

## Modifications of natural rubber (*Hevea brasiliensis*): production, application and comparison

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### ABSTRACT

This paper presents a method for obtaining the gel conductive systems being made of natural rubber (*Hevea brasiliensis*) (NR) and styrene-butadiene rubber (SBR). For this purpose, a natural rubber (*Hevea brasiliensis*), coming from a rubber tree plantation in Ranni, Kerala State, Southwest India, was used. Rubber latex was obtained by making incision in the trunk of Pará rubber tree and then collected, afterward being imported to Poland in 2006. Due to good quality and low price, styrene-butadiene rubber was used in the study as a mixture of 1,4-*cis* and -*trans* forms, composed of 77% butadiene and 23% styrene, No. KER<sup>®</sup> 1507, which was produced at the Dwory Chemical Plant S.A. near Oswiecim, Poland. This rubber was obtained in the process of low-temperature emulsion copolymerisation. As an agent inducing conduction in the rubber systems, divalent metal chlorides, such as BaCl<sub>2</sub>, CaCl<sub>2</sub>, CdCl<sub>2</sub>, CoCl<sub>2</sub>, CuCl<sub>2</sub>, FeCl<sub>2</sub>, MgCl<sub>2</sub>, MnCl<sub>2</sub>, MoCl<sub>2</sub>, NiCl<sub>2</sub>, SnCl<sub>2</sub>, SrCl<sub>2</sub>, or ZnCl<sub>2</sub> (manufactured by Chempur<sup>®</sup>, Poland), and sodium perchlorate, being obtained in the result of sodium hydroxide and perchloric acid synthesis, were used. Active carbon (NORIT<sup>®</sup> SX, manufactured by Chempur, Poland), with a 900m<sup>2</sup>·g<sup>-1</sup> active surface, was also used. For all systems with the divalent metal chlorides mentioned above, specific conductance was determined in the temperature range of 273 K to 313 K. The optimum quantities of doping agents in the form of divalent metal chlorides and active carbon being added to natural rubber (*Hevea brasiliensis*) and styrene-butadiene rubber were determined. It was found that specific conductance for the rubber systems with the addition of divalent metal chlorides and active carbon amounted to 10<sup>-4</sup>-10<sup>-7</sup> S·cm<sup>-1</sup>. On the other hand, specific conductance for sodium perchlorate and active carbon-doped rubbers amounted to 10<sup>-3</sup>-10<sup>-5</sup> S·cm<sup>-1</sup>. The capacitance values for the polymer compositions being doped with divalent metal chlorides are as follows: 8 F/g for the SBR system, and 28 F/g for the NR system.

**Keywords:** natural rubber, styrene-butadiene rubber, electrolytes of polymers, capacitive electrolytes, rubber batteries

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## **1. INTRODUCTION**

The main author and also a pioneer in the field of conductive polymers is a Japanese chemist Hideki Shirakawa who, as sometimes happens, obtained a conductive polymer (polyacetylene) accidentally. While searching for new solutions in the production of polyacetylene, he added by mistake much more catalyser than he intended. Owing to this accident, he obtained a conductive polymer with metallic lustre. At the same time, in the United States of America, Alan G. MacDiarmid and Alan G. Heeger carried out studies on an inorganic polymer, i.e. poly(sulphur nitride), which shows fairly good electrical conductivity. MacDiarmid met Shirakawa in Tokyo and showed a keen interest in polyacetylene which, according to him, could be a good conductor, as well as a safe one. Following their discussions, Shirakawa started to work on “organic metals” in Philadelphia. In a short period of time, this co-operation brought fruition and gave surprising results. It turned out that oxidation of polyacetylene with iodine vapours leads to a huge, about million-fold, increase in the conduction of this polymer. The oxidation process of this polymer mentioned above has been defined as doping, by analogy to a similar phenomenon being characteristic for semiconductors. Introduction of a certain quantity of foreign substance, a doping agent, into semiconductors also leads to a large increase in conduction.

In 2000, Hideki Shirakawa, Alan G. MacDiarmid and Alan G. Heeger were awarded the Nobel Prize in Chemistry for the lifetime achievements in obtaining conductive polymers and their application as polymer electrolytes. The authors of polymer electrolytes are D. E. Fenton, J. M. Parker and P. V. Wright, who obtained polymer electrolytes from poly(ethylene oxide) (PEO) with different salts, such as KSCN, NaSCN, NH<sub>4</sub>SCN, LiSCN and NaI, in which ionic conductivity was tested.

In 1978, M. B. Armand, while dealing with polymer electrolytes, drew conclusions that these polymers could be used in batteries as an electrolyte. It can be noted that since 1978 there has been a sharp increase in the interest in conductive polymers as electrolytes. The synthesis of obtained conductive polymers, in the form of solid polymer or as a polymeric gel, is not difficult. The general method consists in dissolving a polymer in a solvent, usually it is an organic solvent, and then adding metal salts to a polymer, as well as bases or corresponding acids, to polymers of high molecular weight. Conductive polymers have been already produced for more than 30 years. By contrast, conductive rubbers are produced to a very small extent. In international academic journals, there are papers presenting the synthesis of conductive rubbers. However, it was found that conductive rubbers have low values of specific conductance.

Tomasz Borowski, Jacek Kaczmarek, Jarosław Kraśniewski, Maciej Oleksy and Tadeusz Hryniewicz, the authors of a paper in the prestigious Polish journal *Przemysł Chemiczny* (Chemical Industry), No. 8 (2005), pages 607-610, have presented one of the first papers in Poland related to the synthesis of BR- and SBR-based conductive rubbers with NaClO<sub>4</sub> and active carbon.

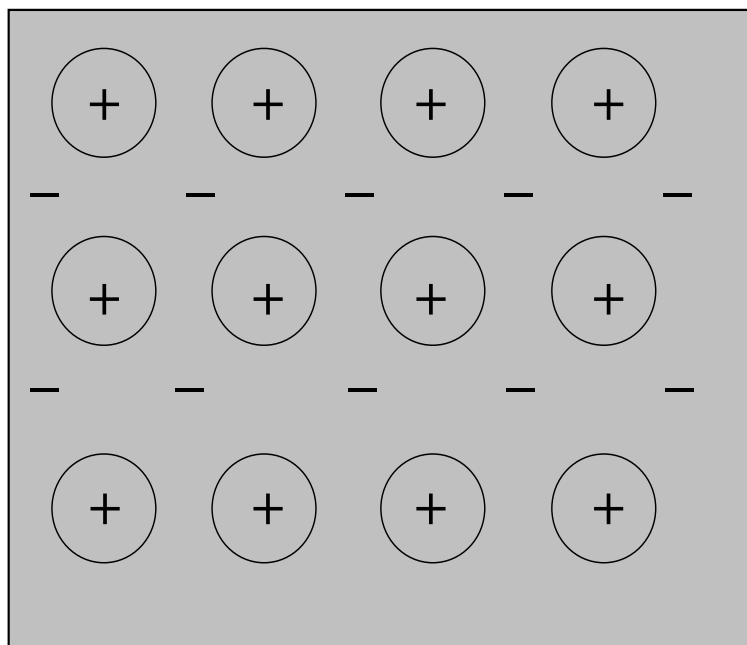
The main objective of this paper is to expand opportunities for obtaining new polymer systems with styrene-butadiene rubber and natural rubber as a doping agent, divalent metal chlorides and sodium perchlorate with the addition of active carbon were used. The polymer systems obtained this way could be applied in the electrochemical and electrical engineering industries.

This paper presents the next scientific stage related to conductive rubbers.

## 2. CONDUCTIVE POLYMERS

### 2. 1. Conductive polymers – introduction

Polymers, plastics of synthetic materials are associated with typical isolators. It is therefore hard to understand that metals are electric charge carriers, as in doped polymers, for instance organic polymers. The difference in terms of physical and chemical traits in both substances in one material seems to be impossible. But it is possible to change the view, which is presented in Figures 1, 2 and 3.



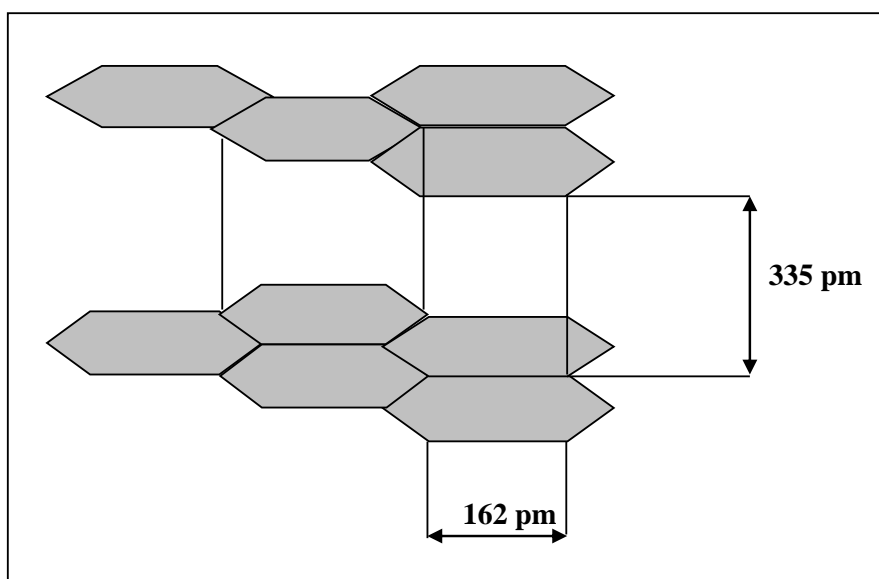
**Fig. 1.** Pictorial diagram of metal crystal structure.

Metallic bonds are composed of positive metal ions and electrons moving freely between them (electron cloud). In metals, conduction consists in the flow of electric charges due to the potential difference.

Conductors are not only metals but also other compounds. A good example is graphite; although it is not a polymer, it also conducts electrical current, though somewhat differently. There are long chains of carbon-carbon bonds in graphite. Graphite owes its good conduction to its specific crystalline structure. Graphite has carbon atoms which are arranged in equilateral hexagons, resembling benzene rings.

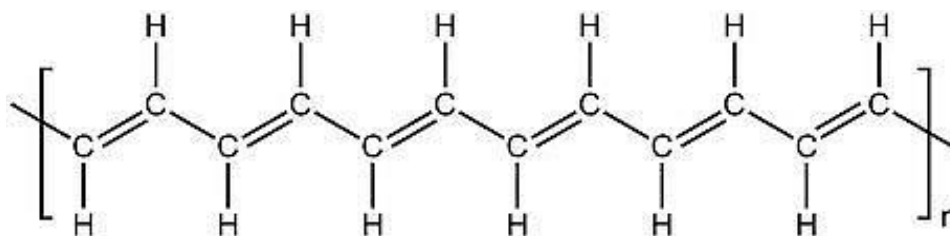
Each carbon atom is linked by covalent bond with three neighbouring atoms. Between respective layers, there are only weak intermolecular forces acting. This causes a high fissility of graphite in planes parallel to respective layers.

Therefore, electrical conductivity is quite high along planes, whereas significantly lower between planes being linked quite loosely (effective conductivity depends therefore on the direction of current flow in relation to the planes of conductors). Figure 2 presents the graphite structure and its distances from respective neighbouring carbons and planes.



