



QUATERNARY AMMONIUM COMPOUND FROM BIO-SOURCE IN THE VULKANIZATION SYSTEM OF ELASTOMERIC COMPOSITIONS

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ABSTRACT

A series of new quaternary ammonium compounds (QAC) was synthesized from plant-derived precursors – furfural and (or) castor oil. Use of QAC as organic activators for sulfur vulcanization of stereoregular and irregular carbon chain dienes rubbers revealed that reactivity of QAC is governed by the presence of functional groups (quaternary nitrogen atoms), the structure of surrounding substituents. QAC containing castor oil trisocyanate and furan, are found to have an optimal effect on vulcanization kinetics, formation of a general complex of properties of elastomeric compositions. Studied QAC was found to outperform equal concentration of stearic acid in terms of initiation properties when used in model elastomeric compositions based on SKI-3 or SKMS-30 ARK. Increasing QAC content from 0.75 to 2.25 wt.h. per 100 wt.p. per rubber, a decrease in vulcanization rate is observed in comparison to stearic acid. It was discovered, that substitution of stearic acid with an equal mass of QAC in compositions for tire treads rubber has positive on the formation of physicommechanical properties of rubber at static and dynamic loads.

Keywords: elastomeric composition, organic vulcanization activator, quaternary ammonium compound, stearic acid substitute, quaternary ammonium salt.

1. INTRODUCTION

Vulcanization is one of the major processes in the manufacturing of rubber articles. A major role in this process is played by organic vulcanization activators [1], the most common of which for sulfur polydiene is stearic acid [2].

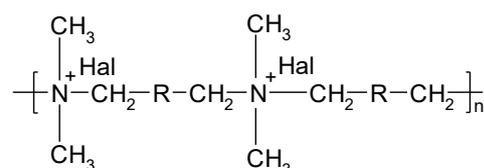
One disadvantage of industrial grades of stearic acid is insufficient solubility in rubbers, which abuses it to diffuse to the surface of rubber mixture, lowering their stickiness [3]. Zinc stearate, formed from the reaction of stearic acid and zinc oxide during processing and vulcanization of elastomeric compositions also has low suability, and after vulcanization deposits in the elastomeric matrix in for of spherulites or micelles, impacting properties of vulcanizates [4]. As such partial or complete replacement of stearic acid in elastomeric compositions becomes a relevant problem. Quaternary ammonium compounds can be an alternative to stearic acid, as an organic activator of sulfur vulcanization system of diene rubber.

In Ukraine, during the 60s of the past century, Bloch, G.A et. al. have conducted studied vulcanization of rubber of general and special application, in presence of cationic surfactants - alkamons and bis- quaternary ammonium chlorides [5, pp. 480-483]. It was found that activating properties of these surfactants depends on their structure and type of accelerators used in rubber mixtures.

Studied surfactants proved to be most effective in combination with tiazole accelerants, which authors have discovered to form N-substituted derivatives of 2-mercaptobenzotizolyl.

W. Sheele [6] describe the solubilizing effect of cationic surfactants N-cetyl-N, N, N'- trimethylammonium bromide и N-benzyl-N-cetyl-N, N'-dimethylammonium chloride, which provides a higher rate of cross-linking and sulfur consumption during vulcanization of polydiens.

During the 90s, USUCT has conducted studies on water-soluble polymers with quaternary nitrogen atom - alkyl aromatic quaternary ammonium salts (PQAC), synthesized in single-stage reaction and general structure:



Studies included not only influence on sulfur vulcanization, but also their modification of mineral fillers [7, pp. 316-428].

Namely, it was found, that as general sulfur rubber vulcanization, PQAC akin to poly-1,5-naphthalene-N, N, N', N'-tetramethylhexamethyldiammonium



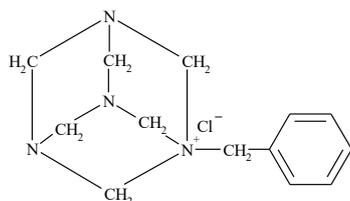
chloride has similar activity to other known activators - stearic acid. Compared to quaternary ammonium salts butyldimethylbenzylammonium bromide and hexyldimethylbenzylammonium bromide, PQAC has a less negative effect on the decrease of induction period of vulcanization, increasing degree of cross-linking.

Based on the activation of sulfur vulcanization of cis-1,4-polyisoprene, PQAC differs depending on the structure. The governing factor in PQAC activation is not only the structure of diamine fragment (diethylenetriamine, hexamethylenediamine) but more so the structure of initial dihalogenide - PQAC decreases with introduction of dibenzylene, dibenzylmethane, naphthalene fragments into their structure.

Organic quaternary ammonium compounds (QAC) spark interest not only as organic activators of sulfur activation but also as accelerants (catalysts) [8, 9], as a replacement for some widely used industrial accelerants that can pose a health hazard due to formation of nitrosamines.

It was found [10], that binary «sodium dialkyl dithiophosphate - polymeric quaternary ammonium salt» shows synergism on different stages of sulfur vulcanization of elastomeric composition based on cis-1,4-polyisoprene, and also in regards to the degree of cross-linking, elasticity and durability. By not being an individual accelerant, PQAC plays the role of co-accelerant in combination with an organophosphorus accelerant.

Based on a study result for QAC synthesized from urotropin and benzyl chloride



in composition for sulfur vulcanization of polydiens [11, 12], it was found that, while rather inactive as an individual accelerant, it synergizes with thiazoles, sulfenamides, thiram and has positive effect kinetic parameters, cross-linking density, the formation of physicomachanical properties of vulcanizates. The binary system of QAC with guanidine accelerant shows antagonism.

No less promising proved to be our study on the synthesis direction of cationic quaternary ammonium compounds using organic matter and their application for sulfur vulcanization of polydiens. For instance, furfuryl alcohol (furfuryl alcohol) - is a large volume product, and is produced world-wide from farming and wood processing byproducts, making use of furfuryl derivatives appealing due to availability and low cost. Structural features and polyfunctionality of the furan ring in the structure of organic compounds promote interaction with various reaction centers.

