Silica recovery from waste obtained in hydrofluoric acid and aluminum fluoride production from fluosilicic acid

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Abstract

A procedure is presented for utilization of waste silicas from hydrogen fluoride synthesis and aluminum fluoride production. A method of purifying silica from fluorine impurities is given. Results of studies on application of by-product silicas from the fluorine processing as fillers for rubber mixtures and urethan elastomers is given. Conditions are presented for preparing chemically pure solutions of sodium and potassium metasilicates of average modules. The surface of the refined silica is modified by using methanol solutions of various silane coupling agents or titanate coupling agent solution in carbon tetrachloride. Effects of the type of the modifier used and of its amount on the strength of butadiene–styrene rubber vulcanizates and urethane elastomers are determined.

Keywords: Silica recovery; Hydrofluoric acid; Aluminum fluoride

1. Introduction

Proper utilization of waste silica obtained in the production of fluorine compounds constitutes a major problem due to economic and ecological reasons. Large amounts of silicas are formed in industrial production of aluminum fluoride and hydrofluoric acid. They differ from each other, however; especially in microstructure, impurities, and the development of outer surface [1, 2]. It is thought that waste silica precipitated from the hydrogen fluoride synthesis might possess interesting application potentials [3]. In the Poznań Chemical Plant R. May in Luboń, hydrofluoric acid is obtained from fluosilicic acid in the reaction with concentrated sulfuric acid (ca. 95%).

$$H_2SiF_6 + H_2SO_4 \rightarrow SiF_4 + 2HF + H_2SO_4,$$

$$SiF_4 + 2H_2O \rightarrow SiO_2 + 4HF.$$
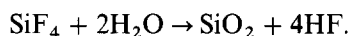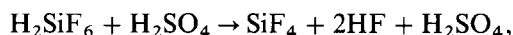
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The HF–H_2O–H_2SO_4 mixture is separated via different ways, such as distillation or HF expulsion by hydrocarbons. Postreaction H_2SO_4, containing HF, is recycled in the decomposition of fluosilicic acid. Silica filtered from the reaction system is a relatively inconvenient waste containing, beside solid, considerable amount of water (up to 70%). The reflux from dumped waste silica and the waters coming from the dumps-washing with atmospheric rain may cause a serious hazard of polluting open waters.
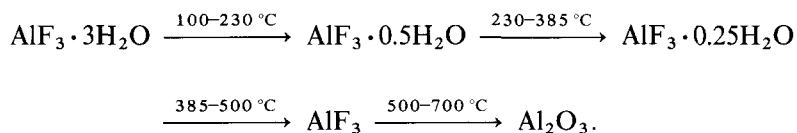
In the process of obtaining aluminum fluoride, silica is formed in the reaction of neutralizing fluosilicic acid with aluminum hydroxide:

$$H_2SiF_6 + 2Al(OH)_3 + xH_2O \rightarrow 2AlF_3 \cdot xH_2O + SiO_2 + 4H_2O.$$
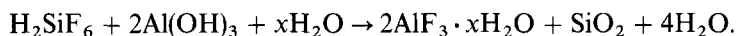
Structure of the precipitated silica depends on many variables: among others, duration of reaction, temperature, the way in which reagents are dosed, structure of $Al(OH)_3$ used in the process, purity of the applied fluorosilicic acid [2]. High temperature and high concentration of fluosilicic acid significantly affect the reaction rate and lead to formation of a well filtrable silica.

The process of obtaining aluminum fluoride involves two operations: neutralization of fluosilicic acid using $Al(OH)_3$ with silica precipitation and crystallization of the hydrated fluoride.

Because of the absence of stable parameters of the procedure, at least such as concentration of free H_2SiF_6 following neutralization, number of crystallization centers, temperature of crystallization (chance of local overheating due to addition of the overheated water steam) the process may follow various routes:

$$AlF_3 \cdot 3H_2O \xrightarrow{100-230\,°C} AlF_3 \cdot 0.5H_2O \xrightarrow{230-385\,°C} AlF_3 \cdot 0.25H_2O$$

$$\xrightarrow{385-500\,°C} AlF_3 \xrightarrow{500-700\,°C} Al_2O_3.$$

At temperatures of 120–140 °C $AlF_3 \cdot H_2O$, which gets decomposed as follows, may be formed:

$$AlF_3 \cdot H_2O \xrightarrow{150\,°C} AlF_3 \cdot 0.8H_2O \xrightarrow{200\,°C} AlF_3 \cdot 0.6H_2O.$$
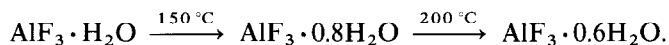
Thus, in theory aluminum fluoride may be reclaimed from oversaturated solutions in the form of one of numerous hydrates, like $AlF_3 \cdot 9H_2O$; $AlF_3 \cdot 5.5H_2O$; $AlF_3 \cdot 3.5H_2O$; $AlF_3 \cdot 3H_2O$; $AlF_3 \cdot H_2O$. In order to obtain $AlF_3 \cdot 3H_2O$, the temperature of crystallization should be kept within 60–100 °C.

Due to the reasons specified above, an investigation of utilization of by-product silicas has been carried out. This investigation heads in five different directions: recycling of waste silica into solutions of sodium or potassium metasilicate (the so-called water glass), Na_2SiO_3 and K_2SiO_3 of different modules [4–7], obtaining active silica as filtration medium in pharmaceutical, food, and other industries [8], production of average medium fillers for polymers or carriers to be used in catalytic mass preparation [9], synthesis of substituent building materials from the by-product

silicas with the use of chalks, application of waste silicas in polishing and cosmetic pastes. The fundamental condition that the waste silicas has to fulfill before it can be applied any further is its purification, i.e. removal of fluorine compounds trapped on its surface. This is very important, especially in the case of waste silicas applied as elastomer fillers.

The search for the sources of a well-dispersed silica filler is now of utmost importance [10–18]. At present, actually only one type of silica filler, labelled Arsil, is produced [19]. It has a form of a highly dispersed active silica and is obtained from sodium metasilicate in a complex process of precipitation by sulfuric acid.

