Development of resource-saving technology for solid waste disposal of industrial gas dehumidifiers of petrochemical enterprises in the process of producing urethane rubbers

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Abstract. Currently, environmental issues are receiving much attention. Considering the fact that several of the largest oil refining and petrochemical enterprises in Russia are concentrated in the Republic of Tatarstan, the improvement of the environmental situation near industrial territories is very important. Previously, the authors of the article investigated the possibility of using wastes of industrial gas dehumidifiers (silica gel and aluminum oxide) as fillers for urethane rubbers of the SKU-OM and SKU-PFL types, both cold and hot cured. Studies have shown that the introduction of silica gel in the injection composition of SKU-OM and SKU-PFL is possible up to 20% of the mass without deterioration of physical and mechanical properties, and spent alumina can be introduced into SKU-OM up to 50% of the mass, which is absolutely not typical for this type of rubber. Thus, the strength properties remain at the level of unfilled analogues, the oil and gas resistance of the compositions increase. Based on these studies, the authors proposed three flowcharts of technological processes, the first of which is a generalized scheme for converting silica gel and alumina waste into secondary material resources, or, basically, into fillers for polymer and rubber mixtures. The second and third schemes are improved flowcharts for the production of injection molded urethane rubbers hot cured (scheme 2) and cold cured (scheme 3). Both schemes can be implemented at enterprises for the production of injection molding polyurethanes, as well as at oil refineries. Economic calculations showed a reduction in the cost of the final polyurethane product by 29% in the case of used silica gel, and by 9% when filling polyurethane with aluminum oxide waste.

To date, the oil producing and oil refining industries are a pillar of stability for sustainable development of the economy of the Republic of Tatarstan. The rapid growth of industrial production in the 60-70s contributed to the emergence of large industrial enterprises on the territory of the Republic such as PJSC Nizhnekamskneftekhim and PJSC Nizhnekamskshina. Having survived the difficult conditions of perestroika, economic crises, these enterprises are not only successful companies, but also are developing steadily, guaranteeing high quality products to consumers. This would not have been possible without the innovative development of enterprises, which implies the constant modernization of production and the introduction of new technologies.
However, it is no secret that the oil refining industry is a manufacturing industry where about 80-85% of all products are produced using catalysts, and the implementation of oil refining processes is associated with many related operations, such as liquefaction of gas fractions, drying of gases used in technological cycles, etc. All this leads to an inevitable increase in the amount of solid industrial waste generated and accumulated annually. Such waste can include deactivated catalysts, adsorbents - dehumidifiers, oil sludge, etc. The negative anthropogenic impact of these wastes, along with the formation of chemically contaminated wastewater and gas emissions into the atmosphere, is obvious and leads to environmental pollution. Waste transportation, its removal from the main technological cycle, as well as storage on specially equipped sludge dumps are costly measures and, in general, are not effective in terms of improving the ecology of territories adjacent to enterprises. It should also be noted that the problem of operational disposal of waste generated is not being solved enough, and the latter also leads to an increase in the mass of stored waste.

A significant part of solid waste from industrial enterprises of hazard class III and IV can be effectively neutralized and disposed of using environmentally friendly technologies, thereby realizing the modern approach to transfer non-utilized waste to the category of secondary raw materials (SRM). The best way to recycle these wastes is using technologies with the application of modern scientific and technological achievements in accordance with the principles of the best available techniques (BAT) [1].

The purpose of the study was to develop a resource-saving technology for the utilization and neutralization of solid waste from gas dehumidifiers used in oil refining processes, and their use in the production of urethane rubbers.

As known, urethane rubbers have a number of unique properties, such as wear resistance, strength, inertness to various fuels and oils. However, their high cost significantly limits the use of products made from this material. Therefore, the current work was focused on the development of a technology for the production of filled polyurethane rubbers using silica gel and alumina as fillers of petrochemical production wastes.

The research is concerned with activated alumina (alumina gel) GOST 8136-85 with a basic substance content of Al₂O₃ -99.5% by mass, used in gas drying and gas purification processes; silica gel GOST 3956-76, the content of the main substance in which was not less than SiO₂-99.5% of the mass.

The following grades of hot-cure urethane rubbers were used as the polymer component: SKU-OM and SKU-PFL and cold-cured SKU-PFL. All rubber types are produced at PJSC Kazan Plant of Synthetic Rubber named after S.M. Kirov. SKU-OM is a polyurethane rubber of triisocyanurate curing scheme. It was synthesized according to the standard procedure based on polyester poly (ethylene adipate) (PEA) with a molecular weight of ~ 2036 g/mol and a mixture of diisocyanates: 2,4- and 2,6-toluene diisocyanate (TDI) at a ratio of 80/20. The catalyst used was a mixture of phenolic Mannich bases - Agidol 51.52.53 with a predominant content of 2,4,6-tris (dimethylaminomethyl) phenol (OM-3). SKU-PFL is an urethane rubber synthesized based on SKU-PFL-100 prepolymer obtained by reacting poly-oxy-tetramethylene-glycol and 2,4-TDI in a 1:2 ratio with a molecular weight of ~ 1300-1500 g/mol; 4.4'-methylene-bis(o-chloroaniline) of the MOCA trademark is the curing catalyst. Standard methods for synthesizing these rubbers can be found in [2].

