UDC 66.094.524.55
DOI: 10.15587/1729-4061.2020.210718

TECHNOLOGY OF OBTAINING WATER-SOLUBLE SURFACE-ACTIVE SUBSTANCES BY THE METHOD OF PHENOL SULFOMETHYLATION

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The object of this study is a technology of the new surface-active substances (SAS) based on sulfomethylated phenol. The study's aim was to improve the technology by a catalytic method, implying the development of industrial schemes for the synthesis processes.

During phenol sulfomethylation, the active conversion of monomers into polymeric substances starts only at a temperature of 110–120 °C; the surface-active substances with an optimal polymeric composition were obtained only at a temperature of 130 °C. In the reaction of phenol sulfomethylation in a water environment at a temperature below 90 °C, obtaining SAS with the required properties takes more than 9 hours. The significant disadvantages of this technique are the relatively low yield of the target product and a significant amount of free phenol in the finished product (over 15 percent).

It is known that a more powerful and less risky technique to accelerate the reaction than rising the temperature is catalysis.

This study investigated the reaction of phenol sulfomethylation under conditions of interphase catalysis. This has made it possible to improve the main technological parameters: the reaction temperature was reduced from 130 °C to 90 °C, the process duration was shortened to 3 hours, to process was conducted at atmospheric pressure. The catalyst used was a cation-active SAS: cetyltrimethylammonium bromide. This makes it possible to simplify the technological scheme of obtaining SAS, that is, to use less energy-intensive and cheap reactors.

A benefit of the proposed technology is the low-waste, single-stage production, and the use of available raw materials: phenol, formaldehyde, and sodium sulfite. During the study, the products were obtained that are similar, in terms of the surface-active properties, to the NF Dispersant, which is widely used in the industry. This makes it possible to expand the range of multifunctional surface-active substances with better bio destruction than products based on naphthalene and lignin.

According to the results of studying the samples obtained, the scope of their application has been proposed. The resulting products have been tested, with positive results, as the anion-active SAS, used as dispersants in the production of organic dyes, as aligners when dyeing textiles, and as plasticizing additives for concrete mixtures

Keywords: phenol, formaldehyde, cetyltrimethylammonium bromide, sulfomethylation, interphase catalysis, surface-active substances, dispersant

Received date 27.07.2020
Accepted date 21.08.2020
Published date 31.08.2020

1. Introduction

The modern market puts forward high requirements for the quality of synthetic surface-active substances (SSAS) and opts for multifunctional products [1]. There are new approaches to methods of obtaining SAS. They imply the simplification and cost reduction of the technology, with the focus shifting to environmental protection.

Among the anion-active multifunctional SASs, those substances are in greatest demand that perform simultaneously the functions of dispersants of solids and stabilizers of water and non-water systems. These include, first of all, the NF Dispersant, S3 Superplasticizer, SS Dispersant, lignosulfonates.

However, the low bio destruction of naphthalene derivatives and complex and expensive technology of obtaining such substances encourages the search for alternative SAS. Therefore, the use of phenol, which is an affordable raw material and has better biodegradation compared to naphthalene and lignin, has been suggested as a starting raw material. The production of multifunctional SASs based on phenol and formaldehyde has not been studied in detail. Therefore, it is a relevant task to develop their synthesis, to investigate their properties, and to devise an industrial, high-efficient, easy to operate, environmentally friendly technology of their production, which is of significant interest, both scientifically and practically.

2. Literature review and problem statement

Among all surface-active substances, the anion SAS enjoyed the greatest demand on the world market in 2019, due to their low price [2]. Synthetic multifunctional anion-active SASs have been the leaders in terms of their application in many sectors of national economies. These are the unique surfactants because they represent water-soluble polymers with several functional groups [3]. In the industry, they are used in the production of finishing forms of dyes and pigments [4–6], when coloring fabrics, paper, leather. They are the plasticizers of concrete mixtures [7] used in residential, industrial construction, and the construction of highways [8].

The most well-known multifunctional SASs, which are used as dispersant and stabilizers, are the products of the condensation of naphthalene sulfonic acid with formaldehyde. Naphthalene derivatives are applied as agents to clean up oil spills [9], to stabilize suspensions of raw porcelain tiles [10], as the superplasticizers of cement mixtures [11, 12], concrete additives [13], etc.

Also widespread in many industrial areas are lignosulfonates (sulfite alkalis) – the products of cellulose processing [14, 15]. They are used as the dispersants of cement supplements [16], of concrete [17, 18], as dye dispersants [19], water-coal suspension [20], and so on.

However, SASs based on lignin and naphthalene derivatives possess low bio destruction [21]. Biodegradation of aromatic hydrocarbons plays an important role in cleaning the environment and is widely studied. The works published in recent years have shown that the issue of the bio destruction of naphthalene and its derivatives [22] and lignin [23] in natural conditions and in the industry is quite relevant. Paper [24] addressed the anaerobic conditions of carbohydrate biodegradation, including naphthalene. The authors successfully cultivated the strains of microorganisms that survive in an environment containing naphthalene derivatives; in the amount not exceeding 0.01–10 mg/kg of microbiomes. Work [25] investigated the possibility of naphthalene bio destruction in soils and obtained a positive result; however, the presence of *n*-heptane significantly reduces the performance, affecting the viability of microorganisms in such an environment. Therefore, the issue of replacement of naphthalene as a raw material for obtaining SAS is relevant [26]. The improvement of the technology, as well as the search for a raw material base for obtaining similar SAS, started in the 1960s. At that time, phenol and formaldehyde were chosen as source raw materials.