2. Experimental

2.1. Materials

Waste silicas were provided by the Poznań Chemical Plant of Dr. R. May in Luboń, and it was a direct product of hydrofluoric acid synthesis and aluminum fluoride production. Silica surfaces were modified by the following proadhesive compounds from the silane coupling agents (Union Carbide):
   A-172 vinyl-tri-(β-methoxyethoxy)silane,
   A-189 γ-mercapto-propyltrimethoxysilane,
   A-1893 β-mercapto-ethyltriethoxysilane,
   A-1100 -γ-aminopropyl-triethoxysilane,
   A-1120 N'β-(aminoethyl)-γ-aminopropyl-trimethoxysilane,
   A-151 vinyltriethoxysilane,
   A-174 γ-metacryloxypropyltrimethoxysilane,
   A-187 γ-glycydoxypropyltrimethoxysilane,
and titanate coupling agent (Kenrich Petrochemicals)
   :KR-TTS isopropyl, triisostearoyl titanate.
   Silica C-5 [20], KS-300 (made by Hoesch, Germany), Arsil [19], and pyrogenic silica (produced by Degussa, Germany) were also employed, for comparison.

2.2. Procedure and methods

Prior to the application of waste silicas, obtained upon hydrofluoric acid synthesis and aluminum fluoride production in elastomers processing, all its by-production impurities (in particular HF and H_2SiF_6) were removed. The impurities were removed via a washing procedure. To this effect, waste silica was treated on a filter with hot water, and subsequently the silica was dried at 105 °C. Aqueous solutions formed as a result of silica washing contained dissolved fluorine compounds (mainly fluorides and fluosilicates). They were passed through a layer of calcium oxide. Thus defluorinated water was recycled back to the process of purifying crude silica.

Production of aluminum fluoride separation of silica from the original filtrate containing hydrated aluminum fluoride ($AlF_3 \cdot xH_2O$) does not follow identical pattern for all samples. In some cases the silica is separated in the form of a fine sediment,

Table 1
Examples of the filtered out silica with aluminum fluoride production

No	H_2SiF_6 concentration (g/dm^3)	Amount of water out filtered silica (%)	Amount of AlF$_3$ in silica (%)		Bulk density	Specific surface area (m^2/g)	Water absorption (g/100 g)	Dibutyl-phthalate absorption (g/100 g)
			After washing in water	After washing in HCl				
1	150	43.0	1.37	2.48	185	24.5	350	370
2	200	30.7	0.92	1.96	260	14.7	290	290
3	175	39.5	1.09	2.60	230	20.3	320	310
4	195	40.1	0.42	1.26	240	21.3	330	300
5	180	36.2	0.59	0.92	230	20.8	310	300
6	195	30.4	0.67	1.67	255	14.0	280	290
7	165	46.5	0.17	2.52	170	23.8	350	360
8	210	31.9	0.87	1.17	270	16.2	290	290
9	195	34.6	0.10	0.34	250	18.5	300	310

suspended in large volumes of water and in the other cases – in the coarse – granular form, easily filtrable and adsorbing on its surface lower amounts of water. During separation, application of exceedingly high temperatures and too high concentrations is associated with the risk of fluoride crystallization before the silica is filtered out, which in this case contains large impurities in the form of aluminum fluoride. Purification of silica is difficult since aluminum fluoride is poorly water soluble. It should be mentioned that the hydrated aluminum fluoride begins to crystallize very fast and, therefore, the rate of filtering out the silica is of principal importance.

Table 1 presents chosen examples of the filtered out silica. Due to low solubility of $AlF_3 \cdot xH_2O$ in water, the silica was purified in hot water or in 20% hydrochloric acid.

The silicas under study were centrifuged and dried to determine the content of humidity, silica, fluorine, aluminium, magnesium, and iron [4]. The specific surface area for the waste silica was established using a comparative chromatography method [21]. The size of molecules was examined by a technique of transmission electron microscope, an indirect method of one-step replica [22], using the JEM-7A electron microscope (Japan). The degree of whiteness was determined in a Zeiss leucometer (Germany). Other physico-chemical parameters (bulk density, water and dibuthyl phthalate absorption) were established according to the widely accepted research methods for fillers strengthening polymer systems.

Unpurified silicas, obtained directly from production, were used to obtain sodium and potassium metasilicate solution. The solutions of sodium metasilicate or potassium metasilicate were obtained by dissolving waste silicas in solutions of sodium hydroxide or potassium hydroxide under elevated pressure, in an autoclave constructed particularly for the purpose, from alkali-resistant steel [7]. In order to remove fluoride ions and fluorosilicate ions, the attempts to dissolve waste silicas in NaOH or KOH were performed adding solid hydroxides, $Ca(OH)_2$, $Ba(OH)_2$, $Mg(OH)_2$,

directly to the autoclave. Addition of the compounds amounted to 1.0% to 3.0% (w/w). The water-insoluble sediment, containing the unreacted silica and fluorides of alkaline earth metals, were separated by filtration from sodium metasilicate solution. In order to improve filtering ability of the solution, Ropol 24 (0.1% w/w) and diatomaceous earth, Dicalit (USA production, 4 g/dm^3 of sodium metasilicate solution), were added.

Silica surface was modified by applying silane and titanate coupling agents. In the case of the former, modification was run in methanol–water (4:1) solution, while titanate was dissolved in carbon tetrachloride. In the modification process, the equipment used consisted of a closed, V-shaped vessel set in motion, with a doser of the modifying solution and a stirrer placed inside [23, 24]. For waste silica modification, a solution containing 0.5–3.0 weight parts of modifying substance per 100 weight parts of the filler was used. Quality of the modified silicas obtained was tested by calorimetric studies, which involved measurements of the heat of immersion of the silicas in water (polar liquid) and benzene (nonpolar liquid). In the studies, the KRM-type differential calorimeter was used [25]. In addition, hydrophobization degrees (N) of silica modified surfaces were calculated by the formula

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

where $(H_i^B)_m$ is the heat of immersion of the surface of modified silica in benzene and $(H_i^B)_n$ the heat of immersion of the surface of unmodified silica in benzene.

Unmodified and modified waste silicas were tested in rubber mixtures. To this effect, Ker 1500 butadiene-styrene rubber (produced by the Chemical Plant in Oś-więcim) was used. Composition of the mixture was as follows (in weight parts): Ker 1500 (100); zinc oxide (3); stearic acid (2); waste silica (50); accelerator DM (2.2); accelerator M (1.4); sulphur (2). Vulcanization was run in a hydraulic press with a steam heater at 143 °C, under press cylinder pressure of 150 atm, for 20–40 min.

The subsequent step involved testing the effect of trace amounts of fluorine compounds contained in waste silica, on the aging processes of rubber. The measuring process was based on a comparison of mechanical properties of rubber noted directly after vulcanization with analogous parameters determined after aging, which occurred under the following conditions: temperature: 50 °C, 100 °C; time: 144 h, 72 h.

These measurements were conducted in a thermostatic dryer, which assured a constant flow of air of a given temperature.

