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IMPROVEMENT OF CRYSTALLISATION STAGE IN PRODUCTION OF SULFAMIC ACID

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Abstract: Identified the basic requirements for the quality of sulfamic acid in all areas of its application. Was described by a method of industrial production technology sulfamic acid. There was designed laboratory installation to study the crystallization process. The paper studies the influence of temperature and cooling rate on the size distribution, the mass fraction of the basic substance, bulk density and flowability. There was defined dependence of the yield of the target substance from the initial and final temperature selection. Recommendations on production sulfamic acid with the designed size of crystals are given.

Currently, the sector of household chemicals has good prospects. The level of consumption of various commodities in this segment (detergents and cleaners, washing powder, etc.) per capita is much lower than in Europe and the United States, but it is constantly growing. Is amended and expands range of products, producers complement the product line products in different price ranges [1].

SulfAmic acid (**SAA**) gained widespread in industry, namely:

– in the production of detergents;

– cleaning of industrial equipment from mineral deposits, "milk" and "beer" stone;

– removal of carbonate deposits (limescale) with heat-exchange equipment, radiators, household dishware;

– production of fireproof materials and herbicides;

– processing treatment of oil wells in order to increase reservoir recovery.

In all application sectors of sulfamic acid presented a series of stringent requirements for particle size distribution, bulk density, flowability, physical-chemical properties, transport and storage of the finished product. The finished product has to comply with the following parameters: the concentration of the target substance is not less than 99.5 %; mass fraction of sulfate – ions to 0.04 %; content of water-insoluble impurities not more than 0.08 %; bulk density of 1200 kg/m^3; flowability 2–3 s.

Despite the fact that the production of sulfamic acid in Russia can completely provide for the needs the internal market, consumers prefer acids imported from China, India and Indonesia. A comparative analysis of technologies of foreign competitors with the domestic producer [2], come to the fore the problem of saving energy and resources, as well as improvement of quality indicators. Industrial synthesis of sulfamic acid comprises reacting urea with sulfur trioxide and sulfuric acid, i.e. with oleum

$$NH_2CONH_2 + SO_3 + H_2SO_4 \rightarrow 2NH_2SO_3H + CO_2\uparrow.$$

The basis of the process of obtaining the sulfamic acid is the reaction of sulfonation urea with oleum with a mass fraction of 24 % sulfuric anhydride at

a temperature of 60…70 ºC, followed by isolation of the finished product on water at a temperature of 10…20 ºC, filtration and drying.

Crystallization stage plays a crucial role in shaping the quality characteristics of the products [3, 4]. The importance of crystallization also stresses the fact that problems at this stage affect not only the quality of the finished product, but also create additional energy costs in the final stages of production. On the basis of the applied technology (sulfonation urea → selection → crystallization → filtration → drying) it is necessary to improve the crystallization stage.

The main technological parameters that influence the shape and size of the crystals are the cooling rate and hydrodynamic regime in the reactor. Completeness of recovering the target substance and the formation of crystalline structure is also dependent on the initial and final temperatures of the crystallization process. Investigation of the crystallization process of sulfamic acid was conducted on a laboratory setup consisting of a thermostat with a thermometer, a drive with a frequency regulator, reactor with the coil and a stirring apparatus (Fig. 1).

The reactor was filled with distilled water and with the fed hot water in the coil it is heated to the required temperature. The required initial temperature of the slurry T_0 is maintained by a thermostat. The suspension is kept at a predetermined temperature until complete dissolution of the acid.

The cooling water is supplied in the coil after keeping for 30 minutes and then suspension cooled to a final temperature of 15 ºC. The resulting slurry of sulfamic acid is filtered on a Buchner funnel. Investigation of the crystallization process was carried out in two directions: the influence the cooling rate and temperature regime on the particle size distribution of sulfamic was determined acid and the effect of temperature of the crystallization and filtration on impurity content, concentration and yield of the desired substance was calcualated.

To assess the effect of cooling rate on particle size distribution there were performed three series of experiments. In the first series at an initial slurry temperature of 60 ºC cooling rates were 0,01 ºC/min; 0,1 ºC/min; 0,2 ºC/min. In the second and third series the initial temperature was respectively 70 and 80 ºC, with the same cooling rates (Fig. 2). From these graphs it can be concluded that the maximum size of the crystals of sulfamic acid (40…45 microns) was obtained at a cooling rate of 0,01 ºC/min and the initial temperature of the slurry 80 ºC. A number of experiments for revealing crystallization parameters, which have a significant impact on the trapping of impurities by crystals and yield of sulfamic acid, were conducted.