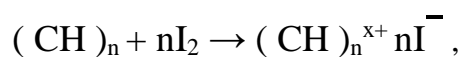
**Fig. 2.** Graphite structure.

One of the simplest conductive polymers which can be produced is polyacetylene. In polyacetylene, there is a system of double bonds conjugated with each other and thereby an energy band is formed being a path on which electrons can move.

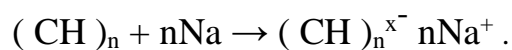


**Fig. 3.** Chemical structure of polyacetylene.

This is not enough for polymers to conduct electrical current; one more condition must be met. A polymer must be in the excited state, i.e. it should be oxidised, for instance by doping it with iodine:

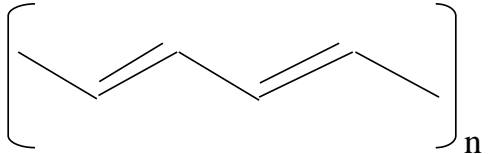
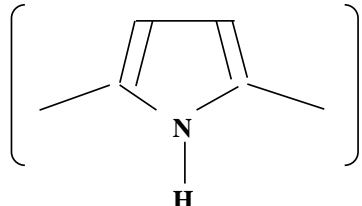
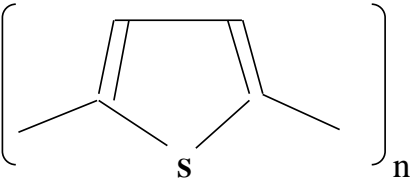
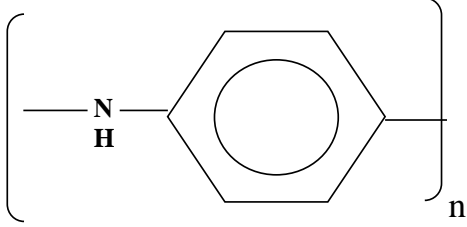
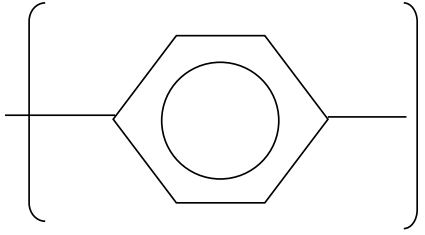


or it should be led to reduction, for instance by doping it with sodium:



It is true that electrical conductivity of a polymer being doped with iodine or sodium increases even to  $10^9$  times, equalling to the conductivity of metals.

However, polyacetylene is a material of quite low durability so that it could be applicable more widely. At present, many different conductive polymers, which are more durable and show high conductivity, are known (Fig. 4).

Name of polymer	Structural example
Polyacetylene	
Polypyrrole	
Polythiophene	
Poly( <i>p</i> -aniline)	
Poly( <i>p</i> -phenylene)	

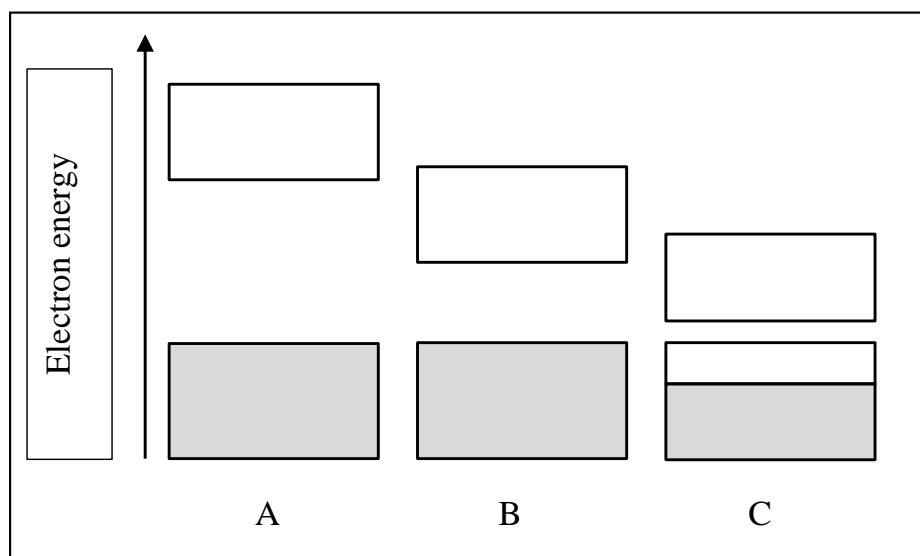
**Fig. 4.** Selected conductive polymers.

Electrons in an energy band are developed from the overlap of orbitals. They may have any energy but only in a strictly defined range (Fig. 5). A polymer contains usually more energy bands, separated by a wider or a narrower energy gap, but electrons can not have energy corresponding to the area between these bands.

The energy level for isolators is shown in Figure 5. A band with lower energy (valence band) is completely filled with electrons, whereas an empty band with higher energy (conduction band) is separated from the valence band by a quite wide energy gap. Such a wide gap makes the material to be an isolator.

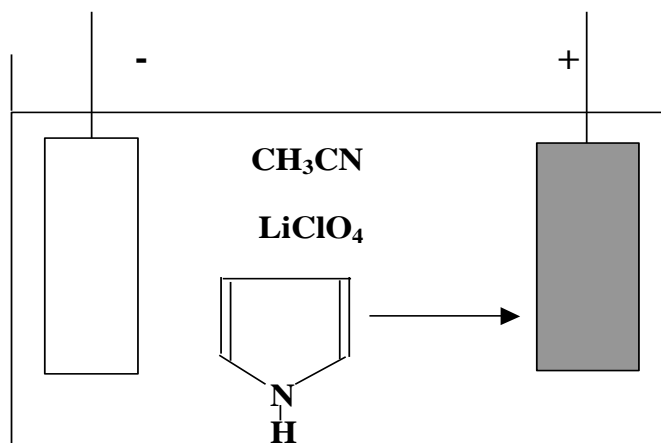
For semiconductors (Fig. 5B), the situation is quite different. Energy gap is slightly smaller. Thus, there could be an electron transition from the valence band to the conduction band under the influence of heat or solar radiation. With this phenomenon, there could be a transfer of electrical charges, as well as a deficit of electrons, which induces more freedom in the valence band.

In metallic-type conductors, the valence band is filled partially, therefore only minimal energy is needed for an electron to excite the conduction band and consequently allow it to move freely in a metal (Fig. 5C).



**Fig. 5.** Diagram of energy levels' occupancy:  
A) isolator; B) semiconductor; C) metal

Conductive polymers may also be obtained from monomers by electrochemical reaction. A good example is the production of polypyrrole. To produce conductive polypyrrole, a solution of polypyrrole in a solvent, e.g. acetonitrile ( $\text{CH}_3\text{CN}$ ) and lithium perchlorate, should be prepared to ensure the conduction of electrolyte, which is presented in Figure 6. Additionally, polypyrrole is partly oxidised and consequently its conduction increases. A positive charge of the polymer chain is compensated by perchlorate anions. Electrodes are placed in such a solution. After the voltage has been switched on, conductive polypyrrole will start to deposit on the positive electrode. Thanks to the fact that polypyrrole conducts electrical current, it is possible to obtain different polymer thickness.



**Fig. 6.** Production of polypyrrole by electrochemical method  $(\text{C}_4\text{H}_3\text{N})_n$ .

Modified conductive polymers can be divided into three basic groups. The first of them is acid-modified polymers. They are otherwise called proton conductive polymers. The acids being most frequently applied for polymer doping are  $\text{HClO}_4$ ,  $\text{H}_2\text{SO}_4$  and  $\text{H}_3\text{PO}_4$ . Also organic acids can be used but more often as additional doping agents in production of conductive polymers.

The second group of conductive polymers is commonly called alkaline conductive polymers. They are obtained by doping polymers with alkaline solutions. The most popular bases being applied to obtain conductive polymers are sodium and potassium hydroxides.

The third group of conductive polymers and, at the same time, the largest one in terms of diversity is polymers doped with salts of inorganic acids.

Studying the properties of conductive polymers requires co-operation of specialists from various fields of science: organic and inorganic chemistry, physical chemistry, electrochemistry, materials engineering, electronics, etc. Linking the polymer systems of good conduction properties, resistant to chemical factors, having physical properties of plastics, and moreover incorporation of optical properties and easiness to obtain polymers, brings a great chance for different applications in practice.

As early as in 1977, the awareness of this fact has been present in the American daily newspaper “Wall Street Journal” which wrote then: “If permanently conductive plastics will be obtained, the number of conceivable applications is surprisingly large”.

At present, conductive polymers have found their application as materials for the production of electrochromic indicators, photo-elements, plastic batteries, polymer sensors, fuel cells, electrochemical capacitors, polymer batteries, and many others.

### 3. EXPERIMENTAL SCOPE

- A) Determination of specific conductance according to temperature (273 K to 313 K);
- B) Determination of the capacitance of selected composite systems;
- C) Example practical application of the polymer compositions obtained:



- coatings with anti-corrosive and anti-electrostatic properties,
- sodium-based rubber batteries.

## 4. PRODUCTION OF CONDUCTIVE RUBBERS

### 4. 1. Production of conductive natural rubber

#### *Stage 1 – Dissolution of natural rubber*

Raw natural latex tends to coagulate, forming elastic and extensible rubber. In order to prevent this process, it was immediately added to toluene with a purity of 99% (toluene was manufactured by Spectrum Chemicals, Edayar, Cochin-683 502, India, Code: T 0105) after collection from the Pará rubber tree (*Hevea brasiliensis*).

The natural rubber latex secured in such a way was imported to Poland from Southwest India.

Development of the synthesis of conductive rubbers required at the first stage the precipitation of natural rubber from toluene and its re-dissolution in toluene in order to make precisely defined molecular mass calculations. To precipitate natural rubber, methanol (99.8%, manufactured by Chempur<sup>®</sup>, Poland) was used. To re-dissolve natural rubber, toluene (99.5%, manufactured by Chempur<sup>®</sup>, Poland), was used. Dissolution proportions: 3 grams of natural rubber, after its previous precipitation from the toluene solution mentioned above, were added to 40 cm<sup>3</sup> of toluene.

The solution of natural rubber was left for 12 hours, shaking it from time to time. After 12 hours, the rubber was dissolved again in toluene. A solution of natural rubber in toluene, of white oil consistency, was obtained.