Application studies on silicas in rubber were also carried out on a commercial scale. Waste silica was introduced into natural rubber and the composition of thus prepared mixture was as follows: natural rubber RSS I (100); zinc oxide (5); silica (58.60); Polnox R (1); accelerator DM (0.80); accelerator D (1.20); stearin (3); sulfur (2.5). For the sake of comparison, the above mixture was also prepared for the following compounds used as fillers: silica C-5, KS-300 and Arsil. The optimum of natural rubber vulcanization was determined using an oscillating rheometer (Monsanto).

Some selected waste silicas (mainly, those modified with aminosilanes) were used as polyurethane fillers. For synthesis of polyurethane, toluelene diisocyanate (Izocyn
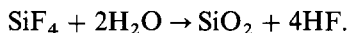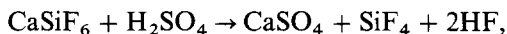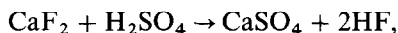
T-80, produced by "Zachem" Bydgoszcz, isocyanate groups content-42%), polyoxy-propylene glycol (Rokopol 2002, produced by Nadodrzański Plant of Organic Chemistry "Rokita", Brzeg Dolny, average molecular weight 2000), polyoxypropylene triol (Rokopol 330, produced by Nadodrzański Plant of Organic Chemistry "Rokita", Brzeg Dolny, average molecular weight 3600) and suitable filler were used. Catalyst of the synthesis was mercuryphenyl oleate (Bayer, Germany) [9].

3. Discussion of results

A scheme of the equipment used for waste silica with HF production purification is shown in Fig. 1. According to the first version (Fig. 1(a)), crude silica directly after the hydrofluoric acid synthesis is placed on a filter, where it is periodically washed with hot water (80 °C). Partially water-soluble fluorides are washed off in the excess of water. In order to reduce the amount of water used for this purpose, it is applied in portions and after one washing it is directed onto liquid-containing vessels placed in series. By a proper valve regulation and using the circulating pump, the vessels supply water of different degree of saturation with fluorine compounds derived from washing the previous silica portions on a filter. Water of the highest degree of saturation with fluorine compounds, after a subsequent elution of silica newly placed on a filter, is transferred onto an equipment which removes fluorides dissolved in it. Water can be purified via two ways. According to the first method, a properly prepared active layer containing calcium oxide, or, in the case of low concentration, an anion-exchange layer is applied. In this method, circulation of water in the system is practically closed. Through an intermediate vessel, pump, and heat-exchanger, purified water is directed on a filter in order to wash successive portions of waste silica.

According to the second version (Fig. 1(b)), fluorides are washed in similar conditions in hot water, yet for purification of waste silica, a battery of vacuum filters arranged in series is applied. The filters operate on a cascade-like basis, so that on the last filter water after the elution of the first filter cake is maximally saturated with fluorine compounds and thus directed into the regeneration equipment, which, as in the first method, can operate in two systems.

After regeneration of water on the bed of calcium oxide, water soluble fluorine compounds are transformed into insoluble sediment of CaF_2 and $CaSiF_6$. The bed containing insoluble fluorine compounds is used in HF production, where it is decomposed by sulfuric acid according to the following reactions:

$$CaF_2 + H_2SO_4 \rightarrow CaSO_4 + 2HF,$$

$$CaSiF_6 + H_2SO_4 \rightarrow CaSO_4 + SiF_4 + 2HF,$$

$$SiF_4 + 2H_2O \rightarrow SiO_2 + 4HF.$$

This is the way fluorine cycle closes in the proposed method of silica utilization.

As indicated by the presented data (Table 1) samples of waste silica from AlF_3 production, which are filtered out with higher amounts of adsorbed water, exhibit higher specific surface and lowest bulk density. They show also better water absorption
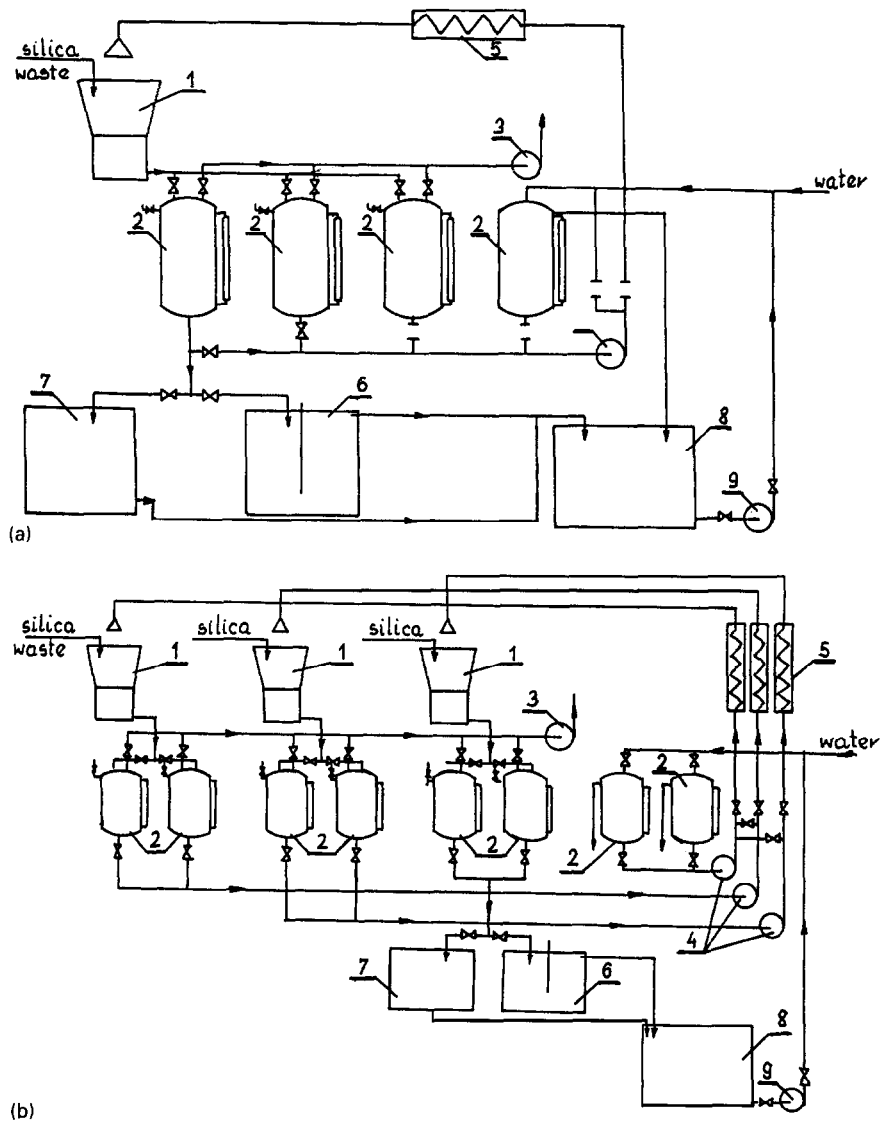
Fig. 1. Equipment for purification of waste silica from hydrofluoric acid production. (a) Version I – adaptation of single filter to purification of silica in hot water. (b) version II – adaptation of filters battery: (1) filter; (2) liquid-containing vessels; (3) vacuum pump; (4) circulating pump; (5) heat exchanger; (6) vessel with active layer containing calcium oxide; (7) vessel with anion-exchanger layer; (8) vessel with purified water; (9) circulating pump.

