Vol. 2, No. 2, 2008 Chemical Technology

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TECHNOLOGICAL AND ECOLOGICAL ASPECTS OF THE PRACTICAL APPLICATION OF QUATERNARY AMMONIUM SALTS IN PRODUCTION OF SYNTHETIC EMULSION RUBBERS IN RUSSIA

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Received: November 26, 2007

Abstract. In the review physical and chemical aspects and technological parameters of the rubbers production processes from industrial latex with application of ammonium halogenides, tetraalkylammonium salts, poly-(N,N-dimethyl-2-oxypropyleneammonium) chloride, poly-N,N-dimethyl-N,N-diallylammonium chloride, and his copolymer with SO_2 are considered. A significant ecological effect of polymeric flocculants application is shown.

Key words: quaternary ammonium salts, rubber, latex, flocculants, ecology.

1. Introduction

Coagulation of the rubber emulsion is one of the main stages during production of synthetic emulsion rubbers. A routine and quite efficient way of emulsion rubbers extraction from latexes is the application of inorganic salts (first of all NaCl) under acidification of the coagulating system with a mineral acid [1]. It is known that for coagulation of 1 ton of the industrial emulsion of different rubbers (butadiene-styrene, butadiene-nitrile, polybutadiene ones or others) a required quantity of NaCl is from 250 to 1500 kg. Mineral salts in the process of wastewater treatment at waste disposal plants are not decomposed and entrapped but drained to the natural wells. This results in pollution of the environment, soil, and drinking water salinization. For example, if production capacity of emulsion butadiene-styrene rubbers is of 100000 tons per year waste discharge of salts in the form of aqueous solution attains 30000 tons per year just from the extraction workshops. Thus, at emulsion rubbers production the annual waste discharge from the extraction workshops to the natural wells is of hundred thousand tons of NaCl and other salts, causing an irreversible ecological damage.

The most efficient way of perfection of the rubbers from latexes extraction technology is the elaboration of brand new coagulating agents providing a decrease of salt components consumption or their complete elimination from the technological process. Such coagulating agents can be water-soluble ammonium salts, particularly quaternary ammonium salts (QAS).

However, only in Russia a full-scale investigation work in the field has been made including:

- the study of physical-chemical processes of latexes coagulation for industrial rubbers production with the use of cationic polyelectrolytes;
- the study of rubbers properties, their mixtures, and vulcanizates;
- applied investigations of possible application of cationic polyelectrolytes in industry.

Previously, flocculation mechanisms of polystyrene latexes [2-4] and some rubbers [4-7] with the use of QAS were investigated. However, the works aimed at solving the chemical and technological problems of the industrial production of synthetic emulsion rubbers were made later in Russia.

This article presents the results of the investigations conducted by the authors concerning the application of different QAS as coagulating and flocculating agents of the industrial latexes used in the production of synthetic rubbers. The works that are directly aimed at the elaboration of the new approaches to the technology of extraction of synthetic rubbers from butadiene-styrene latexes are considered in most details.

According to the abbreviations accepted in Russia emulsion rubbers are denoted as follows:

- SKS-30 – butadiene-styrene rubber (styrene content is 30 %);
- SKMS-25 – butadiene-(α-methyl) styrene rubber (styrene content is 25 %);
- EPB – emulsion polybutadiene;
- SKN-26 SM – butadiene-nitrile rubber (acrylonitrile content is 26 %);
- Letters A, R, K, P, M, O, C after the numbers denote: A – a rubber of low-temperature polymerization, R – regulated, K – colophony emulsifier, P – waxed emulsifier, M – oil-filled, O – oxide-filled, and C – carbon-filled (technical carbon).