#### *Stage 2a – Synthesis of polymer electrolyte: NR + BaCl<sub>2</sub> or CaCl<sub>2</sub> or CdCl<sub>2</sub> or CoCl<sub>2</sub> or CuCl<sub>2</sub> or FeCl<sub>2</sub> or MgCl<sub>2</sub> or MnCl<sub>2</sub> or MoCl<sub>2</sub> or NiCl<sub>2</sub> or SnCl<sub>2</sub> or SrCl<sub>2</sub> or ZnCl<sub>2</sub>*

In order to obtain an electrolyte solution, 1 to 5 grams of BaCl<sub>2</sub> or CaCl<sub>2</sub> or CdCl<sub>2</sub> or CoCl<sub>2</sub> or CuCl<sub>2</sub> or FeCl<sub>2</sub> or MgCl<sub>2</sub> or MnCl<sub>2</sub> or MoCl<sub>2</sub> or NiCl<sub>2</sub> or SnCl<sub>2</sub> or SrCl<sub>2</sub> or ZnCl<sub>2</sub> had to be dissolved in 40 cm<sup>3</sup> methanol (99.5 %). To the rubber solution being prepared at Stage 1, a solution of BaCl<sub>2</sub> or CaCl<sub>2</sub> or CdCl<sub>2</sub> or CoCl<sub>2</sub> or CuCl<sub>2</sub> or FeCl<sub>2</sub> or MgCl<sub>2</sub> or MnCl<sub>2</sub> or MoCl<sub>2</sub> or NiCl<sub>2</sub> or SnCl<sub>2</sub> or SrCl<sub>2</sub> or ZnCl<sub>2</sub> with methanol is added, respectively, and thoroughly mixed.

A rubber electrolyte precipitates almost immediately in the form of gel. Such an electrolyte system with natural rubber automatically cross-links with atmospheric oxygen after 24 hours when submitted to air drying. After this time, the rubber system is submitted to conductivity tests.

#### *Stage 2b – Synthesis of polymer electrolyte: NR + BaCl<sub>2</sub> or CaCl<sub>2</sub> or CdCl<sub>2</sub> or CoCl<sub>2</sub> or CuCl<sub>2</sub> or FeCl<sub>2</sub> or MgCl<sub>2</sub> or MnCl<sub>2</sub> or MoCl<sub>2</sub> or NiCl<sub>2</sub> or SnCl<sub>2</sub> or SrCl<sub>2</sub> or ZnCl<sub>2</sub> + active carbon*

Before obtaining a rubber electrolyte with the addition of active carbon, the maximum quantity of BaCl<sub>2</sub> or CaCl<sub>2</sub> or CdCl<sub>2</sub> or CoCl<sub>2</sub> or CuCl<sub>2</sub> or FeCl<sub>2</sub> or MgCl<sub>2</sub> or MnCl<sub>2</sub> or MoCl<sub>2</sub> or NiCl<sub>2</sub> or SnCl<sub>2</sub> or SrCl<sub>2</sub> or ZnCl<sub>2</sub> possible to be added to the natural rubber solution in toluene (Stage 1) was determined. This quantity was determined and it amounts to 5 grams for each divalent metal chloride. After adding a quantity larger than 5 grams of BaCl<sub>2</sub> or

CaCl<sub>2</sub> or CdCl<sub>2</sub> or CoCl<sub>2</sub> or CuCl<sub>2</sub> or FeCl<sub>2</sub> or MgCl<sub>2</sub> or MnCl<sub>2</sub> or MoCl<sub>2</sub> or NiCl<sub>2</sub> or SnCl<sub>2</sub> or SrCl<sub>2</sub> or ZnCl<sub>2</sub>, difficulties begin to appear in the precipitation of rubber electrolyte from the solution as an electrolyte being made of natural rubber in the form of gel. These difficulties consist in the non-homogenous form of gel.

Divalent metal chlorides, BaCl<sub>2</sub> or CaCl<sub>2</sub> or CdCl<sub>2</sub> or CoCl<sub>2</sub> or CuCl<sub>2</sub> or FeCl<sub>2</sub> or MgCl<sub>2</sub> or MnCl<sub>2</sub> or MoCl<sub>2</sub> or NiCl<sub>2</sub> or SnCl<sub>2</sub> or SrCl<sub>2</sub> or ZnCl<sub>2</sub>, in the quantity of 5 grams are being dissolved in 40 cm<sup>3</sup> methanol and added to the natural rubber solutions prepared earlier with the addition of active carbon, containing from 0.5 to 2.5 grams of active carbon (Fig. 7.). After mixing, the rubber electrolyte precipitates almost immediately from the solution. Such an electrolyte system is left for one day following its removal from the solution. After one day, the rubber system is submitted to conductivity tests.

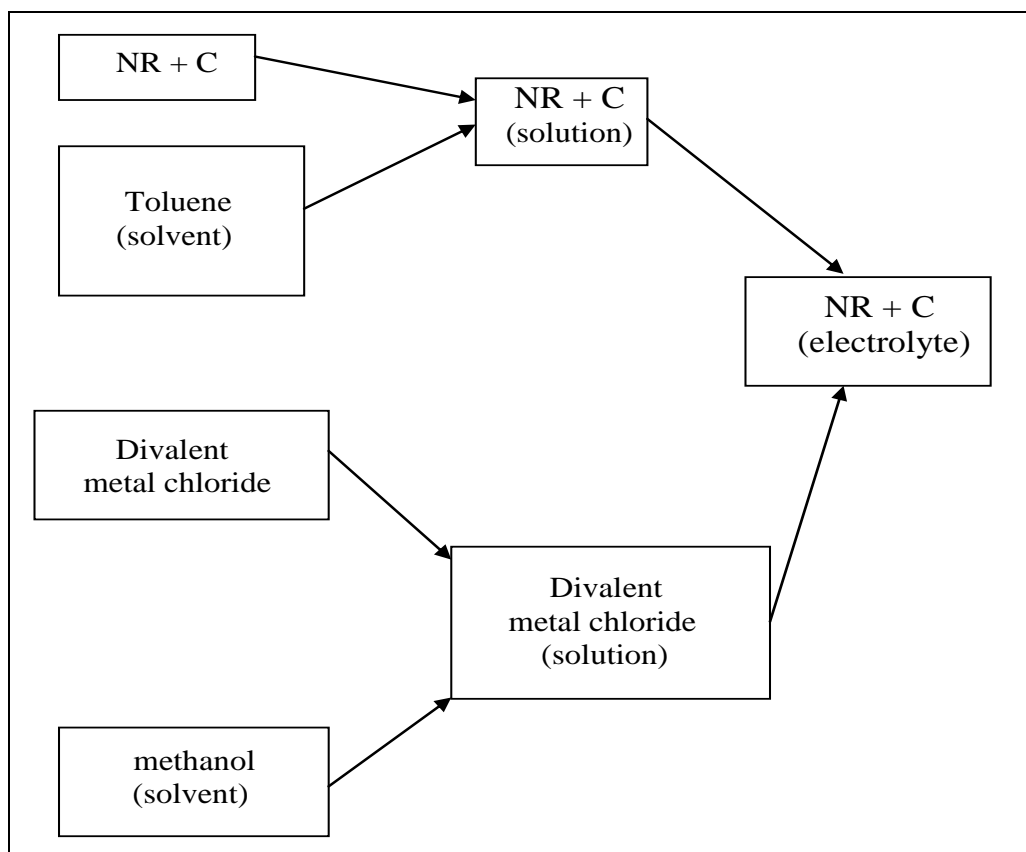


Fig. 7. Diagram of conductive natural rubber (NR) preparation.

#### 4. 2. Production of conductive styrene-butadiene rubber

##### Stage 1 – Dissolution of styrene-butadiene rubber

Styrene-butadiene rubber dissolves well in toluene. To 3 grams of finely cut SBR, 40 cm<sup>3</sup> of toluene are added. After three days, the polymer left at room temperature becomes an oily substance; it dissolves completely.

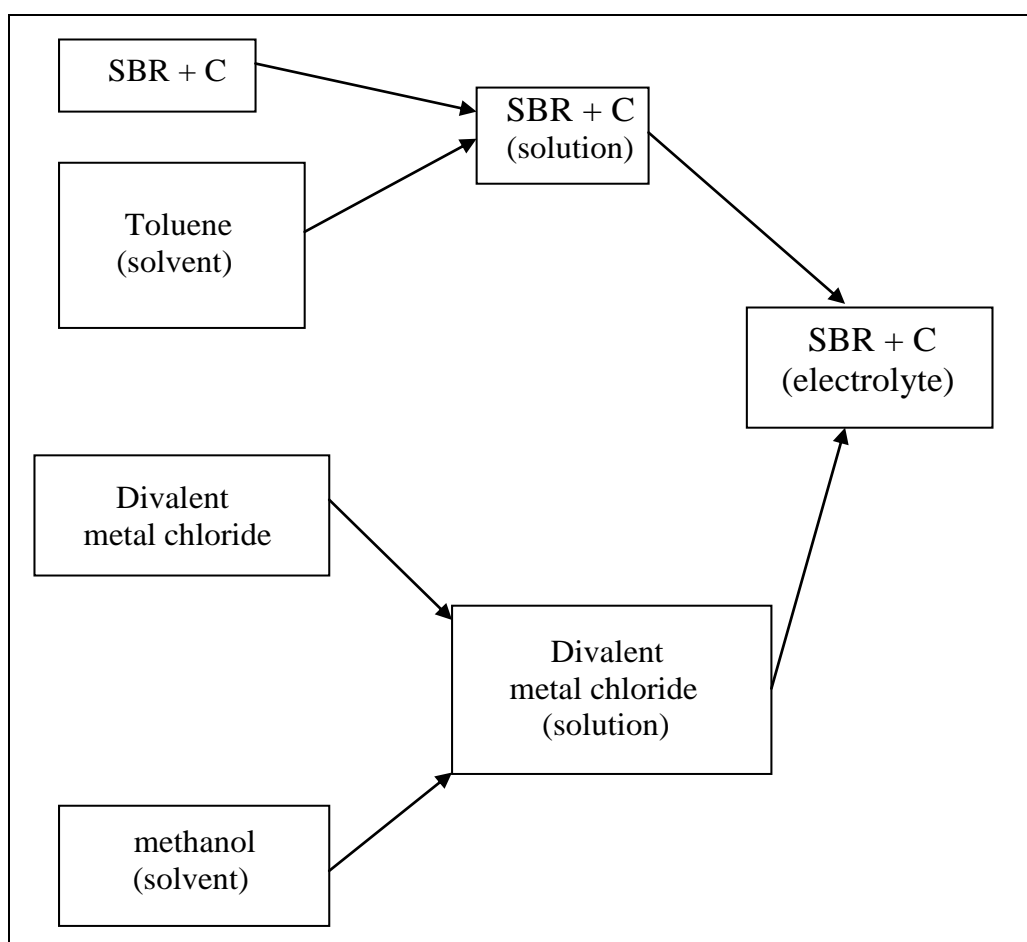
*Stage 2a – Synthesis of polymer electrolyte: SBR + BaCl<sub>2</sub> or CaCl<sub>2</sub> or CdCl<sub>2</sub> or CoCl<sub>2</sub> or CuCl<sub>2</sub> or FeCl<sub>2</sub> or MgCl<sub>2</sub> or MnCl<sub>2</sub> or MoCl<sub>2</sub> or NiCl<sub>2</sub> or SnCl<sub>2</sub> or SrCl<sub>2</sub> or ZnCl<sub>2</sub>*

Before obtaining a rubber electrolyte, the maximum quantity of BaCl<sub>2</sub> or CaCl<sub>2</sub> or CdCl<sub>2</sub> or CoCl<sub>2</sub> or CuCl<sub>2</sub> or FeCl<sub>2</sub> or MgCl<sub>2</sub> or MnCl<sub>2</sub> or MoCl<sub>2</sub> or NiCl<sub>2</sub> or SnCl<sub>2</sub> or SrCl<sub>2</sub> or ZnCl<sub>2</sub> possible to be added to the styrene-butadiene rubber solution. The method is the same as in Stage 2a.

