Peat and mineral anticaking agents for powdered nitrile-butadiene rubbers

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Abstract. The article discusses caking of loose materials and main methods of its prevention. The main characteristics of nitrile-butadiene rubber are outlined. It is possible to obtain hydrophobic-modifying additives during thermochemical degradation of organic matter peat. The author presents a method for analyzing anticaking agents based on peat and mineral compositions. The comparative analysis of the effectiveness of anticaking agents made of kaolin and chalk is made. It is established that the treatment of powdered nitrile butadiene rubber with a hydrophobically modified chalk makes it possible to reduce its ability to cake by 22.5 times during long-term storage compared with the control sample.

1. Introduction

Organic, mineral, amorphous and crystalline substances belonging to the class of high-molecular compounds are widely used in various areas of industrial production. Amorphous polymers that possess high-elasticity properties – elastomers are of particular significance. Compared to other polymers they have a lower glass transition temperature. Natural and synthetic elastomers – rubbers – possess elasticity, hydrophobicity and electrical insulation properties [1].

Currently, the range of rubber products has more than 36,000 items with the separation of raw materials for their manufacture into general- and special-purpose rubbers. Particularly, nitrile-butadiene rubbers (NBR) are the products of polymerization of butadiene and acrylonitrile. NBR are one the most spread special-purpose rubbers that are currently produced in about 20 countries.

Nitrile butadiene rubbers and their vulcanizates are highly resistant to the exposure of mineral oils and fats. Oil and benzine resistance of such rubbers increases along with the increase of content of acrylic acid nitrile in them. NBR vulcanizates compare favorably to other rubbers vulcanizates because of their higher resistance to heat aging and abrasion. Rubber products based on NBR can be used for a long time at 120°C with air exposure and at 150°C in different oils [1]. Therefore, they are used in the manufacture of various rubber technical products: rings, bushings, hoses, cuffs, etc. Rubber based on them is used as anti-corrosion materials for internal coatings of devices operating in aggressive environments.

Nitrile-butadiene rubbers are produced in briquetted, granulated or powder form. Nitrile-butadiene rubbers are stored in polyethylene, paper or tissue bags.

The powder form of rubber allows using of modern loose material dispensers on industrial production lines. This increases the accuracy of dispensing of components and consequently increases the quality of end product. In addition, production costs are reduced due to partial automation of the production cycle. However, the storage of rubber in a powder form results in particles sticking
together due to complex interaction of different forces. The process of caking is aggravated by the storage of bags with powdered rubber under pressure.

Caking refers to the ability of loose materials to lose their flowability during long-term storage due to the interactions between their particles. The main causes of caking include [2, 3, 13]:

- appearance of capillary forces due to an increase in the moisture content of the loose material;
- formation of crystallization bridges between particles as a result of the growth of crystals from substances dissolved in water;
- occurrence of autoadhesion interactions at the interface of two or more particles.

Capillary forces and formation of crystallization bridges in the «moistening – drying» cycle are crucial for disperse soluble systems, for example, mineral fertilizers.

In the case of rubbers that possess hydrophobic properties, autoadhesion forces are the main factor of caking. Autoadhesion is considered to be a diffusion process. It depends on the temperature and can occur both with pressure and without it. Pressure has a positive effect on the process of autoadhesion due to the increase in the contact area. The increase in temperature weakens the intermolecular bonds and intensifies thermal motion of the segments of rubber macromolecules. This facilitates the mutual penetration of areas of the hydrocarbon chains of two or more particles that are in direct contact.

In order to avoid caking of powdered rubbers and other loose materials, they are occasionally dried or stirred. In addition, methods of dry or wet surface treatment of particles or granules of loose bodies are used to avoid caking. The main task of such treatment is to prevent or minimize the moistening of the particles and their contact with each other during storage and transportation.