In this paper, we summarize results of studies on the synthesis of quaternary ammonium compounds from plant matter precursors (furfuryl and (or) castor oil) and use of QAC as an organic activator for sulfur vulcanization of elastomeric compositions based on carbon chain diene rubber for general applications.

2. MATERIALS AND METHODS

2.1 QAC and their Synthesis

Synthesis of furfuryl-containing quaternary ammonium compounds QAC-1 - QAC-4 has been conducted according to the generalized scheme shown on Figure-1 [13]

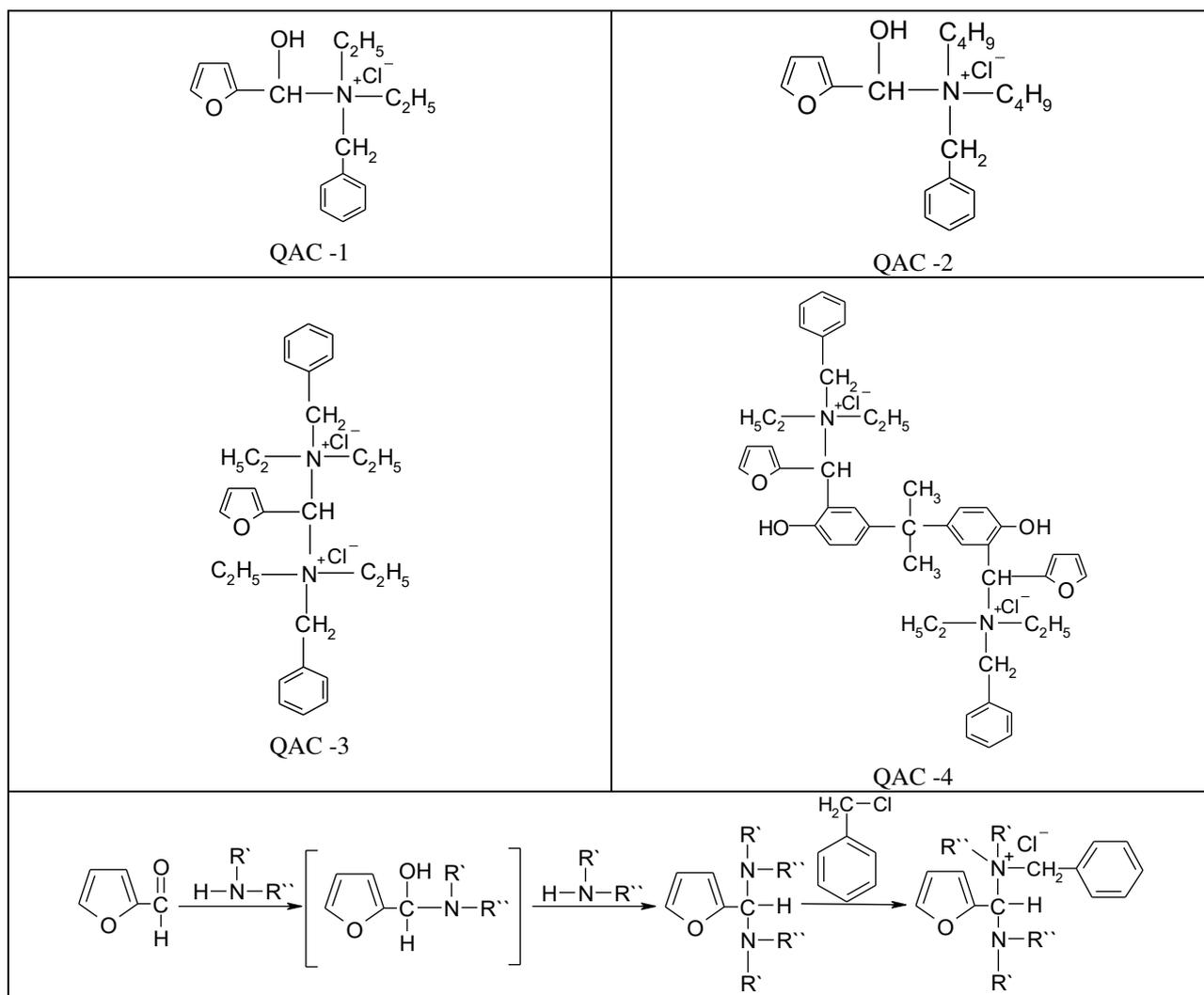


Figure-1. The generalized synthesis procedure of QAC -1 - QAC-4.

Compound QAC-5 was synthesized based on castor oil hydrazide, according to a scheme shown in Figure-2 [14].