Divalent metal chlorides, BaCl<sub>2</sub> or CaCl<sub>2</sub> or CdCl<sub>2</sub> or CoCl<sub>2</sub> or CuCl<sub>2</sub> or FeCl<sub>2</sub> or MgCl<sub>2</sub> or MnCl<sub>2</sub> or MoCl<sub>2</sub> or NiCl<sub>2</sub> or SnCl<sub>2</sub> or SrCl<sub>2</sub> or ZnCl<sub>2</sub>, in the quantity of 1 to 5 grams are being dissolved in 40 cm<sup>3</sup> of methanol and added to the solution of styrene-butadiene rubber prepared earlier.

After mixing, the rubber electrolyte precipitates almost immediately from the solution. Such an electrolyte system is left for a few hours following its removal from the solution. After this time, the rubber system is submitted to conductivity tests.

*Stage 2b – Synthesis of polymer electrolyte: SBR + BaCl<sub>2</sub> or CaCl<sub>2</sub> or CdCl<sub>2</sub> or CoCl<sub>2</sub> or CuCl<sub>2</sub> or FeCl<sub>2</sub> or MgCl<sub>2</sub> or MnCl<sub>2</sub> or MoCl<sub>2</sub> or NiCl<sub>2</sub> or SnCl<sub>2</sub> or SrCl<sub>2</sub> or ZnCl<sub>2</sub> + active carbon*



**Fig. 8.** Diagram of conductive styrene-butadiene rubber (SBR) preparation.

Before obtaining a rubber electrolyte with the addition of active carbon, the maximum quantity of BaCl<sub>2</sub> or CaCl<sub>2</sub> or CdCl<sub>2</sub> or CoCl<sub>2</sub> or CuCl<sub>2</sub> or FeCl<sub>2</sub> or MgCl<sub>2</sub> or MnCl<sub>2</sub> or MoCl<sub>2</sub> or NiCl<sub>2</sub> or SnCl<sub>2</sub> or SrCl<sub>2</sub> or ZnCl<sub>2</sub> possible to be added to the styrene-butadiene rubber solution (*Stage 1*).

This quantity was determined and it amounts to 5 grams for each divalent metal chloride. After adding a quantity larger than 5 grams of BaCl<sub>2</sub> or CaCl<sub>2</sub> or CdCl<sub>2</sub> or CoCl<sub>2</sub> or CuCl<sub>2</sub> or FeCl<sub>2</sub> or MgCl<sub>2</sub> or MnCl<sub>2</sub> or MoCl<sub>2</sub> or NiCl<sub>2</sub> or SnCl<sub>2</sub> or SrCl<sub>2</sub> or ZnCl<sub>2</sub>, difficulties begin to appear in the precipitation of rubber electrolyte from the solution as a styrene-butadiene rubber electrolyte in the form of gel.

These difficulties consist in the non-homogenous form of gel. Divalent metal chlorides, BaCl<sub>2</sub> or CaCl<sub>2</sub> or CdCl<sub>2</sub> or CoCl<sub>2</sub> or CuCl<sub>2</sub> or FeCl<sub>2</sub> or MgCl<sub>2</sub> or MnCl<sub>2</sub> or MoCl<sub>2</sub> or NiCl<sub>2</sub> or SnCl<sub>2</sub> or SrCl<sub>2</sub> or ZnCl<sub>2</sub>, in the quantity of 5 grams are being dissolved in 40 cm<sup>3</sup> of methanol and added to the styrene-butadiene rubber solutions prepared earlier with the addition of active carbon, containing from 0.5 to 2.5 grams of active carbon. After mixing, the rubber electrolyte precipitates almost immediately from the solution (Fig. 8). Such a rubber electrolyte system is left for a few hours following its removal from the solution. After this time, the rubber system is submitted to conductivity tests.

## 5. METHODS FOR MEASUREMENT OF POLYMER SYSTEMS

### 5. 1. Polymer conduction

A major determinant of polymer conduction is specific conductance of conductive polymers, i.e. conductivity [ $\gamma$ ]. It is a material constant, a physical quantity characterising the materials in terms of their ability of conduction.

Conductivity is a measure of the reciprocal of resistivity (specific resistance), which can be determined from the formula presented below:

$$R = \frac{\rho \cdot L}{S_x} \Rightarrow \rho = \frac{R \cdot S_x}{L}$$

where: R – resistance of conductor [ $\Omega$ ]

L – length of conductor [cm]

S<sub>x</sub> – surface of conductor [cm<sup>2</sup>]

$\rho$  – resistivity (specific resistance [ $\Omega \cdot \text{cm}$ ])

Determination of conductivity:

$$\gamma = \frac{1}{\rho}$$

where:  $\gamma$  - conductivity (specific conductance), [ $\Omega^{-1} \cdot \text{cm}^{-1}$ ] or [ $\text{S} \cdot \text{cm}^{-1}$ ].

## 5. 2. Conduction measurement

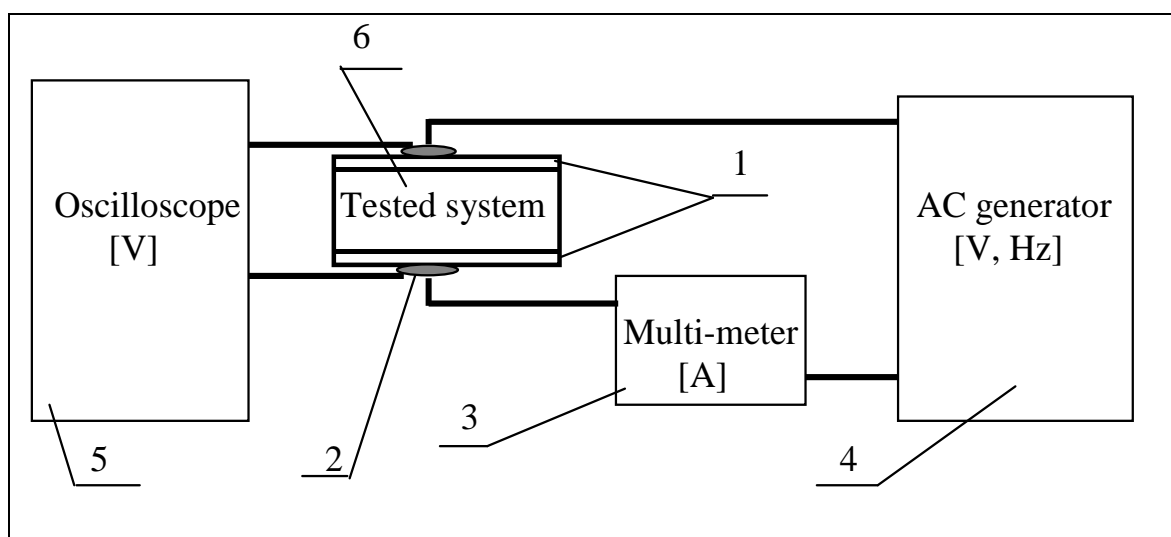
The systems of conductive polymers were tested on copper plates. These copper plates were washed earlier with carbon tetrachloride (CCl<sub>4</sub>) and rinsed with hot water. Thereafter, they were submitted to a 4-hour chemical polishing in a solution composed of:

H <sub>3</sub> PO <sub>4</sub> (80%)	500 cm <sup>3</sup>
CH <sub>3</sub> COOH (glacial)	300 cm <sup>3</sup>
HNO <sub>3</sub> (60%)	200 cm <sup>3</sup>

Onto the copper plates prepared in such a way, with an area of 0.88 cm<sup>2</sup> each, the polymer + divalent metal chloride) + active carbon system, 0.1 cm thick, was placed.

In order to determine specific conductance of the systems obtained, they were submitted to tests using alternating current, of constant frequency 10 kHz. For this purpose, the following equipment was used, the diagram of which is presented in Figure 9.

HEWLETT PACKARD/AGILENT 33120A (15 MHz) FUNCTION/ARBITRARY WAVEFORM Generator  
 AGILENT 3458A 8 ½ DIGIT multi-meter  
 HEWLETT PACKARD Infinium Oscilloscope 500 MHz 1GSa/s



**Fig. 9.** Measuring diagram for the conductivity of polymer system tested  
 1 – copper plates, 2 – cable-copper plate connection point, 3 – multi-meter,  
 4 – alternator, 5 – oscilloscope, 6 – polymer electrolyte

## 6. AGGREGATED MEASUREMENT RESULTS

### 6. 1. Results for the conductivity of modified natural rubber with the addition of active carbon

Tables 1 to 13 present the results for the conductivity of modified natural rubber with the addition of BaCl<sub>2</sub>, CaCl<sub>2</sub>, CdCl<sub>2</sub>, CoCl<sub>2</sub>, CuCl<sub>2</sub>, FeCl<sub>2</sub>, MgCl<sub>2</sub>, MnCl<sub>2</sub>, MoCl<sub>2</sub>, NiCl<sub>2</sub>, SnCl<sub>2</sub>, SrCl<sub>2</sub>, or ZnCl<sub>2</sub> and active carbon.

**Table 1.** Conductivity of rubber composite for the constant concentration of 3 g NR in 40 cm<sup>3</sup> toluene and the variable quantity of active carbon in the temperature range of 273 K to 313 K for the NR + BaCl<sub>2</sub> + active carbon system

Quantity of active carbon	Temperature 273 K [S·cm <sup>-1</sup> ]	Temperature 283 K [S·cm <sup>-1</sup> ]	Temperature 293 K [S·cm <sup>-1</sup> ]	Temperature 303 K [S·cm <sup>-1</sup> ]	Temperature 313 K [S·cm <sup>-1</sup> ]
0.5 g	10 <sup>-8</sup>	10 <sup>-8</sup>	10 <sup>-8</sup>	10 <sup>-8</sup>	10 <sup>-8</sup>
1 g	10 <sup>-7</sup>	10 <sup>-7</sup>	10 <sup>-7</sup>	10 <sup>-7</sup>	10 <sup>-7</sup>
1.5 g	10 <sup>-7</sup>	10 <sup>-7</sup>	10 <sup>-7</sup>	10 <sup>-7</sup>	10 <sup>-7</sup>
2 g	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>
2.5 g	3.7·10 <sup>-6</sup>	3.8·10 <sup>-6</sup>	3.8·10 <sup>-6</sup>	4.2·10 <sup>-6</sup>	4.3·10 <sup>-6</sup>

**Table 2.** Conductivity of rubber composite for the constant concentration of 3 g NR in 40 cm<sup>3</sup> toluene and the variable quantity of active carbon in the temperature range of 273 K to 313 K for the NR + CaCl<sub>2</sub> + active carbon system