Study [27] describes a method of phenol sulfomethylation by treating it with a mixture containing formaldehyde, heptahydrate sodium sulfite, sodium hydroxide, and water. The treatment was carried out at a temperature of 95 °C for 6 hours. The resulting solution was acidified and concentrated in crystalline sediment. Under these conditions, the yield of monosulfomethylated phenol amounted to 28–37 % by weight with a significant amount of disulfomethylated phenol. The concentrated solution is proposed to be used to produce impregnating solutions.

At present, the scientific literature has almost no information about the synthesis of new multifunctional anion-active SAS based on phenol.

Several techniques and technologies of obtaining water-soluble SASs based on phenol and formaldehyde are described.

Recent studies have found that the most suitable method is the sulfomethylation using sodium sulfite in an alkaline environment.

The most common method is the method of obtaining such SAS in several stages.

Paper [28] used sodium bisulfite, sodium sulfite, phenol, and formaldehyde as raw materials. Sulfomethylated phenol-formaldehyde resin was obtained by phenol sulfomethylation and condensation polymerization. At the first stage, when obtaining sodium hydroxymethylsulphonate, the optimal conditions were *n* (sodium bisulfite):*n* (sodium sulfite):*n* (formaldehyde)=1:1:2,3; the reaction temperature, 60 °C; the reaction time, 3 hours. The optimal conditions for phenol sulfomethylation were *n* (sodium hydroxymethylsulphonate):*n* (phenol)=0.7:1; the reaction temperature, 90 °C; the reaction time, 1 hour; pH=9. The optimal conditions of condensation polymerization were *n* (sodium hydroxymethylsulphonate):*n* (phenol):n (formaldehyde)=0.7:1:1.2; pH=9; the reaction temperature, 100 °C; the reaction time, 3 hours. The disadvantages of this method are the multistage course of the process and the long duration of synthesis.

Paper [29] describes the obtaining of fillers based on phenol, lignin, and formaldehyde. The methylated lignin-novolac resin was synthesized using modified methylated lignosulfonate. The replacement of phenol with ammonium lignosulfonate was 30 % by weight. The molar ratios of phenol:lignosulfonate and phenol-lignosulfonate:formaldehyde were 1:0.27 and 1:0.76, respectively. The synthesis involved four stages. Initially, there was a reaction of lignosulphonate, phenol, and oxalic acid (0.5 % by weight of the ratio to phenol) at a temperature of 100 °C. Aldehyde (37 % by weight) was then added; the heating lasted for 90 minutes. After the second stage, the water was distilled off. The resin was washed with water. The described method also has disadvantages: the multi-stage course of the process and the content of free phenol in the product that exceeds the amount of lignin-novolac resin.

Paper [30] reports the results of studying the processes and composition of products obtained via the consistent effect on phenol exerted by formaldehyde and sodium sulfite. The stage of sulfomethylation was carried out at a temperature of 90 °C for 2.5 hours. The main products of the reaction are sodium salts of sulfo-acids containing fragments with methyl groups in their structure, whose number depends on the synthesis conditions. The disadvantage of this method is that it produces mainly monomers with some content of di- and trimers and the complete absence of oligomers. The resulting products are suggested to be used as additives to concrete mixtures.

After analyzing data in the literature, a series of studies of the reaction of phenol sulfomethylation were conducted in order to obtain SAS [31]. Studies of the interaction of phenol, formaldehyde, and sodium sulfite were performed in a water-alkaline environment at different parameters (the temperature, aging time, the ratio of starting reagents). In order to study the impact of various factors on the dynamics of transformations of reagents, the sulfomethylation of phenol was carried out in the temperature interval of 90–150 °C and at the different molar ratio phenol (Ph):formaldehyde (FA):-sodium sulfite:water within 1:(1.1–1.5):(0.2–1):(17–19).

The synthesis of a water-soluble SAS was carried out as follows. Sodium sulfite was dissolved in water with the simultaneous heating of the solution to a temperature of 30–40 °C. At this temperature and continuous stirring, an estimated amount of formaldehyde was introduced. After 15 minutes, the reaction mass was supplemented with the required amount of phenol. The resulting mass was heated to a temperature of 60 °C and aged for two hours. Next, the temperature was increased in the range from 90 °C to 150 °C; aging was performed at a set temperature for 2–3 hours.

The resulting product of the SAS synthesis was filtered from impurities, dried, and analyzed.

The criteria for evaluating the reactions were selected the following:

1) the conversion rate of phenol in a reaction mass;
2) the dynamics of polymeric fractions' formation;
3) the surface-active properties of reaction products.

The best surface-active properties were demonstrated by samples, which were obtained at a temperature of 130 °C. This is confirmed by the nature of changes in the surface tension depending on a change in the concentration of their water solutions. Under a given technology, we managed to synthesize products whose dependence of surface tension (α, din/cm) is similar to the isotherm of the surface tension of the known NF Dispersant. The optimal ratio of the high molecular (HMF) and low-molecular (LMF) fractions in the product of phenol sulfomethylation, obtained at a temperature of 130 °C, at which it has the best surface-active properties, was determined: HMF/LMF=1.42–1.5. Their stabilization capacity (*A*) was $6.7 \cdot 10^{-3}$ g/dm^3, the value of the critical concentration of micelle-formation (CCM) was 2.1 g/dm^3. It was determined that the ratio of HMF/LMF is one of the main characteristics of the finished product. It was established that the water-soluble SSAS, obtained using the method of phenol sulfomethylation, is low-toxic and refers to class 3 of danger [32]. Samples with the optimal surface-active properties, obtained at 130 °C, were taken as a comparison sample for further research.