and dibutyl phthalate absorption. The silica particles are precipitated in the form of fine particles (of the lower mean particle diameter). Due to augmented surface activity of the sample (higher specific surface), the silicas exhibit on their outer surface higher numbers of silanol groups, which their hydrophylic character. In the situation, the

Table 2
Chemical composition of waste silicas directly after production and following purification on the filter press

Composition (% weight)	Waste silica from HF production	Silica after purification (Variant I)	Silica after purification (Variant II)
SiO_2	57.8	88.2	88.5
Moisture	30.7	3.4	3.5
Al_2O_3	1.2	0.2–0.3	0.2
F^-	1.6	0.1–0.2	0.1
CaO	0.18	0.02	0.01
MgO	0.05	0.02	0.01
Fe^{2+} and Fe^{3+}	0.21	0.01	0.02
P_2O_5	0.12	0.01	0.01

Composition (% weight)	Waste silica from AlF_3 production	Silica after purification in hot water	Silica after purification in HCl
SiO_2	54.6	87.5	87.7
Moisture	32.8	4.2	4.4
Al_2O_3	2.3	1.8	0.2
F^-	1.4	0.7	0.2
CaO	0.15	0.05	0.01
MgO	0.10	0.03	0.01
Fe^{2+} and Fe^{3+}	0.30	0.05	0.01
P_2O_5	0.25	0.10	0.02

silica easily adsorbed large quantities of water (e.g. through hydrogen bonds). The data of the Table 1 indicate that fine granular silica and sediments are precipitated in the case of using more concentrated fluosilicic acid to produce the hydrated aluminum fluoride. The phenomenon may result from occlusion on the silica surface of the excess of fluosilicic acid, which hampers increase in grain size. In such cases silica is precipitated in the form of a very fine sediment.

Results of the analysis of chemical composition of silica obtained directly from HF synthesis and after purification with hot water on filters according to the two methods described above are shown in Table 2. Physico-chemical parameters of the refined and dried by-product silicas are given in Table 3. As follows from the tables, the physico-chemical parameters of waste silica after washing with water are al- most identical, independent of the filtration variant used. In further studies on surface modification, waste silica washed on a battery according to variant II was used.

Sodium metasilicate and potassium metasilicate solutions obtained in the absence of hydroxides of alkaline earth metals exibited properties incompatible with sub- sequent use of the metasilicates in production of white silica and silicate fillers. The solutions showed relatively high modules (2.7–2.9) with practically complete absence of solid suspensions. The greatest disadvantage of their subsequent application,

Table 3
Physico-chemical properties of waste silicas after purification in hot water
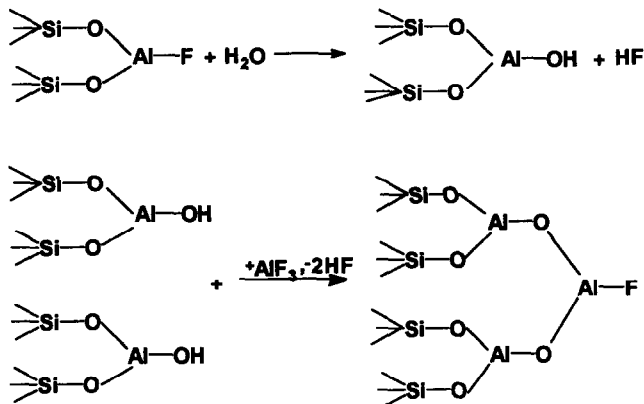
Physico-chemical parameters	Silica after purification (Variant I)	Silica after purification (Variant II)
Appearance	White powder	White powder
Structure	Amorphous	Amorphous
pH water dispersion	6.0	6.0
Specific weight, g/cm^3	2.05	2.06
Bulk density, g/dm^3	150	150
Packing density, g/dm^3	225	220
Water absorption, g/100 g	350	350
Dibuthyl phthalate absorption, g/100 g	380	400
Whiteness, %	80.5	81.3
Specific surface area, m^2/g	30.4	30.5
Average particle size, nm	100	100

however, involved presence of fluoride ions, in amounts occassionally exceeding even 1%. Principal aim of our studies was to obtain sodium and potassium metasilicate solutions containing minimum fluoride contamination, so that the silicas produced would contain at most 0.1–0.3% fluorides. For this purpose, we used hydroxides of alkaline earth metals (calcium, barium or magnesium) to trap fluoride ions. Addition of hydroxides of alkaline earth metals in appropriate amounts permitted to significantly reduce fluoride content in products of solubilization under pressure of waste silicas. As evident from the data of Fig. 2, the best effect was obtained using hydroxides of barium and calcium. When addition of Ba(OH)$_2$ reached 3% related to the mass of solid subjected to solubilization, fluoride content in the obtained sodium and potassium metasilicate solutions decreased to, approximately, 0.1–0.4%. On the other hand, application of magnesium hydroxide only insignificantly decreased fluoride ion content (Fig. 2).

The most extensive elimination of fluorides obtained using Ba(OH)$_2$ can be explained by the very high water solubility of the compound, as compared to that of Mg(OH)$_2$ and Ca(OH)$_2$ (at 80 °C, approximately 101.4 g Ba(OH)$_2$, but only $9.4 \cdot 10^{-2}$ g Ca(OH)$_2$ and even less Mg(OH)$_2$ can be dissolved in 100 ml water). In such conditions, the dissociated Ba^{2+} and F$^-$ ions are the first expected to form barium fluoride, as compared to corresponding reactions of calcium and magnesium ions.

The water insoluble waste sediment containing besides silica fluorides of alkaline earth metals, is also used in HF production, similarly as the sediment obtained from water regenerated by washing waste silica in the proposed installation.