Powdered kaolin, chalk, kieselguhr, talc and other materials – inert fine dispersed systems – are used as anticaking agents of dry surface treatment (or dusting) for powdered rubber. Such additives, with the exception of talc, do not possess hydrophobic properties. In the case of mineral fertilizers, they are used to absorb liquid or gaseous moisture, compensating for the hydration of the water-soluble matter. It is obvious that, as a result of the particles surface treatment of hydrophobic rubber with a hygroscopic substance, an upper layer of hydrophilic mineral carrier is formed between these particles. In relation to such a layer, undesirable caking factors described above may occur. However, inert finely dispersed systems that do not initially possess hydrophobic properties can be modified with various water-repellent additives. Such a composition can prevent the main causes of caking of powdered rubber and a number of other bulk materials.

Today there is a relatively large number of hydrophobic additives that are obtained from products and wastes of oil-processing. Organosilicon liquids (or silicone oils) as well as some products of wood chemical processing are better water-repellant agents. Analysis of the results of scientific research on the thermochemical processing of peat, carried out in Russia in the twentieth century and the beginning of the 21st century [5–8], made it possible to develop a new direction in the use of compounds extracted from its organic matter. Their physical and chemical properties allow hydrophobic modification of a wide range of mineral dispersed materials. Despite the fact that the main part of the organic matter of peat consists of hydrophilic components [9-11], it also contains bitumens consisting of waxes, resins, oils and paraffins. Bitumens obtained from peat are hydrophobic components of peat organic matter [1, 3, 12]. It is known that organic matter of peat undergoes chemical composition change during its thermal processing. The character of such changes depends on the amount and time of thermal exposure. As a result of thermochemical conversion, the organic matter of peat decomposes into individual components, which transit from the class of hydrophilic into the category of hydrophobic matters. Moreover, these are of all aggregative states (solid, liquid, gaseous). Thus, one of the main tasks is to obtain and apply them to the treated surface. This method was implemented upon obtaining of model hydrophobically-modified cement [12]. Currently, it is analyzed whether it is possible to replicate it to other types of mineral dispersed materials. In particular, this paper proposes the treatment of hydrophilic materials – chalk and kaolin – for their subsequent use as anticaking agents for NBR according to the developed method.
2. Materials and methods
The approach is based on the fact that chalk and kaolin are part of the basic composition of a number of rubber mixtures used for specific operating conditions: roll coatings in the textile industry, for shock absorbers with benzine and oil resistance, for various protective coatings, etc. Moreover, their amount in the compositions can vary in a wide range of concentrations.

The method of hydrophobic treatment of kaolin and chalk was as follows. Peat hydrophobic semi-finished product obtained from cotton-grass-sphagnum peat with decomposition degree of 25-30% was introduced to the mineral material. To increase the particle dispersion and homogeneity of their mixing, as well as to create conditions for the formation of primary adhesion contacts, the mixture was placed in a ball mill. An additional grinding of the mixture was carried out in the mill for 5 minutes with a speed of 56-60 rpm. The choice of parameters was made based on the design features of the mill, as well as the optimal quality characteristics of the organomineral mixture.

The obtained two-component composition was activated in a laboratory reactor installation according to the method described in detail in the previous papers [4, 12]. During activation, a protective water-repellent film coating is formed on the surface of the mineral particles from bitumen compounds released during heat treatment. The presence of the film does not adversely affect the flowability of the powder.

The hydrophobic composition was used for the treatment of powdered NBR with particles size lower than 1 mm. The concentration of the components was: 90% of NBR and 10% of the anticaking additive. To model the process of storage under pressure, the control and experimental samples were poured into a special device (Fig. 1). A 1 kg weight was placed on the cylinder head, which created additional pressure on the material.

![Figure 1. Scheme of the installation for determining of caking during the storage of dispersed materials](image)

The experiments of caking of the samples were carried out in seven and thirty days of storage under a pressure of 14.2 KPa, a temperature of 20-25°C and a relative humidity of 70-80%.