2. Results and Discussion

2.1. Low-molecular ammonium salts

In [8] a reduction of coagulating activity of ammonium halogenides was observed in a series of $NH_4F > NH_4Cl > NH_4Br > NH_4J$ for the discharge intensity of these salts equal to 20, 25, 50 and 100 kg/ton of rubber (pH = 2.5–3.0; temperature is 333 K). Efficiency of SKS-30 ARK and ARKPN rubber extraction from latexes in the presence of NH_4Cl under the influence of different parameters was studied in details in [9]. The analysis of the rubber properties as well as compounded rubbers and vulcanizing agents on their basis demonstrated that these properties do not change in fact under the change of the commonly applied coagulating agent NaCl by NH_4Cl (see Table 1).

Using SKS-30 ARKP and SKS-30 ARK latexes as an example it was shown [10, 11] that with the use of Me_4NCl, Et_4NCl, Et_4NBr and *n*-Bu_4NI a complete coagulation of latex can be achieved for the consumption standards of 60–150 kg/ton of rubber. These values are 2–5 times less than the consumption standard for the industrial coagulating agent – NaCl.

In general, coagulating ability of all the low-molecular salts was not very high.

2.2. Mixtures of the routine coagulating agents with poly-N,N-dimethyl-N,N-diallylammonium chloride

By the example of SKS-30 ARKP (ARK, AKO, ARKM) and butadiene-(α-methyl) styrene latexes SKMS-30 ARKP (ARK, ARKM) of industrial rubbers [12-15] it was shown that addition of PDMDAACl to the routine coagulating agents (NaCl, leather glue, protein hydrolyzate) created the following advantages:

Table 1

Properties of SKS-30 ARKPN rubbers extracted with the use of NaCl and NH_4Cl as well as rubber compounds and rubber resins

Quality performance	Coagulating agents	
	NaCl	Ammonium chloride
Mooney viscosity	45	46
Conditional toughness under stretching, MPa	25.0/26.9	27.5/26.9
Relative extension under fracture, %	690/670	675/650
Relative residual deformation after fracture, %	16/18	14/16
Rebound elasticity, %	42/40	41/39
Content of antioxidant (Agidol-2), %	1.0/1.0	1.2/1.0
Mass fraction of organic acids, %	4.92	6.06
Mass fraction of saponaceous organic acids, %	0.16	0.05
Loss of mass under drying, %	0.17	0.12
Mass fraction of the bound styrene, %	22.5	22.5

- a long-term preservation of protein coagulating agents in aqueous solutions at 293–295 K without their decomposition and appearance of unpleasant smells;
- a part of each of the coagulating agents in a composition of 2- or 3-component mixture was considerably less than in case of their individual usage, resulting in 1.5–2.0 time reduction in a leather glue consumption;
- application of NaCl- PDMDAACl mixtures enabled a 5–10 times NaCl consumption reduction to the values of 20–50 kg/ton of rubber;
- complete coagulation was attained in a wider range of pH values pH = 2.5–4.5 making it possible to reduce consumption of H_2SO_4 from 15–18 to 8–12 kg/ton of rubber;
- consumption rate of PDMDAACl was 0.4–1.2 kg/ton of rubber;
- the extracted rubbers satisfied the Standard of the USSR (GOST) and technical specifications (TU) requirements for the corresponding grade marks of rubbers;
- the properties of the vulcanizates did not yield to the properties of the check samples.

All of the oil-filled rubbers and their vulcanizates satisfied the requirements of the Russian national standards for the corresponding grade marks of rubbers [13, 14]. The role of PDMDAACl was decisive in the experiments; increasing the dosage of PDMDAACl to more than 2 kg/ton of rubber demonstrated the possibility of complete elimination of NaCl from application.

2.3. Poly-N,N-dimethyl-N, N-diallylammonium chloride

Since according to [12-15] individual PDMDAACl is an efficient flocculating agent for the industrial emulsions of rubbers a large amount of investigations concerning the influence of different parameters (latex and coagulating

agent concentrations, polyelectrolyte consumption and its molecular mass, temperature of the process) on the process of extraction and on the properties of different rubber grade marks – SKS and SKMS was performed. The rubbers extracted with the use of NaCl were used as the reference samples [15-20].

