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Investigation of the process of latex coagulation by cationic surfactants

In the article the estimation of coagulating ability using cationic electrolytes is shown. It was found that in the case of using low molecular weight cationic electrolyte, the completeness of the release of rubber from latex is achieved at their consumption of 20–30 kg/t of rubber. A feature of the behavior of cationic surfactants in the latex coagulation has been established. It is shown that the consumption of cationic surfactants corresponds to the consumption of polymer cationic electrolytes. Also, a hypothesis was put forward that cationic surfactants violate the aggregate stability of latex systems and the mechanism of action, which is based on the interaction of cationic surfactant micelles with latex globules carrying anionic surfactants on the surface is proposed. The use of cationic surfactants can eliminate the use of sodium chloride in the industry of separating emulsion styrene-butadiene rubber from latex, as well as solve some environmental problems. The final stage of the investigation was to determine the parameters of rubber compounds and vulcanizates based on the rubber. These rubbers, rubber compounds and vulcanizates correspond to standard parameters.

Keywords: latex, coagulation, cationic surfactants, rubber, rubber compounds, vulcanizates, parameters, environment.

Introduction

The chemical and petrochemical industry has been actively developing in recent years. The introduction of new technologies, hardware design of processes, catalytic systems and initiators makes it possible to increase the productivity of the process, the quality of the products obtained, reduce environmental pollution and make more complete and rational use of natural resources [1, 2].

Synthetic rubbers obtained by emulsion polymerization have a set of required properties and are widely used in the tire and rubber industry, in composite materials for various purposes, etc. [3, 4]. However, their production is in conflict with the regional ecology. One of the problematic stages in the production of rubbers obtained by emulsion polymerization is the stage of separation from latex. This is due to the fact that in the process of separating rubbers from latex, salt coagulating agents are used, the consumption of which is tens (metal salts of the second group of the periodic system) and hundreds of kg/t of rubber (metal salts of the first group of the periodic system). Therefore, at present, an important and urgent task is aimed at developing new technologies and technical solutions that can reduce the consumption of salts or completely eliminate their use in the technology of production of emulsion rubbers [5]. Quaternary ammonium salts are promising in this regard. The review paper [5] shows the prospects of their application in the technology of rubber isolation from latex. The consumption of low-molecular and high-molecular quaternary ammonium salts is less than that of sodium chloride and other salts. However, the high cost of these salts, as well as the impossibility of their usage in some variants of latex technology largely deters from their integration in the synthetic rubber industry.

In the literature there is no information about the use of cationic surfactants (CPAV) in the technology of rubber isolation from latex [5]. CPAV are available reagents that are widely used in various industrial sectors [6, 7].

The aim of this paper is to study the possibility of using CPAV in the production technology of styrene-butadiene rubbers.

Experimental

The latex coagulation process (Table 1) was researched using cationic surfactants produced on an industrial scale [8].

Table 1

Characteristics of styrene-butadiene latex produced by emulsion rubbers (SBR)

Parameter	Value
Dry residue, wt%	21.3
Surface tension, mH/m	57.1
pH latex	9.5
Content of bound styrene, wt. %	22.7

The coagulating process was carried out at 21±1 °C. Aqueous solutions of cationic surfactants: dodecylpyridinium chloride with concentrations ~2 wt%, decylpyridinium chloride ~2 %, cetylpyridinium bromide ~2 %, cetyltrimethylammonium bromide ~2 %, alkylbenzyldimethylammonium chloride ~2 %, and sodium chloride — 20 wt%, N,N-dimethyl-N,N-diallylammonium chloride — 5 wt%, poly- N,N-dimethyl-N,N-diallylammoniumchloride — 2 wt% were used as coagulating agents. An aqueous solution of sulfuric acid with a concentration of ~ 2.0 wt% was used as an acidifying agent. The resulting rubber crumb was separated from the aqueous phase (serum), washed with warm water and dehydrated in a drying cabinet at 80–85 °C. The completeness of coagulation was assessed visually by the transparency of the serum and gravimetrically by the mass of the resulting rubber crumb. The following substances were used for the extraction of rubber from latex: dodecylpyridinium chloride (DDPC); decylpyridinium chloride (DPC); cetylpyridinium bromide (CPB); cetyltrimethylammonium bromide (CTMAB); alkylbenzyldimethylammonium chloride (ABDMAH).

