New Solution to the Technology of Halogenated Butyl Rubber

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Abstract

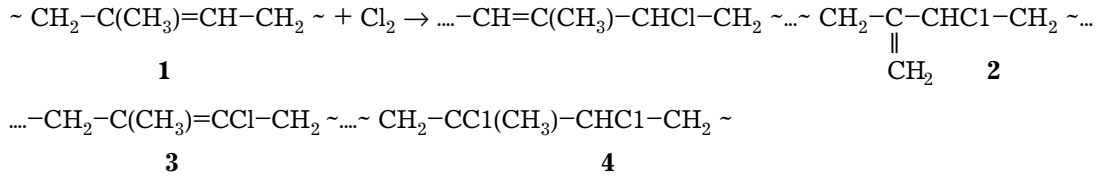
Chlorination of butyl rubber by molecular chlorine in solution relates to the class of fast chemical reactions. A new continuous method of obtaining chlorobutyl rubber in the industry is proposed on the basis of small-size tubular turbulent devices of the jet type; the method provides many ecological and technological advantages.

INTRODUCTION

Halogenated derivatives of butyl rubber were investigated for the first time in the 1940ies; in the 1950ies, at first bromobutyl rubber and then chlorobutyl rubber was obtained on the industrial scale. Each of the halogenated elastomers has its own advantages and shortcomings; an urgent need for them in rubber-processing and tire industry, in particular in the hermetic layer of tubeless tires, has substantially broadened the scale of their production. It should be noted that the industrial production of halogenated butyl rubber has substantially surpassed the fundamental knowledge in this area.

Four forms of isomers are characteristic of chlorobutyl rubber (CBR) which is obtained by chlorination of the copolymer of isobutylene with isoprene, that is, butyl rubber (BR) with the substitution of hydrogen atom for chlorine atom in the isoprene links (Scheme 1).

The analysis of the samples provides evidence of the predominant content of exomethylene groups in the product (structure **2**): 70–90 %. The content of endomethylene groups (structure **1**) is about 9 %. The molecules can also contain saturated groupings (structure **4**):



Scheme 1.

up to 1 %, which are formed mainly at low temperature [1–4].

Chlorobutyl rubber exhibits valuable performance characteristics like BR (low gas permeability, stability to ozone, *etc.*) but differs by increased stability to atmospheric action, UV light, many chemical reagents, improved dynamic properties in comparison with other rubbers, exhibited also under rather rigid performance conditions; it is also characterized by increased vulcanization rate and the ability for joint vulcanization with other elastomers [3–5].

The analysis of the existing production facilities showed that the industrial methods of obtaining CBR are technologically complicated [3–6]. At present, the only method applied in industry to obtain CBR is chlorination of BR with molecular chlorine in solution. This process includes several stages which are rather power-consuming:

1) Preparation of the BR solution (as a rule, in aliphatic hydrocarbons),

2) Chlorination of the BR solution with gaseous chlorine,

3) Neutralization of the formed CBR,

4) Washing the CBR solution from salts, *etc.*,

5) Introduction of a stabilizing antioxidant and anti-agglomerator into CBR,

6) Degassing, CBR isolation and drying.

Almost all the stages of the process involve mixing reservoirs of large volume equipped with intense mechanical mixing units, and in some cases also heat-exchangers, and also large washing columns (Fig. 1).

A specific feature of the process is the necessity to use high-viscous 10–15 % solutions of rubbers (CBR or BR) in an organic solvent (about 350 MPa s and higher).

Chlorination of the BR solution is usually carried out with gaseous chlorine mixed with nitrogen. In this case, the volume of the gas mixture is 6–7 or more times larger than the volume of high-viscous BR solution in an organic solvent. This requires special attention when making optimal conditions for the chlorination of BR in the liquid – gas system, first of all realization of the small-bubble (foam) regime when mixing the reagent flows of the gas and viscous liquid. It is also necessary to exclude the possibility of the formation of a mode of gas flow through the liquid preventing incomplete dissolution of chlorine in the liquid reaction mixture and leading to the emis-