Lower solubility of waste silica from AlF$_3$ production (as compared to silica from HF production) in sodium hydroxide solution reflects formation on the surface of the silica of complex compounds of the following type [26].

$$\equiv Si-O \diagdown \atop \equiv Si-O \diagup Al-F + H_2O \longrightarrow \equiv Si-O \diagdown \atop \equiv Si-O \diagup Al-OH + HF$$

$$\equiv Si-O \diagdown \atop \equiv Si-O \diagup Al-OH \quad + \quad \equiv Si-O \diagdown \atop \equiv Si-O \diagup Al-OH \quad \xrightarrow{+AlF_3 \cdot 2HF} \quad$$

The formed surface complexes may enter into reaction with NaOH, forming aluminates. Thin layer of the compounds formed at the silica surface significantly inhibits penetration of NaOH molecules into silica grain interior in this manner decreasing solubility of silica. Unfavorable effect of aluminum compounds on solubility of silica samples from which fluorine compounds were leached off using hydrochloric acid. In this case solubility of the waste silica is comparable with solubility of silica produced during HF production. However, sodium metasilicate solutions obtained from the acid leached silica are filtered with difficulties.

Result of studies on the effect of $NaOH/SiO_2$ and KOH/SiO_2 ratios on the module of the obtained solutions and their chemical composition are shown in Table 4. The obtained solution of potassium metasilicate may be of particular significance for production of silicate paints. The paints exhibit high permeability for water steam, good coating capacity, high whiteness and they are resistant to the effect of light.

The effect of proadhesive coupling agents used for waste silica surface modification on its hydrophobicity was examined using a calorimetric method. Increase in the value of the heat of immersion of silica surface in benzene indicates increased hydrophobicity of its surface. Results of studies on heats of immersion of waste silica surface in water and benzene are presented in Table 4. Only results obtained for selected proadhesive agents are given. Dependence of the heats of immersion in water of the surface of silica modified with mercaptosilane A-189 and aminosilane upon the amount of silane used is demonstrated in Figs. 3(a) and (b), respectively.

As evident, from the data of Table 5, all proadhesive agents induced an increased hydrophobization of waste silica surface, the increase being the highest for titanate proadhesive agent – isostearoyl titanate KR TTS (hydrophobization degree N for 3 weight parts per 100 weight parts of silica amounted to almost 50%). When silane coupling agents had been applied for modification, lower degrees of hydrophobization were obtained – from 25% to 40%, depending on the amount of modifier used. Of special notice was an increase in the heat of immersion in water of the surface of
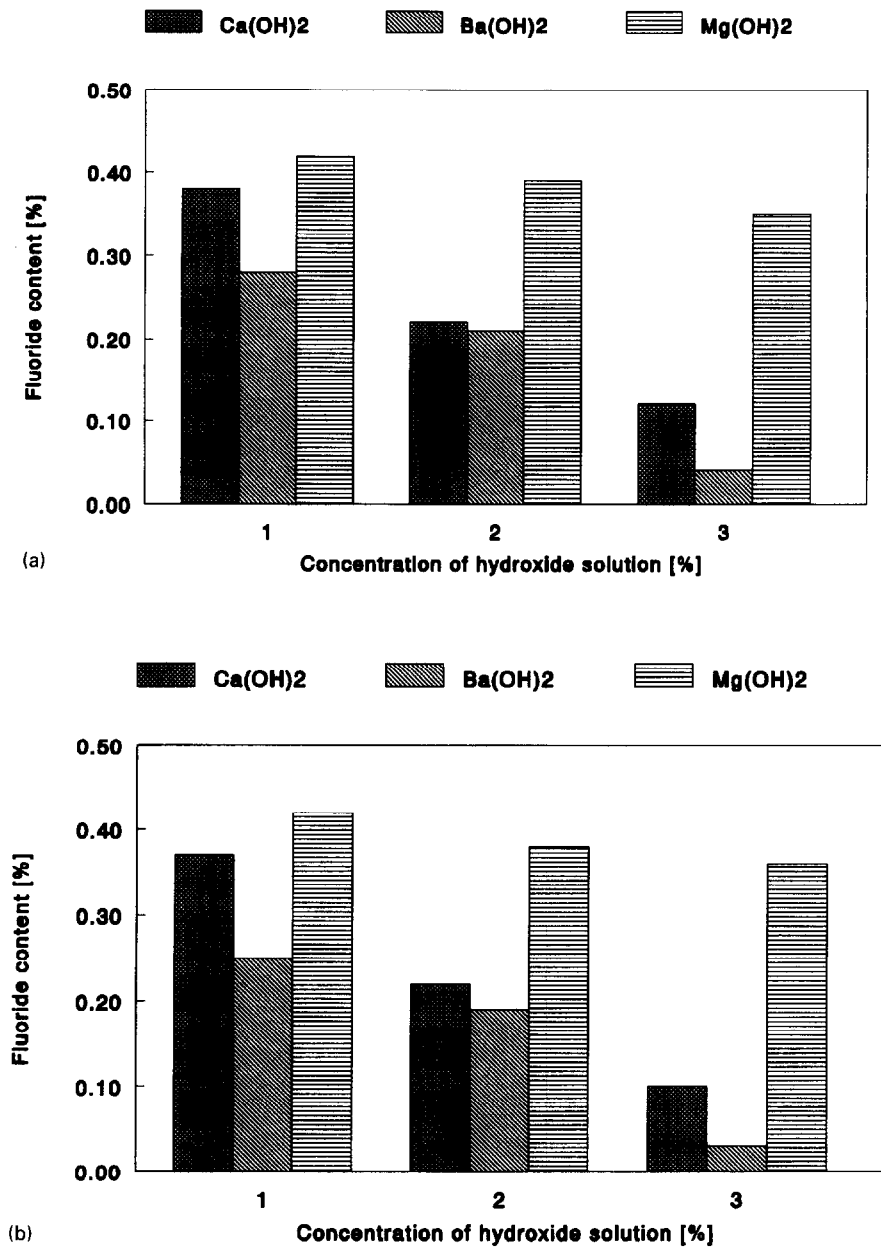
Fig. 2. Fluorine contents in metasilicate solutions, obtained from waste silica from HF production in presence of hydroxides of alkaline earth metals: (a) sodium metasilicate solution; (b) potassium metasilicate solution.

