



DEVELOPMENT OF TECHNOLOGY FOR SYNTHESIS OF LIQUID TECHNICAL DETERGENT FROM SECONDARY ALKALINE SOLUTION OF NAVOIYAZOT JSC

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Abstract. The article presents the results of a study to solve the problem of recycling the technological alkaline solution, which is considered as a secondary raw material that forms 2000 tons per year in the production of polyvinyl chloride by “NAVOIYAZOT” JSC. A composition of a liquid technical detergent based on synthetic surfactants and an alkaline solution formed during the synthesis of vinyl chloride has been developed. The following methods were used in the studies: potentiometry, IR spectroscopy and viscometry, and the foaming ability of the studied samples was determined using a Ross-Miles device according to GOST 22567.1-77. The physicochemical properties of the developed composition were established, on the basis of which laboratory regulations for the production of technical detergent were drawn up. The possibility of creating an industrial technology for the production of technical detergent based on a secondary product - a technological alkali solution is shown, which will increase the profitability of polyvinyl chloride production and solve one of the environmental problems of “NAVOIYAZOT” JSC.

Key words: secondary raw materials, ecology, alkali, surfactant, detergents, synthesis, physicochemical properties, technology, application.

Аннотация. В статье представлены результаты исследования по решению проблемы утилизации технологического щелочного раствора, который рассматривается как вторичное сырье, образующее 2000 тонн в год на производстве поливинилхлорида АО “НАВОИЙАЗОТ”. Разработан состав жидкого технического моющего средства на основе синтетических ПАВ и щелочного раствора, образующегося при синтезе винилхлорида. В исследованиях использовали следующие методы: потенциометрию, ИК-спектроскопию и вискозиметрию, а пенообразующую способность исследуемых образцов определяли с помощью прибора Росс-Майлза по ГОСТ 22567.1-77. Установлены физико-химические свойства разработанной композиции, на основании которых составлен лабораторный регламент производства технического моющего средства. Показана возможность создания промышленной технологии производства технических моющих средств на основе второстепенного продукта - технологического раствора щелочи, что позволит повысить рентабельность производства поливинилхлорида и решить одну из экологических проблем АО “НАВОИЙАЗОТ”.

Ключевые слова: вторичное сырье, экология, щелочь, ПАВ, моющие средства, синтез, физико-химические свойства, технология, применение.

Annotatsiya: Maqolada “NAVOIYAZOT” AJ polivinilxlorid ishlab chiqarishda yiliga 2000 tonna hosil qiluvchi ikkilamchi xomashyo hisoblangan texnologik ishqoriy eritmani qayta ishlash muammosini hal qilish bo'yicha tadqiqot natijalari keltirilgan. Sintetik sirt faol moddalar va vinilxlorid sintezi jarayonida hosil bo'lgan ishqoriy eritma asosida suyuq texnik yuvish vositasining tarkibi ishlab chiqilgan. Tadqiqotlarda quyidagi usullar qo'llanildi: potentsiometriya, IQ spektroskopiya va viskometriya va o'rganilayotgan namunalarning ko'piklanish qobiliyati GOST 22567.1-77 bo'yicha Ross-Miles qurilmasi yordamida aniqlandi. Ishlab chiqilgan kompozitsiyaning fizik-kimyoviy xususiyatlari o'rnatildi, uning asosida texnik yuvish vositalarini ishlab chiqarish bo'yicha laboratoriya reglamentlari tuzildi. Ikkilamchi mahsulot – texnologik ishqorli eritma asosida texnik yuvish vositalarini ishlab chiqarishning sanoat texnologiyasini yaratish imkoniyati ko'rsatilgan, bu polivinilxlorid ishlab chiqarish rentabelligini oshiradi va “NAVOIYAZOT” AJning ekologik muammolaridan birini hal qiladi.



Kalit so'zlar: ikkilamchi xom ashyo, ekologiya, ishqor, sirt faol modda, yuvish vositalari, sintez, fizik-kimyoviy xossalari, texnologiyasi, qo'llanilishi.

Introduction

One of the significant events that took place in the UZKIMYOSANOAT concern in 2020 is the launch of the polyvinyl chloride production plant of NAVOIYAZOT JSC with a capacity of 100,000 tons per year. When producing vinyl chloride (PVC) using the introduced technology, 2000 tons of alkali solution are released per year as a secondary product. This, in turn, leads to environmental pollution, which forces the urgent development of technology for its processing to produce a new, value-added commercial product, which is an urgent task.