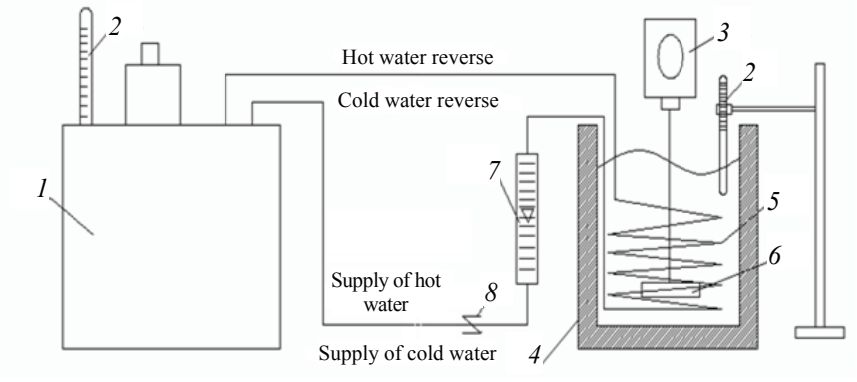
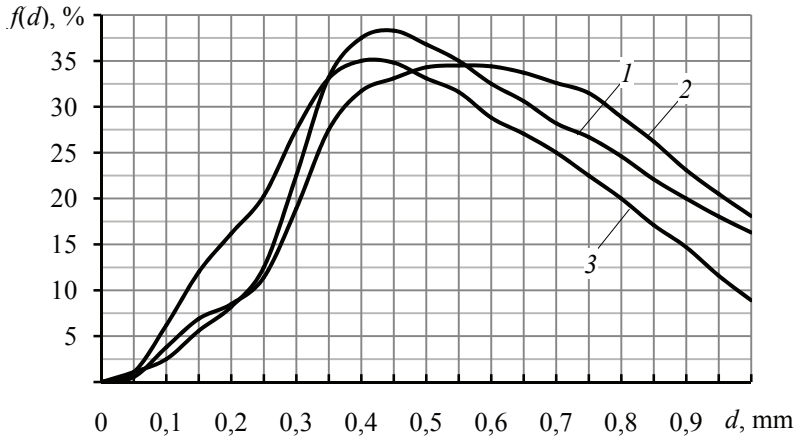


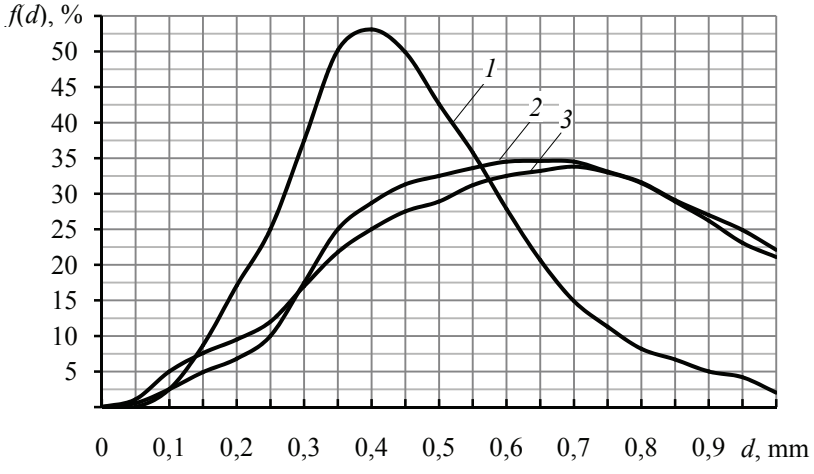
Fig. 1. The laboratory setup for the study of the crystallization process of sulfamic acid:
1 – thermostat; *2* – thermometer; *3* – drive with the frequency regulator; *4* – reactor; *5* – coil; *6* – stirring device; *7* – rotameter; *8* – clip

In the investigations we used solutions of sulfamic acid, prepared by sulfonation of urea 15 % excess of oleum. The feed solution had the following composition, %: NH_2SO_3H – 41,4; H_2SO_4 – 48,9; $(NH_3)_2SO_4$ – 9,65. As a result of the analysis and comparison of the composition of the solution of sulfamic acid and the crystalline product it was found to be the main impurity, contamination level which exceeds the permissible values in the solution, is ammonium sulfate - the main product of hydrolysis of sulfamic acid.

Given that the sulfonation urea is carried out with 15 % excess of oleum, the presence an acidic environment increases the rate of hydrolysis (to 2…2.5 times), and decreases the temperature of initiation of hydrolysis. In order to mitigate the high level of acidity in the crystallization stage, sulfomass is fed on the water to bring the total mass concentration, in terms of sulfuric acid, in the range 270…300 g/dm^3.