The drawback of this technology is the necessity of sulfomethylation reaction at a temperature of 130 °C. The synthesis at high temperatures and under pressure requires special equipment (autoclave), which creates the complexity of the current reaction control, additional water consumption for cooling the autoclave, etc.

Studying the possibility of accelerating the reaction of phenol sulfomethylation is of interest, in terms of obtaining SAS at low temperatures.

It is known that a more powerful and less risky way to accelerate the reaction, rather than rising the temperature, is catalysis [33]. Introduction to the reaction environment of substances, such as SAS, capable of forming micelles, to orient the molecules of reagents to each other in a way that increases the surface of their contact. At the same time, a stable solution of organic matter forms in the solvent, in which this substance does not dissolve or dissolves little without the presence of SAS. This leads to an increase in the reaction rate.

Therefore, it is advisable to continue the proposed area of research in order to improve the technology of the synthesis of an anion multifunctional SAS.

3. The aim and objectives of the study

The aim of this study is to improve the technology of an anion-active SAS with high dispersible and stabilization properties.

To accomplish the aim, the following tasks have been set:

– to determine the optimal conditions for the synthesis of a water-soluble SAS by the method of phenol sulfomethylation;

– to devise a fundamental technological scheme of the process of obtaining SAS using the method of phenol sulfomethylation in a water environment;

– to identify possible areas of the practical application of the resulting product of phenol sulfomethylation.

4. Determining the optimal conditions for the synthesis of a water-soluble SAS by the method of phenol sulfomethylation

In order to reduce the temperature, we studied the influence of interphase catalysts on the process of phenol sulfomethylation. The chosen catalyst was a cation-active SAS – the quaternary ammonium salt of cetyltrimethylammonium bromide (CTMAB). The process of phenol sulfomethylation was carried out in a water-alkaline environment. To obtain a product of the reaction close in properties to the NF Dispersant, sulfomethylation was carried out at the ratio phenol:formaldehyde: sodium sulfite equal to 1:1.5:0.5:18. The amount of the catalyst was calculated depending on the amount of water in the reaction mass within 0.09–0.18 g/dm^3. After loading all the components, the reaction mixture aged for two hours at a temperature of 60 °C; the temperature then was increased to 90 °C to carry out the condensation process.

It was established that the production of a water-soluble surfactant in the presence of the CTMAB catalyst can be carried out by the method of sulfomethylation in one stage under conditions of interphase catalysis. This reduces the reaction temperature to 90 °C, instead of 130 °C, without a catalyst. It is shown that the resulting product in its physical, chemical, and surface-active properties meets the requirements that characterize water-soluble SASs, obtained in synthesis conditions without the presence of a catalyst at a temperature of 130 °C. The synthesized product (Dispersant SMF-90), obtained by the method of interphase catalysis of phenol sulfomethylation, is similar in the main properties to the NF Dispersant, which is widespread in the industry. The optimal amount of the catalyst in our study was 0.18 g/dm^3 of the amount of water being loaded.

An additional advantage of sulfomethylation in a water-alkaline environment is that such an environment is formed by the hydrolysis of sodium sulfite in the following reaction:

$$Na_2SO_3+H_2O \rightarrow NaHSO_3+NaOH.$$

This does not require additional sodium hydroxide in the reaction mass to form an alkaline environment.

The interaction of formaldehyde with sodium hydrosulfite leads to the formation of sodium oxymethylsulfite:

$$CH_2O+NaHSO_3 \rightarrow HOCH_2SO_3Na,$$

which reacts with phenol. Schematically, the equation of condensation reaction and phenol sulfomethylation can be recorded as follows:

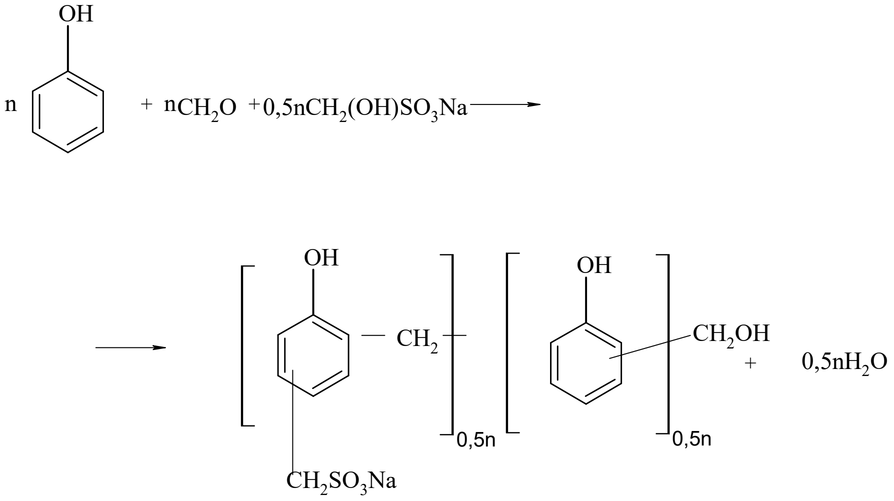

Fig. 1. Schematic equation sulfomethylation of phenol

Based on the data obtained in the process of research on the synthesis of a water-soluble surfactant using the catalyst CTMAB, as well as data given in the scientific literature, the probable mechanism of action of the catalyst is proposed. It is assumed that the process of phenol sulfomethylation passes through the stage of formation of the intermediate complex (an ion pair) between the catalyst and oxymethylsulfite. Next, such a pair is transferred from the water phase into organic with the reaction progress, which can be described by the following equation:

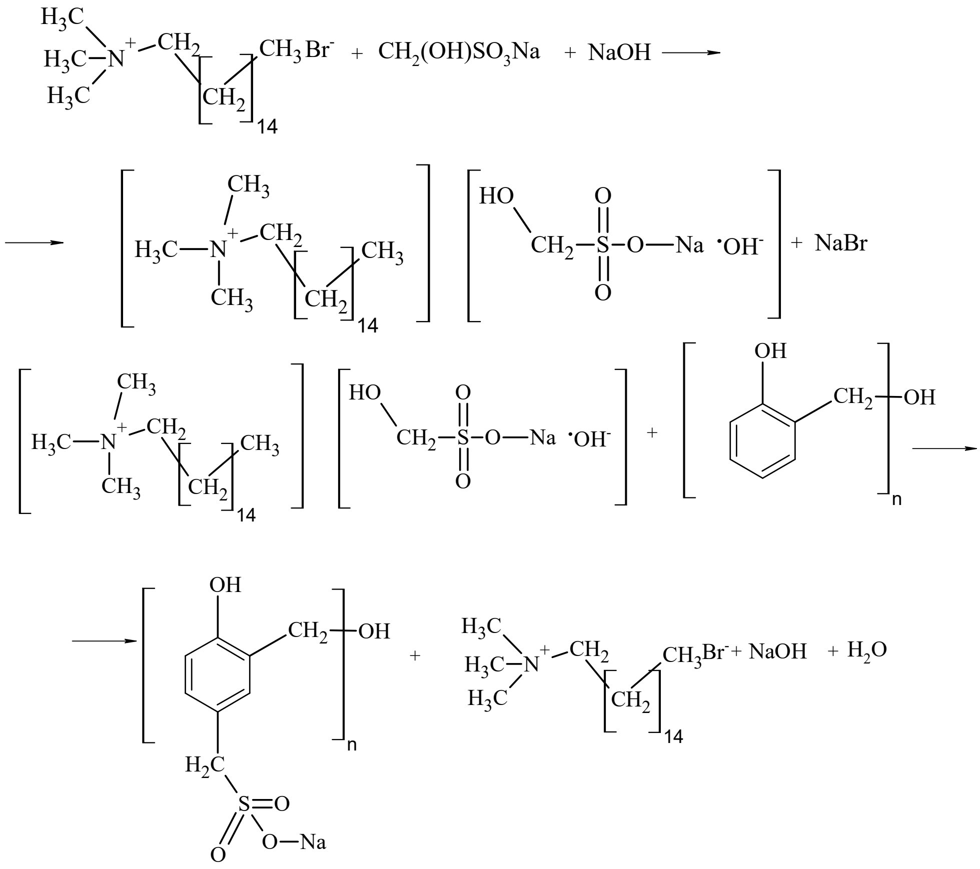

Fig. 2. Probable mechanism of sulfomethylation of phenol under conditions of interphase catalysis

Based on our study, the basic quality indicators of Dispersant SMF-90 were established.

Table 1

Basic quality indicators of Dispersant SMF-90

No.	Indicator title	Norm	
		Dry product	Liquid product
1	Physical appearance	Powder, from light brown to brown color	Liquid, brown or red-brown color
2	Water mass fraction, %, not exceeding	5	60–65
3	Mass fraction of substances, insoluble in water, in conversion to dry product, %, not exceeding	0.1	0.1
4	Indicator of activity of hydrogen ions (pH) of the dispersant water solution with a mass fraction of substances of 2.5 %	7–9	7–9

The surface-active properties of substances are evidenced by their behavior in water solutions. Fig. 1 shows the isotherms of the surface tension of water solutions of the resulting substances (curve – 1) with a concentration of up to 10 % compared to samples obtained at 130 °C (curve – 2).

Fig. 3 shows that the product of the reaction, catalyzed by CTMAB at a temperature of 90 °C, is close in properties to the comparison sample obtained at 130 °C.

The resulting products are the surface-active substances that demonstrate the dispersible and stabilizing properties. We studied the influence of the phenol sulfomethylation products on the colloidal-chemical properties of disperse systems, namely dispersing capacity.

To determine the influence of the resulting products of phenol sulfomethylation on the process of dispersion, we conducted a series of dispersing the dye Cube Blue O compared to the NF Dispersant (sodium dinaphthylmethane disulfide). The dispersion was carried out in a laboratory bead mill, using as a mulish body glass beads measuring 0.8–1.0 mm in a ratio of 1:1 to suspension (by mass) at the concentration of solid phase F=10 % for 8 hours. We dispersed at the optimal concentration of the dispersant, that is, 20 % by weight of the dye. We controlled the change in the particle size of the dye using a microscopic technique. Every 30 minutes of the dispersion, we selected suspension samples for a dispersion analysis by the sedimentation method. The results are given in Table 2.

The end of dispersal was determined by when the size of the bulk of the dye particles reached η=1–2 μm, which meets the basic requirements for the output forms of dyes. Particles of the dye of different sizes and shapes take part in dispersion. In the presence of different dispersants, they are subjected to mechanical effects of different nature, so as a result there are suspensions with a wide range of particle distribution by size.

The distribution of dye particles, dispersed in the presence of the NF Dispersant, a phenol sulfomethylation product at 130 °C, and a product of phenol sulfomethylation at 90 °C in the presence of CTMAB, have the same tendency (Table 2): in the first 30–60 minutes, there is an active grinding of large particles (aggregates) of the dye, which have less strong bonds. Simultaneously with the destruction of aggregates, there is the adsorption of SAS on the newly formed surfaces and the destruction of these surfaces. Over the next 180 minutes, there is a slowdown in dispersion with the formation of primary dye particles. When the duration of dispersion increases to 300–360 minutes, the dimensions of particles do not change.