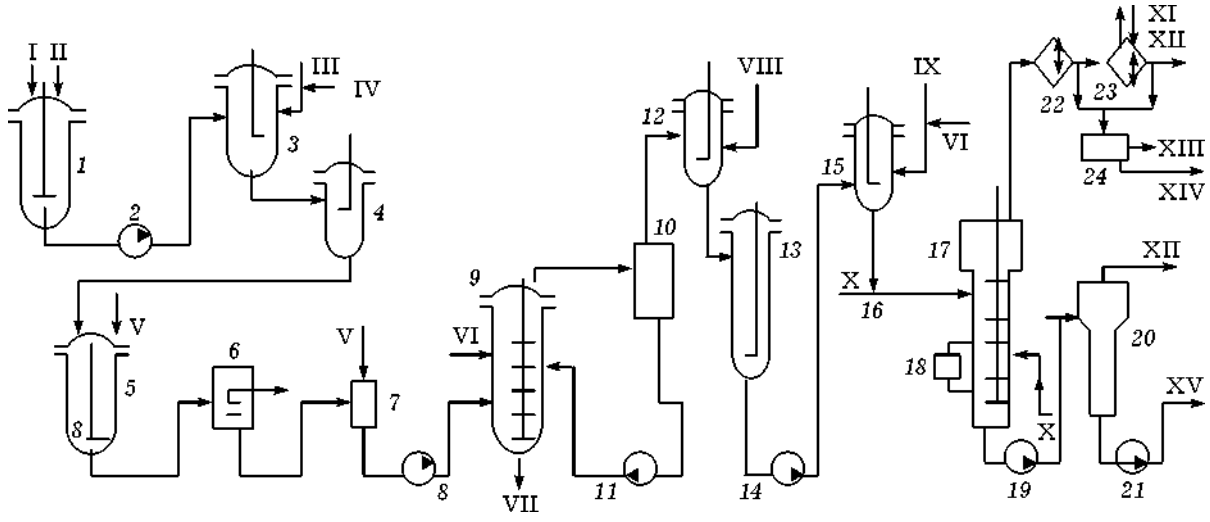


Fig. 1. Conventional technological scheme of chlorobutyl rubber synthesis [4]: *1* – apparatus for preparation of butyl rubber solution; *2, 8, 11, 14, 19, 21* – pumps; *3, 12* – intensive mixing devices with mechanical mixers; *4, 5* – voluminous mixing chambers (*4* – chlorinator, *5* – neutralizing vessel); *6* – filter; *7* – collector; *9* – washing column with a mixer; *10, 24* – settling vessels; *13* – equalizing basin; *15* – voluminous apparatus; *16* – injector; *17* – degassing unit; *18* – throttling device; *20* – vacuum degasser; *22, 23* – condensers. Flows: I – solvent, II – butyl rubber crumbs, III – chlorine, IV – nitrogen, V – aqueous alkali solution, VI – water, VII – washing water for purification, VIII – the solution of stabilizing antioxidant, IX – suspension of anti-aggloemrating agent, X – steam, XI – cooling agent, XII – to the vacuum pipeline, XIII – benzine for drying, XIV – water for steam stilling of organic compounds, XV – pulp to concentrating unit.

sion of chlorine into the atmosphere, which is inadmissible in modern industry. Because of this, in order to intensify the process of BR chlorination in large-volume mixing reactors, an additional chlorination apparatus is used, which is a special centrifugal pump or a volume-free reactor where the BR solution and a mixture of chlorine with nitrogen are fed. To provide the necessary residence time for the reacting mixture, recycling is provided [3, 6]. Disadvantages of this flowchart include not only high resource and power consumption but also worsening of the ecological safety pf CBR production.

EXPERIMENTAL

In Russia, investigations of elastomer chlorination had been carried out since 1960ies, but there was no realization of production. At present, works are being carried out on the creation of a large-scale production of halogenated BR at the Nizhnekamskneftekhim Co. Among other advances, it is planned to use new approaches to the halogenation process. A new continuous ecologically safe method of obtaining CBR involving small-sized tubular turbulent devices allowing one to conduct chemical processes in displacement mode in highly turbulent flows has been recently developed and tested experimentally [7–10].

It should be stressed that it is principally important for the realization of the new continuous process of CBR synthesis that the rate constant of the bimolecular BR chlorination reaction be not less than 10–100 l/(mol s).

According to the literature data, the time of chlorination reaction within temperature range 290–325 K is less than 60 s; in the specific case (that is, for the chlorination of a 15–16 % solution of BR in methyl chloride at 328 K, the mass of molecular chlorine being 3–3.5 % of the rubber mass) it is equal to (7.5 ± 2.5) s [4]. It follows from these data that for C_0 = 0.05 mol/l

$$K = \frac{1}{t_{\text{chem}}} \frac{C_x}{C_0 (C_0 - C_x)} \quad (1)$$

where K is the rate constant of chemical reaction; C_0 are the initial reagent concentrations, mol/l; C_x is the concentration of the formed product, mol/l; t_{chem} is the time of chlorination reaction, s.

