Prospect of using beet molasses in the production of synthetic rubbers

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Abstract. The production of high-molecular compounds requires improvement in manufacturing technology. Promising instrumentation of technological processes, new raw materials are being introduced, that in some cases makes it possible to improve the composite materials, use valuable hydrocarbon raw materials more fully and efficiently, and reduce the pressure on the environmental. All this applies to the production of synthetic rubbers. It is important to select new coagulating systems used in the technology of rubber separation from latex, since the coagulation stage is one of the most material-intensive and energy-intensive and problematic from an environmental perspective. In this paper, we studied the possibility of using a beet-sugar production by-product - beet molasses - in the technology for producing styrene-butadiene rubber of the SKS-30 ARK brand to reduce the aggregative stability of latex systems. The completeness of rubber separation was achieved at consumption of 200 kg / t and sulfuric acid consumption of 15 kg / t of rubber. In this case, the pH of the system increased from 3 to 5.5. Increasing the consumption of sulfuric acid to 40 kg / t of rubber allowed reducing the consumption of molasses to 90 kg / t of rubber and stabilizing the acidity of the coagulated system. Synergism in the action of these components was established for the first time and allowed reducing the consumption of coagulating agent by 2–3 times. Synergism of these components was first established and allowed reducing the consumption of a coagulating agent by a factor of 2–3. Based on the rubber obtained, rubber mixtures were prepared using standard components and vulcanized. Rubber based on SKS-30 ARK meets the requirements.

1. Introduction
Reducing environmental risks is an important and urgent task of our time. To solve this problem, the processing and using waste and by-products of existing plants is a priority and allows more fully and efficiently use secondary resources. This is especially important in cases where expensive and scarce raw materials are used to produce the target product. Moreover, the most promising developments are based on the integrated processing and use of available secondary resources.

One of such large-tonnage products is molasses - a by-product of sugar beet production, which can serve as a source for valuable food and feed products [1–4].
The use of molasses in the technology for the production of high-molecular compounds was due to the fact that, in addition to the main products, the sugar production generates a significant amount of waste that is currently not being used effectively enough, and their disposal in the solid waste storage fields causes significant harm to the environment. For example, the beet-sugar industry of the Russian Federation annually processes up to 40 million tons of beets. In this case, the main waste is obtained: tops - 50-70 tons, fresh pulp 70-90 tons, filtration sludge 8-12 tons and molasses 4-6% by weight of beets. Of particular interest is molasses. The use of molasses as a secondary raw material allows comprehensive resolution of the issue of its disposal. It is important to note that molasses contains compounds containing nitrogen and, in particular, betaines. It was shown in [5] that nitrogen-containing compounds can lead to a decrease in the aggregative stability of disperse systems. Therefore, research on the use of molasses as a coagulating agent is of interest from both a scientific and a practical point of view. Betaines contain in their structure a fragment capable of reacting with anionic emulsifiers to form ion-salt complexes. The formation of such complexes can be due to the fact that betaines create intrasalt forms, since they contain two oppositely charged groups in the molecules: the positive charge is provided by the ammonium group, and the negative charge is provided by the carboxylate group. In this case, we are dealing with a bipolar ion.

2. Materials and methods
For the study, latex of styrene-butadiene rubber SKS-30 ARK, manufactured on an industrial scale was selected. Latex indicators are presented in Table 1.

Table 1. Characteristics of styrene-butadiene latex SKS-30 ARK

| Name of parameter                      | Value  |
|----------------------------------------|--------|
| Dry residue (solid), %                 | 20.5   |
| Content of bound styrene, %            | 22.5   |
| Surface tension, mN / m                | 64.2   |
| Latex particle radius, nm              | 39     |

The main characteristics of molasses are as follows: solubility in water - complete, mass fraction of solids - not less than 75.0%, mass fraction of sucrose (beet sugar) - not less than 43.0%, mass fraction of the amount of fermentable sugars - not less than 44.0%, pH – 6.5-8.5.

Rubber was separated from latex according to the procedure described in [6].

3. Results
The results of the first studies on the use of molasses in the process of reducing the aggregative stability of latex systems showed that it has a number of features that were not observed in such classic coagulating agents as sodium chloride, as well as cationic polyelectrolytes [7, 8].

It was found that with a stable consumption of the acidifying component - sulfuric acid (15 kg / t of rubber), a decrease in the aggregate stability of latex is achieved with a dosage of molasses 190-200 kg / t. A decrease in acidity of the coagulated system and an increase in pH from 3.0 to 5.0-5.5 were noted. A decrease in acidity of the coagulated system does not allow the complete conversion of carboxylic acid soaps to carboxylic acids, that stabilizes the dispersion, and its destabilization requires an increased consumption of molasses, corresponding to the consumption of sodium chloride.

It was possible to reduce the molasses consumption by increasing the consumption of sulfuric acid: increasing the consumption of sulfuric acid from 15 to 37-40 kg / t of rubber allows reducing the consumption of molasses from 200 to 70-90 kg / t of rubber.

Using the design of experiments, an assessment of the influence on the rubber separation process of such parameters as the coagulation temperature and the consumption of sulfuric acid and molasses was made. Regression equations are obtained that describe the influence of the above factors on the rubber separation process from latex. The dominant factors are the consumptions of molasses and sulfuric
acid. The coagulation process should be carried out at temperatures not exceeding 30 °C. The use of elevated temperatures (above 50 °C) leads to a decrease in the completeness of coagulation.

The mathematical model obtained by performing the full factorial experiment has the form of a linear equation.