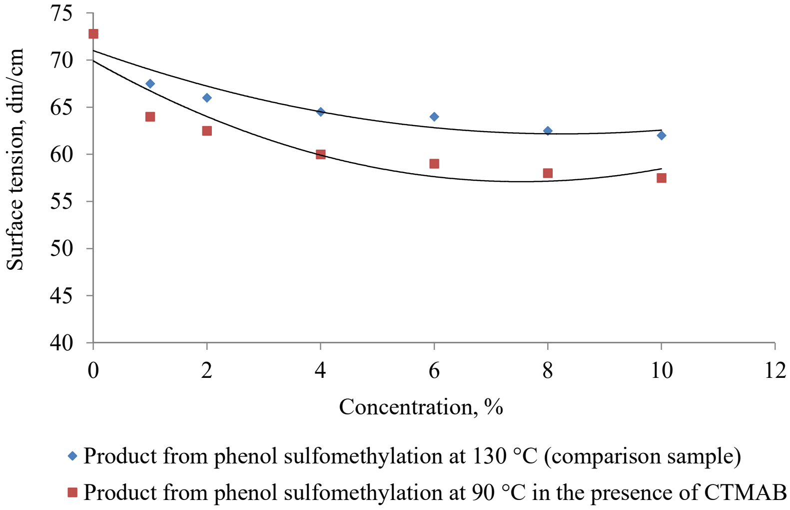

Fig. 3. Isotherms of the surface tension of the products' water solutions

Table 2

Dynamics of change in the size of dye particles during dispersion

Time, min	Size of dye particles when dispersing with different Dispersant, microgram		
	NF Dispersant	The product of phenol sulfomethylation at 130 °C	The product of phenol sulfomethylation at 90 °C in the presence of CTMAB
5	20	20	20
30	6	8	10
60	4	6	7
90	3	4	5
120	3	3.5	4
150	2.9	3.5	3.7
180	2.8	3	3.5
210	2.7	2.5	3
240	2.3	2.5	3
270	2.1	2.4	3
300	2	2.3	3
330	2	2.3	3
360	2	2.3	3

Thus, it was determined that the product of phenol sulfomethylation at 90 °C in the presence of CTMAB manifests the dispersing properties. It makes it possible to grind the dye's aggregates to the size of the bulk of the particles of 2–3 μm n and to obtain the highly-disperse pastes with the dye particles up to 1–2 μm.

5. Technological scheme of obtaining the Dispersant SMF-90 and its main characteristics

Based on laboratory tests, we devised the technology of obtaining the Dispersant SMF-90, proposed the flowchart (Fig. 4) and the technological scheme (Fig. 5) of the process. The proposed technology makes it possible to carry out phenol sulfomethylation in one stage, to reduce the reaction temperature from 130 °C to 90 °C, which simplifies the hardware of the technological scheme.

The flowchart includes the main and auxiliary stages of the process, namely:

1. Main stages:

– phenol sulfomethylation in an aquatic environment;

– reaction mass filtration;

– drying of the obtained product.

2. Auxiliary stages:

– the preparation of sodium sulfite water solution;

– the preparation of the catalyst water solution (CTMAB).

Taking into consideration the developed flowchart, the technological scheme of the synthesis of the Dispersant SMF-90 using the method of phenol sulfomethylation as a single-stage process (Fig. 5) is proposed.

The technological scheme includes the following basic devices: a synthesis reactor, a reaction mass filter, and a spray dryer. Auxiliary equipment includes preparation devices of sodium sulfite and catalyst solutions, capacitors-refrigerators, montage, a reaction mass receiver, a cyclone, a sleeve filter, and a packing line for dried dispersant.

The technological process of obtaining the Dispersant SMF-90 is carried out as follows.

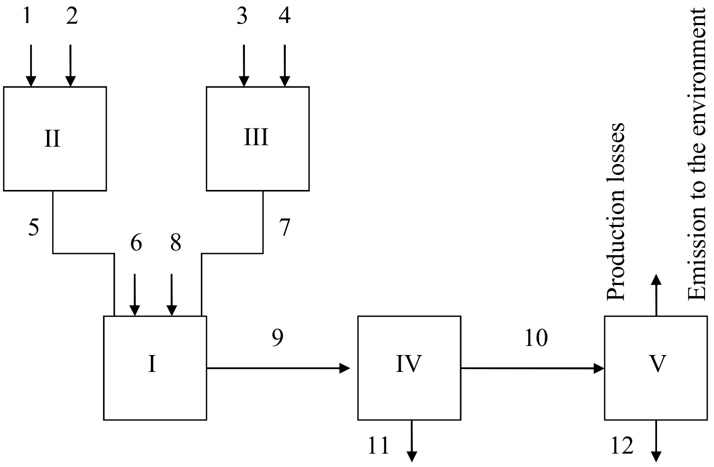

Fig. 4. Flowchart of the Dispersant SMF-90 synthesis technology:
I — unit of the principal process — phenol sulfomethylation;
II — auxiliary process unit — the preparation of a sodium sulfite water solution;
III — auxiliary process unit — the preparation of a water solution of the catalyst (cetyltrimethylammonium bromide);
IV — hot reaction mass filtration unit; V — drying unit;
1 — sodium sulfite, 2 — water, 3 — catalyst, 4 — water,
5 — sodium sulfite water solution, 6 — formaldehyde,
7 — catalyst water solution, 8 — phenol,
9 — hot reaction mass,
10 — filtrate after filtration,
11 — finished product Dispersant SF-90 in the form of water solution,
12 — finished product Dispersant SMF-90 in the form of dry powder