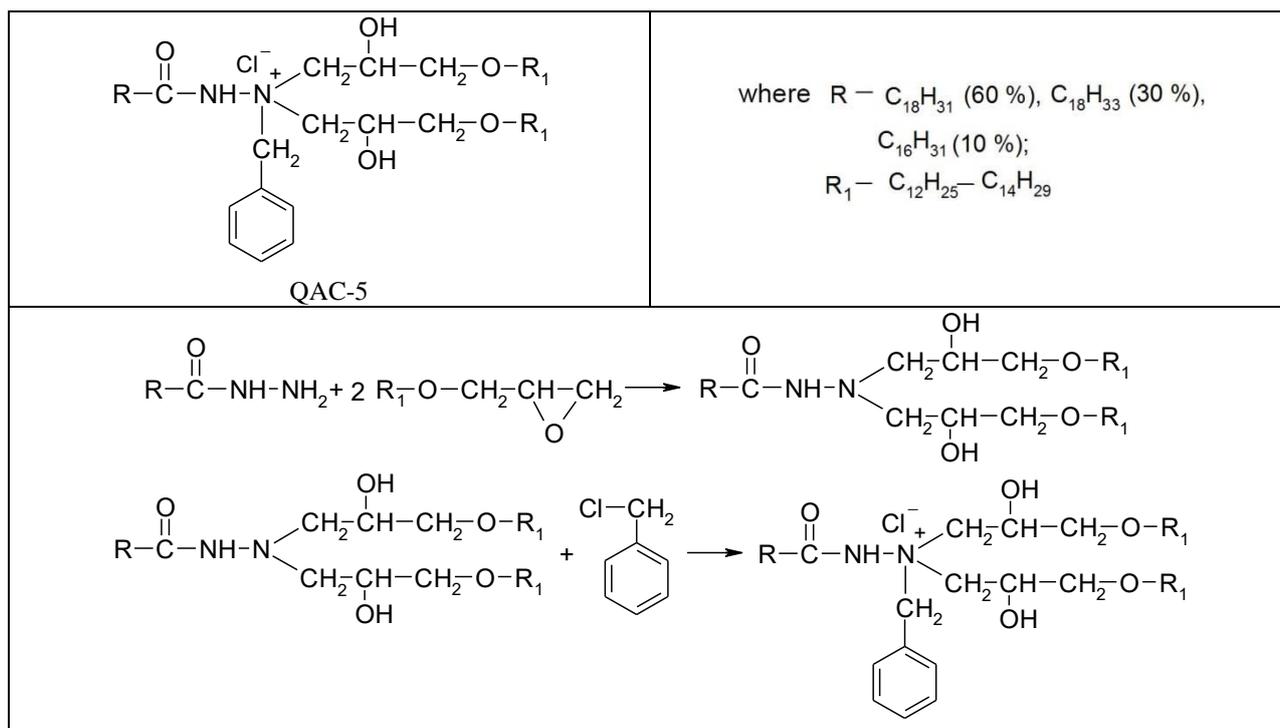
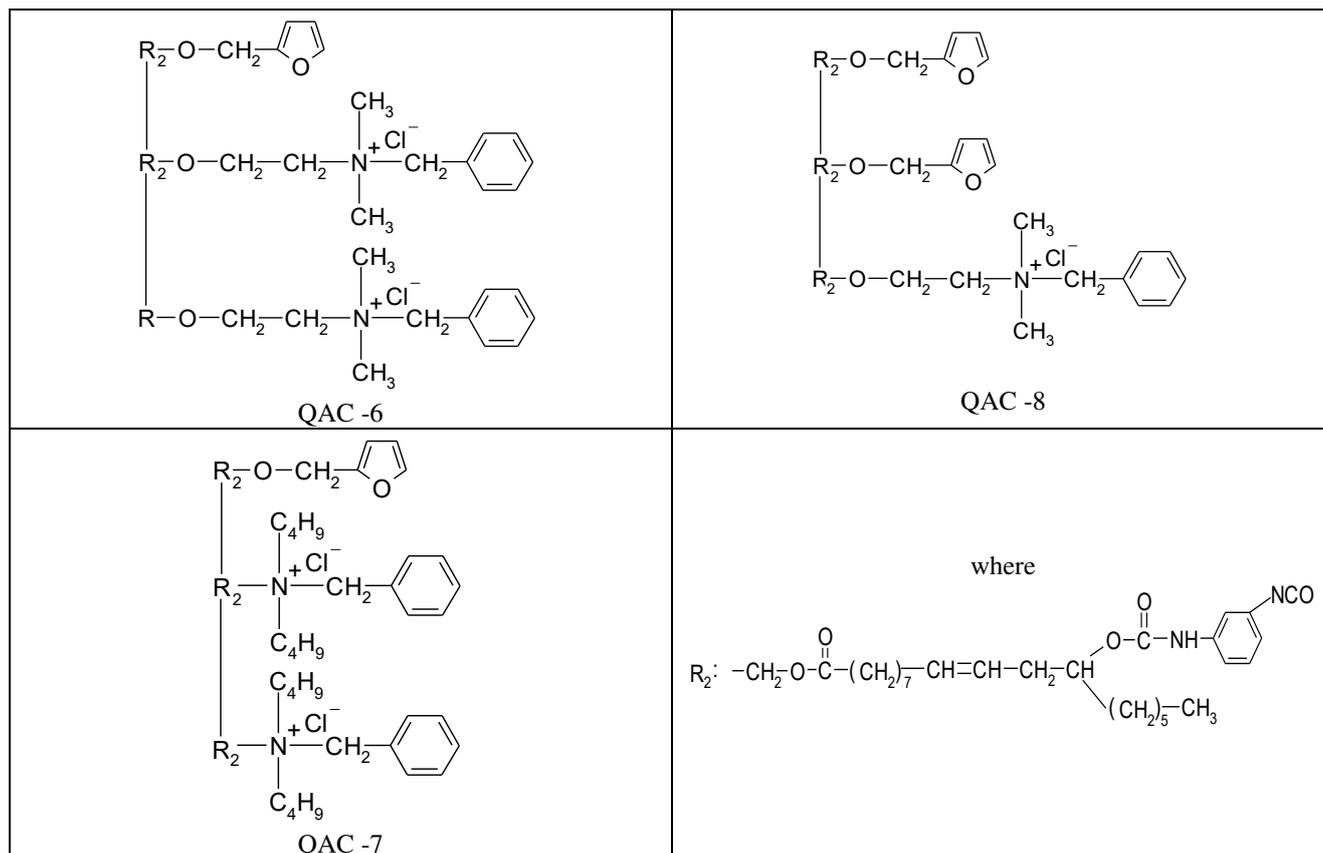


Figure-2. The generalized synthesis procedure of QAC-5.

Compounds QAC -6 - QAC -8 were synthesized from castor oil triisocyanate [15] and have the following structure:



The kinetic feature and structure of initial compounds was studied by means of IR-spectroscopy [13-15]. Synthesized compounds were transparent liquids with

different viscosity, with colors from orange to dark-brown and were soluble in benzene.