Results and Discussion

The conducted studies have established (Table 2) that the amount of rubber crumbs released naturally increases with an increase in the consumption of all the coagulating agents studied. However, a number of interesting features were also noted in the behavior of CPAV during the coagulation of styrene-butadiene latex, which was not previously noted when using other agents used in the isolation of rubber from latex.

Results of the research are presented in Table 2.

Table 2

Experimental results obtained in the isolation of rubber from emulsion latex using various coagulating agents

TYPE OF COAGULANT	Sodium chloride						
Temperature, °C	20/60						
Consumption of sodium chloride кg·t^{-1} of rubber	10	30	50	70	100	120	150
Rubber outlet (20°C), mass %	34.5	56.3	74.7	80.5	85.6	90.5	97.1
Rubber outlet (60°C), mass %	22.7	50.9	72.2	80.2	83.6	89.9	95.6
Evaluation of complete coagulation	icc	icc	icc	icc	icc	icc	cc
TYPE OF COAGULANT	N,N-dimethyl-N,N-diallylammonium chloride						
Temperature, °C	20						
Consumption of coagulating agent, кg·t^{-1} of rubber	1	3	5	10	15	20	25
Rubber outlet, mass %	34.7	58.9	67.2	78.2	87.6	90.9	96.3
Evaluation of complete coagulation	icc	icc	icc	icc	icc	icc	cc
TYPE OF COAGULANT	Poly- N,N-dimethyl-N,N-diallylammonium chloride						
Temperature, °C	20						
Consumption of coagulating agent, кg·t^{-1} of rubber	0.25	0.50	0.75	1.00	1.50	2.00	2.50
Rubber outlet, mass %	13.3	25.8	44.7	69.8	86.8	92.9	95.5
Evaluation of complete coagulation	icc	icc	icc	icc	icc	cc	Cc
TYPE OF COAGULANT	Dodecylpyridinium chloride						
Temperature, °C	20						
Consumption of coagulating agent, кg·t^{-1} of rubber	0.25	0.50	0.75	1.00	1.25	1.50	-
Rubber outlet, mass %	12.7	20.9	42.2	80.2	89.1	93.6	
Evaluation of complete coagulation	icc	icc	icc	icc	icc	cc	-

Continuation of Table 2

TYPE OF COAGULANT	Decylpyridinium chloride						
Temperature, ºC	20						
Consumption of coagulating agent, кg·t^{-1} of rubber	0.25	0.50	0.75	1.00	1.50	2.00	2.50
Rubber outlet, mass %	27.3	37.8	59.9	85.0	91.4	92.1	94.4
Evaluation of complete coagulation	icc	icc	icc	icc	cc	cc	cc
TYPE OF COAGULANT	Cetylpyridinium bromide						
Temperature, ºC	20						
Consumption of coagulating agent, кg·t^{-1} of rubber	0.25	0.50	0.75	1.00	1.50	2.00	2.50
Rubber outlet, mass %	17.5	50.2	50.8	75.0	90.2	93.2	95.2
Evaluation of complete coagulation	icc	icc	icc	icc	icc	cc	cc
TYPE OF COAGULANT	Cetyltrimethylammonium bromide						
Temperature, ºC	20						
Consumption of coagulating agent, кg·t^{-1} of rubber	0.25	0.50	0.75	1.00	1.50	2.00	2.50
Rubber outlet, mass %	28.8	50.2	66.4	75.0	85.6	93.2	94.2
Evaluation of complete coagulation	icc	icc	icc	icc	icc	cc	cc
TYPE OF COAGULANT	Alkylbenzyldimethylammonium chloride						
Temperature, ºC	20						
Consumption of coagulating agent, кg·t^{-1} of rubber	0.50	1.0	1.5	2.0	2.5	3.0	
Rubber outlet, mass %	40.3	57.7	71.6	83.8	93.9	93.0	
Evaluation of complete coagulation	icc	icc	icc	icc	cc	cc	