The mass of the extracted coagulum was shown to increase with the increase of PDMDAACl amount added to the latex [17, 18]. Flocculation completeness was achieved for the consumption rate of PDMDAACl ≈ ≈ 4 kg/ton of rubber and application rate of H_2SO_4 ≈ ≈ 15 kg/ton of rubber. Here the application rate of cationic polyelectrolyte required for attaining of a complete SKS-30 ARK latex coagulation depends on the temperature: an optimal coagulation temperature was 333 K. The application of higher temperatures did not result in a considerable increase of a coagulum yield. For the temperatures of 293 and 353 K flocculation curves did not in fact depend on the value of PDMDAACl molecular mass (172000, 62000 and 16000). The concentration of the initial aqueous solution of cationic polyelectrolyte did not have any considerable effect on its consumption rate necessary for complete extraction of rubber from latex.

The extracted rubbers very slightly differed from the check samples by their chemical composition and satisfied the requirements of the Russian standards. The main quality coefficients of vulcanizates on the basis of the experimental and check samples were equivalent (see Table 2). However, rubber compounds on the basis of SKS-20 ARK rubber extracted with the use of PDMDAACl were vulcanized more rapidly. According to [17-19] the role of vulcanization activators could belong to polymer QAS remained in the rubber after its flocculation and/or products of its interaction with the components of emulsion system.

The investigation of the flocculation of the emulsive polybutadiene (EPB) [21] showed that the consumption rate value for PDMDAACl was 8.0 kg/ton of rubber. At 333–353 K the rate value was reduced to 5.0 kg/ton of rubber. The change of concentration of the operation PDMDAACl solution from 2.0 to 45.0 % did not have any effect on its consumption rate value. For H_2SO_4 consumption rate value 11–15 kg/ton of rubber a complete latex flocculation takes place. However the amount of coagulum was regularly reduced from 96–98 % to 94–96 % under decrease of H_2SO_4 consumption rate value from 10 to 9 kg/ton of rubber. Thus it can be concluded the process of flocculation is less sensitive to the dosage of H_2SO_4 than under the use of NaCl as a coagulating agent. Rubbers, rubber compounds, and vulcanizates of EPB extracted with the use of PDMDAACl and NaCl were equivalent by the main quality parameters. Just as in case of butadiene-styrene rubbers EPB rubber compounds were vulcanized a little more rapidly (Table 3) [21].

Similar regularities were found for latex flocculation process of butadiene-nitrile rubber SKN-26 SM with the use of PDMDAACl [16] as well as for its two fractions with mean-viscous molecular masses of $11.5 \cdot 10^4$, $2.3 \cdot 10^4$, $17.4 \cdot 10^4$, respectively.

2.4. PDMDAACl copolymer with sulphur dioxide

Flocculation activity of alternative low-molecular copolymer of N,N-dimethyl-N,N-diallylammonium chloride with sulphur oxide (PDMDAACl-OS) was studied

Table 2

Properties of SKS-30 ARK rubbers extracted with the use of PDMDAACl and NaCl as well as rubber compounds and vulcanizates based on these rubbers

Quality performance	Flocculating agent	
	PDMDAACl	NaCl
Mass content, %		
free organic acids	6.3-6.8	5.8
bound organic acids	absent	0.15
antioxidant VTS-150	1.3	1.3
ashes	0.12	0.18
bound styrene	22.5	22.5
Mooney viscosity	54	52
Loss of mass at 378 K, %	0.13	0.19
Duration of vulcanization, min	60	80
Elastic recovery, mm	3.0	3.0
Strain under 300 % extension , MPa	9.4	8.3
Toughness under extension, MPA	27.8	28.8
Relative extension under fracture, %	580	630
Relative residual deformation after fracture, %	14	10
Rebound elasticity, %	40	42

Table 3

Properties of rubbers extracted with the use of NaCl and flocculating agent PDMDAACl as well as rubber compounds and vulcanizates based on oil-filled EPB