2.2 Elastomeric Compositions

Effect of synthesized QAC as bioorganic activators for sulfur vulcanization was evaluated using model unsaturated elastomeric composition based on diene rubber - stereoregular isoprene rubber SKI-3 (GOST 14925-79), amorphous butadiene- α -methyl styrene rubber SKMS-30 ARK (TU 38.40355-99) and SKMS-30 ARKM-15 (GOST 11138-78), and elastomeric composition for making tire treads, which is based on the combination of general application isoprene SKI-3 + cis-butadiene SKI (FOGST 14924-75) + butadiene- α -methylstyrene SKMS-30 ARKM-15 [13-18].

For instance, elastomeric compositions based on SKI-3, studied in paper [14], had following composition (wt.p.): rubber - 100.0; sulfur - 2.0; zinc oxide - 5.0; sulfenamide CBTS (N-cyclohexyl-2-benzothiazolylylsulfenamide) - 0.8; organic vulcanization activator - 2.0. In reference to rubber mixtures, the organic activator was either absent or was replaced with equal doses of stearic acid. Rubber mixture was prepared in two stages: initial rubber mix was prepared using a laboratory rubber mixer ($V=2 \text{ dm}^3$) at unloading temperature 75°C ; organic activators were added on laboratory rollers.

2.3 Testing Methodology

Technological characteristics of rubber mixtures were evaluated according to acting standards [19] and known methods [7, pp. 20-22, etc.] Viscosity of rubber mixtures and tendency to premature vulcanization were determined using MV 2000E. Vulcanization

characteristics of elastomeric compositions were studied by recording vulcanization curves using rheometer «Monsanto 100S» according to GOST 12535-84, using rheometer MDR 3000 (Mon-Tech Werkstoffprüfmaschinen GmbH, Deutschland) according to ASTM D 6601-02 using MonControl software, and according to the method described in [20, pp. 177-181]. Elasto-relaxation properties of rubber were studied using tearing machine RMI-5 (GOST 28840-90). Shore hardness was measured using analog Shore durometer (ISO 868). Rebound elasticity was measured using a resillometer.

3. RESULTS AND DISCUSSIONS

3.1 QAC in Model Compositions based on CYS-1,4-Polyisoprene

The influence of different QAC on vulcanization kinetic of elastomeric composition based on stereoregular cis-1,4-polyisoprene SKI-3 at 155°C is shown in Figure-3. When compared to stearic acid, the studied QAC, in general, seem to better initiate sulfur vulcanization, which is evidenced by decreased induction period and increased torque at vulcanization plateau. The initiation effect of QAC varies with their type: maximum value of relative vulcanization degree is observed in presence of QAC-5; shortest induction period - QAC-4; longest induction period (close to composition with stearic acid) - QAC-5. Depending on the type of QAC, the duration of the induction period increases in series: QAC-4 < QAC-1 < QAC-8 < QAC-5.

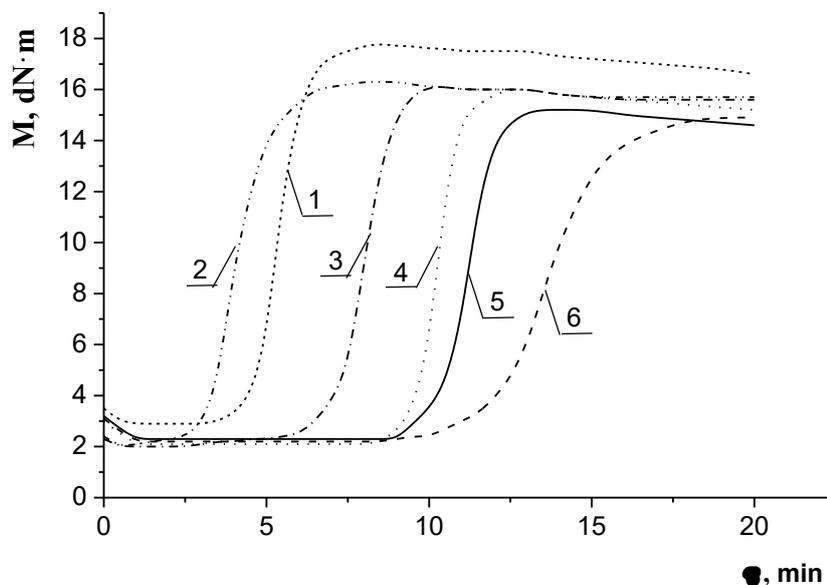


Figure-3. Kinetic curves at 155°C for model elastomeric composition based on synthetic isoprene rubber SKI-3 with 2.0 wt.p. of organic activator: 1 - QAC-1; 2 - QAC-4; 3 - QAC-8; 4 - QAC-5; 5 - stearic acid; 6 - no organic activator.



The advantage of QAC over stearic acid in (Table-1), studied in paper [14].
 initiation activity is observed for all temperature range

Table-1. Kinetic parameters of sulfur vulcanization of model rubber mixture based on synthetic isoprene rubber SKI-3 with different activators.

Parameter	Organic activator								
	QAC-1			QAC-7			Stearic acid		
	Vulcanization temperature, °C								
	155	160	175	155	160	175	155	160	175
k_2, min^{-1}	0.64	0.85	2.3	0.45	0.62	0.96	0.29	0.33	0.88
t_i, min	4.8	4.3	2.3	4.9	4.0	1.9	12.8	9.6	3.8
t_{dis}, min	5.0	4.5	2.5	5.5	4.5	2.0	13.5	10.2	4.0

For instance, the parameter of nominal vulcanization rate constant in primary period k_2 , for elastomeric composition with most active compound QAC -1, is two times higher than that for compositions with stearic acids. QAC-1 results in the value of k_2 at 160°C on the same level as that for stearic acid at 175°C.

When compared to stearic acid, QAC as organic activators can provide equal nominal vulcanization rate constant k_2 , induction period duration t_i , and total accelerant consumption time t_{his} , for rubber mixture based on cis-1,4-polyisoprene, at process temperatures lower by 10 - 15°C. Based on the values of t_{dis} (Table. 1), QAC is also able to improve the activity of vulcanization accelerant and lower initiation temperature.

