 | 15.9 | 18.5 | 380 | 10 | 77.7 |
| + 2 wt/wt A-174 | 72 | 19.0 | 20.9 | 360 | 10 | 80.5 |
| + 2 wt/wt Titanate I | 73 | 19.2 | 21.1 | 360 | 12 | 80.3 |
| + 2 wt/wt KR TTS | 74 | 20.3 | 22.9 | 340 | 8 | 83.5 |
| + 2 wt/wt KR 33 CS | 74 | 19.4 | 22.5 | 340 | 10 | 82.1 |

$H$ – Shore hardness
M-300 – 300% Modulus
$R_r$ – Tensile strength
$E_r$ – Relative elongation
$E_t$ – Tension set
$R_{rd}$ – Tearing strength

stabilizers on the surface of precipitated calcium carbonate, the carbonate may be introduced to the plastics in large amounts. The amount of the introduced filler may vary from 5 to 100 weight parts per PVC, depending on the required physical properties of the ready-made products. The precipitated calcium carbonate is introduced to the PVC mixture mainly in order to reduce the price of the product, but also to improve some mechanical properties, e.g., impact strength, and to increase dielectric properties.

Addition of the modified calcium carbonates practically did not affect the onset of PVC gelation, which occurred at 1.5 min. However, it exerted a clear influence on the gelling period, stability, and the rotation moment of the PVC film. Especially the turning moment is of importance here, as it determines the degree of a given mixture's plasticity at a given temperature (the higher the moment, the lower the degree of plasticity.) As follows from Table 7, the precipitated calcium carbonate modified with triisostearoyltitanate (at the amount of both 1 or 2 weight parts) and carbonate modified with isopropyl, trimethacryl titanate (at the amount of 2 weight parts) are of special interest.

Depending on the amount of the modifier used, the safe processing time ranges from 23.5 to 25.0 min. In these cases, the values of turning moment decrease, which is indicative of an increase in the plasticity degree of the film and which elicits improvement of its strength parameters. For calcium carbonate modified with silane A-174, plasticity and stability of PVC film increase only slightly.

Physico-chemical examinations for silicate pigments, both unmodified and modified, are given in Table 8.

Volume of the sedimentation of silicates samples in aqueous media is determined to characterize

Table 6. Physico-mechanical properties of polyurethanes filled with unmodified and modified fillers.

| Fillers content wt/wt polymer | M-100 [MPa] | $R_r$ [MPa] | $E_r$ [%] | $H$ [° Sh] | Hysteresis loop [%] |
|---|---|---|---|---|---|
| 0 | 0.76 | 0.92 | 100 | 38 | 1.00 |
| Precipitated calcium carbonate unmodified | | | | | |
| 5 | 0.72 | 0.95 | 135 | 39 | 1.25 |
| 10 | 0.70 | 1.30 | 130 | 42 | 1.32 |
| 20 | 0.95 | 1.48 | 130 | 49 | 3.15 |
| 30 | 1.10 | 1.65 | 205 | 55 | 6.30 |
| $CaCO_3$ modified with 2 wt/wt A-174 | | | | | |
| 5 | 0.91 | 1.10 | 130 | 40 | 1.45 |
| 10 | 0.98 | 1.35 | 130 | 42 | 1.60 |
| 20 | 1.12 | 1.68 | 160 | 48 | 3.30 |
| 30 | 1.40 | 2.12 | 180 | 54 | 7.00 |
| $CaCO_3$ modified with 2 wt/wt KR 33 CS | | | | | |
| 20 | 1.25 | 2.01 | 180 | 48 | 4.15 |
| 30 | 1.66 | 2.28 | 200 | 55 | 7.12 |
| Sodium-aluminum silicate ANS-15 unmodified | | | | | |
| 5 | 1.45 | 1.68 | 120 | 58 | 0.85 |
| 10 | 1.68 | 2.25 | 130 | 62 | 2.15 |
| 20 | 2.40 | 3.33 | 220 | 63 | 9.05 |
| 30 | 2.65 | 4.05 | 230 | 65 | 12.80 |
| ANS-15 modified with 2 wt/wt A-174 | | | | | |
| 20 | 2.80 | 4.10 | 230 | 64 | 10.15 |
| 30 | 3.05 | 4.82 | 240 | 65 | 13.63 |
| ANS-15 modified with 2 wt/wt KR 33 CS | | | | | |
| 20 | 2.80 | 4.15 | 230 | 64 | 10.20 |
| 30 | 3.02 | 4.70 | 230 | 64 | 10.80 |
| AS-2 modified with 2 wt/wt A-174 | | | | | |
| 20 | 2.95 | 4.26 | 240 | 65 | 11.05 |
| 30 | 3.35 | 5.15 | 240 | 65 | 12.60 |
| AS-2 modified with 2 wt/wt KR 33 CS | | | | | |
| 20 | 2.90 | 4.30 | 240 | 65 | 10.95 |
| 30 | 3.20 | 5.00 | 250 | 65 | 11.83 |

M-100 – 100% Modulus
$R_r$ – Tensile strength
$E_r$ – Relative elongation
$H$ – Shore hardness

the so-called refinement of the sample or its "looseness." The greater the volume of silicate following precipitation, the higher is the refinement of silicate. This is a very important quality of pigments, which implies high covering power. As follows from Table 8, high covering power has been observed for sodium-aluminum and aluminum silicates modified especially with titanate coupling agents (in many cases, the sedimentation volume exceeds 2.0 cm$^3$).