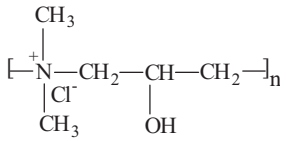
Quality performance	Flocculating agent	
	PDMDAACl	NaCl
Mass content, %		
free organic acids	6.0	5.6
bound organic acids	absent	0.10
antioxidant VTS-150	0.25	0.25
ashes	0.12	0.18
oils of PN-6K	0	15
Loss of mass at 378 K, %	0.15	0.20
Mooney viscosity	40	40
Strain under 300 % extension, MPa	12.0	10.3
Toughness under extension, MPa	17.7	18.6
Relative extension under fracture, %	430	480
Relative residual deformation after fracture, %	6	10
Plasticity	0.37	0.37

for the industrial latex samples of SKS-30 ARK and EPB [23]. The completeness of the flocculation for SKS-30 ARK latex was attained at the flocculating agent supply rate of 18–20 kg/ton of rubber, while for EPB latex it was 14–15 kg/ton of rubber. The introduction of the increased amount of sulphuric acid as the acidifying agent under the optimal discharge rate of PDMDAACl-OS did not have a considerable effect on the amount of the obtained coagulum. However, the influence of H_2SO_4 dosage was more significant under reduced discharge rate of the flocculating agent. For example, discharge rate of PDMDAACl-OS was almost twice reduced up to 9.0 kg/ton of rubber for the discharge rate of sulphuric acid equal to 8.0 kg/ton of rubber. The rubber compounds on the basis of SKS-30 ARK rubber resin extracted from the latex with the flocculating agent of PDMDAACl-OS were vulcanized more rapidly than the check sample due to the presence of the flocculating agent or the products of its interaction with the components of the emulsion system. The physico-mechanical quality indexes of the vulcanizates on the basis of SKS-30 ARK rubber correspond to the requirements of the Russian standards.

Similar regularities were observed under the flocculation of EPB latex. For the discharge rate of PDMDAACl-OS 10.8 kg/ton of rubber completeness of the flocculation for EPB latex was attained under the discharge rate of H_2SO_4 6.0 kg/ton of rubber. Thus, the use of PDMDAACl-OS as a flocculating agent would require its high-precision dosage.

2.5. Poly-(N,N-dimethyl-2-oxypropyleneammonium) chloride

Dependence of the flocculation process for SKS-30 ARK latex on the concentration of the dispersed phase in the presence of poly-(N,N-dimethyl-2-oxypropyleneammonium) chloride (PDMOPACl) was investigated in [24]. The formula of this salt is:



A maximum (optimal point) of flocculation was found just as in case of latexes extracted with the use of PDMDAACl. According to [24] this maximum was associated with two factors (neutralization and bridge) that can influence the flocculation mechanism. The value of the concentration of the dispersed phase in the range of 50, 100, 150 g/l was insignificant in the discharge rate value of the flocculating agent.

The change of the temperature did not have any considerable effect on the process of rubber extraction from latex. Nevertheless, a slight increase of mass of the forming coagulum was observed with the increase of the temperature from 293 to 353 K at the initial stage of the extraction process (for low discharge rate of PDMOPACl). Decrease of PDMOPACl discharge rate from 4 to 3 kg/ton of rubber allowed attaining complete flocculation of SKS-30 ARK latex only at high temperatures of 353–368 K and discharge rate of acidifying agent of up to 30 kg/ton of rubber. If the discharge rate of PDMOPACl was reduced to 2 kg/ton of rubber complete extraction of the rubber would not be achieved even at these temperatures.

The discharge rate of the acidifying agent demonstrated a greater influence on the flocculation process than the temperature and concentration of the dispersed phase in the investigated intervals. For example,

under discharge rate of PDMOPACl ~ 4 kg/ton of rubber mass of the formed coagulum was regularly increased with the increase of the introduced H_2SO_4. Coagulum mass attained ~ 100% for the discharge rate of sulphuric acid 15 kg/ton of rubber that proved to be the optimal technological parameters of the process.