Quantity of active carbon	Temperature 273 K [S·cm <sup>-1</sup> ]	Temperature 283 K [S·cm <sup>-1</sup> ]	Temperature 293 K [S·cm <sup>-1</sup> ]	Temperature 303 K [S·cm <sup>-1</sup> ]	Temperature 313 K [S·cm <sup>-1</sup> ]
0.5 g	10 <sup>-7</sup>	10 <sup>-7</sup>	10 <sup>-7</sup>	10 <sup>-7</sup>	10 <sup>-7</sup>
1 g	10 <sup>-7</sup>	10 <sup>-7</sup>	10 <sup>-7</sup>	10 <sup>-7</sup>	10 <sup>-7</sup>
1.5 g	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>
2 g	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>
2.5 g	1.4·10 <sup>-6</sup>	1.4·10 <sup>-6</sup>	1.4·10 <sup>-6</sup>	1.4·10 <sup>-6</sup>	1.5·10 <sup>-6</sup>

**Table 3.** Conductivity of rubber composite for the constant concentration of 3 g NR in 40 cm<sup>3</sup> toluene and the variable quantity of active carbon in the temperature range of 273 K to 313 K for the NR + CdCl<sub>2</sub> + active carbon system

Quantity of active carbon	Temperature 273 K [S·cm <sup>-1</sup> ]	Temperature 283 K [S·cm <sup>-1</sup> ]	Temperature 293 K [S·cm <sup>-1</sup> ]	Temperature 303 K [S·cm <sup>-1</sup> ]	Temperature 313 K [S·cm <sup>-1</sup> ]
0.5 g	10 <sup>-7</sup>	10 <sup>-7</sup>	10 <sup>-7</sup>	10 <sup>-7</sup>	10 <sup>-7</sup>
1 g	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>
1.5 g	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>
2 g	10 <sup>-5</sup>	10 <sup>-5</sup>	10 <sup>-5</sup>	10 <sup>-5</sup>	10 <sup>-5</sup>
2.5 g	3.7·10 <sup>-5</sup>	3.7·10 <sup>-5</sup>	3.8·10 <sup>-5</sup>	4.0·10 <sup>-5</sup>	4.3·10 <sup>-5</sup>

**Table 4.** Conductivity of rubber composite for the constant concentration of 3 g NR in 40 cm<sup>3</sup> toluene and the variable quantity of active carbon in the temperature range of 273 K to 313 K for the NR + CoCl<sub>2</sub> + active carbon system

Quantity of active carbon	Temperature 273 K [S·cm <sup>-1</sup> ]	Temperature 283 K [S·cm <sup>-1</sup> ]	Temperature 293 K [S·cm <sup>-1</sup> ]	Temperature 303 K [S·cm <sup>-1</sup> ]	Temperature 313 K [S·cm <sup>-1</sup> ]
0.5 g	10 <sup>-8</sup>	10 <sup>-8</sup>	10 <sup>-8</sup>	10 <sup>-8</sup>	10 <sup>-8</sup>
1 g	10 <sup>-7</sup>	10 <sup>-7</sup>	10 <sup>-7</sup>	10 <sup>-7</sup>	10 <sup>-7</sup>
1.5 g	10 <sup>-7</sup>	10 <sup>-7</sup>	10 <sup>-7</sup>	10 <sup>-7</sup>	10 <sup>-7</sup>
2 g	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>
2.5 g	2.1·10 <sup>-6</sup>	2.1·10 <sup>-6</sup>	2.1·10 <sup>-6</sup>	2.1·10 <sup>-6</sup>	2.1·10 <sup>-6</sup>

**Table 5.** Conductivity of rubber composite for the constant concentration of 3 g NR in 40 cm<sup>3</sup> toluene and the variable quantity of active carbon in the temperature range of 273 K to 313 K for the NR + CuCl<sub>2</sub> + active carbon system

Quantity of active carbon	Temperature 273 K [S·cm <sup>-1</sup> ]	Temperature 283 K [S·cm <sup>-1</sup> ]	Temperature 293 K [S·cm <sup>-1</sup> ]	Temperature 303 K [S·cm <sup>-1</sup> ]	Temperature 313 K [S·cm <sup>-1</sup> ]
0.5 g	10 <sup>-7</sup>	10 <sup>-7</sup>	10 <sup>-7</sup>	10 <sup>-7</sup>	10 <sup>-7</sup>
1 g	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-7</sup>
1.5 g	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>
2 g	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>
2.5 g	3.5·10 <sup>-6</sup>	3.7·10 <sup>-6</sup>	3.8·10 <sup>-6</sup>	3.9·10 <sup>-6</sup>	4.0·10 <sup>-6</sup>

**Table 6.** Conductivity of rubber composite for the constant concentration of 3 g NR in 40 cm<sup>3</sup> toluene and the variable quantity of active carbon in the temperature range of 273 K to 313 K for the NR + FeCl<sub>2</sub> + active carbon system

Quantity of active carbon	Temperature 273 K [S·cm <sup>-1</sup> ]	Temperature 283 K [S·cm <sup>-1</sup> ]	Temperature 293 K [S·cm <sup>-1</sup> ]	Temperature 303 K [S·cm <sup>-1</sup> ]	Temperature 313 K [S·cm <sup>-1</sup> ]
0.5 g	10 <sup>-7</sup>	10 <sup>-7</sup>	10 <sup>-7</sup>	10 <sup>-7</sup>	10 <sup>-7</sup>
1 g	10 <sup>-7</sup>	10 <sup>-7</sup>	10 <sup>-7</sup>	10 <sup>-7</sup>	10 <sup>-7</sup>
1.5 g	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>
2 g	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>
2.5 g	6.6·10 <sup>-5</sup>	6.7·10 <sup>-5</sup>	6.7·10 <sup>-5</sup>	6.8·10 <sup>-5</sup>	7.0·10 <sup>-5</sup>

**Table 7.** Conductivity of rubber composite for the constant concentration of 3 g NR in 40 cm<sup>3</sup> toluene and the variable quantity of active carbon in the temperature range of 273 K to 313 K for the NR + MgCl<sub>2</sub> + active carbon system

Quantity of active carbon	Temperature 273 K [S·cm <sup>-1</sup> ]	Temperature 283 K [S·cm <sup>-1</sup> ]	Temperature 293 K [S·cm <sup>-1</sup> ]	Temperature 303 K [S·cm <sup>-1</sup> ]	Temperature 313 K [S·cm <sup>-1</sup> ]
0.5 g	10 <sup>-8</sup>	10 <sup>-8</sup>	10 <sup>-8</sup>	10 <sup>-8</sup>	10 <sup>-8</sup>
1 g	10 <sup>-7</sup>	10 <sup>-7</sup>	10 <sup>-7</sup>	10 <sup>-7</sup>	10 <sup>-7</sup>
1.5 g	10 <sup>-7</sup>	10 <sup>-7</sup>	10 <sup>-7</sup>	10 <sup>-7</sup>	10 <sup>-7</sup>
2 g	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>
2.5 g	9.0·10 <sup>-6</sup>	9.0·10 <sup>-6</sup>	9.5·10 <sup>-6</sup>	9.5·10 <sup>-6</sup>	1.0·10 <sup>-5</sup>

**Table 8.** Conductivity of rubber composite for the constant concentration of 3 g NR in 40 cm<sup>3</sup> toluene and the variable quantity of active carbon in the temperature range of 273 K to 313 K for the NR + MnCl<sub>2</sub> + active carbon system

Quantity of active carbon	Temperature 273 K [S·cm <sup>-1</sup> ]	Temperature 283 K [S·cm <sup>-1</sup> ]	Temperature 293 K [S·cm <sup>-1</sup> ]	Temperature 303 K [S·cm <sup>-1</sup> ]	Temperature 313 K [S·cm <sup>-1</sup> ]
0.5 g	10 <sup>-7</sup>	10 <sup>-7</sup>	10 <sup>-7</sup>	10 <sup>-7</sup>	10 <sup>-7</sup>
1 g	10 <sup>-7</sup>	10 <sup>-7</sup>	10 <sup>-7</sup>	10 <sup>-7</sup>	10 <sup>-7</sup>
1.5 g	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>
2 g	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>
2.5 g	1.7·10 <sup>-6</sup>	1.7·10 <sup>-6</sup>	1.7·10 <sup>-6</sup>	1.8·10 <sup>-6</sup>	1.8·10 <sup>-6</sup>

**Table 9.** Conductivity of rubber composite for the constant concentration of 3 g NR in 40 cm<sup>3</sup> toluene and the variable quantity of active carbon in the temperature range of 273 K to 313 K for the NR + MoCl<sub>2</sub> + active carbon system

Quantity of active carbon	Temperature 273 K [S·cm <sup>-1</sup> ]	Temperature 283 K [S·cm <sup>-1</sup> ]	Temperature 293 K [S·cm <sup>-1</sup> ]	Temperature 303 K [S·cm <sup>-1</sup> ]	Temperature 313 K [S·cm <sup>-1</sup> ]
0.5 g	10 <sup>-8</sup>	10 <sup>-8</sup>	10 <sup>-8</sup>	10 <sup>-8</sup>	10 <sup>-8</sup>
1 g	10 <sup>-8</sup>	10 <sup>-8</sup>	10 <sup>-8</sup>	10 <sup>-8</sup>	10 <sup>-8</sup>
1.5 g	10 <sup>-7</sup>	10 <sup>-7</sup>	10 <sup>-7</sup>	10 <sup>-7</sup>	10 <sup>-7</sup>
2 g	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>
2.5 g	1.2·10 <sup>-5</sup>	1.3·10 <sup>-5</sup>	1.4·10 <sup>-5</sup>	1.4·10 <sup>-5</sup>	1.6·10 <sup>-5</sup>



**Table 10.** Conductivity of rubber composite for the constant concentration of 3 g NR in 40 cm<sup>3</sup> toluene and the variable quantity of active carbon in the temperature range of 273 K to 313 K for the NR + NiCl<sub>2</sub> + active carbon system

Quantity of active carbon	Temperature 273 K [S·cm <sup>-1</sup> ]	Temperature 283 K [S·cm <sup>-1</sup> ]	Temperature 293 K [S·cm <sup>-1</sup> ]	Temperature 303 K [S·cm <sup>-1</sup> ]	Temperature 313 K [S·cm <sup>-1</sup> ]
0.5 g	10 <sup>-8</sup>	10 <sup>-8</sup>	10 <sup>-8</sup>	10 <sup>-8</sup>	10 <sup>-8</sup>
1 g	10 <sup>-7</sup>	10 <sup>-7</sup>	10 <sup>-7</sup>	10 <sup>-7</sup>	10 <sup>-7</sup>
1.5 g	10 <sup>-7</sup>	10 <sup>-7</sup>	10 <sup>-7</sup>	10 <sup>-7</sup>	10 <sup>-7</sup>
2 g	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>
2.5 g	3.4·10 <sup>-6</sup>	3.5·10 <sup>-6</sup>	3.5·10 <sup>-6</sup>	3.5·10 <sup>-6</sup>	3.6·10 <sup>-6</sup>

**Table 11.** Conductivity of rubber composite for the constant concentration of 3 g NR in 40 cm<sup>3</sup> toluene and the variable quantity of active carbon in the temperature range of 273 K to 313 K for the NR + SnCl<sub>2</sub> + active carbon system