Table 4
Chemical analysis of metasilicate solutions (reaction time: 2 h, temperature 145 °C, pressure: 5 atm)

Waste silica after HF production

(a) Sodium metasilicate solution

$NaOH/SiO_2$	Na_2O (%)	SiO_2 (%)	Module M_K	F^- (%)	Insoluble solid phase (%)
1:2.0[a]	6.5	16.5	2.53	1.10	4.05
1:2.5[a]	6.3	17.1	2.72	1.15	3.20
1:3.0[a]	6.1	17.4	2.86	1.15	2.85
1:2.0[b]	6.6	16.8	2.54	0.15	2.03
1:2.5[b]	6.2	17.5	2.82	0.20	1.85
1:3.0[b]	6.0	17.7	2.95	0.18	1.83

(b) Potassium metasilicate solution

KOH/SiO_2	K_2O (%)	SiO_2 (%)	Module M_K	F^- (%)	Insoluble solid phase (%)
1:2.0[c]	5.7	14.7	2.58	0.16	2.15
1:2.5[c]	5.4	14.9	2.76	0.16	2.03
1:3.0[c]	5.1	15.0	2.94	0.12	1.96

Waste silica after AlF_3 production

(a) Sodium metasilicate solution

$NaOH/SiO_2$	Na_2O (%)	SiO_2 (%)	Module M_K	F^- (%)	Insoluble solid phase (%)
1:3.0[a]	6.5	17.8	2.74	1.29	5.25
1:3.0[b]	6.6	17.9	2.71	0.20	5.20
1:3.0[c]	6.5	18.3	2.82	0.22	5.15

(b) Potassium metasilicate solution

KOH/SiO_2	K_2O (%)	SiO_2 (%)	Module M_K	F^- (%)	Insoluble solid phase (%)
1:3.0[c]	6.3	18.0	2.86	0.21	5.05

[a] Unpurified silica.
[b] Unpurified silica + 2% $Ba(OH)_2$.
[c] Unpurified silica + 2% $Ca(OH)_2$.

Table 5
Heats of immersion in water (H_i^W) and in benzene (H_i^B), specific surface areas and hydrophobization degrees of waste silicas (unmodified and modified with silane and titanate coupling agents)

Proadhesive agent	Content (% weight)	S (m²/g)	H_i^W (J/g)	H_i^B (J/g)	N[a] (%)
Unmodified silica	—	30.5	11.0	10.9	—
Mercaptosilane A-189	1	29.0	7.0	15.0	27.3
	2	29.0	5.6	16.8	35.1
	3	28.6	4.5	18.0	39.4
Mercaptosilane A-1893	1	29.2	7.4	14.5	24.8
	2	29.0	6.7	16.2	32.7
	3	28.8	5.5	17.4	37.4
Aminosilane A-1100	1	29.0	12.9	14.1	22.7
	2	29.3	13.6	16.2	31.9
	3	29.1	14.7	17.4	36.3
Vinylsilane A-172	1	29.1	7.5	14.6	25.3
	2	29.2	6.4	16.2	32.7
	3	29.0	5.2	17.5	37.7
Titanate KR TTS	1	29.5	6.7	18.4	40.9
	2	29.6	4.9	20.0	45.5
	3	29.5	3.8	21.3	48.8

[a] Hydrophobization degree.

silicas modified with aminosilanes A-1100 and A-1120 (Table 5, Fig. 3). This was probably due to the interaction between water molecules and amino groups of silane, adsorbed on the surface of silica, which lead to formation of hydrogen bonds.

Physico-mechanical indices of rubber vulcanizates, filled with waste silica unmodified or modified with different amounts of proadhesive agents, are compiled in Table 6. As follows from the data, addition of waste silica only slightly reduced rubber elasticity. Similarly, unmodified waste silica hardly improved tensile strength and moduli of the vulcanizates. This implies, then, that unmodified silica has exhibited low activity and, thus, may be applied in rubber products which do not require high values of those parameters. In contrast, application of modified silica considerably improved physico-chemical parameters of filled butadiene–styrene rubbers. Surface modification of these silicas with silane coupling agents, performed according to methodology developed in our laboratory, lead to formation of vulcanizates of higher tensile strength and to a marked increase of their modules.

Silicas modified with proadhesive agents may be considered to represent fillers of average activity. Of all the silane proadhesive agents used, the most favorable modifying influence was observed for mercaptosilanes A-189 and A-1893. This was demonstrated by the fact that styrene–butadiene rubber vulcanizates filled with waste silicas modified with 2–3 weight parts of silane coupling agents showed the highest values of moduli and tensile strength parameters. However, the effect on the value of the parameters was most favorable when rubber was filled with waste silica modified with 1-3 weight parts of isostearoyl titanate.
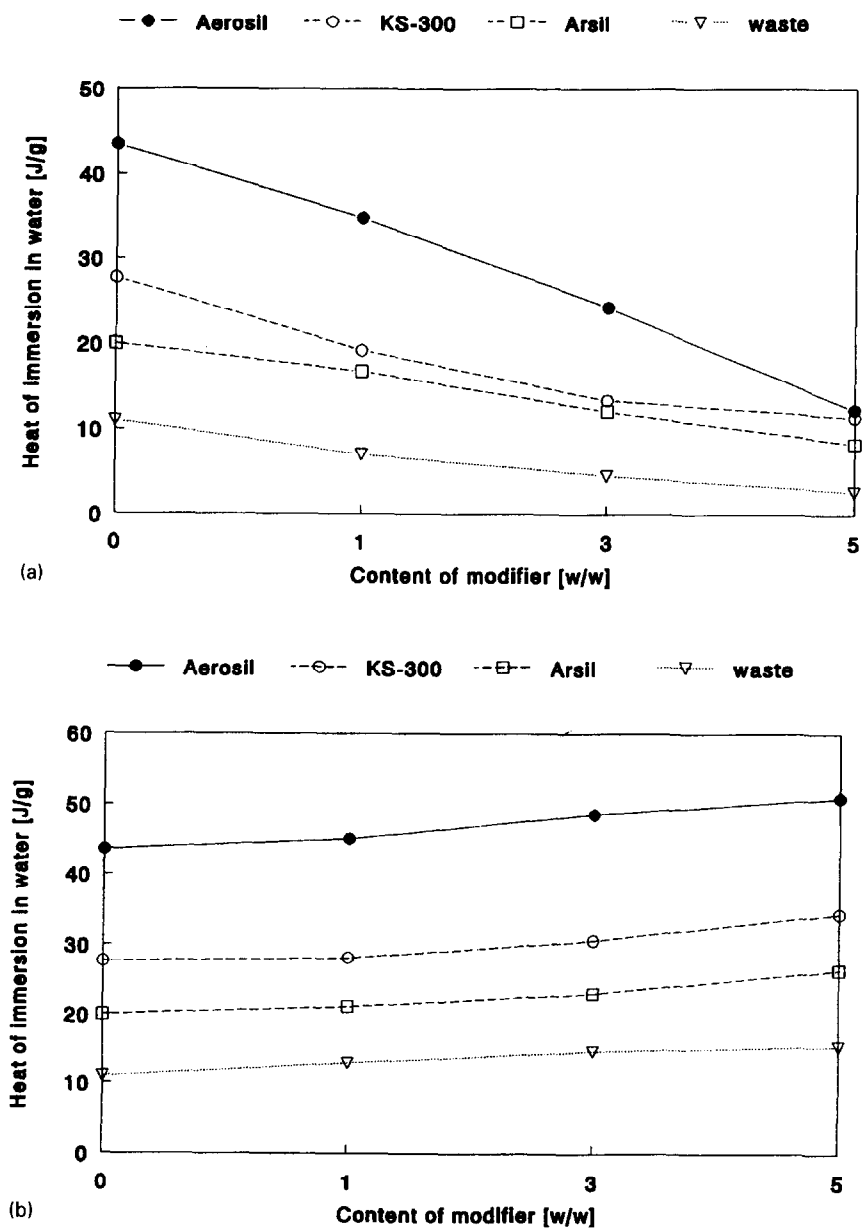
(a)