It was found [14], that maximum initiation effect on kinetic parameters of vulcanization, degree of cross-linking, better influxes on the formation of elastic-resilient characteristic on rubber mixtures and rubbers from SKI-3 is demonstrated by QAC-1, which was synthesized from furfural and diethylamine, and has lowest molecular mass among studied QAC, meaning the highest concentration of quaternary nitrogen atoms in rubber mixture.

Long induction period (close to stearic acid), high rate and degree of vulcanization, elasto-resilient is provided by composition based on SKI-3 and compound QAC-5, synthesized from vegetable oil hydrazide and monoglycidyl ether of C₁₂-C₁₄ fraction alcohols.

QAC synthesized from triisocyanate of castor oil, furfural, dimethylethanolamine (QAC-7), from furfural, diethylamine and bisphenol A (QAC-4) [14], with large molecular mass and high content of aromatic fragments also capable of initiating sulfur vulcanization of cis-1,4-polyisoprene, but are worse than stearic acid in terms of formation of technological and physicomachanical properties of elastomeric compositions.

It is found that the quaternary ammonium compound we prepared from precursor originated from plant matter, are superior to stearic acid in terms of kinetic parameters of SKI-3 vulcanization. Their activity depends on molecular mass and number of aromatic fragments in the structure. Compounds QAC-7, QAC -4, QAC -1 can be recommended for rapid sulfur vulcanization systems, which provide kinetic parameters of cis-1,4-polyisoprene on the level of traditional stearic acid, while at vulcanization temperatures lower by 10 - 15°C. Experimental compound QAC-5 can be used instead of stearic acid in sulfur vulcanization composition for diene-based rubber while maintaining properties of the final product.

3.2 QAC in Model Composition based on Butadiene- α -Methylstyrene Rubber

Influence QAC synthesized from castor oil triisocyanate and (or) furfuryl alcohol QAC-2, QAC -6, QAC -7, QAC -8, as organic activators at 1.5 wt.p. on properties of rubber mixtures, was studied using model compositions of unsaturated elastomers of synthetic non-crystallizing amorphous butadiene- α -methylstyrene rubber with irregular structure SKMS-30 ARK. Study on the dosage of QAC-7 in range 0 - 2.25 wt.p. per 100 wt.p. of rubber was conducted in comparison to the same content of stearic acid [15].

Based on kinetic curves of SKMS-30 ARK vulcanization at 155°C (Figure-4), quaternary ammonium compounds synthesized from castor oil isocyanate are similar in effect to stearic acid. The introduction of furfuryl-based QAC-2 results in significant process acceleration on all stages.

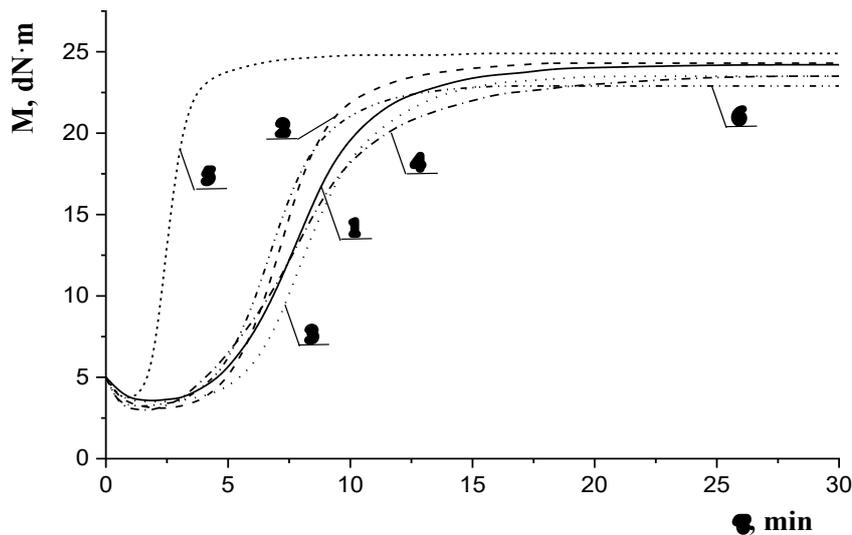


Figure-4. Kinetic curves of sulfur vulcanization of elastomeric compositions based on butadiene- α -methylstyrene rubber SKMS-30 ARK without activator (1), with stearic acid (2) and quaternary ammonium compounds: QAC-5 (3), QAC -8 (4), QAC -2 (5), QAC -6 (6).

Meaning, compounds QAC-6 and QAC-7, synthesized with castor oil triisocyanate fragments have activating effect on sulfur vulcanization of SKMS-30 ARK which is close to that of stearic acid. Compounds QAC-2, based on furfurool, dibutylamine, benzene chloride, which have lower molecular mass and a higher concentration of quaternary nitrogen, show better ignition properties than other QAC or stearic acid.

Studies of QAC-7 concentration on properties of elastomeric composition revealed, that increasing concentration from 0.75 wt.p. to 2.25 wt.p. per 100.0 wt.p. of rubber, results in a lower rate of sulfur vulcanization of SKMS-30 ARK [15], which differentiates effect of QAC from stearic acid.

3.3 «Structure-Properties» Dependency for QAC as an Organic Activator

Because the main reaction center of QAC in the sulfur vulcanization process of polydienes is quaternary nitrogen [5], the studied compounds that equal concentration per 100 wt.p. of rubber in mixture differed in a concentration of active centers. As such, we evaluated

«structure-properties» dependency of QAC as an activator in model rubber mixtures based on SKMS-30 ARKM-15 [19, p. 182] at an equal concentration of quaternary nitrogen per 100 wt. p. of rubber.

Considering results of previous studies [12, 13], concentration of compounds with single quaternary nitrogen was chosen as 2.0×10^{-3} moles per 100 wt.p. of rubber; concentration was halved for QAC with 2 quaternary nitrogen atoms.