According to the technological regulations, in position 11 of the PVC production of NAVOIYAZOT JSC, a technological solution with an average NaOH content of up to 1.0% is released, and the Na₂CO₃ content is 12.0%. Considering such a high content of sodium ions in this technological solution, it was proposed to use it to obtain a technical detergent [1]. The reaction of alkali with surfactants makes it possible to obtain detergents that are widely used both in the national economy and in industry. Its chemical activity, water solubility and ability to dissolve in various solvents determine its areas of application [2]. The production of synthetic detergents (SD) is one of the most dynamically developing industries and occupies a stable market position [3]. Therefore, the world's manufacturers of SD are focused on the active development of numerous innovative technologies in the field of developing new compositions of detergents, producing SD of various states of aggregation, and searching for fundamentally new approaches to the essence of the washing action [4]. The introduction of new technologies for the production of SD is aimed at increasing the functionality of manufactured products, their safety for humans and the environment, and efficiency [5].

It should be noted that Uzbekistan is in dire need of various types of detergents, but due to the lack of production of the necessary chemical reagents in the country, this problem is still awaiting a solution [1]. One of the solutions to this problem is the organization of industrial production of technical detergent using secondary raw materials of an alkaline solution at NAVOIYAZOT JSC.

Research methods

The objects of the study were samples taken at different times from the process solution at the JSC NAVOIYAZOT plant during the synthesis of PVC, nonionic surfactant - COCODEA (coke oil diethanolamine); ampholytic surfactant – “Betaine-30” (cocamidopropyl betaine) [6] and compositions obtained by their interaction.

The content of NaOH and Na₂CO₃ in their joint presence in the solution was determined by titration according to the procedure [7]. Potentiometric titration of solutions was carried out in an “Ionomer 130” ion meter with a glass -silver chloride electrode, which was previously calibrated using buffer solutions.

IR spectrophotometric studies were carried out according to the method [8] in the laboratory of physicochemical research at the Center for Advanced Research using a Nicoletis 50 Fourier spectrometer infrared device (Thermo Fisher Scientific), which has a large database of IR spectra of various chemicals in the range of 4000-400 cm⁻¹.

Viscometer measurements of polymer solutions were carried out in the temperature range 15-35°C in an Ubbelohde capillary viscometer [9]. The temperature in the thermostat was achieved with an accuracy of 0.20C. The flow time of the solution was determined with a



class 2 stopwatch. The relative viscosity was calculated from the flow time of the solution and solvent using the well-known formula [9].

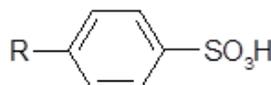
Foaming ability was determined using a Ross-Miles device for the samples under study according to GOST 22567.1-77 [1]. The solutions were thermostated and then the pipette stopcock was opened. After the solution had flowed out of the pipette, the stopwatch was turned on and the height of the resulting foam column was measured in millimeters ($H_{0\text{measured}}$). Then, after 5 minutes, the height of the resulting foam column was measured in millimeters ($H_{5\text{measured}}$).

Results and its discussion

During the work, samples of the process solution were taken at different periods. It has been established that the average NaOH content in the studied samples of the technological solution of NAVOIYAZOT JSC reaches 0.94-0.98%, and the Na_2CO_3 content reaches 11.39-11.53%. The recording of IR spectra showed the presence of low molecular weight polyvinyl chloride oligomers in the process solution [8].

As is known [4], the composition of SD includes surfactants (surfactants), which perform the main work. Surfactant molecules, adsorbed on a mud particle, "attract" it to water, tear it away from the surface, preventing the particles from sticking back and sticking together, which leads to the particles going into solution. Due to its high wettability, the surfactant solution easily penetrates into the smallest pores and destroys large particles of contaminants [10].

Based on the goal, to establish optimal conditions for obtaining SD in laboratory conditions from the secondary product of JSC NAVOIYAZOT - an alkali solution, its interaction with an anionic surfactant - alkylbenzenesulfonic acid of the LABSA brand, according to a certificate produced by Clean Chemicals LLC in the city of Tashkent, was studied by viscometry. LABSA surfactant contains 97% of the main substance, has a light brown color, chemical formula:



where R - $\text{C}_{10-14}\text{H}_{21-29}$.

Also used in the studies were the ampholytic substance "Betaine-30" consisting of a 30% aqueous solution of cocamidopropyl betaine and the nonionic "COCODEA" consisting of a 70% aqueous solution of diethanolamine coke oil, according to the manufacturer's certificate. It has been established that the anion-exchange substance "LABSA" is the best component from a scientific point of view for obtaining a technical detergent based on a secondary product - an alkali solution of NAVOIYAZOT JSC. A temperature of 25°C is the most optimal for producing detergents.

