Synthesis And Properties Of New Ionophors Based On Oil And Fat Industry Waste

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ABSTRACT

Using characteristic ion of the fraudulent resins is considered in article in sorption process gold of the extraction. They Are Presented: scheme of the technological process of the syntheses efficient ionit incorporated phosphorus gossypol resins; the mode to technologies of the reception ionit introduction phosphoric group gossypol of the resin; the technical features ionit phosphorus containing gossypol of the resin on base gossypol resins butter to fatty industry TSh 86-38: 2006.

It Is Installed that received ionit possible applying ion for extraction of the non-ferrous metals, as follows for extraction ion honeys from concentrated solution hydra metallurgical production and is determined that, ion exchange runs only then, when ion gene group dissociation.

It Is Revealled that received ionit the phosphoric group gossypol of the resin for extraction and sorptions ion non-ferrous metals corresponds to the confirmed specificationes, in accordance with which is planned to issue in the manner of grain, applicable as sorbent for extraction ion non-ferrous metals from concentrated solution.

It Is Determined that received by syntheses phosphoric group gossypol of the resin efficient ionit, after washer with water and after hydrolysis saves its spherical form and in this form possible send on stock-room.

KEYWORDS

Ion-exchange resins, sorption process, gold recovery, synthesis, effective ion exchanger, heavy metal ion recovery, phospholized gossypol resin.
INTRODUCTION

The properties of ion exchange resins are widely used in the extraction of gold in production. In the process of beneficiation of ground gold-bearing ores, an important role is played by insoluble solid high-molecular substances - ion exchangers. The presence of ionic (active) groups in the solution makes it possible to absorb electrolyte solutions — positively or negatively charged paths due to their presence.

In practical terms, preference is given to ion exchangers based on synthetic ion-exchange resins.

The structure of macromolecules of ion-exchange resins is a flexible interwoven strands of polymer molecules whose chains are composed of hydrocarbon and have cross-links in videograms. Groups are fixed on the matrix.

The existing charge of fixed ions is neutralized by the moving ions inside the resin, which have the opposite sign, the so-called counterions. Due to the bonds between fixed ions and counterions, ionogenic groups are formed. Due to the mobility of counterions, they enter into an exchange reaction with ions of the same sign in solution.

It is accepted that an ion exchanger matrix with fixed negative ions is called a polyanion, and with fixed positive ions it is called a polycation.

In cases where fixed ions carry a negative charge, the ion exchanger can exchange cations and therefore is called a cation exchanger, but if the ion charge is positive, then the ion exchanger is capable of exchanging anions and is accordingly called anion exchanger.

MATERIALS AND METHODS

When contacting with electrolyte solutions occurs, the cation exchanges exchange the counterions contained in their structure, for example, H + cation exchangers - for an equivalent amount of another cation in solution:

\[ HR^+Na^+Cl^- \leftrightarrow NaR+H^++Cl^- \]

Accordingly, in cases of contact with electrolyte solutions, anion exchangers exchange the counterion in their structure, for example, OH- anion for an equivalent amount of another anion present in the solution:

\[ ROH+Na^+Cl^- \leftrightarrow RCl+Na^++OH^- \]

here R is the ion exchanger frame; the ion exchanger phase is indicated by a bar.

The nature of the fixed ion has a great influence on the ion-exchange properties of the resin. The most commonly used fixed ions for cation exchangers are -SO_3^-, -COO^-, -PO_3^{2-}, and for anion exchangers - NH_3^+, = NH_2^+, = NH^+, N^-

It was found that ion exchange occurs only when the ionogenic group is dissociated. Considering the degree of dissociation of the ionic group containing H + or OH- ion as a counterion, ion-exchange resins are divided into strongly - or weakly acid cation exchangers and strongly - or weakly basic anion exchangers.

So, ionic groups of water like -SO_3H or -PO_3H_2 almost completely turn out to be dissociated in solutions. In view of this, cation exchangers containing these groups are strongly acidic. It
should be noted that strongly acidic cation exchangers are predisposed to exchange cation exchangers in a wide pH range, i.e. in acidic, neutral and alkaline environments. Accordingly, cation exchangers containing a weakly dissociating carboxyl group — COOH — are weakly acidic and exhibit ion-exchange properties only in an alkaline medium.

It is known that strongly basic anion exchangers are capable of exchanging anions, both in acidic and alkaline environments, and as ionogenic groups they contain well-dissociating groups of quaternary ammonium or pyridine bases or salts.

It has been proved that the ion exchange ability of these ion exchangers is due to the fact that, having weakly basic properties, the amino groups and the pyridine group in an acidic environment attach a proton (like ammonia), forming the corresponding ionic group with an acid anion.

It should be noted that in alkaline and neutral environments the salt formed enters the hydrolysis process, losing the attached acid molecule, and as a result, the ability to exchange ions. Given the above, such anion exchangers can only be used in acidic environments.