Rubber compounds and vulcanizates did not surrender the check sample (Table 4) [24].

2.6. Implementation of the new technology in the industry of Russia

The performed investigations demonstrated high efficiency of the utilization of QASs as flocculating agents. Due to its unique set of properties the most perspective one proved to be PDMDAACl. By elaborating the technological conditions for the process of rubber extraction from latex in the laboratory the following was achieved:

- PDMDAACl was proven to be a high-efficient flocculating agent for rubber latexes;
- optimal technological parameters of the flocculating process for latex were elaborated;
- application of cationic polyelectrolyte PDMDAACl has no negative effect on the properties of the obtained rubbers, rubber compounds, and vulcanizates based of these compounds.

Table 4

Properties of rubber compounds and vulcanizates on the basis of SKS-30 ARK rubber extracted with the use of NaCl and PDMOPACl flocculating agents and rubber resins

Quality performance	NaCl	PDMOPACl
Mooney viscosity	53.0	42.5
Carrer placticity, arb. un	0.30	0.28
Recovery, mm	1.86	1.84
Optimum of vulcanization at 416 K, min	80	60
Conditional strain under 300 % stretching, MPa	8.4	14.0
Conditional toughness under stretching, MPa	27.0	27.6
Relative extension under fracture, %	600	540
Relative residual deformation, %	16	15
Rebound elasticity, %		
at 293 K	37	32
at 373 K	50	46
Shore hardness, arb. un.	59	65
Shopper-Schlobach abrasion, 10^{-3} cm^3/m	1.80	1.31
Resistance to the growth of cuts up to 12 mm with a puncture, thousands of cycles	39200	115200
Conditional toughness under stretching after ageing (373 K, 72 h)	18.0	20.0
Relative extension after ageing (373 K, 72 h)	242	257

During the period of 1992–1994 the implementation of the obtained laboratory results was performed at the synthetic rubber plant, namely:

- operating modes of the industrial flocculation for SKS-30 latex were completely elaborated;
- more than 372 tons of SKS-30 rubber was produced;
- application of PDMDAACl did not require considerable changes in the technology of rubber extraction from latexes, no capital investments were needed either;
- the factory treatment works operated in normal mode;
- the produced rubber satisfied the Russian standards.

Thus, transition to the new technology of all the manufacturers of emulsion rubbers of only SKS marks in Russia (the production volume is about 240000 tons) can significantly reduce the annual ecological damage by:

- ceasing the discharge of 100000–135000 tons of sodium chloride a year
- decreasing the amount of industrial waste discharge by 8–10 % (240000 m^3 per year).

3. Conclusions

As a result of the performed investigations the fundamental of a new exclusive ecologically reasonable industrial technology of latex flocculation for the emulsion rubbers with the use of cationic polyelectrolyte poly-N,N-dimethyl-N,N-diallylammonium chloride was elaborated. This technology was practically implemented in the Russian industry.

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ТЕХНОЛОГІЧНІ ТА ЕКОЛОГІЧНІ АСПЕКТИ ПРАКТИЧНОГО ЗАСТОСУВАННЯ ЧЕТВЕРТИННИХ СОЛЕЙ АМОНІЮ У ВИРОБНИЦТВІ СИНТЕТИЧНИХ ЕМУЛЬСОВАНИХ КАУЧУКІВ В РОСІЇ

Анотація. *Розглянуто фізичні та хімічні аспекти і технологічні параметри виробництва каучуків з промислового латексу із застосуванням галогенідів амонію, тетраалкіламонієвих солей, полі(N,N-диметил-2-оксипропіленамоній)хлориду, полі-N,N-диметил-N,N-діаліламоній хлориду та його кополімеру з SO_2. Показано важливий екологічний вплив полімерних флокулянтів.*

Ключові слова: *четвертинні солі амонію, каучук, латекс, флокулянт, екологія.*