Glass plates painted with the obtained pigments suspended in a bleached linen oil were radiated with a quartz lamp (6 h) and exposed to the action of $H_2S$, $SO_2$, and $NH_3$. In all these cases,

Table 7. Estimation of the quality of PVC film filled with modified precipitated calcium carbonate.

| Coupling agent | Content of coupling agent [wt/wt] | Temp. of PVC mixture [C] | Onset of PVC gellation [min] | Gelling period [min] | Safe procesing time [min] | Max. turning moment [pm] | Min. turning moment [pm] |
|---|---|---|---|---|---|---|---|
| No coupling agent | – | * **<br>181(140) | 1.5 | 5.5 | 21.5 | 2400 | 1130 |
| A-174 | 1 | 180(135) | 1.5 | 5.5 | 22.0 | 2350 | 1110 |
| | 2 | 180(135) | 1.5 | 6.0 | 22.0 | 2300 | 1100 |
| Titanate I | 1 | 178(136) | 1.5 | 7.0 | 22.5 | 2200 | 1080 |
| | 2 | 178(135) | 1.5 | 7.5 | 23.0 | 2150 | 1080 |
| KR TTS | 1 | 175(125) | 1.5 | 8.5 | 24.0 | 2050 | 1050 |
| | 2 | 174(125) | 1.5 | 9.5 | 25.0 | 2000 | 1020 |
| KR 33 | 1 | 170(124) | 1.5 | 8.0 | 23.5 | 2100 | 1070 |
| CS | 2 | 174(125) | 1.5 | 9.0 | 24.0 | 2000 | 1060 |

*) temperature during preparation of PVC mixture
**) the number in parentheses stand for the temperature in a crusher during the mixture packing.

Table 8. Measurements of properties typical of unmodified and modified pigments (for selected sodium-aluminum and aluminum silicates).

| Sample | Residue volume [cm$^3$] | Re-emission [%] | | | | |
|---|---|---|---|---|---|---|
| | | standart plate*) | light | post | | |
| | | | | H$_2$S | SO$_2$ | NH$_3$ |
| ANS-15 unmodified | 1.7 | 67.5 | 67.3 | 67.3 | 67.2 | 67.6 |
| ANS + 1 wt. A-174 | 1.7 | 67.5 | 67.4 | 67.4 | 67.3 | 67.4 |
| ANS + 2 wt. A-174 | 1.8 | 67.5 | 67.4 | 67.3 | 67.4 | 67.4 |
| + 1 wt. KR TTS | 1.8 | 67.5 | 67.4 | 67.4 | 67.4 | 67.4 |
| + 2 wt. KR TTS | 2.0 | 67.5 | 67.5 | 67.4 | 67.4 | 67.4 |
| + 1 wt. KR 33 CS | 1.8 | 67.5 | 67.4 | 67.4 | 67.4 | 67.4 |
| + 2 wt. KR 33 CS | 1.9 | 67.5 | 67.4 | 67.5 | 67.4 | 67.5 |
| AS-2 unmodified | 1.8 | 69.5 | 69.0 | 69.1 | 68.8 | 68.8 |
| AS + 1 wt. A-174 | 1.9 | 69.5 | 69.2 | 69.1 | 69.1 | 69.0 |
| + 2 wt. A-174 | 2.0 | 69.5 | 69.3 | 69.2 | 69.1 | 69.1 |
| + 1 wt. KR TTS | 2.1 | 69.5 | 69.3 | 69.3 | 69.3 | 69.2 |
| + 2 wt. KR TTS | 2.3 | 69.5 | 69.5 | 69.4 | 69.4 | 69.3 |
| + 1 wt. KR 33 CS | 2.1 | 69.5 | 69.3 | 69.3 | 69.3 | 69.4 |
| + 2 wt. KR 33 CS | 2.2 | 69.5 | 69.4 | 69.4 | 69.4 | 69.4 |

*) the leukometer was titrated by a plate with a barium sulfate of re-emission equal to 68.7% a white filter was applied.

either only a minimum decrease of re-emission in comparison to the standard was observed, or none at all, which testifies to a high resistance of these white silicates to the reagents. In practice, almost no darkening of glass plates painted with these silicates is observed.

## References

1. K.L. Mittal, ed.: "Silanes and other coupling agents" VSP, Utrecht, 1992.
2. Monte SJ, Sugerman G, Seeman DJ. Titanate coupling agents-current applications (V). Bull N KR 0577-6
3. Krysztafkiewicz A (1987) Chemia Stosowana, 31:443
4. Brewis D (1988) J Adhesion 26:215
5. Leidheiser H, Jr., Funke W (1987) J Oil Colour Chem Assoc, 70, 121
6. Yoldas BE (1982) J Mater Sci, 21:1087
7. Pike RA (1986) Int J Adhesion Adhesives, 6:21
8. Domka L (1979) Szklo i Ceramika, 30:133
9. Domka L (1990) J Adhes Sci Technol 4:1
10. Krysztafkiewicz A, Maik M, Rager B, Powder Technology (in press)

11. Paryjczak T (1975) "Chromatografia gazowa w badaniach adsorpcji i katalizy", PWN, Warszawa,
12. Domka L, Krysztafkiewicz A, Krysztafkiewicz W (1982) Pat. PRL nr 119:358
13. Domka L, Marciniec B, Krysztafkiewicz A (1983) Pat. PRL nr 115:671
14. Zielenkiewicz W, Kurek T (1966) Przem Chem 45:247
15. Krysztafkiewicz A, Domka L, Wieczorek W (1985) Colloid Polym Sci 263:804
16. Krysztafkiewicz A, Maik M (1987) Colloid Polym Sci 265:704

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