Reducing Anthropogenic Impact on Hydrosphere Related to Synthetic Rubber Manufacture by Means of Their Formulation Technology Enhancement

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Abstract. Negative impact of industrial sewage waters on the state of water objects requires the development of measures for reducing the volume of wastes disposal and searching for the solutions on the decrease or complete exclusion of toxic reagents from industrial processes. The use of emulsive rubbers made of latex as tin chloride coagulant (IV) allows reducing the level of sewage water pollution due to the decreased volume electrolyte velocity and the absence of the necessity to use sulphuric acid as an aciditating agent.

1. Introduction
The condition of natural environment requires the mankind to review the model of society interaction with its technical resources and nature. Actually, the sustainable development concept is based upon this statement. The condition of water resources has not improved for last decades: water resources reduce in their number while their quality deteriorates. A negative trend relates to the increasing anthropogenic influence on the water reservoirs at the background of increasing needs in such resource. The inflow of industrial sewage waters into water objects causes its pollution, sometimes accompanied by eutrophication processes. Among the main pollutants of water eco-systems one can point to oil products, phenols, synthetic surface active materials, heavy metals. Here one can note mostly anthropogenic impact on the pollution of organic nature and ingestion of heavy metals to water reservoirs [1-5]. Flowing to water reservoirs with sewage waters, metals tend to accumulate in sea-floor sediments and benthic organisms or transform into more toxic substances.

In many cities natural&anthropogenic water reservoirs - water collecting areas - are the places where high pollution levels keep being registered. This phenomenon is explained by the impact of industrial sewage waters which do not correspond to regulatory requirements [1, 2, 4]. As a result of ingredient pollution water reservoir eco-systems change, and these changes include biodiversity reduction, dominant species change, development of separate taxonomic groups of organisms, mostly cyanobacteria, which can pose threat not only for the environment but also for the human due to the increased generation of cyanotoxines [6, 7]. Acknowledging the need to reduce the anthropogenic
impact on water reservoirs one applies new approaches to sewage treatment, however, the most reasonable is to develop technology allowing for the reduction or exclusion of the pollutant inflow to sewage waters.

Chemical and petrochemical companies make the largest impact into the pollution of surface water reservoirs. At the same time the demand for the products from these areas remains significant and keeps growing [8]. In a total of synthetic rubbers consumed in the world a half of this number consists of emulsion polymerization rubbers used for the manufacture of rubber products, including tire manufacture [9]. However, at the manufacture of emulsive rubbers there is a problem of high coagulant consumption, in particular, sodium chloride, and the use of sulphuric acid as an acidating agent which causes synthetic rubber losses and negatively influences the hydrosphere state generating sewage waters. At the same time one of the key tasks of the state policy in the environmental development of the Russian Federation until 2030 is preventing and reducing current negative impact on the environment. This task may be resolved both by means of introducing modern pollution control equipment and by means of improving existing technologies.

In connection with the aforementioned the paper purpose is the search for optimal coagulants the application of which in the process of emulsion synthesized rubbers will allow reducing the level of sewage waters pollution with metals.

2. Methods and materials
As research objects the authors selected styrene-butadiene-rubber SKS-30 ARK and various coagulants - electrolytes – sodium chloride solutions (24 % wt.) and lithium, potassium, magnesium, aluminum, tin (II) and tin (IV) chlorides (10 % wt.). As an acidating agent the authors used the sulphuric acid solution (2% wt.). To conduct the process of rubber separation from latex, the authors used a coagulation unit made in the form of the tank with a mixing device. 20 ml of latex were added to the tank, after that it was placed into a thermostat for 20 minutes. Further coagulant solutions and the acidating agent - sulphuric acid - were added to latex, and due to this the media pH was equal to 2.2-3.0. To conduct a comprehensive research of various factors impact on the coagulation process, the authors applied the method of experiment planning (full factor experiment for all coagulants by the plan $2^3$ and $2^4$). The advantage of this planning method consists in the revealing and exclusion of mutual influence of the factors under research on the output characteristics of the system under study [10].