Upon expiration of the storage period, the contents of the cylinders (compacted NBR, Fig. 2) with the respective groups of samples were removed from the internal detachable device and subjected to pulsed destruction on a specially designed experimental setup (Fig. 3) using the following procedure.
Figure 2. Appearance of the experimental sample of rubber located in a two-piece cylinder

Figure 3. Experimental setup for determining caking of samples of loose materials: 1 - stand, 2 - set of sieves, 3 - experimental sample, 4 - tripod; 5 - hollow tube; 6 - crystallizer

A test sample was put to the plastic tube fixed in the laboratory tripod, the top part of which was at a height of 150 cm.

Moving under the action of gravity down the tube with the acceleration of free fall, it fell into the crystallizer and partially or completely destroyed. Next, the contents of the crystallizer were subjected to sieve analysis using sieves with round cells of dimensions 10, 7, 5, 3, 2, 1 mm. The purpose of the analysis was to determine the mass of material in loose and aggregated states. In addition, the degree of aggregation of particles.

3. Results & Discussion

The experiments allowed establishing the following change in the quality characteristics during storage of nitrile-butadiene rubbers (Table 1). In the first seven days, the proportion of caked mass (the oversize fraction on a sieve with a mesh size of $d = 1$ mm) in the control sample was 57.27%. It is characteristic that its main part (39.05%) remained on a sieve with a mesh size of $d = 10$ mm. In experimental samples, the best indicators were obtained by treating NBR with hydrophobically-modified chalk – 1.82%. When hydrophobic kaolin was used as an anticaking agent, the caking rate was 13.8 times higher – 25.19%. It is noteworthy that relatively large agglomerates ($d > 5$ mm) did not
form when using hydrophobically modified chalk in seven days. With the increase in the storage time up to 30 days, the trends identified above persist, and the quality indicators deteriorate significantly – in the control sample, the amount of caked mass is 96.55%. Moreover, the majority are agglomerates with a size greater than 10 mm (Figure 4, a). In the samples treated with hydrophobically-modified chalk and kaolin the caking rates were 11.03% and 96.43%, respectively. Moreover, the main part of the sample, treated with chalk, almost completely retained its flowability (Figure 4, b). The substantial part of the material (~ 89%) passed through the sieve with a 1 mm mesh.

![Image](https://example.com/image.png)

**Figure 4.** Appearance of samples of NBR destroyed after 30 days storage:
- a - control; b - treated with hydrophobically-modified chalk

**Table 1.** Comparative sieve analysis of the control and experimental samples of powdered nitrile-butadiene rubber after storage

| Sieve residue, mm | Control sample of NBR | Fraction content, g / % | Experimental sample of NBR treated with hydrophobically-modified chalk | kaolin |
|------------------|-----------------------|-------------------------|---------------------------------------------------------------------|--------|
|                  | 7 days of storage      |                         |                                                                     |        |
| $d > 10$         | 11.78 / 39.05          | 0 / 0                   | 0.94 / 3.72                                                         |        |
| $7 < d < 10$     | 0.92 / 3.05            | 0 / 0                   | 0.39 / 1.54                                                         |        |
| $5 < d < 7$      | 0.54 / 1.78            | 0 / 0                   | 0.16 / 0.64                                                         |        |
| $3 < d < 5$      | 0.75 / 2.48            | 0 / 0                   | 0.3 / 1.19                                                          |        |
| $1 < d < 3$      | 3.29 / 10.91           | 0.44 / 1.82             | 4.57 / 18.10                                                        |        |
| $d < 1$          | 12.89 / 42.73          | 23.80 / 98.18           | 18.89 / 74.81                                                       |        |
| Total weight, g  | 30.16 / 100            | 24.24 / 100             | 25.25 / 100                                                         |        |
|                  | 30 days of storage     |                         |                                                                     |        |
| $d > 10$         | 28.06 / 94.12          | 0.5 / 2.14              | 20.18 / 92.36                                                       |        |
| $7 < d < 10$     | 0.13 / 0.43            | 0.1 / 0.43              | 0.11 / 0.51                                                         |        |
| $5 < d < 7$      | 0.09 / 0.30            | 0.1 / 0.43              | 0.25 / 1.14                                                         |        |
| $3 < d < 5$      | 0.13 / 0.43            | 0.09 / 0.38             | 0.13 / 0.59                                                         |        |
| $1 < d < 3$      | 0.38 / 1.27            | 1.79 / 7.65             | 0.4 / 1.83                                                          |        |
| $d < 1$          | 1.03 / 3.45            | 20.81 / 88.97           | 0.78 / 3.57                                                         |        |
| Total weight, g  | 29.81 / 100            | 23.39 / 100             | 21.85 / 100                                                         |        |
Thus, the choice of chalk as a mineral carrier for the production of hydrophobic anticaking agents makes it possible to fully implement the principle of forming on its surface solid bitumen nano-films extracted from organic matter of peat during thermochemical exposure [4, 12]. In this regard, it was necessary to establish how the anti-agglomeration properties of natural chalk change after its hydrophobic treatment.