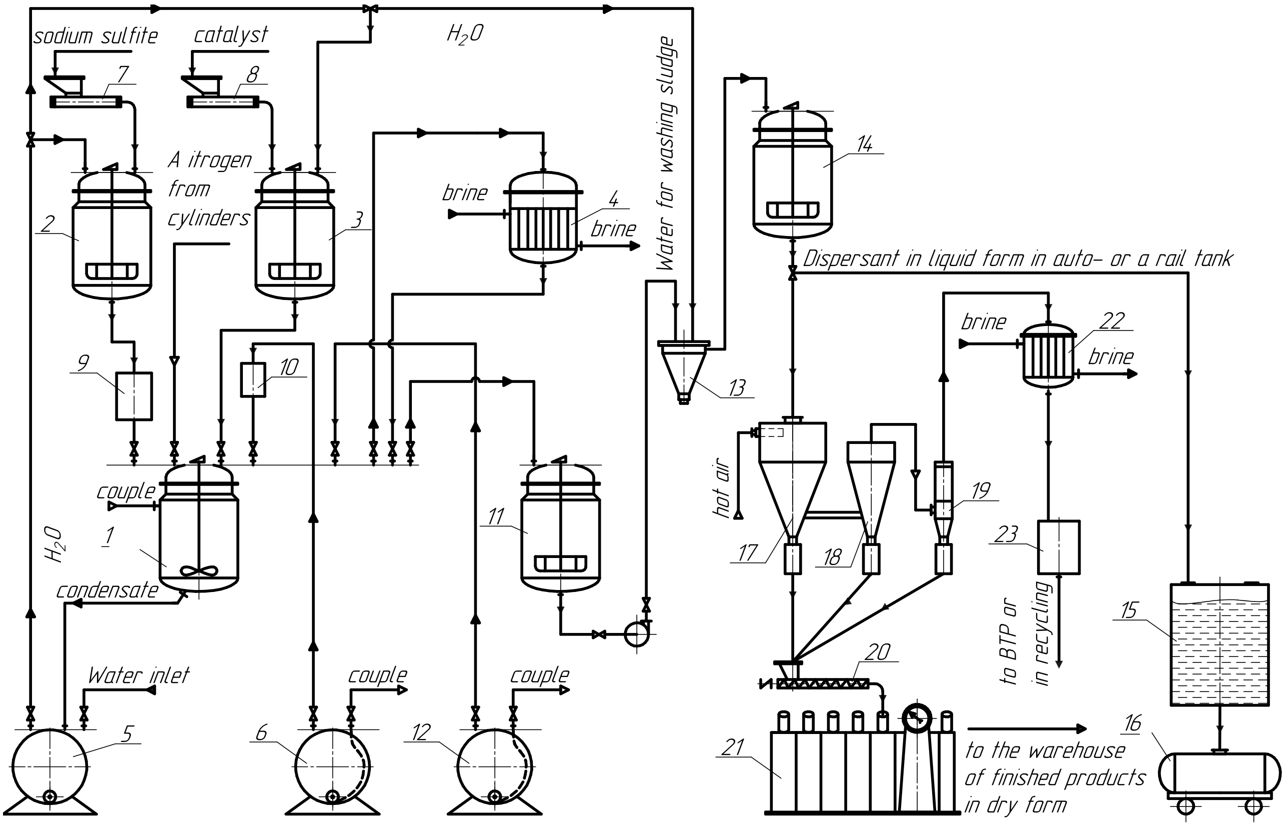

Fig. 5. Technological scheme of obtaining the Dispersant SMF-90: 1 – apparatus with a steam heating shirt and cooling with water; 2, 3 – devices for the preparation of water solutions of sodium sulfite and the catalyst; 4 – capacitor; 5, 6, 12 – montage for water and condensate, phenol, and formaldehyde, respectively; 7 – sodium sulfite bunker; 8 – catalyst bunker; 9 – measuring tank for sodium sulfite solution; 10 – measuring tank for phenol; 11 – receiver of reaction mass; 13 – filter; 14 – receiver of the filtered dispersant solution; 15 – storage container for a dispersant in liquid state; 16 – loading into the railway tank to dispatch liquid dispersant to the customer; 17 – spray dryer; 18 – cyclone; 19 – sleeve filter; 20 – screw storage of dried dispersant; 21 – packing line for packaging the dried Dispersant SMF-90 into small containers; 22 – direct heat exchanger; 23 – condensate container

5. 1. Main process stages

5. 1. 1. Phenol sulfomethylation in an alkaline environment

Sulfomethylation is carried out in the reactor (1) made of stainless steel. Before loading the raw materials, the reactor (1) is checked for tightness by the rarefication of at least 0.05 MPa. After that, the machine (1) is blown out with nitrogen for air displacement for 5–10 minutes. Next, the machine (1) is fed from the machine (2) through the measuring unit (9) a solution of sodium sulfite and formaldehyde from montage (12); the reagents are stirred for 30 minutes. Then, from the machine (3), we load the catalyst solution in water, and, from the measuring unit (10), phenol is fed by gravity.

Loading all the components is carried out when running a mixer. After loading all the components, the machine (1) is sealed; the refrigerator (4) is then enabled, which operates in a reverse mode. The reaction mass is heated to a temperature of 60 °C by feeding water vapor at a pressure not exceeding 0.3 MPa; at this temperature, it is aged for 2 hours. The vapors of phenol and formaldehyde, from the machine (1), enter the refrigerator (4), condensate in it, and return to the machine (1).

