Technology of receiving a ferriferous pigment from production wasters of synthetic rubber

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Abstract. In article the technology of processing of one of production wastes of synthetic rubber – the fulfilled adsorbent applied in the course of production of butadiene and containing significant amounts of compounds of copper and iron is offered. The description of laboratory researches on receiving from the specified withdrawal of a ferriferous pigment for paint and varnish and construction materials and also copper vitriol is shortly given. The schematic diagram of installation developed by results of the conducted researches is provided, the short description of technological process is given.

Important aspect in the solution of environmental problems is the question of resource-saving. As a rule, the majority of types of natural resources are exhaustible and not renewable, especially sharply this question rises concerning the ore minerals which are raw materials for production of metals. Therefore, search of new sources of raw materials for production of traditional products, in particular use of secondary raw materials for extraction of valuable metal-containing connections, gains the increasing value in recent years.

The greatest number of research and development is carried out to areas of processing of industrial wastes for the purpose of extraction from them useful and valuable components, in particular, of metals.

In this regard, the most perspective raw sources are the fulfilled catalysts, adsorbents, slags, slimes and other types of waste containing metals [1 - 5].

Object of the researches presented in this work is industrial waste – the fulfilled coal adsorbent which is formed in the course of production of butadiene – monomer for receiving synthetic rubber, and containing a significant amount of compounds of copper and iron.

The purpose of researches was studying of a possibility of processing of the specified withdrawal with receiving a ferriferous pigment for production of paint and varnish and construction materials.

It is known that at production of paints and construction materials with use of ferriferous pigments, the cost of the pigment as raw materials for its production are rather scarce and expensive [6] is a considerable share of prime cost of finished goods. It is obvious that receiving a pigment from secondary raw materials – industrial wastes, will allow not only to solve a problem of chemical environmental pollution as a result of accumulation of toxic withdrawal and to save traditional ore raw materials, but, owing to involvement of a cheap source of raw materials in production of pigments, to considerably reduce the price of cost of production of the paint and varnish and construction materials made on their basis.
As it was told above, a research object – the fulfilled adsorbent is formed during the extraction of butadiene from the pyrolysis fraction of oil by chemisorption with copper-ammonia solution, based on the ability of monovalent copper salts to form complexes with diene hydrocarbons at low temperatures.

Copper-ammoniac solution is under production conditions used in recycling therefore, after a butadiene desorption, has to be exposed to cleaning in the coal filter for the purpose of removal of polymers of acetylene connections from it and other impurity which are formed as a result of collateral reactions. As the filtering material in filters active coal on which surface impurity are adsorbed most often is applied. At decrease in adsorptive ability, coal is exposed to replacement by fresh therefore a significant amount of toxic withdrawal – the fulfilled adsorbent is formed. Owing to presence at structure of the specified copper acetylenide waste, capable to self-ignition at contact with air oxygen, right after unloading of adsorbent from the filter, the process of burning out of carbon and hydrocarbon impurity continuing within 4-6 months for which the fulfilled adsorbent is stored on the specialized platform of temporary storage begins. Upon termination of burning out process, the appearance and structure of the studied withdrawal considerably change. According to results of analyses, the fulfilled adsorbent represents powder of red-brown color, humidity of 0.48 %, with a size of particles from 50 to 500 microns. The average content of the main components in the fulfilled adsorbent after passivation the following:

- iron oxides – 43 – 47 %;
- copper oxides – 30 – 35 %;
- aluminum oxides – 13 – 16 %.

It is obvious that mix of such structure can be successfully used as secondary raw materials for receiving compounds of iron and copper [7].

Laboratory researches on processing of the fulfilled adsorbent included two stages of processing: extraction of iron with receiving a ferriferous pigment and extraction of copper with receiving copper vitriol. Practically, process of extraction of metals of the fulfilled adsorbent represents serial processing it hydrochloric and sulfuric acids.

In a ceramic glass fill in 320 ml of the distilled water and warm it up to 40 ºC on an electric tile. In the small portions at continuous hashing add 100 g of the fulfilled adsorbent to the warmed water. Then in solution in the small portions flow 175 ml of the concentrated hydrochloric acid for office of iron.

Reaction proceeds according to the following equation

\[ Fe_2O_3 + 6HCl = FeCl_3 + 3H_2O. \]

Reaction is carried out within 15 minutes at a temperature about 55 ºC and continuous hashing. As a result of reaction the brown deposit which is filtered on the paper filter is formed and wash with the distilled water of 5 - 6 times in the portions 50 ml. After that the deposit is dried up at a temperature of 100 ºC in a drying cabinet. The received brown fine powder has the following chemical composition:

- chloride of iron (III) – 57.97 %;
- oxide of iron (III) – 26.98 %;
- impurity – 15.06 %.

The filtrate is warmed up to 65 ºC and flow in the small portions at continuous hashing 30 ml of 92 % sulfuric acid. Through the bubbling device, air is supplied with a mass flow rate, for increase in speed of reaction add 2 g of copper vitriol to solution.

Reaction happens within 1 hour at a continuous bubbling and temperature 70 ºC.

Formation of copper vitriol happens according to the following equations of reactions
\[ Cu_2O + H_2SO_4 \rightarrow Cu_2SO_4 + H_2O, \]

\[ 2Cu_2SO_4 + 2H_2SO_4 + O_2 \rightarrow 4CuSO_4 + 2H_2O. \]

After completion of reaction mix is filtered, the deposit is washed with the distilled water. The received deposit has white color and, according to results of the analysis, contains about 95% of oxide of aluminum (III).