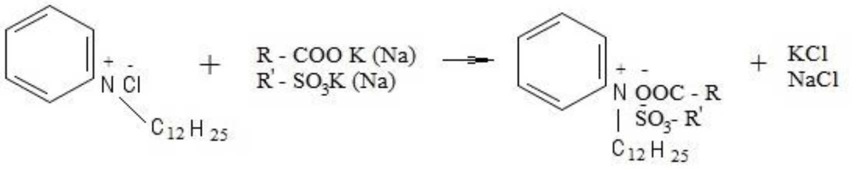
Notes. Abbreviations: icc — incomplete coagulation; cc — complete coagulation. The pH of the aqueous phase (serum) — 3,0; consumption of sulfuric acid — 15,0 kg·t^{-1} rubber.

What is the peculiarity in the behavior of CPAV as agents of coagulation?

The results presented in Table 2 indicate a sharp difference in the efficiency of the coagulating action of low molecular weight cationic reagents, which differ in their colloidal characteristics: the consumption of micelle-forming CPAV (DDPC, CPC, CTAB) is an order of magnitude less than the consumption of similar in chemical structure DMDAAH, which does not have the ability to micelle (2.0–2.5 kgt^{-1}, and 20.0–25.0 kgt^{-1}, respectively). Micelle-forming low molecular weight CPAV are close to (and sometimes exceed) the high molecular weight analog of DMDAAH the VPK-402 reagent in terms of their effectiveness in latex coagulation. The high coagulating capacity of the polymer cationic reagent VPK-402 is due to the fact that in the case of cationic polyelectrolyte, the combined effect of two astabilizing mechanisms acts – neutralization and bridging, the second mechanism enhances the effect of the first one.

The above-mentioned feature in the behavior of CPAV is probably related to their micelle-forming ability. In this case, the coagulation process will be based on the interaction of latex globules carrying adsorption layers of anionic surfactants on the surface not with individual molecules of the cationic electrolyte, but with CPAV micelles (Fig. 1), i.e., a kind of polycondensation reaction will occur with the release of a low-molecular product — an inorganic salt (sodium chlorides) and the formation of an unstable complex latex globule-CPAV micelle.

The disintegration of this complex will be accompanied by the release of the water-insoluble product of the interaction of CPAV with anionic surfactant into the sediment according to the scheme:



Or in general:

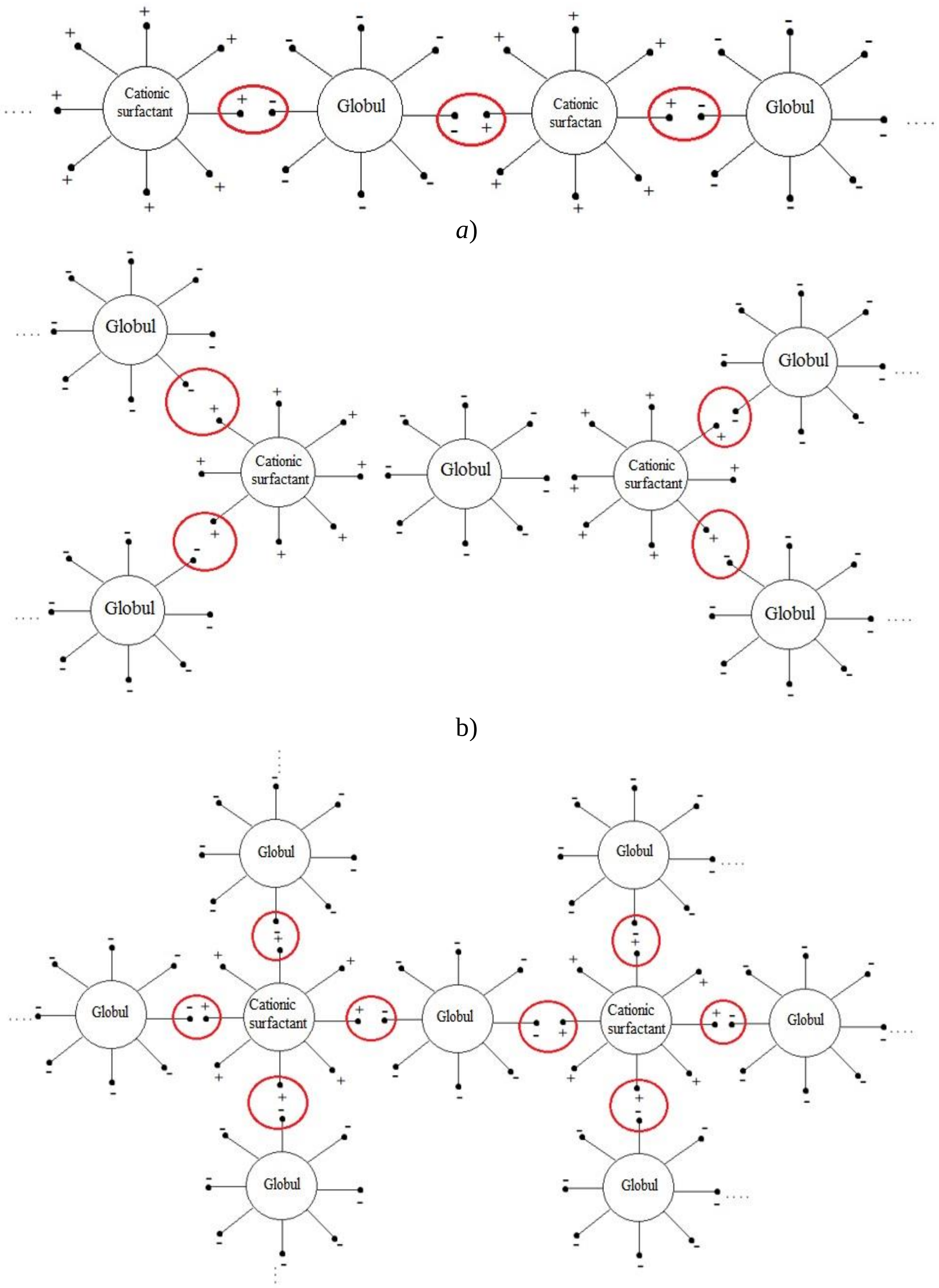
$$n\text{R–COOK} + n(\equiv\text{N}^+ - \text{C}_{(10\text{–}16)})\text{Cl}^- \rightarrow ((\equiv\text{N}^+ - \text{C}_{(10\text{–}16)})\text{–OOC–R})_n + n\text{KCl}$$

where n is greater than 1.

In an acidic medium, the decomposition of low-stability polymer-complex structures occurs:

$$((\equiv\text{N}^+ - \text{C}_{(10\text{–}16)})\text{–OOC–R})_n + \text{H}_2\text{SO}_4 \rightarrow (\equiv\text{N} + -\text{C}_{(10\text{-}16)})\text{HSO}_4^- + \text{R–COOH}$$

A hypothetical model of the interaction of latex micelles with CPAV allows us to explain the observed (Table 3) the effect of the length of the hydrocarbon radical of CPAV on the process of isolation of rubber from latex. Thus, when the radical contains 10–12 carbon atoms, a bi-beam structure is most likely formed (Fig. 1*a*), and when the radical contains 16 carbon atoms, the size of the micelle increases and the coagulation process can occur with the formation of 3 and 4 beam structures (Fig. 1*b*, *c*). This is also reflected in the consumption of cationic surfactants. These hypothetical considerations are supported by some simple calculations. Namely, we found how many micelles per 1 globule of latex are approximately at the time of the introduction of CPAV in the full coagulation mode (for CTAB, CPC, DPC) (Table 3) [9, 10]. The data in Table 3 show that the number of micelles surrounding the globule at the initial moment of coagulation significantly exceeds the number of latex globules, so there are sufficient grounds for the hypothetical scheme shown in Figure 1.



a)

b)

c)

Figure 1.The proposed scheme of interaction of negatively charged latex globules with micelles of cationic surfactants (*a*) with a relatively short length of the hydrocarbon radical (*n*C = 10–12) and (*b*), (*c*) a long radical length (*n*C = 16)

Conclusion

Using cationic surfactants in the rubber industry makes it possible to achieve the complete latex coagulation at the expense of the corresponding cationic polyelectrolyte. A hypothesis about the effect of cationic surfactants on the destabilization of the latex aggregate stability is proposed. The process mechanisms occurring during the introduction of a cationic surfactant in a latex system stabilized by anionic surfactants has been introduced.