As can be seen from Figure-5, unfilled rubber mixtures based non-crystallizing amorphous rubber with irregular structure SKMS-30 ARKM-15 with experimental compounds at 145°C , are characterized by S-curves of vulcanization kinetics, akin to stearic acid but differ in duration of induction period, rate and relative degree of vulcanization cross-links. Judging by values of nominal vulcanization constant (k_2) at 155°C (Table-2) at studied concentration, have better performance in terms of initiation degree than 2.0 wt.p. stearic acid, providing duration of induction period (t_i) and total accelerant consumption time (t_{dis}) on level of elastomeric composition with known activator.

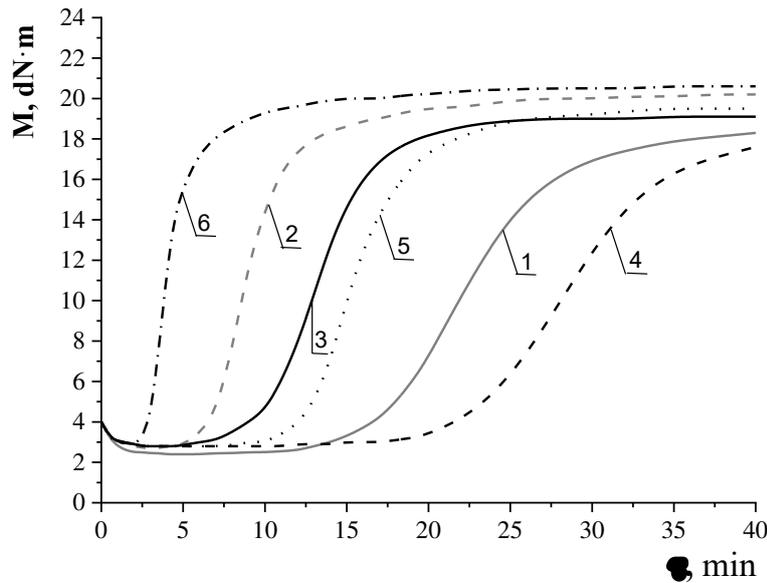


Figure-5. Kinetic curve of sulfur vulcanization at 145⁰C of elastomeric composition based on SKMS-30 ARKM-15 with different activators:

- 1 - stearic acid (2.0 wt.p.);
- 2 - no organic activator;
- 3 - QAC-6 (2.0 wt.p.);
- 4 - QAC-1 (0.7 wt.p.);
- 5 - QAC-2 (0.6 wt.p.);
- 6 - QAC-3 (0.5 wt.p.).

Table-2. Kinetic characteristics of sulfur vulcanization at of elastomeric composition based on SKMS-30 ARKM-15 at 155⁰C with different activators.

Parameter	Organic activator					
	Stearic acid	No activator	QAC-6	QAC-1	QAC-2	QAC-3
t_i , min	5.5	2.5	4.5	10.0	5.0	2.0
t_{dis} , min	6.0	3.0	5.0	11.0	6.0	2.5
k_2 , min ⁻¹	0.24	0.48	0.36	0.21	0.31	0.78

Influence of organic activators on vulcanization process was evaluated as ratio between parameter of elastomeric composition with activator and parameters of control (initial) elastomeric composition [13]. It was found (Figure-6), that compounds QAC-6, QAC-1 and QAC-2, similar to stearic acid, prolong induction period relative to

control mixture, by 1,8 - 4,0 times, lowering value of nominal vulcanization rate constant by 1.3 - 2.3 times. Only in case when QAC-3 was introduced to rubber mixture, the induction period decreased by 1.25 times, and nominal rate constant increased by 1.62.

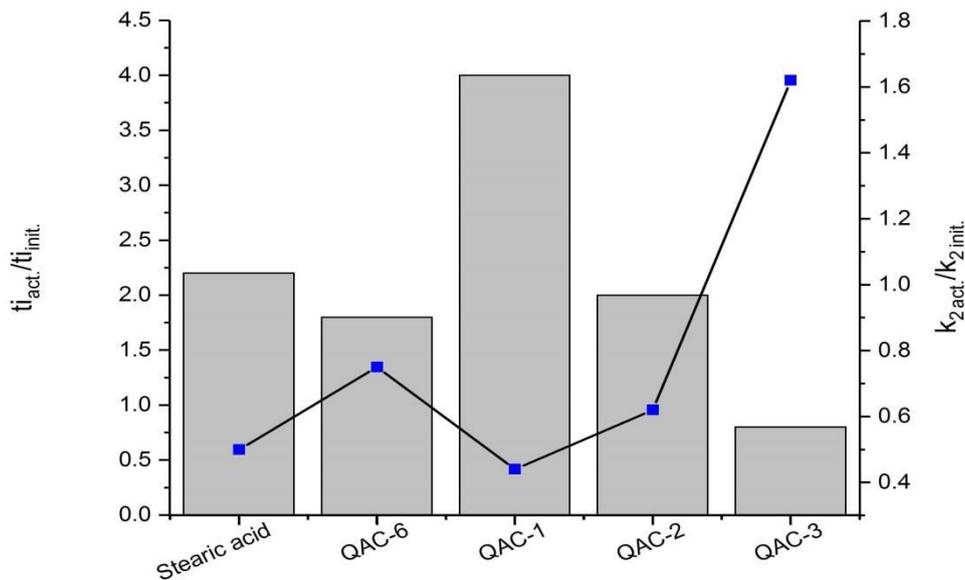


Figure-6. Relative effect of organic vulcanization activators on cross-linking period $t_{i,act}/t_{i,init}$ (█) and nominal vulcanization rate constant $k_{2,act}/k_{2,init}$ (—■—) for elastomeric compositions based on SKMS-30 ARKM-15 at 155°C.

Based on minimum torque value (S_{min}) of rubber mixtures (Table 3), introduction of quaternary ammonium compounds does not decrease viscosity of rubber mixtures, and rubbers that contain show relative cross-linking degree ($S_{max} - S_{min}$) are close to elastomeric compositions with stearic acid.