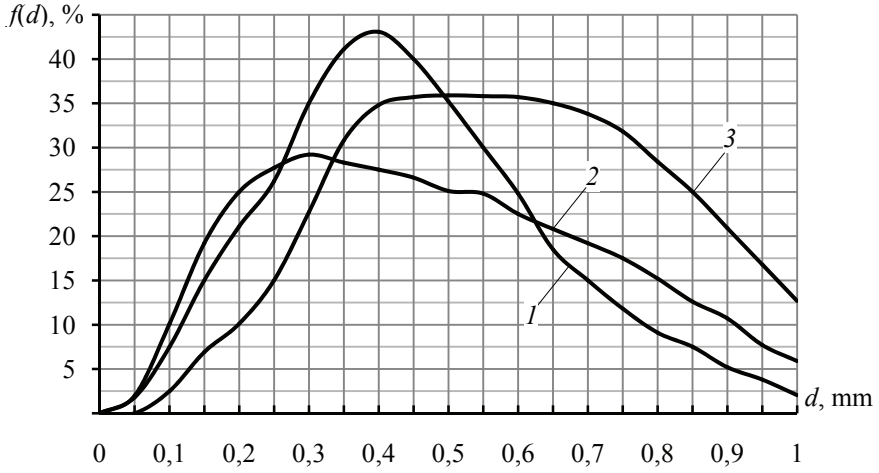


a)



b)

Fig. 2. The distribution function of sulfamic acid crystals depending on the initial temperature of the solution at a cooling rate of 0,01 ºC/min (*a*), of 0,1 ºC/min (*b*): *1* – 60 ºC; *2* – 70 ºC; *3* – 80 ºC



c)

Fig. 2. Continued. The distribution function of sulfamic acid crystals depending on the initial temperature of the solution at a cooling rate of 0,2 ºC/min (*c*):
1 – 60 ºC; *2* – 70 ºC; *3* – 80 ºC

In this regard, the experiments were conducted in two stages: was studied the mechanism of transition of specified impurity in crystalline the precipitate of sulfamic acid was determined influence of temperature regime selection and filtration on yield the target product.

During research crystallization temperature interval was varied in the range of 20 to 80 ºC. In the experiment was determined influence temperature regime on the trapping of impurities by the crystals of sulfamic acid. So offset the initial crystallization temperature the region of higher values and the shift of the final temperature of selection in the region of lower values lead to a definite decrease in the content of impurities (Fig. 3).

In the second stage of the study was defined the influence of temperature of selection and filtration on the product yield and the mass fraction of sulfamic acid.

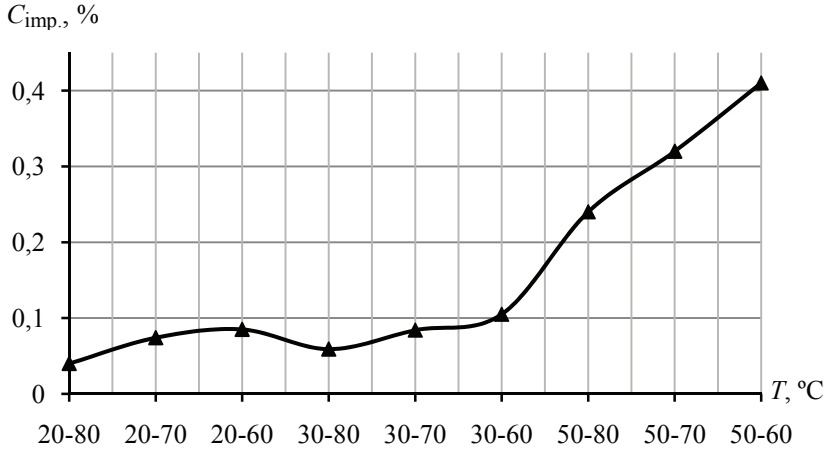


Fig. 3. The dependence of the mass fraction of impurities from the temperature range of crystallization

Two series of experiments were performed. In the first series, filtering was carried out at a temperature corresponding to the final temperature of selection (in the range of 20 to 60 ºC). In the second series, the filtration temperature was constant (20 ºC) while the temperature of selection was varied in the same range as that in the first series. Based on these results were constructed graphs (Fig. 4, 5).

On the basis of these experiments it can be concluded that the shift of initial crystallization temperature into the region higher values and the offset of final temperature of selection into the region lower value leads to reduction of the content of impurities (from 0.58 to 0.06 %). It was also established that the smallest the hydrolysis occurs at a temperature of 20 ºC selection – from 0,3 to 0,6 %. The losses of product due to the hydrolysis are from 1.5 to 3 % with increasing temperature of selection. Thus, reducing temperature of selection to 20 ºC may lead to an increase in yield of 1,8…2,3 %.