In addition to strongly- and weakly basic anion exchangers, there are mixed basic anion exchangers (multifunctional). Such anion exchangers contain simultaneously strongly basic quaternary ammonium (or pyridine) groups and weakly basic amino groups (or pyridine groups).

Functionally ion-exchange resins synthesize monomeric molecules of organic compounds as a result of polymerization or polycondensation reactions. The obtained ionic groups are introduced into the starting monomers or the finished matrix.

The use of polymerization-type ion exchangers based on styrene and divinylbenzene (DVB) is also common, the latter copolymerizing to form a spatial copolymer.

Divinylbenzene, which connects the linear chains of polystyrene, performs the bridge-forming function. By changing the ratio between the amount of styrene and DVB, you can adjust the distance between the transverse bonds (change the degree of “crosslinking”) and thereby vary the size of the resin cells. Thus (large and small ions) it becomes possible to synthesize resins with varying degrees of selectivity. Thus, by artificially increasing the degree of cross-linking (the amount of DVB), one can minimize the exchange of large ions while maintaining the exchange of small ions (“sieve” effect).

As a result of copolymerization, the obtained styrene and DVB polymer serves as a feedstock for the production of many ion-exchange resins. After treatment of this copolymer with concentrated sulfuric acid, a strongly acidic cation exchanger containing sulfo group SO3H is obtained. In order to obtain anion exchangers, the copolymer is chloromethylated with the corresponding ether.

Next, amination of the resulting chloromethylated copolymer is carried out, resulting in various types of anion exchangers. The type of amine used determines the basicity of anion exchange resin. In cases of amination with ammonia with primary or secondary amines, weakly basic anion exchangers are obtained. The forming part of the tertiary amino groups interacts with chloromethyl groups of other copolymer molecules, forming
salt groups of quaternary ammonium bases. As a result, in the resins obtained by this method, along with weakly basic groups, 10–20% of strongly basic groups are contained. In fact, when using tertiary amines, strongly basic anion exchangers are obtained, and mixed anion exchangers can be obtained from mixtures of amines of different basicities.

Widespread ion exchange resins with clearly defined physical pores - macroporous ion exchangers. These ion exchangers are obtained by introducing into the reaction mass during the polymerization of some inert organic solvent (for example, higher hydrocarbons or alcohols), which is captured by the mass and then removed by distillation from the spatial polymer. Having the structure of a hardened sponge, such ion exchangers are objects with a developed inner surface, reaching 40-60 m² per 1 g of ion exchanger versus 0.1-0.2 m² for ordinary (gel) ion exchangers. Containing large pores and channels facilitating the diffusion of ions to active centers, macroporous ion exchangers are characterized by enhanced kinetic properties.

As a rule, ion-exchange resins are obtained in the form of granules of regular spherical shape ranging in size from 0.5 to 3 mm.

After immersion in water, the ion exchangers swell, absorbing a certain amount of water. The ingress of water into the ion exchanger is justified by the tendency of the ions in the resin to hydrate (it is believed that the ion exchanger is a highly concentrated solution, tending to lower the concentration). Facilitation of the penetration of ions into the ionite grain accelerates ion exchange and is associated with the swelling of ion exchangers, the expansion of the spatial network of the resin and an increase in its volume. The degree of swelling of the ion exchanger depends on the number of ionogenic groups and the degree of crosslinking of the matrices (framework rigidity).

In addition to the above, the degree of swelling of the ion exchanger also depends on the concentration of the solution, and in concentrated solutions it is weaker than in dilute solutions, which is characterized by a coefficient of swelling equal to the ratio of the specific volume of the swollen resin to the specific volume of the resin in air-dry form. Variation in the swelling coefficient can be observed over a fairly wide range. For example, for styrene and DVB-based ion exchangers, it varies from 1.5–2 for highly crosslinked resins (15–20% DVB) to 5–10 for weakly crosslinked (0.5–2% DVB).

An important characteristic of an ion exchanger is its exchange capacity, i.e. the amount of ions that can be absorbed by a unit mass of ion exchanger. There are full, equilibrium and working exchange capacities.

The total exchange capacity reflects the maximum number of ions that can be absorbed by the resin when all the exchangeable ionogenic groups are completely saturated, which is determined by the concentration of ionogenic groups in the resin. In cases of polyfunctional resins, the total exchange capacity is distinguished by individual types of active groups. Naturally, for each ion exchanger, the total exchange capacity is a constant value. Usually it is expressed in milligrams - equivalents per 1 g of ion exchanger in the air - dry state.

Equilibrium exchange capacity is the number of ions of a certain type absorbed by a resin in equilibrium with a solution of a certain
composition. The indicated equilibrium exchange capacity is not constant, it depends on the composition of the solution (concentration of the extracted ion, the presence of impurities, etc.), determined by the statistical method. In this case, the sample is kept in contact with a solution of a certain composition for a certain time, sufficient to establish equilibrium, after which the amount of ion absorbed is determined. The units of measurement of the equilibrium exchange capacity are milligrams-equivalents or milligrams of the extracted component per 1 g of ion exchanger in the air-dry state.