Analysis of rheokinetic characteristics of rubber mixtures at 155°C (Table-3), revealed that minimum parameter values of vulcanization initiation time (t_{s2}),

optimal vulcanization time (t_{c90}), highest ($V_{c,max}$) is demonstrated by rubber mixture with QAC-3. Relative to stearic acid, QAC-1 slows down sulfur vulcanization, resulting in longest time initiation time (t_{s2}); longest optimal vulcanization time on cross-linking stage (t_{c90}), lowest values of vulcanization rate ($V_{c,max}$) and relative cross-linking degree ($S_{max} - S_{min}$), maximum reversion stability $T@Rev98$.

Table-3. Rheometric parameters of sulfur vulcanization of elastomeric compositions based on SKMS-30 ARKM-15 at 155°C with different organic activators.

Parameter	Organic activator					
	Stearic acid	No activator	QAC-6	QAC -1	QAC -2	QAC -3
S_{min} , dN·m	2.47	3.02	3.19	3.41	3.19	3.22
$S_{max} - S_{min}$, dN·m	38.65	40.80	38.43	36.31	39.73	38.88
t_{s2} , min	5.49	2.66	4.05	9.14	4.88	1.26
t_{c90} , min	15.45	7.38	11.13	21.31	12.36	4.01
$V_{c,max}$, dN/min	7.06	16.65	9.71	4.78	9.95	30.57
$T@Rev98$, min	53.49	44.02	34.61	64.86	41.59	43.50

Based on rheokinetic parameter values, which characterize sulfur vulcanization of rubber mixtures based on SKMS-30 ARKM-15 at temperature 155°C (Table-3) a following activity series is proposed: QAC-3 > QAC -6 > QAC-2 > stearic acid > QAC-1. And quaternary ammonium compounds, which show high reactivity during induction period, lowering its duration, tend to initiate accelerated sulfur vulcanization during main period.

Regarding effect of QAC structure on their activity in sulfur vulcanization of elastomeric composition based on synthetic butadiene- α -methylsterene rubber

SKMS-30 ARKM-15, at equimolar concentrations (2.0×10^{-3} moles per 100 wt.p. of rubber) of quaternary nitrogen atoms, it can be concluded that QAC-2 with dobutyl radicals has significantly higher activity than, than QAC-1 with diethyl radicals in the structure. QAC-3, with symmetric quaternary nitrogen atoms relative to furfuryl fragment, demonstrated high initiation activity among studied furfuryl containing QAC. Branched structure of QAC-6, synthesized from castor oil triisocyanate has negligible effects on its activity relative to compounds with lower molecular mass, such as QAC-2.



As such, reactivity of studied QAC, similar to vulcanization accelerants [8], is determined by presents of vulcanization active functional groups– quaternary nitrogen atom and influence of surrounding substitutes.

3.4 QAC based on Castor Oil and Furfurol in Tire Composition

The effectiveness of QAC in compositions for industrial application, was evaluated using elastomeric

composition for making tire tread by substituting equal mass of standard activator - stearic acid, with QAC [15].

It was found (Table-4), substitution of industrial activator with experimental doesn't lower values of technological parameters of rubber mixtures, doesn't change S-shaped character of kinetic curve, and possibly, mechanism of sulfur vulcanization of rubber mixture (Figure-7).

Table-4. Technological and vulcanization characteristics of industrial elastomeric compositions based rubbers SKI-3, SKD, SKMS-30 ARKM15, for making tire treads with different vulcanization activators.

Parameter	Organic activator(2.0 wt. p.)	
	Stearic acid	QAC-8
Karrer plasticity, arb. u.	0.38	0.36
Cohesive resilience, MPa	0.19	0.19
Vulcanization parameters at 155°C:		
Time before vulcanization initiation (t_s), min	6.7	6.5
Time before vulcanization optimum (t_{C90}), min	15.0	13.4
Vulcanization rate (R_v), min^{-1}	12.0	14.5
Vulcanization rate ($V_c = M_{t_{C90}} - M_{t_s} / t_{C90} - t_s$), $\text{dN}\cdot\text{m}/\text{min}$	2.3	2.8
Cross-linking induction period (t_i), min	7.8	7.5
Accelerant consumption tim (t_{dis}), min	9.1	9.0
Nominal vulcanization rate constant (k_2), min^{-1}	0.15	0.20

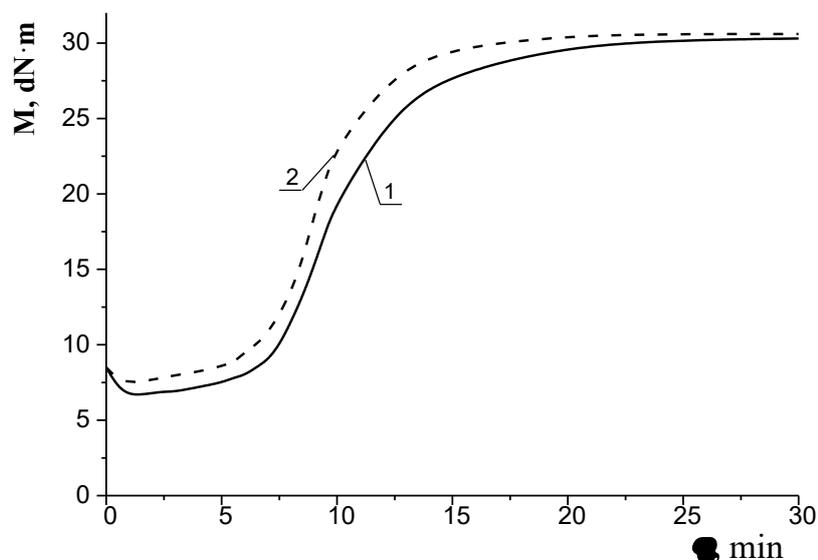


Figure-7. Kinetic curves of sulfur vulcanization of tread elastomers Compositions with stearic acid (1) and QAC-8 (2) at 155°C.