Quantity of active carbon	Temperature 273 K [S·cm <sup>-1</sup> ]	Temperature 283 K [S·cm <sup>-1</sup> ]	Temperature 293 K [S·cm <sup>-1</sup> ]	Temperature 303 K [S·cm <sup>-1</sup> ]	Temperature 313 K [S·cm <sup>-1</sup> ]
0.5 g	10 <sup>-7</sup>	10 <sup>-7</sup>	10 <sup>-7</sup>	10 <sup>-7</sup>	10 <sup>-7</sup>
1 g	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>
1.5 g	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>
2 g	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>
2.5 g	1,3·10 <sup>-5</sup>	1,3·10 <sup>-5</sup>	1,3·10 <sup>-5</sup>	1,3·10 <sup>-5</sup>	1,3·10 <sup>-5</sup>

**Table 12.** Conductivity of rubber composite for the constant concentration of 3 g NR in 40 cm<sup>3</sup> toluene and the variable quantity of active carbon in the temperature range of 273 K to 313 K for the NR + SrCl<sub>2</sub> + active carbon system

Quantity of active carbon	Temperature 273 K [S·cm <sup>-1</sup> ]	Temperature 283 K [S·cm <sup>-1</sup> ]	Temperature 293 K [S·cm <sup>-1</sup> ]	Temperature 303 K [S·cm <sup>-1</sup> ]	Temperature 313 K [S·cm <sup>-1</sup> ]
0.5 g	10 <sup>-7</sup>	10 <sup>-7</sup>	10 <sup>-7</sup>	10 <sup>-7</sup>	10 <sup>-7</sup>
1 g	10 <sup>-7</sup>	10 <sup>-7</sup>	10 <sup>-7</sup>	10 <sup>-7</sup>	10 <sup>-7</sup>
1.5 g	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>
2 g	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>
2.5 g	4.5·10 <sup>-5</sup>	4.6·10 <sup>-5</sup>	4.7·10 <sup>-5</sup>	4.7·10 <sup>-5</sup>	4.9·10 <sup>-5</sup>

**Table 13.** Conductivity of rubber composite for the constant concentration of 3 g NR in 40 cm<sup>3</sup> toluene and the variable quantity of active carbon in the temperature range of 273 K to 313 K for the NR + ZnCl<sub>2</sub> + active carbon system

Quantity of active carbon	Temperature 273 K [S·cm <sup>-1</sup> ]	Temperature 283 K [S·cm <sup>-1</sup> ]	Temperature 293 K [S·cm <sup>-1</sup> ]	Temperature 303 K [S·cm <sup>-1</sup> ]	Temperature 313 K [S·cm <sup>-1</sup> ]
0.5 g	10 <sup>-7</sup>	10 <sup>-7</sup>	10 <sup>-7</sup>	10 <sup>-7</sup>	10 <sup>-7</sup>
1 g	10 <sup>-7</sup>	10 <sup>-7</sup>	10 <sup>-7</sup>	10 <sup>-7</sup>	10 <sup>-7</sup>
1.5 g	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>
2 g	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>
2.5 g	7.3·10 <sup>-5</sup>	7.3·10 <sup>-5</sup>	7.4·10 <sup>-5</sup>	7.5·10 <sup>-5</sup>	7.6·10 <sup>-5</sup>

## 6. 2. Results for the conductivity of modified styrene-butadiene rubber the addition of active carbon

Tables 14 to 26 present the results for the conductivity of modified styrene-butadiene rubber with the addition of BaCl<sub>2</sub>, CaCl<sub>2</sub>, CdCl<sub>2</sub>, CoCl<sub>2</sub>, CuCl<sub>2</sub>, FeCl<sub>2</sub>, MgCl<sub>2</sub>, MnCl<sub>2</sub>, MoCl<sub>2</sub>, NiCl<sub>2</sub>, SnCl<sub>2</sub>, SrCl<sub>2</sub>, or ZnCl<sub>2</sub> and active carbon.

**Table 14.** Conductivity of rubber composite for the constant concentration of 3 g SBR in 40 cm<sup>3</sup> toluene and the variable quantity of active carbon in the temperature range of 273 K to 313 K for the SBR + BaCl<sub>2</sub> + active carbon system

Quantity of active carbon	Temperature 273 K [S·cm <sup>-1</sup> ]	Temperature 283 K [S·cm <sup>-1</sup> ]	Temperature 293 K [S·cm <sup>-1</sup> ]	Temperature 303 K [S·cm <sup>-1</sup> ]	Temperature 313 K [S·cm <sup>-1</sup> ]
0.5 g	10 <sup>-7</sup>	10 <sup>-7</sup>	10 <sup>-7</sup>	10 <sup>-7</sup>	10 <sup>-7</sup>
1 g	10 <sup>-7</sup>	10 <sup>-7</sup>	10 <sup>-7</sup>	10 <sup>-7</sup>	10 <sup>-7</sup>
1.5 g	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>
2 g	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>
2.5 g	1.5·10 <sup>-5</sup>	1.5·10 <sup>-5</sup>	1.5·10 <sup>-5</sup>	1.6·10 <sup>-5</sup>	1.7·10 <sup>-5</sup>

**Table 15.** Conductivity of rubber composite for the constant concentration of 3 g SBR in 40 cm<sup>3</sup> toluene and the variable quantity of active carbon in the temperature range of 273 K to 313 K for the SBR + CaCl<sub>2</sub> + active carbon system

Quantity of active carbon	Temperature 273 K [S·cm <sup>-1</sup> ]	Temperature 283 K [S·cm <sup>-1</sup> ]	Temperature 293 K [S·cm <sup>-1</sup> ]	Temperature 303 K [S·cm <sup>-1</sup> ]	Temperature 313 K [S·cm <sup>-1</sup> ]
0.5 g	10 <sup>-7</sup>	10 <sup>-7</sup>	10 <sup>-7</sup>	10 <sup>-7</sup>	10 <sup>-7</sup>
1 g	10 <sup>-7</sup>	10 <sup>-7</sup>	10 <sup>-7</sup>	10 <sup>-7</sup>	10 <sup>-7</sup>
1.5 g	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>
2 g	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>
2.5 g	1.7·10 <sup>-6</sup>	1.7·10 <sup>-6</sup>	1.7·10 <sup>-6</sup>	1.8·10 <sup>-6</sup>	1.8·10 <sup>-6</sup>

**Table 16.** Conductivity of rubber composite for the constant concentration of 3 g SBR in 40 cm<sup>3</sup> toluene and the variable quantity of active carbon in the temperature range of 273 K to 313 K for the SBR + CdCl<sub>2</sub> + active carbon system

Quantity of active carbon	Temperature 273 K [S·cm <sup>-1</sup> ]	Temperature 283 K [S·cm <sup>-1</sup> ]	Temperature 293 K [S·cm <sup>-1</sup> ]	Temperature 303 K [S·cm <sup>-1</sup> ]	Temperature 313 K [S·cm <sup>-1</sup> ]
0.5 g	10 <sup>-7</sup>	10 <sup>-7</sup>	10 <sup>-7</sup>	10 <sup>-7</sup>	10 <sup>-7</sup>
1 g	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>
1.5 g	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>
2 g	10 <sup>-5</sup>	10 <sup>-5</sup>	10 <sup>-5</sup>	10 <sup>-5</sup>	10 <sup>-5</sup>
2.5 g	2.5·10 <sup>-5</sup>	2.5·10 <sup>-5</sup>	2.7·10 <sup>-5</sup>	2.8·10 <sup>-5</sup>	2.9·10 <sup>-5</sup>

**Table 17.** Conductivity of rubber composite for the constant concentration of 3 g SBR in 40 cm<sup>3</sup> toluene and the variable quantity of active carbon in the temperature range of 273 K to 313 K for the SBR + CoCl<sub>2</sub> + active carbon system

Quantity of active carbon	Temperature 273 K [S·cm <sup>-1</sup> ]	Temperature 283 K [S·cm <sup>-1</sup> ]	Temperature 293 K [S·cm <sup>-1</sup> ]	Temperature 303 K [S·cm <sup>-1</sup> ]	Temperature 313 K [S·cm <sup>-1</sup> ]
0.5 g	10 <sup>-7</sup>	10 <sup>-7</sup>	10 <sup>-7</sup>	10 <sup>-7</sup>	10 <sup>-7</sup>
1 g	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>
1.5 g	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>
2 g	10 <sup>-5</sup>	10 <sup>-5</sup>	10 <sup>-5</sup>	10 <sup>-5</sup>	10 <sup>-5</sup>
2.5 g	5.2·10 <sup>-5</sup>	5.3·10 <sup>-5</sup>	5.3·10 <sup>-5</sup>	5.4·10 <sup>-5</sup>	5.5·10 <sup>-5</sup>

**Table 18.** Conductivity of rubber composite for the constant concentration of 3 g SBR in 40 cm<sup>3</sup> toluene and the variable quantity of active carbon in the temperature range of 273 K to 313 K for the SBR + CuCl<sub>2</sub> + active carbon system

Quantity of active carbon	Temperature 273 K [S·cm <sup>-1</sup> ]	Temperature 283 K [S·cm <sup>-1</sup> ]	Temperature 293 K [S·cm <sup>-1</sup> ]	Temperature 303 K [S·cm <sup>-1</sup> ]	Temperature 313 K [S·cm <sup>-1</sup> ]
0.5 g	10 <sup>-7</sup>	10 <sup>-7</sup>	10 <sup>-7</sup>	10 <sup>-7</sup>	10 <sup>-7</sup>
1 g	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>
1.5 g	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>
2 g	10 <sup>-5</sup>	10 <sup>-5</sup>	10 <sup>-5</sup>	10 <sup>-5</sup>	10 <sup>-5</sup>
2.5 g	5.0·10 <sup>-5</sup>	5.0·10 <sup>-5</sup>	5.2·10 <sup>-5</sup>	5.3·10 <sup>-5</sup>	5.5·10 <sup>-5</sup>

**Table 19.** Conductivity of rubber composite for the constant concentration of 3 g SBR in 40 cm<sup>3</sup> toluene and the variable quantity of active carbon in the temperature range of 273 K to 313 K for the SBR + FeCl<sub>2</sub> + active carbon system

Quantity of active carbon	Temperature 273 K [S·cm <sup>-1</sup> ]	Temperature 283 K [S·cm <sup>-1</sup> ]	Temperature 293 K [S·cm <sup>-1</sup> ]	Temperature 303 K [S·cm <sup>-1</sup> ]	Temperature 313 K [S·cm <sup>-1</sup> ]
0.5 g	10 <sup>-7</sup>	10 <sup>-7</sup>	10 <sup>-7</sup>	10 <sup>-7</sup>	10 <sup>-7</sup>
1 g	10 <sup>-7</sup>	10 <sup>-7</sup>	10 <sup>-7</sup>	10 <sup>-7</sup>	10 <sup>-7</sup>
1.5 g	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>
2 g	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>
2.5 g	3.9·10 <sup>-5</sup>	4.0·10 <sup>-5</sup>	4.1·10 <sup>-5</sup>	4.3·10 <sup>-5</sup>	4.6·10 <sup>-5</sup>

**Table 20.** Conductivity of rubber composite for the constant concentration of 3 g SBR in 40 cm<sup>3</sup> toluene and the variable quantity of active carbon in the temperature range of 273 K to 313 K for the SBR + MgCl<sub>2</sub> + active carbon system