The filtrate obtained after separation of the aluminum oxide (III) precipitate is evaporated in a water bath and dried with air at room temperature until copper sulfate crystals are obtained.

The products received as a result of researches were analysed for the purpose of definition of their suitability to application.

So, for definition of characteristics of the received pigment, paints on the basis of varnish and drying oil were made and put on standard trials [8]. As a result of tests it is established that the paint and varnish coatings applied with the paints made with application of the received pigment almost completely conform to requirements imposed to such coverings. Characteristic of key indicators of paints in comparison with the required values is given in table 1.

| Table 1. Characteristic of key indicators of the paints and varnishes made with use of the received pigment. |
|---------------------------------------------------------------|
| Name of an indicator | Desired value | Actual value |
| Paint on the basis of varnish | | |
| Paint on the basis of drying oil | | |
| Paint on the basis of varnish | | |
| Paint on the basis of drying oil | | |
| 1. Film durability at blow, kgf·sm | 50 | 45 | 50 |
| 2. Film bend, mm | 1,0 | crack | 1,0 |
| 3. Hardness, conventional unit. | 0,1 - 1,0 | 0,213 - 0,25 | 0,102 - 0,412 |
| 4. Adhesion, point | 4 | 4 | 4 |
| 5. Glitter, % | 60 - 70 | 63 | 4 |
| 6. Covering ability, g/m² | 170 | 170 | 150 |

The key controlled indicators of the copper vitriol received as a result of complex processing of the studied withdrawal also conform to the requirements to this commodity product shown by normative documents and can be recommended for application in agriculture and other areas [9]. Characteristic of the received copper vitriol, in comparison with the specified requirements, is given in table 2.

Thus, as a result of carrying out laboratory researches the basic possibility of complex processing of the fulfilled adsorbent – withdrawal of production of synthetic rubber – with receiving commodity products was established: a brown ferriferous pigment for production of paint and varnish and construction materials and also copper vitriol.

| Table 2. Characteristic of the copper vitriol received as a result of researches. |
|-------------------------------|
| Indicator | Required value [9] | Actual value |
| Brand B, premium | Brand B, grade the first |
| Mass fraction of the main substance CuSO₄·5H₂O, %, not less | 98,1 | 96,0 | 95,0 - 97,0 |
Mass fraction, %, no more:

|       |       |       |
|-------|-------|-------|
| iron  | 0,2   | 0,25  |
| H₂SO₄ | 0,012 | 0,012 |
| arsenic |       | 0,05 - 0,02 |
| insoluble rest | 0,012 | 0,05 - 0,02 |

On the basis of the obtained data the technological scheme of unit for processing of the studied withdrawal submitted in figure 1 was designed.

**Figure 1.** The schematic diagram of unit for processing of the fulfilled adsorbent.

Processing of the fulfilled adsorbent is carried out in 2 stages: receiving pigment and receiving copper vitriol.

Process of receiving a pigment is carried out in reactor 4 supplied with the mixing device and a shirt of heat exchange.

Loading of the reactor is made in the following sequence.

The desalinated water is pumped in reactor 4 and heats up to 40 °C. The mixer turns on and dispensing of the fulfilled adsorbent from loading bunker 1 is made. Hydrochloric acid is dosed in the reactor 4 of capacity 3.

Reactionary mix is kept 15 minutes at a temperature of 55 °C and continuous hashing; after the specified time the reacted mix moves in filter 6 for office of a deposit. The deposit from filter 6 goes for washing in mixer 7 where mixes up with the desalinated water and comes to filter 9 for office of washing water.

The deposit washed from acid from filter 9 moves on tape dryer 10 where it is dried up heated up to 200 °C air. From the dryer the final product – a pigment is unloaded.

The filtrate from filter 9 is pumped out in a water supply line in reactor 4.

Process of receiving copper vitriol is carried out in reactor 14 supplied with the mixing device and a shirt of heat exchange.

Loading of reactor 14 is made in the following sequence.
The filtrate from filter 6 containing copper ions moves in reactor 14 and heats up to temperature of 65 °C. The mixer turns on, air in the bubbling device moves and dispensing of sulfuric acid in the reactor is made. For increase in speed of reaction, in reactor 14 a small amount of copper vitriol from bunker 15 moves.

The reaction mixture is kept for 1 hour at a temperature of 70°C, constant stirring and bubbling with air; after this time, the reacted mixture is fed into the filter 18 to separate the precipitate. The deposit from filter 18 comes on washing to mixer 19 where mixes up with desalinated water, and further comes to filter 21 for office of washing water.

The filtrate from filter 18 representing solution of copper vitriol pump 23 moves in a crystallizer 24 where there is a process of allocation of crystals of copper vitriol of solution.

Hold time of solution – 1 hour; after the specified time mix of crystals and uterine solution goes to centrifuge 26 for office of crystals of copper vitriol.

The wrung-out crystals move in dryer 27 where they are dried up by air at 20°C. Uterine solution from centrifuge 26 is pumped out in capacity 29.

The offered technological scheme of unit for processing of the fulfilled adsorbent – withdrawal of production of synthetic rubber – with receiving a ferriferous pigment and copper vitriol, can be the basis when developing industrial technology.

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