Previous studies conducted by the authors revealed the possibility of using the waste substances specified in the research objects as fillers for polyurethane compositions [3 - 5]. In the works, it was shown that the silica gel content in SKU-OM urethane rubbers can be increased to 15 wt-%, and in the SKU-PFL polyurethanes of cold and hot curing, up to 20 wt-%. It was noted that silica gel gives polyurethane compositions increased heat resistance, which greatly expands the range of operational capabilities of the finished product. In urethane rubbers of the SKU-OM grade, the content of aluminum oxide was brought up to 50% of the mass without significant loss of strength and elasticity, which is not typical for filled products. Such a high content of filler significantly reduces the cost of the product and at the same time solves the issue of recycling and disposal of waste.
A basic technological flowchart for the collection of aluminum oxide and silica gel waste for their further use as fillers for polymeric materials was developed (figure 1).

![Diagram of the collection process](image)

**Figure 1.** The basic technological flowchart for the production of fillers for polyurethane compositions from silica gel and aluminum oxide wastes.

The technological scheme includes the following stages:

- Collection of silica gel and alumina waste in special receiving bins.
- Filtering out and fractionation of collected waste from coarse impurities, which are cinder and nozzles after unloading from columns using sieves and screens.
- Milling the treated waste using mills of various designs to the particle sizes of the fractions specified by the customer.
- Collection of powdered ground waste, washing and steaming the mill before milling another type of waste.
- Drying the shredded waste in the oven with varying moisture content.
- Cooling the shredded fraction under vacuum to prevent moisture condensation on the resulting filler.
- Packaging of commercial products in bags or polypropylene sealed containers without air.

If necessary, there is the possibility of creating another stage after fractionation - roasting or waste treatment to give them filler properties for polyurethanes, since there is a likelihood of chemical contamination of the waste with residues of those substances with which they previously interacted. In this case, assuming, the catalyst can be returned to its previous activity and use it not as a filler, but as a finished catalyst. Researches in this area also remain relevant.

The results of the study developed a basic flow chart of the technology for producing two grades of hot cure urethane rubbers SKU-OM and SKU-PFL filled with silica gel waste (figure 2).

The technological scheme includes the following stages:

- Collection of silica gel waste.
- Milling of silica gel waste to a powder state with preliminary separation of large fractions on special equipment.
- Separation of the powder mass and selection for the synthesis of polymer fractions with a particle size of not more than 42 microns.
- Drying the milled silica gel to remove adsorbed moisture and absorbed gases. The process is carried out in an electronic thermostat at a temperature of at least 180°C for 180 minutes; the residual moisture content should not exceed 0.2 ± 0.05% of the mass.

Then the rubbers SKU-OM and SKU-PFL of hot curing are obtained on the same installation, but with some technological features. For example, for the synthesis of SKU-OM in the technological process, the following stages must be present:
Figure 2. The basic technological flow chart of the use of silica gel waste in the production of hot cure polyurethane grades SKU-PFL and SKU-OM.

- Degassing of polyester at an elevated temperature in order to remove excess moisture. Process parameters: temperature 100±5°C, vacuum 2-5 mm Hg (267-667 Pa), thorough mixing, degassing time of 60-120 minutes. The residual moisture content should not exceed 0.03% of the mass.

- Synthesis of SKU-OM urethane rubber: TDI reagent and OM-3 catalyst are introduced into a mixture of polyester with a filler-silica gel cooled to 50 ± 5°C. The reaction mass is thoroughly mixed for at least two minutes, while degassing 2-5 mm Hg (267-667 Pa).

For SKU-PFL urethane rubber, the production line should include the following stages:

- Degassing of the SKU-PFL-100 prepolymer with silica gel added to it. The content of silica gel varies depending on the degree of filling of the final polymer. Degassing parameters: temperature 100-5°C, vacuum 2-5 mm Hg (267-667 Pa), and mixing time 60±5 minutes.

- Synthesis of SKU-PFL: a molten curing agent 4,4'-methylen-bis- (ochloraniline) of the MOCA trademark is introduced into a mixture of SKU-PFL-100 prepolymer and silica gel, cooled to 50 ± 5°C. Then the reaction mass is thoroughly mixed for at least two minutes while degassing 2-5 mm Hg (267-667 Pa).