Quantity of active carbon	Temperature 273 K [S·cm <sup>-1</sup> ]	Temperature 283 K [S·cm <sup>-1</sup> ]	Temperature 293 K [S·cm <sup>-1</sup> ]	Temperature 303 K [S·cm <sup>-1</sup> ]	Temperature 313 K [S·cm <sup>-1</sup> ]
0.5 g	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>
1 g	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>
1.5 g	10 <sup>-5</sup>	10 <sup>-5</sup>	10 <sup>-5</sup>	10 <sup>-5</sup>	10 <sup>-5</sup>
2 g	10 <sup>-5</sup>	10 <sup>-5</sup>	10 <sup>-5</sup>	10 <sup>-5</sup>	10 <sup>-5</sup>
2.5 g	8.0·10 <sup>-5</sup>	8.1·10 <sup>-5</sup>	8.1·10 <sup>-5</sup>	8.2·10 <sup>-5</sup>	8.3·10 <sup>-5</sup>

**Table 21.** Conductivity of rubber composite for the constant concentration of 3 g SBR in 40 cm<sup>3</sup> toluene and the variable quantity of active carbon in the temperature range of 273 K to 313 K for the SBR + MnCl<sub>2</sub> + active carbon system

Quantity of active carbon	Temperature 273 K [S·cm <sup>-1</sup> ]	Temperature 283 K [S·cm <sup>-1</sup> ]	Temperature 293 K [S·cm <sup>-1</sup> ]	Temperature 303 K [S·cm <sup>-1</sup> ]	Temperature 313 K [S·cm <sup>-1</sup> ]
0.5 g	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>
1 g	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>
1.5 g	10 <sup>-5</sup>	10 <sup>-5</sup>	10 <sup>-5</sup>	10 <sup>-5</sup>	10 <sup>-5</sup>
2 g	2.7·10 <sup>-5</sup>	2.8·10 <sup>-5</sup>	2.8·10 <sup>-5</sup>	2.7·10 <sup>-5</sup>	2.6·10 <sup>-5</sup>
2.5 g	6.2·10 <sup>-5</sup>	6.2·10 <sup>-5</sup>	6.6·10 <sup>-5</sup>	6.6·10 <sup>-5</sup>	7.1·10 <sup>-5</sup>

**Table 22.** Conductivity of rubber composite for the constant concentration of 3 g SBR in 40 cm<sup>3</sup> toluene and the variable quantity of active carbon in the temperature range of 273 K to 313 K for the SBR + MoCl<sub>2</sub> + active carbon system

Quantity of active carbon	Temperature 273 K [S·cm <sup>-1</sup> ]	Temperature 283 K [S·cm <sup>-1</sup> ]	Temperature 293 K [S·cm <sup>-1</sup> ]	Temperature 303 K [S·cm <sup>-1</sup> ]	Temperature 313 K [S·cm <sup>-1</sup> ]
0.5 g	10 <sup>-7</sup>	10 <sup>-7</sup>	10 <sup>-7</sup>	10 <sup>-7</sup>	10 <sup>-7</sup>
1 g	10 <sup>-7</sup>	10 <sup>-7</sup>	10 <sup>-7</sup>	10 <sup>-7</sup>	10 <sup>-7</sup>
1.5 g	10 <sup>-7</sup>	10 <sup>-7</sup>	10 <sup>-7</sup>	10 <sup>-7</sup>	10 <sup>-7</sup>
2 g	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>
2.5 g	8.3·10 <sup>-6</sup>	8.3·10 <sup>-6</sup>	9.1·10 <sup>-6</sup>	1.0·10 <sup>-5</sup>	1.1·10 <sup>-5</sup>

**Table 23.** Conductivity of rubber composite for the constant concentration of 3 g SBR in 40 cm<sup>3</sup> toluene and the variable quantity of active carbon in the temperature range of 273 K to 313 K for the SBR + NiCl<sub>2</sub> + active carbon system

Quantity of active carbon	Temperature 273 K [S·cm <sup>-1</sup> ]	Temperature 283 K [S·cm <sup>-1</sup> ]	Temperature 293 K [S·cm <sup>-1</sup> ]	Temperature 303 K [S·cm <sup>-1</sup> ]	Temperature 313 K [S·cm <sup>-1</sup> ]
0.5 g	10 <sup>-7</sup>	10 <sup>-7</sup>	10 <sup>-7</sup>	10 <sup>-7</sup>	10 <sup>-7</sup>
1 g	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>
1.5 g	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>
2 g	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>
2.5 g	1.1·10 <sup>-5</sup>	1.1·10 <sup>-5</sup>	1.2·10 <sup>-5</sup>	1.2·10 <sup>-5</sup>	1.2·10 <sup>-5</sup>

**Table 24.** Conductivity of rubber composite for the constant concentration of 3 g SBR in 40 cm<sup>3</sup> toluene and the variable quantity of active carbon in the temperature range of 273 K to 313 K for the SBR + SnCl<sub>2</sub> + active carbon system

Quantity of active carbon	Temperature 273 K [S·cm <sup>-1</sup> ]	Temperature 283 K [S·cm <sup>-1</sup> ]	Temperature 293 K [S·cm <sup>-1</sup> ]	Temperature 303 K [S·cm <sup>-1</sup> ]	Temperature 313 K [S·cm <sup>-1</sup> ]
0.5 g	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>
1 g	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>
1.5 g	10 <sup>-5</sup>	10 <sup>-5</sup>	10 <sup>-5</sup>	10 <sup>-5</sup>	10 <sup>-5</sup>
2 g	10 <sup>-4</sup>	10 <sup>-4</sup>	10 <sup>-4</sup>	10 <sup>-4</sup>	10 <sup>-4</sup>
2.5 g	3.0·10 <sup>-4</sup>	3.1·10 <sup>-4</sup>	3.1·10 <sup>-4</sup>	3.3·10 <sup>-4</sup>	3.5·10 <sup>-4</sup>

**Table 25.** Conductivity of rubber composite for the constant concentration of 3 g SBR in 40 cm<sup>3</sup> toluene and the variable quantity of active carbon in the temperature range of 273 K to 313 K for the SBR + SrCl<sub>2</sub> + active carbon system

Quantity of active carbon	Temperature 273 K [S·cm <sup>-1</sup> ]	Temperature 283 K [S·cm <sup>-1</sup> ]	Temperature 293 K [S·cm <sup>-1</sup> ]	Temperature 303 K [S·cm <sup>-1</sup> ]	Temperature 313 K [S·cm <sup>-1</sup> ]
0.5 g	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>
1 g	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>
1.5 g	10 <sup>-5</sup>	10 <sup>-5</sup>	10 <sup>-5</sup>	10 <sup>-5</sup>	10 <sup>-5</sup>
2 g	10 <sup>-5</sup>	10 <sup>-5</sup>	10 <sup>-5</sup>	10 <sup>-5</sup>	10 <sup>-5</sup>
2.5 g	6.2·10 <sup>-5</sup>	6.2·10 <sup>-5</sup>	6.6·10 <sup>-5</sup>	6.6·10 <sup>-5</sup>	7.1·10 <sup>-5</sup>

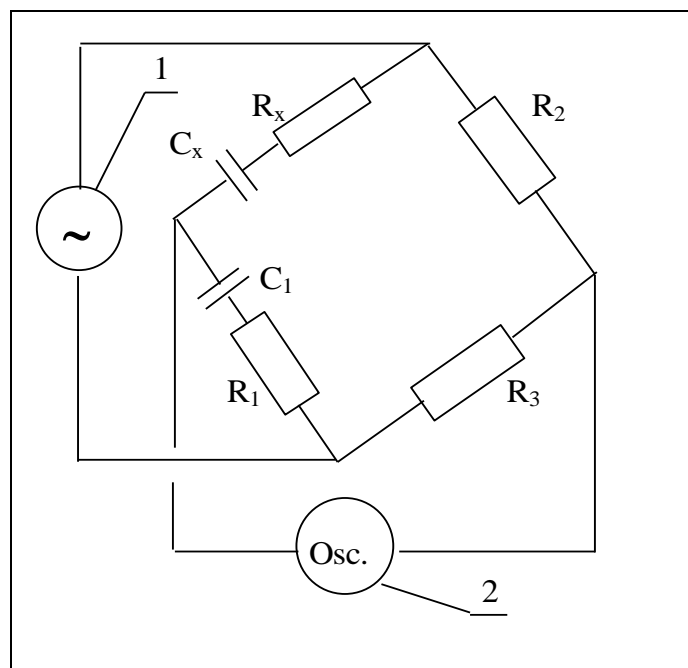
**Table 26.** Conductivity of rubber composite for the constant concentration of 3 g SBR in 40 cm<sup>3</sup> toluene and the variable quantity of active carbon in the temperature range of 273 K to 313 K for the SBR + ZnCl<sub>2</sub> + active carbon system

Quantity of active carbon	Temperature 273 K [S·cm <sup>-1</sup> ]	Temperature 283 K [S·cm <sup>-1</sup> ]	Temperature 293 K [S·cm <sup>-1</sup> ]	Temperature 303 K [S·cm <sup>-1</sup> ]	Temperature 313 K [S·cm <sup>-1</sup> ]
0.5 g	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>
1 g	10 <sup>-5</sup>	10 <sup>-5</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>
1.5 g	10 <sup>-5</sup>	10 <sup>-5</sup>	10 <sup>-5</sup>	10 <sup>-5</sup>	10 <sup>-5</sup>
2 g	10 <sup>-4</sup>	10 <sup>-4</sup>	10 <sup>-4</sup>	10 <sup>-4</sup>	10 <sup>-4</sup>
2.5 g	2.8·10 <sup>-4</sup>	2.8·10 <sup>-4</sup>	2.9·10 <sup>-4</sup>	3.0·10 <sup>-4</sup>	3.1·10 <sup>-4</sup>

## 7. CAPACITANCE VALUES OF SELECTED COMPOSITE SYSTEMS

### 7. 1. Capacitance measurement

A diagram of the system for measuring capacitor properties of polymer composites is presented below. Figure 10 presents a typical diagram of such an electronic circuit.



**Fig. 10.** Diagram of the alternating-current electronic circuit for testing the capacitance of polymer systems:  
 1 – 1.5 V<sub>pp</sub> voltage for a frequency of 1 kHz produced by a Hewlett Packard/Agilent 33120A function/arbitrary waveform generator,  
 2 – settings on a Hung-Chang Protek 3502C Oscilloscope (20 MHz),  
 R<sub>1-3</sub> – resistances set on OD-1-D7a decade resistors,  
 C<sub>1</sub> – capacitance set on a CD-5d decade capacitor.

**Table 27.** Results for the measurement of capacitance for the composite system (SBR) at the constant quantity of 5 grams of CdCl<sub>2</sub>, MoCl<sub>2</sub>, CuCl<sub>2</sub> or ZnCl<sub>2</sub> within the variable range of active carbon from 0.5 to 2.5 grams.