3. Result
In the industry electrolytes are widely applied as coagulating agents characterized by low toxicity, high availability and low net cost. To separate rubber from latex the chlorides of alkaline, alkaline-earth metals, light and polyvalent metals. After conducting the analysis of the emulsive rubber obtaining the authors defined a list of coagulants used at present for industrial rubber manufacture. The main coagulants in the production of emulsive rubbers are sodium and magnesium chlorides requiring the process to be conducted at 50-65°C. One should mention that sometimes organic coagulants are used to manufacture synthetic rubbers, for example, such coagulants as polydiallyldimethylammonium chloride (VPK-402) which have a number of advantages comparing with non-organic coagulants. The advantages may include low consumption (2-4 kg/ton of rubber). However, there is a significant drawback - high antiseptic capacity. In case of its contact with waste treatment facilities at the application of the technology of sewage waters cleaning with the help of activated sludge, the substance destruction takes place.

At the first stage of the research the authors defined the coagulant types the efficiency of which depends on coagulant and aciditating agent consumption. Such dependence was determined for the following coagulants: lithium, sodium, potassium, magnesium, calcium, aluminum, zinc, tin (II). Fig. 1 shows the influence of magnesium chloride and aciditating agent consumption on coagulation.
Figure 1. Influence of magnesium chloride consumption ($q$, kg/ton of rubber) and aciditating agent consumption ($p$, kg/ton of rubber) on coagulation.

\[ Y = -3.140 + 3.570V_1 + 0.100V_2 - 0.002V_3 + 0.045V_4 + 0.013V_1V_2 + 0.005V_1V_4 + 0.001V_2V_3 \]

where $Y$ – yield of the generated rubber crumb, %; $V_1$ – consumption of magnesium chloride, kg/ton of rubber; $V_2$ – aciditating agent consumption, kg/ton of rubber; $V_3$ – process temperature, °C; $V_4$ – mixing time, min.

Legend: кг/т каучука – kg/ton of rubber

At the second stage the search was directed at the revealing of coagulant types the efficiency of which was defined by coagulant consumption and process temperature. The coagulant meeting the requirements is tin chloride (IV) (Fig. 2) [11].

Figure 2. Impact of tin (IV) chloride consumption ($q$, kg/ton of rubber) and temperature (°C) on coagulation.

\[ Y = -27.85 + 5.55V_1 + 0.28V_2 - 0.22V_3 - 0.01V_1V_2 + 0.02V_1V_3 \]
where $Y$ – yield of the generated rubber crumb, %; $V_1$ – tin (IV) chloride consumption, kg/ton of rubber; $V_2$ – acidating agent consumption, kg/ton of rubber; $V_3$ – process temperature, °C.

Legend: кг/т каучука – kg/ton of rubber

As a result of the conducted experiments with the use of tin (IV) chloride, the authors revealed some regularities involving the process kinetics.

Studying the kinetics of rubber separation from latex at the use of the electrolyte of tin (IV) chloride allows observing the reduction in coagulant consumption if the process occurs under decreased temperature (2 °C). The mentioned electrolyte consumption necessary for full rubber separation from latex is lower than aluminum chloride consumption which does not contradict with the Schulze-Hardy rule. In compliance with the Schulze-Hardy rule the increase in cation charge (cation valence) the coagulating electrolyte capacity grows up. Consequently, tin (IV) chloride should have the maximum coagulating effect. However, the increase of the temperature of rubber separation results in coagulant consumption increase: at 40 °C tin chloride consumption was comparable to aluminum chloride consumption while at 80 °C one observed the deviation from the Schulze-Hardy rule as tin chloride consumption exceeded aluminum chloride consumption.

Such deviation from the Schulze-Hardy rule may be observed at neutral coagulation which is not subject to this rule. As tin chloride is also an electrolyte with a multi-charge counter-ion, a so-called non-indifferent electrolyte, at its introduction into latex the temperature rise is accompanied by the decrease of $\xi$-potential down to its recharge for the opposite polarity which results in neutralizing coagulation.

To assess the dependence of rubber separation from latex, the authors considered two values of the temperature, 2 °C (Fig. 3) and 60 °C (Fig. 4), as during industrial manufacture coagulation is conducted at 60 °C.

![Figure 3](image-url)

Figure 3. Impact of tin (IV) chloride consumption ($q$, kg/ton of rubber) and temperature (°C) on coagulation.

$Y = -27.85 + 5.55V_1 + 0.28V_2 - 0.22V_3 - 0.01V_1V_2 + 0.02V_1V_3$

where $Y$ – yield of the generated rubber crumb, %; $V_1$ – tin chloride (IV) consumption, kg/ton of rubber; $V_2$ – acidating agent consumption, kg/ton of rubber; $V_3$ – process temperature, °C.
Figure 4. Dependence of the impact of temperature, coagulant consumption and nature on rubber separation from latex (A, %).