The above statement was also confirmed by studying the change in pH of solutions at different ratios of components in the systems studied. It has been established that the strongest change in the pH of the solution occurs when the anion exchange substance "LABSA" acts as a surfactant, the next is the ampholytic substance "Betaine-30" and the nonionic "COCODEA" has the weakest effect. The results obtained indicate the influence of the chemical nature of the surfactant in the process under study. Thus, the presence of a strong acid group in the structure of the anion exchange substance "LABSA" leads to the greatest change in the pH of the solution. In this series, Betaine-30, which has both an acidic and shellac group in its structure, occupies the middle, and COCODEA, which does not have ionizing groups in its structure, occupies the last place. Although, due to the presence of alcohol groups in the structure of the latter, sodium salts are formed when it interacts with an alkaline solution, which leads to a decrease in the pH of the solution.



A comparison of the results obtained by two independent methods indicates a stronger interaction of the anionic surfactant - "LABSA" with the studied technological solution than the ampholytic surfactant - "Betaine-30" and the nonionic surfactant - "COCODEA". This can be explained, as indicated above, by the presence in the structure of the anionic surfactant - "LABSA" of a strong acidic sulfo group. The presence of industrial production of this surfactant in Uzbekistan makes the creation of a technical detergent based on it and a secondary product of NAVOIYAZOT JSC - an alkali solution - technologically convenient and economically profitable.

One of the important indicators for detergents is foam stability. As is known from the literature [5], the formation of foam allows detergents to wash away various organic substances from the surface. The theory of interaction of detergents with various substances is very widely presented in the scientific literature [2]. Surfactants are substances that have the ability to adsorb at the interface (surface) between two phases (immiscible liquids, for example, fat-water, or solid-liquid systems), thereby reducing surface tension. The latter is understood as an excess of energy or force of intermolecular interaction that arises as a result of the uncompensated intermolecular forces in each phase and manifests itself at their interface. In a physical sense, this excess force is estimated as a measure of the work that must be done to increase the interfacial surface at constant temperature and pressure per unit area [10]. The presence of surfactants adsorbed on the interfacial surface and an increase in temperature leads to a decrease in this surface tension force. This ability of surfactants is usually ensured by their ambiphilicity, that is. the presence in the molecule of both a hydrophobic or lipophilic fragment and a hydrophilic or lipophobic fragment.

Foaming ability was determined using a Ross-Miles device for the samples under study according to GOST 22567.1-77. From Table 1 it can be seen that the height of the foam in the studied systems decreases with the addition of a technological solution, and an increase in its content in the system also leads to a decrease in the stability of the foam. Based on the analysis of the results obtained, it can be concluded that the chemical nature of the surfactant greatly influences the properties under study. The system has the greatest height and stability of the foam when using the anion exchange agent "LABSA" as a surfactant, while "Betaine-30" and "COCODEA" have the weakest characteristics.

Table 1.

**Dependence of the stability of foam solutions on the ratio of components
(surfactant concentration 0.5%, T – 25°C)**

Volume solution Surfactant, ml	Volume of process solution, ml	Initial foam height, mm		Foam height after 5 minutes, mm		Foam stability
		H _{0chan} ge	H ₀	H _{0chang}	H ₅	
Surfactant – aqueous solution of LABSA						
200,0	-	194	192	142	141	0,73
		195	193	144	143	0,74
		194	192	143	142	0,74
195,0	5,0	184	182	134	133	0,72
		185	183	135	134	0,73
		185	182	133	132	0,72
190,0	10,0	180	178	125	124	0,69
		181	179	122	121	0,67



		180	178	124	123	0,69
Surfactant – aqueous solution of COCODEA						
200,0	-	180	178	125	124	0,69
		181	179	126	125	0,69
		180	178	125	124	0,69
195,0	5,0	165	164	98	97	0,59
		165	164	100	99	0,60
		166	165	102	101	0,61
190,0	10,0	145	144	88	87	0,60
		145	144	86	85	0,59
		149	148	88	87	0,59
Surfactant – aqueous solution of Betaine-30						
200,0	-	184	182	131	130	0,71
		185	183	132	131	0,71
		184	182	131	130	0,71
195,0	5,0	174	172	114	113	0,65
		175	173	115	114	0,66
		176	174	113	112	0,64
190,0	10,0	170	169	110	109	0,65
		169	167	112	111	0,66
		168	166	114	113	0,68

At the next stage of work, on the basis of extensive laboratory studies, laboratory regulations for the synthesis of liquid synthetic technical detergent “FZ-26” were developed, which indicated the following important characteristics;

Physical properties: TMS “FZ-26” is a colorless or yellowish liquid with an oily consistency. $d_4^{20}=1,3283$, $d_4^{15}= 1,3332$ g/cm³. Relative viscosity 1.5-1.7 at 25°C. Increasing the temperature to 35°C and above leads to a significant decrease in viscosity. Freezing temperature is less than -10°C. Stable during long-term storage.