For this purpose, a series of experiments with NBR treated with powders of same dispersion from natural and hydrophobically-modified chalk. The results of the experiments (Table 2) demonstrate that the natural chalk, which is a typical hydrophilic material, solves the issues of caking decreasing only for a relatively short time of storage.

| Sieve residue, mm | 7 days of storage | Fraction mass of NBR on the sieve, % | 30 days of storage |
|------------------|------------------|-------------------------------------|-------------------|
|                  | control          | Treated with chalk                  | Treated with hydrophobically-modified chalk |
| $d > 10$         | 68.34            | 0.00                                | 0.00              |
| $7 < d < 10$     | 3.79             | 0.00                                | 0.34              |
| $5 < d < 7$      | 1.54             | 0.00                                | 0.26              |
| $3 < d < 5$      | 2.42             | 0.12                                | 0.52              |
| $1 < d < 3$      | 9.38             | 4.22                                | 2.88              |
| $d < 1$          | 14.54            | 95.66                               | 96.01             |
|                  | $d > 10$         | 92.95                               | 58.21             |
|                  | $7 < d < 10$     | 0.56                                | 0.00              |
|                  | $5 < d < 7$      | 0.37                                | 0.00              |
|                  | $3 < d < 5$      | 0.56                                | 0.96              |
|                  | $1 < d < 3$      | 1.61                                | 7.07              |
|                  | $d < 1$          | 3.95                                | 33.76             |

The experiment time that did not change the tendency to cake for the samples treated both with chalk and hydrophobically-modified chalk was seven days. With a longer storage time (30 days), a sufficiently high caking ability, which is approximately 63% of the control sample (data from the analysis of the fraction above 10 mm), is observed in the nitrile-butadiene rubber treated with chalk. Most likely this is due to the sorption of water vapor from the environment, which eventually begins to condense and moisten the chalk particles during storage. In addition, with the adhesion of rubber particles, moisture condensation occurs on the chalk particles with the subsequent formation of rather large lumps.

In rubber treated with hydrophobic-modified chalk, the caking ability was only 2.3% of the indicator of the control sample. Moreover, the vast majority of it (practically 89%) turned out to be in the undersize product when sifting on a sieve with a mesh of less than 1 mm.

4. Conclusion
Thus, it is experimentally determined that hydrophobic processing of chalk with bitumen compound of peat increases its efficiency as an anticaking agent for powdered nitrile-butadiene rubbers by 2.6 times compared standard chalk and by 22.5 times compared to the control sample. Moreover, a lower price of chalk as a raw material compared to kaolin will increase the economic efficiency of its use in technological processes of obtaining of different types of industrial-rubber products.
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