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Латексті катионды беттік-белсенді заттармен коагуляциялау процесін зерттеу

Мақалада катиондық электролиттердің коагуляциялау қабілеті туралы түсінік кеңейтілген. Төменгі молекулалы катионды электролиттерді қолданған кезде, резеңкеден латекстерді бөліп алудың толықтығына олардың 20-30 кг/т резеңке жұмсау кезінде қол жеткізілетіндігі анықталды. Жүргізілген зерттеулерде стирол-бутадиен каучукты латекстен алу процесінде зерттелген катиондық беттік-белсенді заттармен (ББЗ) әсер етуі барысында ерекшелік байқалды. Катионды ББЗ шығыны полимерлі катионды электролиттің шығынына жақын, ал кейбір жағдайларда одан да аз болатыны көрсетілген. Катиондық беттік-белсенді заттардың латекс жүйелерінің жиынтық тұрақтылығының бұзылуына ықпалы туралы гипотеза алға тартылып, оның әсер ету механизмі ұсынылды, ол катионды ББЗ-дың мицеллаларының бетінде аниондық беттік активті заттарды алып жүретін латекс глобулаларымен өзара әрекеттесуіне негізделген. Осылайша, катионды беттік-белсенді заттарды қолдану натрий хлоридінде және қымбат катионды полимерлі электролитті, эмульсиялы стирол-бутадиенді каучук өндірісінде қолдануды болдырмауға мүмкіндік береді. Катионды ББЗ-ды енгізу кейбір экологиялық мәселелерді шешуге мүмкіндік туғызады. Осы зерттеудің соңғы кезеңінде ұсынылған технологияға сәйкес резеңке негізінде резеңке қоспалары мен вулканизаттардың индикаторларын анықтау болды. Барлық негізгі көрсеткіштер бойынша зерттелетін үлгілер талаптарға сай.

Кілт сөздер: латекс, коагуляция, беттік-белсенді заттар, резеңке қосылыстар, вулканизаттар, қасиеттері, қоршаған орта.

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Исследование процесса коагуляции латекса катионными поверхностно-активными веществами

В статье расширены представления о коагулирующей способности катионных электролитов. Установлено, что в случае применения низкомолекулярных катионных электролитов полнота выделения каучука из латексов достигается при их расходе 20–30 кг/т каучука. Проведенными исследованиями была отмечена особенность в поведении исследуемых катионных поверхностно-активных веществ в процессе выделения бутадиен-стирольного каучука из латекса. Показано, что расход катионных поверхностно-активных веществ близок к расходу (а в некоторых случаях даже меньше) полимерного катионного электролита. Выдвинута гипотеза действия катионных поверхностно-активных веществ на нарушение агрегативной устойчивости латексных систем, предложен механизм его действия, который основан на взаимодействии мицелл КПАВ с латексными глобулами, несущими на поверхности анионные ПАВ. Таким образом, использование катионных поверхностно-активных веществ позволяет исключить применение как хлорида натрия, так и более дорогостоящего катионного полимерного электролита в производстве эмульсионного бутадиен-стирольного каучука. Внедрение КПАВ позволит решить некоторые экологические проблемы. Завершающий этап данного исследования заключался в определении показателей резиновых смесей и вулканизатов на основе каучука, выделенного по предложенной технологии. По всем основным показателям исследуемые образцы соответствовали предъявляемым требованиям.

Ключевые слова: латекс, коагуляция, поверхностно-активные вещества, резиновые смеси, вулканизаты, свойства, окружающая среда.

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