After calculating the regression coefficients and determining their significance using the Student criterion, the equation takes the form:

\[ Y = 51.68 + 11.61x_1 + 11.23x_2 - 10.22x_3 + 4.83x_1x_2 + 2.28x_1x_3 - 3.22x_2x_3 \]

The suitability of the mathematical model was tested using the Fisher test.

When molasses is added to styrene-butadiene latex, at the first stage, anionic surfactants adsorbed on the surface of latex particles react with the components of the coagulant according to the reaction:

\[ [(\text{CH}_3)_3\text{N}^+\text{CH}_2\text{COO}^-] + \text{R}–\text{COONa} \rightarrow [(\text{CH}_3)_3\text{N}^+\text{CH}_2\text{COONa}]\text{R}–\text{COO}^- \]

The acidification of the system can lead to a reaction with cleavage of the formed complex with the release of free carboxylic acid, sodium sulfate and the formation of a new zwitterion:

\[ [(\text{CH}_3)_3\text{N}^+\text{CH}_2\text{COONa}]\text{R}–\text{COO}^- + \text{H}_2\text{SO}_4 \rightarrow [(\text{CH}_3)_3\text{N}^+\text{CH}_2\text{COOH}] + \text{Na}_2\text{SO}_4 + \text{R}–\text{COOH} \]

This contributes to the active agglomeration of the system and the completion of the coagulation process.

The occurrence of this series of sequential and parallel reactions explains the increased consumption of sulfuric acid.

4. Discussion

The analysis of experimental data shows that in order to reduce molasses consumption, an increase in the consumption of sulfuric acid is required, the work with which requires increased safety measures: the use of acid-resistant equipment, personal protective equipment, etc. Therefore, it was necessary to solve the problem of reducing the consumption of sulfuric acid.

It was possible to reduce the consumption of sulfuric acid and stabilize the coagulation process through the use of a combined coagulant consisting of sodium chloride and molasses. The use of a hybrid reagent to destabilize the aggregate stability of the latex system made it possible to achieve the complete rubber separation from latex at sodium chloride consumption of 20–50 kg / t and molasses consumption of 50–30 kg / t of rubber [7,8].

The complete rubber separation is achieved at dosages of the combined coagulant of 70-80 kg / t of rubber, which is 2-3 times less than when sodium chloride and molasses coagulations taken separately. At the same time, the consumption of the salt component in the hybrid coagulant is reduced by 5-8 times, and molasses by 3-7 times. Thus, in this case, a synergism of the coagulating action of the components when they are used together is clearly detected. It is important to note that under these conditions, the required acidity of the environment (pH ~ 3) is achieved without the use of excessive amounts of acidifying agent (specific consumption of sulfuric acid is 15 kg / t of rubber).

The proposed solution for the rubber separation from latex has certain advantages over actual technologies and can be promising for industrial applications.

It should be noted that a decrease in the share of the salt component of the hybrid coagulant (for example, below 15 kg / t of rubber) is impractical, since this entails an increase in the consumption of molasses, an increase in the pH of the environment and, accordingly, an increase in the consumption of sulfuric acid.

The discovered synergistic effect of the coagulating action in the molasses – sodium chloride system is apparently associated with the combined effect of two coagulation mechanisms. The presence of an inorganic salt determines the contribution of the concentration mechanism — a decrease in the potential barrier of repulsion of particles due to compression of the diffuse ionic layers of the emulsifier on their surface. At the same time, a neutralizing mechanism is also observed in an
acidic environment due to the chemical interaction of emulsifier anions and betaine molecules with the formation of an insoluble weakly dissociating ion-salt complex.

The advantage of molasses is that it is non-toxic and safe for human health. One of its most important advantages is complete biodegradation at sewage treatment plants. This reduces the discharge of aqueous effluents into the natural water bodies from the production of synthetic rubbers, which contain a large amount of sodium chloride and other inorganic salt, and are not contaminated at treatment plants, causing irreparable environmental damage.

Emulsion polymerization rubbers have a set of properties required for the tire and rubber industry [9-11]. The tests showed that the vulcanizates obtained on the basis of rubber samples separated by a combined coagulant met the requirements and were similar to the control specimen obtained from latex using sodium chloride (Table 2).

5. Conclusion
The studies have shown that both the consumption of molasses and sulfuric acid influence the process of reducing the aggregate stability of latex. It was found that the consumption of sulfuric acid depends on the consumption of molasses: the higher the consumption of molasses, the higher the dosage of sulfuric acid.

For the first time, synergism in the action of the components of the combined coagulant was noted and it was shown that its use in the technology for the production of emulsion rubbers can reduce the total consumption of coagulating agents by 2–3 times.

The parameters of rubber compounds and vulcanizates obtained on the basis of rubber separated from latex using molasses meets regulatory requirements. The use of molasses in the technology of rubber separation from latex can reduce environmental risks.

| Table 2. Physical and mechanical properties of vulcanizates |
|-------------------------------------------------------------|
| Parameters | Requirements for rubber SKS-30 ARK according to TU 38.40355-99 | Control (coagulant: sodium chloride) | Experimental (coagulant: molasses) |
| Mooney rubber viscosity | 40 – 65 | 55,0 | 62 |
| Nominal tensile strength, MPa | not less than 21,5 | 24,5 | 23,7 |
| Breaking elongation, % | not less than 380 | 520 | 500 |
| Breaking (residual) strain, % | – | 12 | 11 |
| Vulcanizate aging coefficient (100 °C, 72 h) | – | 0,53 | 0,57 |
| - by strength | – | 0,35 | 0,38 |
| - by elongation | – | – | – |

Similar results were obtained on the basis of rubber separated from latex using a hybrid coagulant.
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