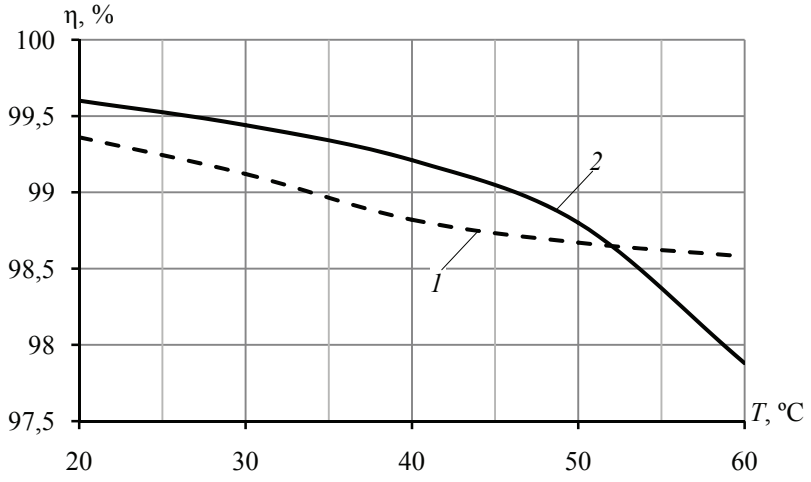


Fig. 4. Influence of temperature selection and filtering on the yield of sulfamic acid:
1 – the first series; *2* – the second

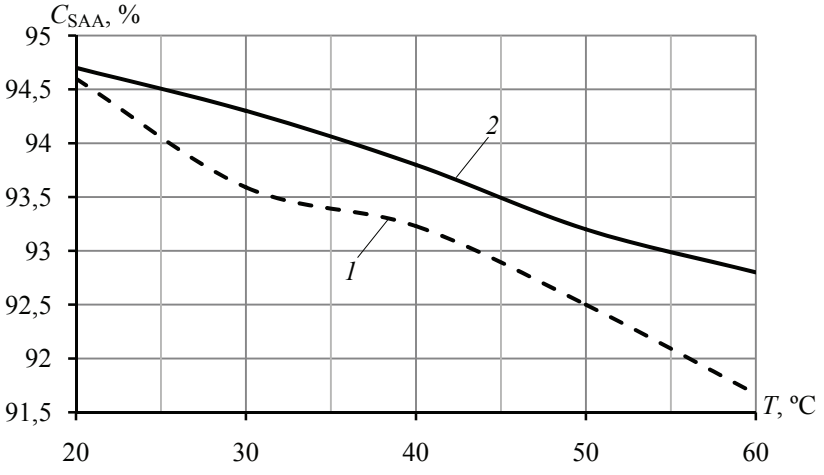


Fig. 5. The dependence of the mass fraction of sulfamic acid from temperature mode:
1 – the first series; *2* – the second

Implementation of the received data into the existing production technology will allow obtaining sulfamic acid with mass fraction of the basic substance to 99.5 %, with a reduction of content of sulfate ions to 0.06 %, with a bulk density and an average of crystals diameter closest to foreign analogues.

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Совершенствование стадии кристаллизации в производстве сульфаминовой кислоты

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Ключевые слова и фразы: выход целевого продукта; гранулометрический состав; кристаллизация; массовая доля основного вещества; насыпная плотность; сульфаминовая кислота; сыпучесть.

Аннотация: Определены основные требования к качеству сульфаминовой кислоты во всех областях ее применения. Приведено описание промышленной технологии получения сульфаминовой кислоты. Разработана лабораторная установка для изучения процесса кристаллизации. Исследовано влияние температурного режима и скорости охлаждения на гранулометрический состав, массовую долю основного вещества, насыпную плотность и сыпучесть. Определена зависимость выхода целевого вещества от начальной и конечной температуры выделения. Разработаны рекомендации для получения сульфаминовой кислоты с желаемым размером кристаллов.

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Vervollkommnung des Stadiums der Kristallisation in der Produktion der Amidosulfonsäure

Zusammenfassung: Es ist der Einfluss des Temperaturregimes und der Geschwindigkeit der Abkühlung auf den granulometrischen Bestand, den Massenanteil des Hauptstoffes, die aufgeschüttete Dichte und die Schüttbarkeit untersucht. Es ist die Abhängigkeit des Ausgangs des zweckbestimmten Stoffes von der Anfangs- und Endtemperatur der Absonderung bestimmt.

Perfectionnement du stade de la cristallisation dans la production de l'acide de sulfamide

Résumé: Est étudiée l'influence du régime de la température et de la vitesse du refroidissement sur la composition granulométrique, la part de masse de la matière essentielle, la densité en vrac et la pulvérilence. Est définie la dépendance de la sortie de la substance de but de la température initiale et finale du dégagement.

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