Chemical properties: TMS “FZ-26” is an acidic solution (pH=5.5-6.0). It interacts with metals such as iron, aluminum, zinc and honey, as well as alkali solutions. Reacts with strong oxidizing agents. Does not react with non-metals and organic saturated polymers such as polyethylene, polypropylene, polyvinyl chloride, polystyrene, methyl methacryl copolymers and others. Stable during long-term storage, as well as exposure to sunlight, radioactive rays and various microbacteria. Destroys in concentrated acids.

Toxicology and safety: TMS “FZ-26” is a composition with a skin-resorptive effect; if it comes into contact with the skin, it causes burns and long-term non-healing ulcers. It also has a general toxic effect, especially on the central nervous system. Damage to the eyes is especially dangerous (possible loss of vision). Toxicity is due to alkali and the presence of strong surfactants.

Solubility: TMS “FZ-26” mixes well with water, alcohol, tetrahydrofuran, dioxane, acetone, dimethylformamide, aromatic acids and other hydrophilic substances. Does not mix with hydrophobic substances.

Based on the literature data, as well as the established physicochemical properties of the developed composition, in order to establish the areas of application of the developed “FZ-26” product, its cleaning ability was investigated at food and processing industry enterprises for washing floors, walls, industrial premises, all types equipment, tanks, pipelines, as well as vacated containers. For example, the developed liquid synthetic technical detergent “FZ-26” was tested in the process of cleaning raw materials from



polyethylene terephthal using special equipment and according to regulatory documents established by LLC "REPROCESSING", the results of which are presented in Table 2.

Table 2.

Dependence of the cleaning ability of a technical detergent means "FZ-26" from concentration (polymer/solution mass ratio=1/10, washing time 20 minutes)

№	Volume, ml		Concentration in solution, %		pH solution	T _{solution} °C	Result
	TMS	Water	NaOH	Na ₂ CO ₃			
1	800	--	1.00	12.00	12	90	clean
2	700	100	0.875	10.50	12	90	clean
3	600	200	0.75	9.00	12	90	clean
4	400	400	0.50	6.00	11	90	clean
5	200	600	0.25	3.00	10	90	dirty
6	100	900	0.10	1.20	8	90	dirty
7 ¹	400	400	0.50	6.00	11	80	clean
7 ²	400	400	0.50	6.00	11	80	clean
7 ³	400	400	0.50	6.00	11	80	clean
7 ⁴	400	400	0.50	6.00	11	80	clean
7 ⁵	400	400	0.50	6.00	11	80	clean

in the 71-75 series, new portions of the polymer were cleaned with the same solution. As a result of laboratory tests, it was found that when the test product "FZ-26" is diluted twice with technical water and when this solution is reused five times, a reliable cleaning effect is achieved.

Also, the results of tests of the liquid synthetic technical detergent "FZ-26" in the process of cleaning containers freed from raw materials (organic reagents) and treating the walls and floors of production premises according to the regulatory documents established by the KASER corporation showed that when diluting the tested product "FZ-26" » industrial water achieves twice the reliable cleaning effect in the above processes.

At the GIGIEN MED enterprise, tests were successfully carried out on the use of the developed SD FZ-26 in the process of degreasing parts, cleaning containers freed from oil products and chemicals (organic reagents), as well as cleaning the walls and floors of production premises.

A commission consisting of representatives of ABK-MEDICAL LLC and developers came to the conclusion that it was appropriate to introduce the developed liquid synthetic technical detergent "FZ-26" in the process of cleaning containers freed from raw materials (organic and inorganic reagents) and walls and floors production premises.

Conclusion

The research carried out will make it possible in the future to create an industrial technology for the production of TMS "FZ-26" based on a secondary product - the technological alkali solution of JSC "NAVOIYAZOT", which will increase the profitability of PVC production and solve one of the environmental problems of this enterprise.

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