Values of kinetic parameters calculate from kinetic curves indicate that both rubber mixture has the same duration of induction period (t_s , t_i) and complete

accelerant consumption (t_{dis}) during the cross-linking stage. QAC differs from stearic acid in that it has higher activity during the main vulcanization period. In the



presence of QAC-8, the vulcanization rate (R_v , V_c Table-4) is higher by more than 20 % and the nautical vulcanization rate constant by a third.

The substitution of stearic acid with QAC-8 has positive effect physic-mechanical properties under normal

conditions, at 100⁰C and after thermal again (Table-5). Dynamic parameters of rubber are improved significantly: fatigue resilience of rubbers with QAC-8 increased by 17%, under normal conditions, and by almost 2 times after thermal aging.

Table-5. Physicomechanical properties of tire protector rubber with different organic activators for sulfur vulcanization.

Parameter	Organic activator(2.0 wt. p.)	
	Stearic acid	QAC-8
Nominal stress at 300% elongation (f_{300}), MPa:	n.u.	
100 °C	8.4	8.4
100 °C x 12 h	7.1	8.1
100 °C x 24 h	12.9	14.2
100 °C x 24 h	13.6	14.2
Nominal stretch resilience (f_p), MPa:		
n.u.	20.6	24.2
100 °C	11.9	14.0
100 °C x 12 h	19.3	20.4
100 °C x 24 h	18.0	19.4
Relative elongation on tear (ϵ), %:		
n.u.	570	650
100 °C	490	560
100 °C x 12 h	410	430
100 °C x 24 h	440	450
Rebound elasticity (S), arb. u.	32	32
Shore hardness (H), arb.u.:	66	66
Dynamic characteristics		
Fatigue resilience on repeated deformation ($\epsilon_{dyn.}=100\%$), thousands of cycles:		
n.u.	300.5	388.3
120°C x 12 h	16.8	33.3

Meaning, the substitution of stearic acid with an equal mass of QAC-8 in the composition of tire tread rubber, has a positive effect on vulcanization kinetics during the main stage, formation physicomechanical characteristics of rubber under static and dynamic loads [15].

3.5 Furfurol-based QAC in Tire Mixtures

QAC-2 was studied as a vulcanization activator for tire tread rubber [13]. QAC-2 was studied as activator sulfur-sulfenamide vulcanization with dosages 0 - 2.0 wt.p. per 100.0 wt.p. of rubber-based and compared to analogous dosages of stearic acid.

It was found that QAC-2 demonstrated higher activity than stearic acid on all vulcanization stages. Intense polydiene vulcanization in presence of QAC-2, which occur at lower activation energy values (Figure-8), indicates it having higher activity than stearic acid, and supports previously established [11, 12] possibility of forming synergistic systems with sulfenamide accelerant

As an alternative to stearic acid, the studied QAC provides required technological properties of rubber mixtures and physicomechanical properties of vulcanizates, and a dosage of 1.0 wt.p. can be used to intensify vulcanization [13].

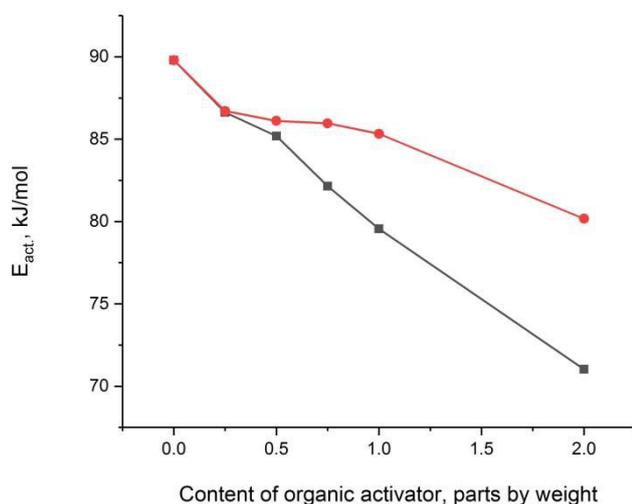


Figure-8. The dependency of effective activation energy $E_{act.}$ of vulcanization for elastomeric compositions based on SKI-3, SKD, SKMS-30 ARKM-15 on type and content of organic activators (■ QAC-2, ● stearic acid).

4. CONCLUSIONS

- With aim of expanding the assortment of organic activates for sulfur vulcanization of diene rubber and search for alternative replacements for stearic acid, we have synthesized a series of new quaternary ammonium compounds using available precursors derived from plant matter - furfural and castor oil.
- Use of QAC as organic activators for sulfur vulcanization of stereoregular and irregular carbon chain dienes rubbers revealed that reactivity of QAC is governed by the presence of functional groups (quaternary nitrogen atoms), the structure of surrounding substitutes.
- When studying model elastomeric compositions of synthetic cis-1,4-polyisoprene and butadiene- α -methylstyrene rubbers it was found that when QAC outperform stearic acid as vulcanization initiators per unit of mass. Their activity is influenced by the presence of aromatic fragments in the structure. QAC synthesized using castor oil triisocyanate, have an effect on sulfur vulcanization similar to that of stearic acid. Lower molecular mass QAC based on furfural rapidly initiates the vulcanization process on all its stages. Increasing QAC content from 0.75 to 2.25 wt.h. per 100 wt.p. per rubber, a decrease in vulcanization rate is observed in comparison to stearic acid.
- At equimolar (2.0×10^{-3} mole per 100.0 wt.p. butadiene- α -methylstyrene rubber) concentration of quaternary nitrogen atom in synthesized QAC, the highest activity is observed for compounds with

symmetric quaternary nitrogen atoms relative to furfuryl fragment.

- Depending on the established activity of synthesized QAC, possible applications for the development of composition for sulfur vulcanization elastomers are proposed. It was discovered, that substitution of stearic acid with an equal mass of QAC in compositions for tire treads rubber has positive effect on the formation of physicomechanical properties of rubber at static and dynamic loads.

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