Q, kg/t of synthetic rubber – coagulant consumption. Coagulation temperature: а – 2 °C; б – 60 °C.
Coagulants – metal chlorides: 1 – tin (IV); 2 – aluminum; 3 – magnesium; 4 – sodium.

Therefore, the authors observe increase in coagulant consumption in case neutralizing coagulation occurs in the range of 20-92 °C.

It should be mentioned that there is no need to use an acidating agent during coagulation as acid environment is generated by the electrolyte itself, namely, by tin (IV) chloride. I.e., at the use of this coagulant one may not add sulphuric acid into a coagulating system. This fact is explained by the process of hydrolysis tin chloride is subject to in the water solution [12, 13]. Hydrolysis can occur in various directions:

- with the formation of hydrochloric and stannic acids
  \[ \text{SnCl}_4 + 6 \text{H}_2\text{O} \rightarrow \text{H}_2\text{Sn(OH)}_6 + 4 \text{HCl} \]
- chlorostannic acid
  \[ 3 \text{SnCl}_4 + 4 \text{H}_2\text{O} \rightarrow 2 \text{H}_2\text{Sn(Cl)}_6 + \text{Sn(OH)}_4 \]

In addition to this process, the formation of chlorostannic acid is possible at interaction of hydrochloric acid with SnCl4

\[ \text{SnCl}_4 + 2 \text{HCl} \rightarrow \text{H}_2\text{Sn(Cl)}_6 \]

The increase of temperature facilitates hydrolysis resulting in the formation of chlorostannic acid \( \text{H}_2\text{[Sn(Cl)}_6\text{]} \) interacting with the components of the emulsion system (surface-active agents) which is a destabilizing factor of the latex system. It allows one not to use sulphuric acid in the industrial process.

\[ \text{H}_2\text{[Sn(Cl)}_6\text{]} + \text{R–COONa}(\text{K}) \rightarrow \text{Na}_2\text{(K)}_2\text{[Sn(Cl)}_6\text{]} + \text{R–COOH} \]

When tin chloride is used as a coagulant at rubber separation from latex the authors note the generation of finely dispersed rubber crumb. This is a negative effect in case one applies a traditional technology of rubber separation from latex as rubber crumb losses increase with rinse waters of separation shops. It demands new technology solutions in terms of the equipment used for the separation of styrene-butadiene-rubber in the form of finely dispersed crumb.

However, one should mention that at the Russian and global market there has been recently the growth of demand in finely dispersed rubber crumb which makes the application of this coagulant rather prospective.

On the basis of the conducted research one can identify the electrolyte showing the highest coagulating activity. Such coagulant is tin (IV) chloride, and the highest efficiency of the coagulating activity is observed at the temperature up to 20 °C which allows reducing energy demands on heating
the coagulating mixture which corresponds to the requirements set for the implementation of the sustainable development concept in the industrial sphere.

The research conducted to study the peculiarities of separating the rubber SKS-30 ARK from latex at adding electrolytes in the form of metal salts with various nature confirm the identified process regularities for other types of emulsive rubbers (SKS-30 ARKPN, SKMS-30 ARK, SKS-30 ARKM-15, SKS-30 ARKM-27).

4. Conclusion
The conducted research allowed making conclusions on the necessity of reducing negative impact of rubber production on the environment due to the reduction of sewage waters and pollutants they contain. A possible solution for the problem of sewage water pollution by oil chemical plants can become the selection of electrolytes applied at coagulation of emulsive rubbers the demand for which keep growing year by year.

Studying the kinetics of synthetic rubber SKS-30 ARK resulted in the identification of the following consistent regularities:

1) the efficiency of rubber separation from latex is significantly defined by the applied coagulant type;

2) the increase in the cation charge of polyvalent salt results in the coagulating capacity increase;

3) the dependence of the coagulation efficiency on the temperature is direct - temperature increase facilitates a faster coagulation;

4) the application of tin (IV) chloride as a coagulating agent allows process conduct at low temperatures (maximum up to 20 °C) without sulphuric acid as an acidating agent. It will reduce the amount of generated sewage waters;

5) the application of tin chloride has an impact on the product dispersity: the amount of the generated finely dispersed crumb increases which, however, can be prospective taking into account the growing demand in finely dispersed rubber crumb;

6) the obtained regularities are fair not only for SKS-30 ARK but also for other types of emulsive rubbers.

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