Depending on the transformation degree of reagents taken in the molar ratio of 1 : 1, $K_{(0.9)} \approx (30 \pm 10)$ l/(mol s) and $K_{(0.99)} \approx (150 \pm 50)$ l/(mol s). The indices 0.9 and 0.99 correspond to reagent transformation degrees of 90 and 99 %.

One can see that the chemical process of CBR synthesis according to the reaction of BR chlorination in solution by molecular chlorine in mixture with nitrogen proceeds rather rapidly.

Similar K values were also obtained in the experimental investigation of CBR obtaining process involving the reaction of BR with chlorine in Nephras solution. In the Nizhnekamskneftekhim JSC, an experimental set-up was mounted with a tubular turbulent reactor for chlorination, which is a jet-type diffuser-converting tube [9], with the diameter d = 0.05 m and the length l = 2 m (the volume of the apparatus is 0.004 m^3). The solution of BR in Nephras was fed into the tubular apparatus at the rate of about 0.21 m^3/h, while the mixture of nitrogen and chlorine (5 : 1 volume ratio) was fed at the rate of 2.1 m^3/h. This provides the linear reagent movement rate (without taking into account the volume occupied by a special filling) V = 0.33 m/s and the corresponding residence time is $t_{\text{res}} = 1/V \sim 6.1$ s.

RESULTS AND DISCUSSION

Since there was no overshoot of molecular chlorine after reaction mixture passed out of the apparatus during the performance of the set-up, we may assume that the conversion of Cl_2 was not less than 99 %. Therefore, $K_{(0.99)} \geq 225$ mol/(l s) ($K_{(0.9)} \sim 20.5$ mol/(l s), which almost coincides with the K value calculated using the above-reported data. This means that the time of chemical reaction $t_{\text{chem}} = [C_0](1/K)$ is rather short and is <0.09 s for the 99 % conversion. For this reason, the liquid-phase chlorination of butyl rubber with molecular chlorine should be related to a new class of chemical processes, *i. e.*, fast chemical reactions for which usually $t_{\text{mix}} > t_{\text{chem}}$ (where t_{mix} is mixing time) and which are distinguished by characteristic specific objects of investigation, methodology of research and new fundamental regularities [7, 8, 11–14]. Chemical process-

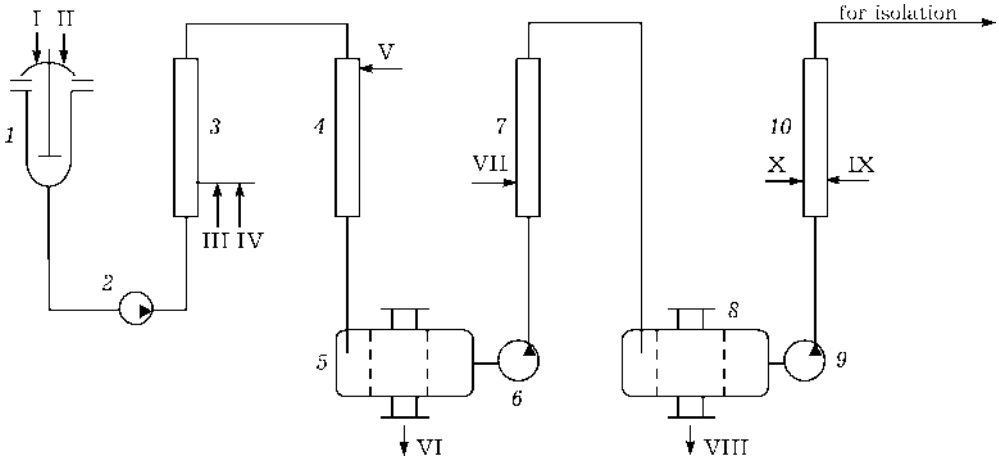


Fig. 2. New technological scheme of the synthesis of chlorobutyl rubber: *1* – the apparatus for preparing butylrubber solution; *2*, *6*, *9* – pumps; *3*, *4*, *7*, *10* – tubular turbulent reactors (*3* – separator, *4* – neutralizer, *7* –washing, *10* – introduction of a stabilizing agent); *5* – vessel to separate CBR and the neutralizing solution; *8* – vessel to separate CBR and washing water. Flows: I – solvent, II – butyl rubber crumbs, III – chlorine, IV – nitrogen, V – neutralizing solution, VI, VIII – drainage of the worked out neutralizing and aqueous solutions, respectively, VII – washing water, IX – solution of stabilizing antioxidant, X – suspension of antiagglomerating agent.