(b)

Fig. 3. Effect of coupling agents used to modify the silica surface on the heat of immersion in water: (a) mercaptosilane A-189; (b) aminosilane A-1120; (●) Aerosil 200; (○) KS-300; (□) Arsil; (▽) waste silica.

Table 6
Physico-mechanical properties of Ker 1500 vulcanizates filled with waste silicas from HF production after purification unmodified or modified (vulcanization time – 40 min)

Type of silane or titanate	Content of proadhesive agent (wt/wt)	H (°Sh)	E^a (%)	M-100 (MPa)	M-200 (MPa)	M-300 (MPa)	E_r (%)	R_r (MPa)	E_t (%)
Unmodified	—	68	44	2.9	3.9	4.8	310	6.1	10
A-172	1	68	44	3.2	4.7	5.9	310	7.4	10
	2	68	44	4.1	6.2	7.2	310	8.6	12
	3	68	45	4.8	6.9	8.0	310	9.4	12
A-189	0.5	69	45	3.5	5.0	5.9	310	7.6	10
	1	69	45	3.9	5.7	6.8	310	8.0	10
	2	68	44	4.7	7.3	8.3	340	10.9	12
	3	70	46	5.8	8.2	9.4	360	12.9	12
A-1893	1	69	45	3.9	5.5	6.7	310	8.0	10
	2	69	46	4.7	7.3	8.2	320	11.1	12
	3	69	45	5.8	8.1	9.4	320	12.5	12
A-1100	1	68	45	3.1	4.4	5.4	310	7.3	10
	2	69	45	3.9	6.0	6.6	310	8.5	12
	3	68	45	4.3	6.6	7.5	310	8.9	12
A-1120	1	69	45	3.3	4.4	5.5	320	7.3	12
	2	69	45	3.9	6.2	6.9	310	8.4	12
	3	69	46	4.5	6.7	7.4	320	9.1	12
A-151	1	68	44	3.3	4.6	5.8	310	7.5	12
	2	68	45	4.1	6.2	7.2	310	8.7	12
	3	68	45	5.0	7.1	8.1	310	9.5	12
A-174	1	68	45	3.5	4.8	5.8	310	7.6	12
	2	68	46	4.3	6.4	7.4	320	9.0	12
	3	68	46	5.1	7.3	8.1	310	10.5	12
A-187	1	69	45	3.5	4.7	5.6	310	7.7	12
	2	68	46	4.3	6.3	7.0	310	8.9	12
	3	68	46	5.1	7.2	7.9	320	9.6	12
KR TTS	1	69	45	4.5	6.0	7.2	310	8.9	12
	2	69	45	5.2	7.7	8.9	320	11.2	12
	3	69	46	6.3	8.8	10.0	320	14.0	12

^{a} Elasticity.

Physico-mechanical parameters of rubber vulcanizates filled with active silicas (C-5, K-300, Arsil and Aerosil) are listed in Table 7. Evidently, the active silicas cross-linked vulcanizates of significantly higher strength parameters (moduli and tensile strength parameters were higher than for vulcanizates filled with unmodified waste silica by 100–150%). The effect of impurities of fluorine compounds, adsorbed on the surface of waste silica on physico-chemical properties of butadiene–styrene rubber vulcanizates was observed upon running studies on aging (Table 8).

Table 7
Physico-mechanical properties of Ker 1500 vulcanizates filled with various silicas (vulcanization time – 40 min)

Silica	H (°Sh)	E_1 (%)	M-100 (MPa)	M-200 (MPa)	M-300 (MPa)	E_r (%)	R_r (MPa)	E_t (MPa)
No filler	48	60	1.9	1.7	—	220	1.9	4
Waste from HF prod.	68	44	2.9	3.9	4.8	310	6.1	10
Waste from AlF₃ prod.	68	43	2.4	3.0	3.9	300	5.2	10
C-5	75	46	5.7	9.1	12.8	360	21.5	20
KS-300	76	41	4.9	8.8	10.5	420	20.7	20
Arsil	70	43	4.1	7.8	10.3	370	20.2	10
Aerosil 200	77	42	6.7	9.2	11.5	300	25.8	6

Table 8
Accelerated vulcanizate aging in air

Probe	Temp. 50 °C, time 144 h				Temp. 100 °C, time 72 h			
	R_r (MPa)	ΔR_r (%)	M-100 (MPa)	Δ(M-100) (%)	R_r (MPa)	ΔR_r (%)	M-100 (MPa)	Δ(M-100) (%)
Waste silica after HF production								
1	3.5	− 42.6	1.5	− 48.3	3.4	− 44.3	1.4	− 51.7
2	3.6	− 41.0	1.7	− 41.4	3.5	− 42.6	1.5	− 48.3
Probe 1 after purification	5.7	− 6.6	2.7	− 6.9	5.7	− 6.6	2.7	− 6.9
Probe 2 after purification	5.8	− 4.9	2.7	− 6.9	5.7	− 6.6	2.7	− 6.9
Waste silica after AlF₃ production								
Raw silica	2.7	− 48.0	1.2	− 50.0	2.6	− 50.0	1.1	− 54.2
After purification in hot water	4.0	− 23.1	1.9	− 20.8	4.1	− 21.2	2.0	− 16.7
After purification in HCl	4.7	− 9.6	2.1	− 12.5	4.7	− 9.6	2.2	− 8.3
KS-300	20.4	− 1.4	4.8	− 2.0	20.5	− 1.0	4.8	− 2.0