5. 1. 2. Condensation stage

After aging the reaction mass for 2 hours at a temperature of 60 °C, the reaction mass temperature in the machine (1) rises to 90 °C; the condensation process lasts for 3 hours.

The vapor of phenol together with the vapor of water formed during the reaction enter the capacitor (4), condense, and return to the machine (1). After that, the reaction mass is cooled to a temperature of 50 °C.

After the condensation reaction, the resulting product of synthesis enters the container (11) by gravity, from where the pump is used to deliver it to the filtering stage in the filter (13) and then on drying in the spray dryer. The dryer includes a drying chamber (17), a cyclone (18), and a sleeve filter (19). The dried dispersant is sent by a screw dispenser (20) for packaging the powder into small containers to the packing line. For a customer of the liquid form, the dispersant from the machine (14) enters the storage container (15), from where it is supplied for loading into an automobile or railway tanks (16).

5. 1. 3. Reaction mass filtration

Hot reaction mass from the container (11) is pumped to the filter (13). After filtering, the filtrate is transferred by the pump for drying to the machine (14).

5. 1. 4. Finished product drying

The drying of water solution of the Dispersant SMM-90 is carried out in a spray dryer made of stainless steel of any type used in the chemical or food industry. Water solution, from the pressure container (14), is fed by gravity into the chamber of the dryer (17). The heat carrier is the air heated to a temperature of 245 °C. The temperature at the outlet from the dryer is 110±5 °C and is adjusted by the rate of the flow of the solution supplied to drying.

A dust-type dispersant is sent after the cyclone (18) for additional cleaning in the sleeve filter (19), where dust particles of the dispersant are caught in the filter material, which is subsequently periodically cleaned. The dried dispersant is fed, from the drying chamber (17), cyclone (18), and sleeve filter (19), to the screw collector (20), from which the finished product is packed in containers and sent to the warehouse.

5. 2. Auxiliary stages:

5. 2. 1. Preparation of sodium sulfite water solution

The device (2) for the preparation of a 40 % solution is a cylindrical steel vertical container with a frame mixer with a rotation frequency of 0.8 s^{-1} and a water-cooling shirt. The device (2) is poured with water according to a meter; it is heated up to a temperature of 40 °C; and then crystalline sodium sulfite is loaded into the device from the weight bunker (7).

After loading the ingredients, somebody switches on the mixer and stir the reaction mass for 30 minutes until sodium sulfite is completely dissolved.

5. 2. 2. Preparation of the catalyst water solution based on cetyltrimethylammonium bromide

The device (3) for the preparation of a catalyst solution is a cylindrical steel vertical container with a frame mixer with a rotation frequency of 0.8 s^{-1} and a water-cooling shirt. The device (3) is poured with water, cooled, and the required amount of cetyltrimethylammonium bromide is loaded from the bunker (8). The solution is stirred for 30 minutes and sent to the machine (1).

6. Advantages of the developed technological scheme

The developed technological scheme of obtaining the Dispersant SMF-90 is rational and environmentally-economically beneficial for the following reasons:

1) it makes it possible to obtain two target products with a yield of 94–95 % by weight in conversion to dry substance – a powder-like product and the liquid water solution of Dispersant SMF-90;

2) the use of the inter-phase catalyst of cetyltrimethylammonium bromide makes it possible to simplify the equipment design of the process by using less energy-intensive reactors (instead of an autoclave);

3) the temperature modes of such a technological process within 90–95 °C make it possible to use hot water and low-temperature water vapor as heat carriers, and, as a refrigerant, technical water, which is cooled by the atmospheric air;

4) the waste of production is solid sediment of the filtration stage in the amount not exceeding 0.1 %;

5) the developed technology makes it possible to use, as the raw materials, the wastewater from enterprises, which includes phenol, for example, wastewater from the production of phenol-formaldehyde resins. The amount of phenol should not exceed the value required for synthesis taking into consideration the ratio of the starting components.

7. Practical use of Dispersant SMF-90 – a product of phenol sulfomethylation

We have tested the resulting dispersant with positive conclusions:

a) on the actual equipment at the enterprise PP “InterGas-Synthesis” (Rubizhne, Ukraine) as a dispersant: samples of the paint FACADE WATER DISPERSION SYNTHEGO-VDS are produced. In the manufacture of the paints, we replaced the dispersant Orotan N-4045 (Rohm and Haas Europe Trading Aps., United Europe), used in line with the enterprise’s formulation, with the Dispersant SMF-90 in equivalent quantity. No technological difficulties were noticed when fabricating the experimental samples of paints. Based on the physical and chemical indicators, the paints meet the requirements and standards set by TU U 24.6-32803942-021:2010. Based on the laboratory tests of the paint samples, it was determined that the Dispersant SMF-90 is suitable for use in the production of water-dispersion paints;