It should be noted that the equilibrium between the ion exchanger and the solution in real technological processes is usually not achieved. Therefore, in these cases, they use the concept of working capacity, treating it as the content of the extracted component, for example, gold, in the ion exchanger under specific sorption conditions. In this case, the working capacity is expressed in the same units as the equilibrium exchange capacity.

RESULT AND DISCUSSION

Before using the properties of ion-exchange resins in the sorption process of gold recovery, it is necessary to synthesize an effective ionite of a phospholized gossypol resin (FGS) based on the technological process proposed by the authors (Fig. 1) [2].

Fig. 1: Flow chart of the synthesis of effective ion exchanger phospholized gossypol resin.

Using pump 2 from the tank-storage 1 through the flow meter 3 gossypol resin is pumped into the reactor 4, heated to 40 - 50° C. Then the temperature in the reactor is raised to 60° C. Foaming indicates the moisture content in gossypol resin, to reduce it, it is necessary to increase the intensity of mixing of the resin. After stirring for 35 - 40 minutes, the release of foam ceases, this indicates the removal of 91 - 92% moisture from gossypol resin. Then, with the help of pump 6, diaxane is added from tank 5 through the flow meter 7. At the same time, copper chips are fed through tank 8 through the weighing meter 9. Using pump 6, the resulting mass is fed through the flow meter 10 to the reactor 11, where aluminum trichloride is
also sequentially from the hopper 15 through phosphor batcher 16 and from tank 12 by means of pump 13 phosphor trichloride enters through batcher 14. Then the temperature in the reactor 11 rises to 60 - 70°C. Then intensive mixing is carried out for 3 hours.

As a result, the effective ion exchanger obtained by synthesis of a phospholized gossypol resin is washed with water, after hydrolysis it retains a spherical shape and is sent to the finished product warehouse in this form.

Carrying out the technological regime shown in Table 1 of metals, an ion exchanger was obtained, which is used, inter alia, for the extraction of non-ferrous ions, namely copper ions from concentrated solutions of hydrometallurgical industries.

### Table 1

**The mode of technology for obtaining ion exchange resin phospholized gossypol resin**

| Name of parameters                                      | unit of measurement | Norm or rated value |
|---------------------------------------------------------|---------------------|---------------------|
| Gossypol resin consumption                              | Ton / liter         | 0,9                 |
| Separation sieve size                                   | mm                  | 0,25 – 1,0          |
| Coarse sieve size                                       | mm                  | 5,0                 |
| Phosphorus trichloride concentration                    | %                   | 99                  |
| Phosphorus trichloride consumption for phospholation    | %                   | until 4             |
| Reactor temperature                                     | °C                  | 60 – 70             |
| Reaction time                                           | hour                | until 3             |

Ionite phospholized gossypol resin is a finished product obtained by forforylation of gossypol resin with the addition of copper chips and in dioxane. The resulting ion exchanger phospholized gossypol resin for the extraction and sorption of non-ferrous metal ions meets the approved technical requirements, according to which it is planned to be released in the form of grain used as a sorbent for the extraction of non-ferrous metal ions from concentrated solutions.

According to physical and technical indicators, the obtained ion exchange resin phospholized gossypol resin meets the requirements and standards specified in the table 2.
Table 2

Technical characteristics of ion exchange resin phospholized gossypol resin based on gossypol resin oil and fat industry TSh 86-38: 2006

| №  | Name of indicators                                      | Norm          | Test methods |
|----|----------------------------------------------------------|---------------|--------------|
| 1  | Appearance                                               | Dark black grain | Visually     |
| 2  | Granulometric composition - grain size, mm               | 0.25 - 1      | IDT 10900-84 |
| 3  | The content of the working fraction of the total mass% not less than | 96            |              |
| 4  | Humidity,%                                              | 15-20         | IDT 10898.1-84 |
| 5  | Phosphorus content,%                                     | 19.4          | IDT 8.531-85 |
| 6  | Bulk weight, g / ml                                      | 0.19          | IDT 20298-74 |
| 7  | Specific volume of swollen ion exchanger in the OH form, ml / g | 2.12         | IDT 10898.4-84 |
| 8  | COE (mEq / hl):                                          |               |              |
|    | Cu from solution (5 g / l) CuSO4                        | 4,0           | IDT 20255.1-89. |
|    | Co from solution (5 g / l) CoSO4                        | 5,5           |              |
|    | Ni from solution (5 g / l) NiSO4                        | 4,8           |              |
| 9  | Mechanical strength,%                                    | 94.0          | IDT 17338-81. |

CONCLUSION

In conclusion, it should be noted that, based on the results of studies carried out in the synthesis process, an effective ion-exchange phospholized gossypol resin was obtained for the extraction of precious metal ions. The properties and the technology of producing ion exchanger for the extraction of rare and precious metal ions from the wastewater of metallurgical plants, including gossipole resin, phosphorus trichloride, aluminum trichloride, and copper shavings, are presented.

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