es belonging to the class of fast reactions should be conducted according to principally new technology using intensively moving technological media created with the help of highly productive small-size tubular turbulent devices of the jet type [7–10, 15]. This technology provides an increase in resource and energy saving by an order of magnitude, in the process productivity by two-three orders, the residence time of reacting mixture in the reaction region decreases and an actual possibility arises to conduct the whole process using the continuous scheme.

For example, in the set-up for CBR production with the capacity of about 1000 t/y chlorinating BR (10–12 % solution in Nephras) with a mixture of molecular chlorine with nitrogen (1 : 5 by volume) (Fig. 2), the main chlorinating reactor is not a traditional mixing-type voluminous reactor but a small-size tubular turbulent jet-type apparatus with the diameter d = 0.089 m and the length l = (4.5 ± 1.5) m (volume 0.02 ± 0.003 m^3) without any mixing and heat exchange devices.

Calculations indicate that the thermal regime in the reaction region does not cause any problems though the BR chlorination process is accompanied with heat release (q = 184 kJ/mol). In the adiabatic mode of operation of the tubular turbulent chlorinating reactor (without cooling), temperature change in the reaction region ΔT determined using equation [14] is $\Delta T = q\Delta Q/(C_p\rho)$, where q is the thermal effect of chlorination reaction, kJ/mol; ΔQ is the amount of the formed product, mol/m^3; C_p is the mean thermal capacity of the reaction mixture, kJ/(kg K); ρ is the mean density of the medium, kg/m^3.

For BR chlorination (12–15 % solution) with molecular chlorine in a tubular apparatus operating in the mode of optimal ideal displacement in tubular flows, temperature rise does not exceed (3 ± 1) °C, that is, the process may be considered to proceed under quasi-isothermal conditions and to require no external or internal cooling.

It is necessary to note that in the technological flowchart of CBR production [3, 4] tubular turbulent jet-type devices of similar design should also be used at other stages of the technological process, in particular for neutralization of the solution of the formed CBR (rate constants of the interaction of mineral acids with alkalis are very high: $K \sim 10^{9 \pm 12}$ l/(mol s), washing CBR solution with water to remove salts, washing the recurrent solvent, introduction of stabilizing antioxidant and anti-agglomerating agent into the CBR solution, and also instead of all the intensive mixers, including volume-free ones, with mechanical mixers (see Fig. 2). In the major part of these stages, tubular turbulent devices have passed thorough approval

tests and are used with high efficiency in some works, for example in the production of synthetic isotactic *cis*-1,4-isoprene rubber of various grades (Kautchuk JSC, Sterlitamak), synthetic ternary ethylene-propylene rubber (SREPT) (Nizhnekamskneftekhim JSC), polymers of isobutylene (Efremovskiy zavod SK JSC, Orgsintez JSC, Sumgait), *etc.*

CONCLUSION

A principally new economically efficient continuous process was developed for the synthesis of chlorobutyl rubber using small-size tubular turbulent reactors of original design operating in high flow turbulence mode at least at four stages of the technological scheme. Comparison with the known scheme of the process of CBR synthesis, for example that shown in Fig. 1 [4], shows that the new process (see Fig. 2) excludes voluminous mixing devices and involves small-size turbulent jet-type reactors in which chlorination takes place, and also neutralization, washing and introduction of stabilizing agents. The process is generally distinguished by compactness and low cost of equipment, power and resource saving, ecological safety, simplicity of services for the jet-type devices, simplicity of the process management, *etc.*

The new method ensures several times increase in the productivity of CBR synthesis process, an increase in the specific productivity of the main device by 2–3 orders of magnitude, substantial decrease in the necessary industrial area, increase in the product quality, *etc.* As a consequence, the technology of synthesis of chlorobutyl rubber is substantially simplified in general, and the prime cost of the product decreases.

It may be assumed that the new process is principally suitable also for obtaining bromobutyl rubber, as well as various chlorinated elastomers.

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