Further technological stages for both rubbers are the same:

- 7) Filling the liquid mass of polyurethane in the form preheated to a temperature of 80±5°C.
- Thermostating SKU-OM and SKU-PFL in forms at a temperature of 80±5°C for 72 hours.

Further, the finished product is removed from the forms. It is left to rest for at least 14 days, since during this time the final formation of polyurethane rubber occurs and the physicomechanical properties of the product reach maximum values [5]. Stage 5-8 can be carried out on existing equipment and in accordance with the technological scheme for the production of urethane rubber, described in the directory of the best available technologies in the field of polymer production [1].
The collection of used waste
Milling
Fractionation
Dewatering
180-300°C, 3 h

Synthesis
(25±5) °C, 2 min
Applying to a substrate
Curing
(25±5) °C, 14 day

Degassing
(2-5) mm Hg,
(100±5) °C, 1-2 h

Figure 3. Schematic diagram of the use of silica gel and alumina waste for the production of cold-cured SKU-PFL rubber.

A basic block diagram of the technology for producing polyurethane SKU-PFL cold cured filled with waste silica gel and aluminum oxide was also developed (figure 3). SKU-PFL cold curing is used as a protective coating for surfaces of various natures (wood, concrete, brick, steel, etc.).

The stages of the basic technological flowchart for the production of cold-cured SKU-PFL filled rubber, filled with waste silica gel and aluminum oxide:

1) Collection and milling of waste using mills of various designs.
2) Separation of crushed waste into fractions in order to obtain particles of the required size.
3) Thermostating of finely dispersed powder in order to remove residual moisture and absorbed gases in an electronic thermostat: silica gel - at a temperature of 180°C, aluminum oxide - at a temperature of 300°C. The temperature control time should be at least 180 minutes; the residual moisture content should vary within 0.2 ± 0.05% of the mass.
4) Degassing of the SKU-PFL-100 prepolymer at a temperature of 100±5 °C under a vacuum of 2-5 mm Hg (267-667 Pa) and mixing for 60-5 minutes.
5) Synthesis of SKU-PFL. For this, the degassed prepolymer is mixed with filler waste, and then a molten curing agent 4,4’-methylene-bis- (o-chloraniline) of the MOCA trademark is introduced into the reaction mixture having a temperature of 25 ± 5 °C. Then the reaction mass is thoroughly mixed for at least two minutes while degassing 2-5 mm Hg (267-667 Pa).
6) Application of liquid polymer mass on the surface to be protected.
7) Extract SKU-PFL at a temperature of 25 ± 5 °C for 14 days to fully cure the composition [4].

PU based on SKU-PFL-100, filled with 20% of the mass with silica gel, has been tested and recommended for use as protection valves for metering pumps of municipal utilities, LLC Dorkomtekhnika Moscow [2].

The use of developed technologies for the production of filled polyurethane compositions reduces the cost of finished products. According to the calculations carried out [2], filling SKU-OM and SKU-PFL with silica gel reduces the cost of the composition by about 29% with an optimum degree of filling of rubber up to 20% of the mass. Filling SKU-OM with aluminum oxide in an amount of 10% of the mass leads to a reduction in the cost of finished products by about 9%.

Thus, the paper presents three fundamental technological flowcharts. The first scheme can be implemented at large oil refineries, such as Nizhnnekamskneftekhim PJSC, TANECO JSC, and Taif OJSC. It will allow enterprises to transfer part of the waste gas dehydrators of gas mixtures into secondary material resources, receiving economic benefits and at the same time implementing environmental programs to reduce the amount of stored waste at the landfills of enterprises. The third
technological scheme can also be implemented at the above enterprises and used to protect and seal their own equipment or for the production of commercial products. The second and third technological flowcharts can be implemented directly at enterprises producing urethane rubbers, for example, at Kazan Synthetic Rubber Plant PJSC.

References
[1] Information Technology Guide on Best Available Technologies 32-2017 Production of polymers, including biodegradable (Moscow:Byuro NTD) p 401
[2] Kozhevnikova I V 2016 Polyurethane Compositions Containing Mineral Oxide Desiccant Waste (Kazan) 178
[3] Sergeeva E A, Safiullina T R, Shmakova O P, Bakirova I N and Zenitova L A 2006 D The structure of injection molded polyurethanes filled with alumina J. of Applied Chemistry 79(7) 1193-7
[4] Kozhevnikova I V, Safiullina T R, Barminova T I and Zenitova L A 2014 S Disposal of dehumidifiers based on aluminum and silicon oxides by producing polyurethane compositions Ecology and Industry of Russia 5 26-30
[5] Kozhevnikova I V, Safiullina T R, Tikhonova S S and Zenitova L A 2014 The use of waste silica gel-based dehumidifiers for polyurethane compositions Ecology and Industry of Russia 4 16-20