b) at the enterprise PAT “Company “Elba” (Kyiv, Ukraine): as a stabilizer of concrete mixtures in the manufacture of paving tiles. Using the equipment, according to the formulation and technology of the enterprise, we fabricated experimental samples of concrete paving tiles based on fine-grained (sandy) concrete in line with GOST 26633-2012 in the climatic execution UHL in line with GOST 15150, which are intended for constructing prefabricated pavements, pedestrian and garden paths, pedestrians areas and sites for public transport passengers. The plasticizing additive used was an experimental batch of the anion-active SAS based on the sulfomethylated products from the condensation of phenol with formaldehyde: Dispersant SMF-90. The tests were conducted in comparison with the plasticizer – technical lignosulfonate (LST in line with TU 13-0281036-05). In terms of quality (setting duration and light-laying), the concrete mixtures made when using the Dispersant SMF-90 are close to the concrete mixtures containing sodium lignosulfinate as a plasticizer in the same quantity. According to the physical and mechanical properties, the fabricated tiles met the requirements set by GOST 17608-91 “Concrete paving slabs. Technical conditions (incl. Change No. 1). Based on the laboratory tests, the experimental samples of Dispersant SMF-130 and Dispersant SMF-90 can be recommended as the plasticizers of concrete mixtures in the production of paving tiles for pedestrian and gardening paths, pedestrian areas, and landing sites of public transport;

c) The results of this work have been implemented at the enterprise TOV “Trade House. Ukrainian resins” (Rubizhne, Ukraine): to improve the technological scheme of the actual production of phenol-formaldehyde resins, for the purpose of using phenol-containing wastewater from the enterprise. The condensation method of phenol with formaldehyde in an aquatic environment, with the simultaneous sodium sulfite sulfonation, tested in the development of experimental and industrial samples of the Dispersant SMF-90, makes it possible to use the phenol-containing wastewater from enterprises.

8. Discussion of results of studying the improvement of the technology of obtaining SAS by the method of phenol sulfomethylation

This work has shown the possibility of obtaining a multifunctional anion-active SAS based on the products of phenol sulfomethylation. The main quality indicators of the obtained SAS, Dispersant SMF-90, were established (Table 1).

It has been proven that the surface-active properties of the resulting products depend on their polymeric composition. The ratio of a high molecular fraction (HMF) and a low-molecular fraction (LMF) within 1.42–1.5 ensures both the high stabilization and dispersion capacities.

The SAS of the optimal polymeric composition was obtained both by the non-catalytic phenol sulfomethylation in a water-alkaline environment at 130 °C and by the catalytic sulfomethylation at 90 °C, by using cetyltrimethylammonium bromide as a catalyst (Fig. 2). According to the surface-active properties (Fig. 3), the resulting product is similar to the known NF Dispersant, and to the products obtained during phenol sulfomethylation under conditions of 130 °C (Table 2).

Thus, by applying the proposed technology (Fig. 5), one can obtain the SMF-90 Dispersant – a product of phenol sulfomethylation under milder conditions in comparison with earlier studies. A temperature drop from 130 °C to 90 °C becomes possible during synthesis within 3 hours in the presence of an inter-phase catalyst (CTMAB). Accelerating the reaction in the presence of the CTMAB catalyst is probably due to the process of the diffusion of the reagents across the border of the interphase: the salts dissolved in water, on the one hand, and the substances dissolved in the organic phase, on the other hand. The reaction of phenol sulfomethylation in the presence of the cetyltrimethylammonium bromide catalyst is not studied in detail, so it is of interest to further study the mechanism of action of the interphase catalysts on the reaction of phenol sulfomethylation in the aquatic environment.

The reaction of phenol sulfomethylation in the aquatic environment makes it possible to use the phenol-containing wastewater from chemical industries, which helps reduce the amount of industrial waters. Research in this area can be useful from an environmental point of view in order to reduce the emissions of wastewater from enterprises into the environment.

9. Conclusions

1. We have investigated the synthesis of water-soluble SASs in one stage by the catalytic method of phenol sulfomethylation. This reduced the reaction temperature to 90 °C instead of 130 °C. the ratio of the starting components phenol:formaldehyde:sodium sulfite:water equals 1:1.5:0.5:18. The catalyst amount is 0.18 g/dm^3 of the amount of water being loaded. According to the surface-active properties, the resulting product is similar to the known NF Dispersant, and to the products obtained during phenol sulfomethylation under conditions of 130 °C.

2. A fundamental low-energy technological synthesis scheme of the Dispersant SMF-90 has been devised, which makes it possible to obtain the finished product in a dry or liquid form. The technology has been suggested, according to which the process of sulfomethylation is carried out in the reactor in one stage at a temperature of 90 °C; it makes it possible to use industrial wastewater as raw materials (phenol), for example, after the production of phenol-formaldehyde resins, the concentration of phenol in which does not exceed 10 %.

3. The resulting target product, in terms of the main properties (stabilizing ability, dispersing ability, a change in the surface tension of water solutions), meets the requirements that relate to industrial dispersants, for example, the NF Dispersant. The possible areas of the practical application of the obtained product have been proposed:

- as a dispersant in the manufacture of paints;
- when dyeing textiles as a leveler;
- as a stabilizer of concrete mixtures in the manufacture of paving tiles.

Thus, the resulting product, Dispersant SMF-90, could be a replacement for naphthalene-containing SASs with low bio destruction. The application of the environmentally friendly and economically beneficial technology of the SMF Dispersant solves the series of the set tasks.

Acknowledgments

This work was carried out in accordance with the plan of research works at the Department of Ecology and Polymer Technology, the Institute of Chemical Technologies at the Eastern Ukrainian National University named after V. Dal (Rubizhne) in the continuation of the state budget theme “The latest technologies and resource-saving technologies in the energy, industry, and agrarian-industrial complex” (DN-56-08, State Registration Number – 0108U000155).

According to economic agreements and cooperation agreements with enterprises PP “InterGasSynthesis” (Rubizhne) and TOV “Trade House. Ukrainian resins” (Rubizhne), the scientific work on the development of technology for obtaining SAS of the anion-active character under ecologically beneficial conditions has been implemented.

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