Tensile strength parameters of vulcanizates containing unrefined waste silica clearly deteriorated under the influence of accelerated aging (the tensile strength decreased by approx. 55% relative to that measured directly after vulcanization). In contrast, vulcanizates containing refined silicas and additionally modified with mercaptosilane showed a minimum tendency to decrease tensile strength parameters upon prolonged aging process (both the tensile strength parameter and the M-100 modulus diminished only by 5–7%, which is in agreement with a standard for rubber products such as packings, corks, etc.). KS-300- silica containing vulcanizates practically have not aged and, thus, may be safely applied in any technology. Thus, studies on aging confirmed
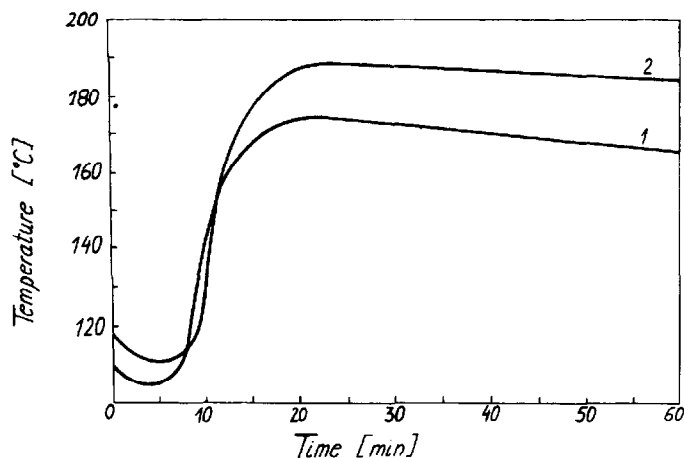
Fig. 4. Curves of the vulcanization course for Ker 1500 rubber compounds filled with silicas: (1) waste silica after purification and modification with 3 w/w of mercaptosilane (A-189); (2) precipitated silica (Arsil).

Table 9
Physico-mechanical properties of vulcanizates filled with tigated silicas (rubber mixtures prepared in technical scale)

Silica	R_r (MPa)	M-300 (MPa)	E_r (%)	H (Sh)
Waste, from HF production (filtered and modified with 3 w/w parts silane A-189)	12.5	4.6	500	62
Arsil	19.5	9.0	525	65
C-5	22.2	10.5	500	65
KS-300	22.0	10.4	510	65

a decidedly negative effect of fluorine compounds on strength parameters of vulcanizates.

Waste silicas obtained from hydrofluoric acid synthesis, after washing with hot water may be successfully used in rubbers as medium-active fillers. It should be remembered, however, that application of purified by-product silicas as elastomer fillers should be confined to products which are not subjected to accelerated processes of aging (e.g. at high temperature and high pressure).

Physico-mechanical parameters of vulcanizates used in a technical scale are given in Table 9, while a rheometric diagram is shown in Fig. 4. Introduction of refined waste silica, obtained from synthesis of hydrofluoric acid into urethan elastomers brought about a regular increase in tensile strength parameters, such as, stress at 100% elongation (Module-100), tensile strength, relative elongation, hardness, etc. [27].

Table 10
Physico-mechanical parameters of polyurethane elastomers filled with silica waste after purification (unmodified or modified with silane coupling agents)

Silica content (%)	M-100 (MPa)	R_r (MPa)	E_r (%)	H (°Sh)
0	0.76	0.92	100	39
10[a]	0.90	1.44	160	43
20[a]	1.25	1.72	160	52
30[a]	1.82	2.04	240	62
40[a]	—	0.80	40	67
30[b]	2.15	2.32	240	62
30[c]	2.75	3.12	250	63
30[d]	2.88	3.39	250	63

[a] Unmodified waste silica.
[b] Waste silica modified with 2 w/w parts of A-189 silane.
[c] Waste silica modified with 2 w/w parts of A-1100 silane.
[d] Waste silica modified with 2 w/w parts of A-1120 silane.

Physico-mechanical parameters of urethan elastomers filled with different amounts of refined, modified, and unmodified waste silicas are listed in Table 10. Optimum values of tensile strength parameters were obtained at 20–30% (w/w) content of silica in the elastomer. Particularly distinct strengthening effects were observed for urethan elastomers filled with waste silicas purified and modified aminosilanes A-1100 or A-1120. The amount of silane used to secure the above effect was important. It was economical to use 2 weight parts of the silanes per 100 weight parts waste silica.

4. Conclusions

(1) In order to remove fluorine impurities (they induce heavy aging processes of polymers filled with waste silicas), waste silicas from the synthesis of hydrofluoric acid and aluminum fluoride were subjected to hot water or HCl solution washing on a battery of filters. Some methods of solutions neutralization following silica washing were developed. Silicas with a satisfactory degree of fluorine leaching were obtained.

(2) The optimum technique of fluoride leaching from sodium and potassium metasilicate solutions involves addition of solid hydroxides of alkaline earth metals directly to the autoclave in which the solutions are prepared. In the course of leaching, sodium metasilicate solution does not, even partially, coagulate under effect of the added electrolytes (the coagulation would lead to sedimentation of silica in form of a gel). Lower solubility of the waste silica from AlF_3 production (as compared to silica from HF production) in sodium hydroxide solution reflects formation of complex compounds on the surface of the silica.

(3) Surface modification of refined waste silica ensures increase in activity of the filler. Surface modification of the silicas with silane and titanate coupling agents increases chemical affinity of fillers to polymers, and in particular, changes their

character from hydrophilic to a hydrophobic one. Activity of waste silicas after modification with silanes, and especially with isostearoyl titanate, increases by approximately, 100–150%, relative to unmodified silica. Modified waste silicas are therefore very useful as rubber and urethan elastomers fillers; their applicability being comparable to the Arsil silica – the only one available on our market.

(4) When butadiene–styrene rubber is filled with waste silicas, the best effect is observed for silicas modified with mercaptosilanes (A-189 and A-1893) and isostearoyl titanate (KR TTS) at the amount of 2–3 weight parts per 100 weight parts of silica.

(5) Dependence of strength parameters of polyurethanes on the content of purified waste silica is extreme in character – elastomer exhibits optimal mechanical strength at 20–30% content of silica in elastomer. When the amount of silica is higher, defects appear in the polyurethane structure lattice and physico-mechanical properties of the polyurethanes deteriorate markedly. Surface modification of waste silica, especially with 2–3 weight parts of aminosilanes (A-1100 and A-1120) causes an evident increase in strength parameters of polyurethanes in comparison with the effects of application of unmodified silicas in the polymers.

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