Styrene-butadiene rubber (SBR) composition	Quantity of active carbon [g]				
	0.5	1.0	1.5	2.0	2.5
	System capacitance [F/g]				
CdCl <sub>2</sub>	0.9	2.3	4.7	6.2	8.0
MoCl <sub>2</sub>	0.8	1.9	3.3	5.6	7.1

CuCl <sub>2</sub>	0.4	0.8	1.4	2.7	4.1
ZnCl <sub>2</sub>	0.9	2.9	4.7	6.2	9.1

**Table 28.** Results for the measurement of capacitance for the composite system (NR) at the constant quantity of 5 grams of MnCl<sub>2</sub>, SnCl<sub>2</sub>, SrCl<sub>2</sub> or ZnCl<sub>2</sub> within the variable range of active carbon from 0.5 to 2.5 grams.

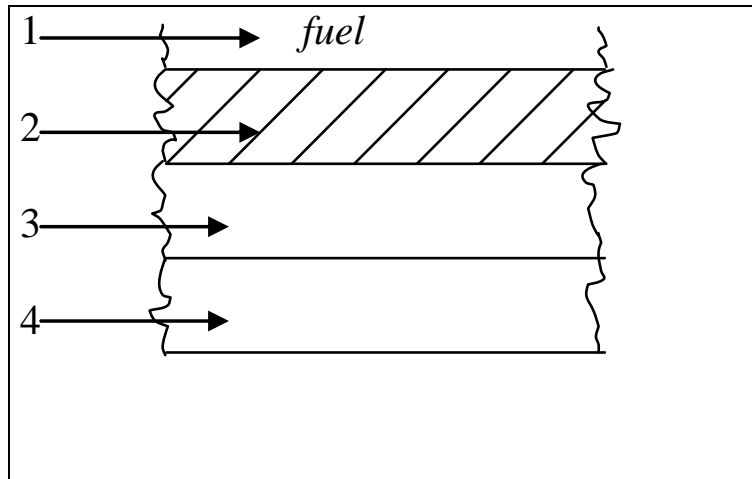
Natural rubber (NR) composition	Quantity of active carbon [g]				
	0.5	1.0	1.5	2.0	2.5
	System capacitance [F/g]				
MnCl <sub>2</sub>	9.0	13.5	16.2	20.6	28.8
SnCl <sub>2</sub>	4.7	8.1	12.4	15.0	19.4
SrCl <sub>2</sub>	23	27	33	36	39
ZnCl <sub>2</sub>	24	28	36	39	41

## 8. EXAMPLE APPLICATION OF POLYMER COMPOSITIONS

A) Anti-corrosion and anti-electrostatic protection of containers with dangerous materials.

Figure 11 presents a diagram of container coating being made of conductive material. A metal container can be coated with rubber electrolyte. Next, this conductive rubber is secured with a bituminous coating.





**Fig. 11.** Diagram of anti-static and anti-corrosion protection on conductive polymer composite: 1 – fuel, 2 – metal container, 3 – conductive polymer, 4 – bituminous coating

Based on the results being obtained in this study, polymer electrolytes in the polymer +  $\text{NaClO}_4$  + active carbon system can be applied (BR – 112  $\Omega$ , SBR – 125,2  $\Omega$ ) as anti-corrosion material for coating the fuel tanks, which is presented in Photo 1 below.



**Photo 1.** The photo shows polymer composite (SBR) testing.

For the rubber electrolyte (NR or SBR) system, the maximum quantity of divalent metal chloride amounts to 5 grams, which was added to the solution containing 3 grams of rubber (NR or SBR) in 40 cm<sup>3</sup> toluene. After adding a quantity of divalent metal chloride larger than 5 grams, difficulties begin to appear in the precipitation of rubber electrolyte in the form of homogenous gel from the solution in both composite systems. After adding active carbon to the rubber systems, the whole system increases its conductive values. Above 2.5 grams of active carbon per 3 grams of rubber (NR or SBR), the rubber electrolyte starts to become brittle and fragile. Therefore, it is possible to consider that such rubber systems, though have low conduction values, are stable at variable temperature.

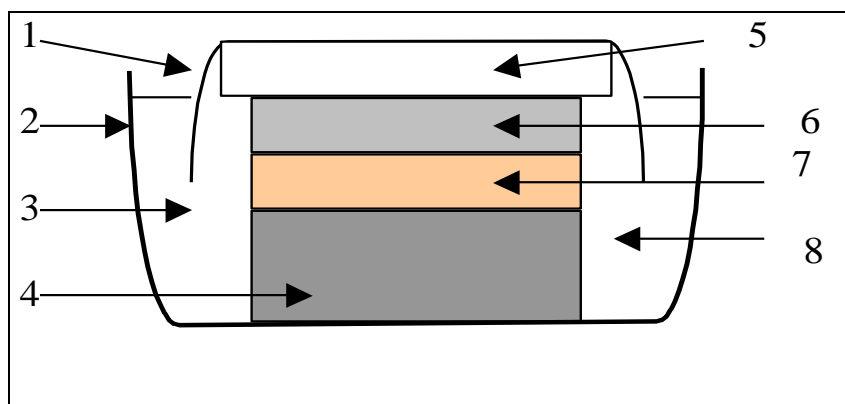
B) Sodium-based rubber batteries being made of NR, BR, SBR composites (Table 29)

Figure 12 presented below shows a diagram of battery which is composed of two metal electrodes (1, 2) isolated from one another by an isolator (3, 8). In the metal casing, being a negative pole [terminal] (1), a discharge electrode (5) is placed. In the centre of this discharge electrode, metallic sodium is placed (6).

In the metal casing, being a positive electrode (2), manganese dioxide is placed (4).

An essential element connecting the anode, i.e. metallic sodium, and the cathode, i.e. manganese dioxide, is a conductive polymer composed of NR, BR or BSR with sodium perchlorate (7), Table 1.

Negative electrode, i.e. metallic sodium (6), has to be connected only with the cathode, i.e. manganese dioxide (4) through a conductive polymer being made of NR, BR or SBR with the addition of sodium perchlorate (7).



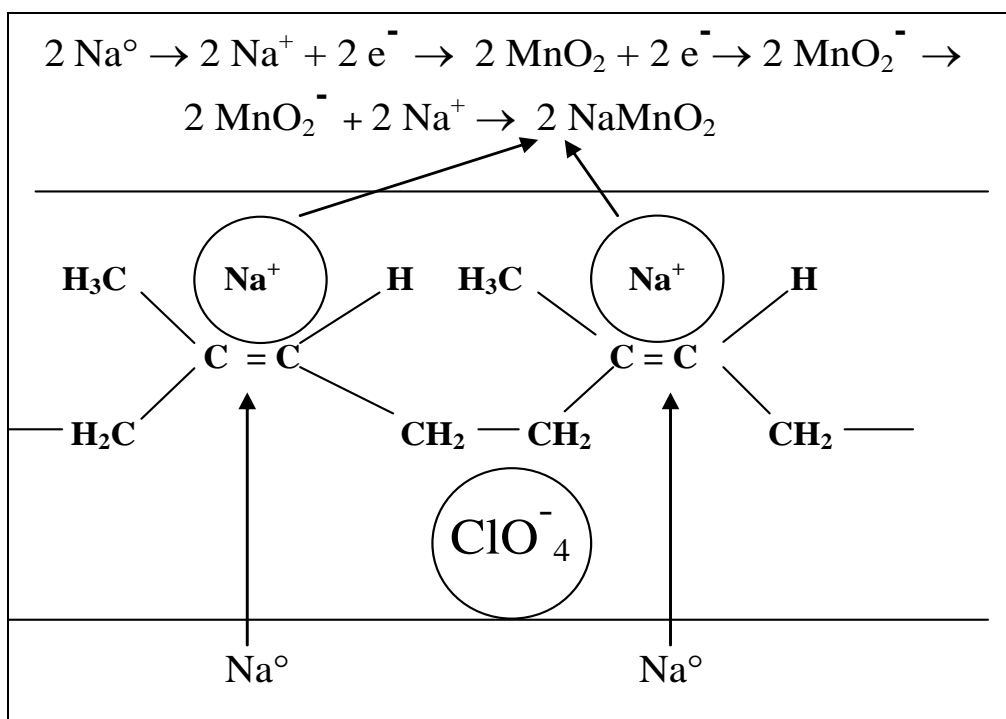
**Fig. 12.** Construction diagram of sodium-ion polymer battery: 1 – metal casing – negative pole (terminal), 2 – metal casing – positive pole (terminal), 3 – isolator, 4 – manganese dioxide, 5 – discharge electrode, 6 – metallic sodium, 7 – polymer + NaClO<sub>4</sub>, 8 – isolator.

On the anode, metallic sodium donates an electron to an energy receiver and moves to the cathode. On the cathode, manganese dioxide (MnO<sub>2</sub>) becomes reduced to manganate anion (MnO<sub>2</sub><sup>-</sup>). Sodium, in the form of cation (Na<sup>+</sup>), diffuses through a conductive polymer, such as NR, BR or BSR with sodium perchlorate, and incorporates into the crystal lattice of manganese dioxide.

The mechanism of conduction is similar to that in lithium button-cell [coin-cell] batteries, which is presented in the diagram below in Figure 13.

**Table 29.** Collected results for the conductivity of rubber composites (NR, BR, SBR) with NaClO<sub>4</sub> at a frequency of 50 kHz.

Polymer system	Temperature 273 K [S·cm <sup>-1</sup> ]	Temperature 293 K [S·cm <sup>-1</sup> ]	Temperature 303 K [S·cm <sup>-1</sup> ]	Temperature 323 K [S·cm <sup>-1</sup> ]
NR + NaClO <sub>4</sub>	2.0·10 <sup>-4</sup>	2.1·10 <sup>-4</sup>	2.3·10 <sup>-4</sup>	2.4·10 <sup>-4</sup>
BR + NaClO <sub>4</sub>	8.1·10 <sup>-5</sup>	8.2·10 <sup>-5</sup>	8.4·10 <sup>-5</sup>	8.5·10 <sup>-5</sup>
SBR + NaClO <sub>4</sub>	9.4·10 <sup>-3</sup>	9.5·10 <sup>-3</sup>	9.6·10 <sup>-3</sup>	9.8·10 <sup>-3</sup>



**Fig. 13.** Diagram and mechanism of operation of rubber battery being made of natural rubber (NR) composition

Such prototype rubber batteries have the following parameters:

- for a sodium-based natural rubber battery - 42 mA / 0.8 V,
- for a sodium-based butadiene rubber battery - 40 mA / 0.9 V
- for a sodium-based styrene-butadiene rubber battery – 48 mA / 1.2 V.

Rubber batteries have low voltage and current and therefore they can be connected serially or in parallel, depending on the needs, to obtain higher voltage-current values.

The performance characteristic of such batteries is relatively long. At the maximum current consumption (circuit closed), such a battery becomes discharged after three months.

## 9. CONCLUSIONS

A characteristic feature of the polymer compositions being obtained is stable specific conductance within the temperature range of 273 K to 313 K, which is presented in Tables 1 to 26 for doping agents in the form of divalent metal chlorides and in Table 29 for sodium perchlorate.

Sodium-based batteries being made of rubber compositions show constant voltage, irrespective of temperature (in the range of 273 K to 323 K).

The polymer compositions being presented in this paper can be used as materials in corrosion chemistry, electrochemistry and electrical engineering as new material compositions to produce capacitors with high capacitance and as materials for rubber batteries.

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