SJIF Impact Factor 2021: 8.013| ISI I.F.Value:1.241| Journal DOI: 10.36713/epra2016 ISSN: 2455-7838(Online)
EPRA International Journal of Research and Development (IJRD)
Volume: 6 | Issue: 6 | June 2021 - Peer Reviewed Journal

TECHNOLOGY OF PRODUCTS OF INTERACTION OF OLEIC ACID AND MALEIC ANHYDRIDE

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ABSTRACT

Nowadays in the world the issue of adaptation of surfactant production technology at those enterprises where they are used as components of various products also remains topical. This can have a positive effect on the general economic situation of small enterprises. Thus, the work considers topical issues of chemistry and technology of surfactants based on oleic acid and maleic anhydride, and is of a recommendatory nature for use in industry.

KEYWORDS: *Maleic anhydride, 1,4-butanediol, Oleic acid, Perchlorethylene, tetrahydrofuran, aspartame.*

INTRODUCTION

To be competitive in the world market, modern industries need to have several basic qualities: to produce environmentally friendly products and have perfect cutting-edge production technologies. The environmental friendliness of products is ensured, first of all, by the nature of the materials and raw materials that are used to obtain it. And the issue of improving technology remains relevant at any time.

Surfactants (surfactants) have found widespread use in our time, which accompany a person, both in his daily life and in the technical sphere. Surfactants based on plant and animal products are considered environmentally friendly and biodegradable. Moreover, such raw materials are renewable and easy to use. An interesting class of "organic" surfactants are derivatives of fats, oils and fatty acids. As a rule, these are products of malleination of vegetable oils or unsaturated fatty acids with non-conjugated multiple bonds. The branched structure of the molecule and the presence of carboxyl groups in combination with the hydrocarbon chain determine the sufficient nonionicity of the molecule, and, as a result, allows the use of such surfactants in non-polar media.

It is the technology of surfactant production based on maleic anhydride (MA) and oleic acid (OA), as an unsaturated fatty acid, that has become the subject of our research.

Analysis of literature data and problem statement. Surfactants derived from products of maleic anhydride and oleic acid are obtained by malleinization of the latter in the melt at 200-220 ° C for 3-5 hours [1-3], followed by their treatment with polyhydric alcohol [1]. Thus, the nonionicity of the molecule is achieved, which allows the use of substances such as, for example, emulsifiers of the second kind. The authors of [4] succeeded in reducing the malleination temperature of unsaturated fatty acids and oils to 150 ° C through the use of catalysts — boron compounds. The authors managed to obtain the product with a yield of 86-96%, which they determined by the amount of unreacted maleic anhydride. Boron compounds are used industrially as catalysts for the oxidation of hydrocarbons, which can affect the quality of the final product of malleination. Determination of the yield of MA products and unsaturated fatty acids from the degree of MA conversion is not quite a correct method, since it can also be used for the formation of by-products. Therefore, the high yield in this case can be considered invalid.

The issue of malleinization of OK and vegetable oils was asked back in the middle of the twentieth century, however, with the beginning of the

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two thousandth, this topic became relevant again. Thus, in [5, 6], it is reported about ten new oil demulsifiers based on the product of MA and OA, followed by esterification with various polyhydric alcohols at the anhydride group.

In addition to the unsaturated fatty acids themselves, cis-isomers of their esters can react with maleic anhydride, as shown in [4, 2, 7] in the first half of the 20th century, and also much later in 2008 [8]. At the same time, in the last of the listed works, the kinetics of malleinization of cis-forms of alkyl esters of highly oleinized sunflower oil was investigated. The authors also noted that in the reaction of malleination of OA, two different reaction mechanisms occur simultaneously: allylic addition and new interaction. This is confirmed by the simultaneous presence of isomers with and without a shift in the OC molecule among the products.

The relationship between the various pathways for malleination of unsaturated fatty acids is shown in [7]. Here, ethyl oleate was reacted with MA at 210 ° C. The resulting product was oxidized with an alkaline solution of potassium permanganate and the ratio of the final products was evaluated. Thus, it has been proved that under the indicated conditions it is the new mechanism with the movement of the double bond that prevails, in the ratio 1: 2.

Modern science makes it possible to more accurately determine and identify the structural differences in the products of interaction between MA and OA [9]. For this, a mass spectroscopy technique has been developed.

As can be seen from the sources considered, between oleic acid and maleic anhydride at temperatures of the order of 150-300 ° C, interaction is possible according to several mechanisms: allyl, new and radical. In this case, the reaction product is a mixture of isomers obtained by all three types of interaction.

There are no other references to a decrease in the temperature regime of the malleination process of unsaturated carboxylic acids, primarily oleic acid, in the literature.

Therefore, we were faced with the task of considering the possibility of interaction between MA and OK in milder conditions, different from industrial ones.

MATERIALS AND METHODS

Isolation of a pure crystalline reaction product requires a series of successive dissolutions and filtrations, which should also be provided for in the technology and in the technological production scheme.

The whole technology can be represented in the form of the following block diagram of stages and flows (Fig. 1).

So the synthesis proceeds at the first stage at the boiling point in the main apparatus (Fig. 1 block I), where perchlorethylene, oleic acid and maleic anhydride are loaded (Fig. 1, flows 1, 2, 3). Then the hot reaction mass (Fig. 1, stream 4) is fed to the purification filtration (Fig. 1, block II), from where the first brown precipitate formed during the synthesis is discharged for drying (Fig. 1, stream 6). The filtrate is overloaded (Fig. 1, flow 5) to the next filtration stage (Fig. 1, block III). There it is cooled to normal temperature, and the resulting mixed precipitate (Fig. 1, stream 7) is sent for secondary dissolution in perchlorethylene (Fig. 1, stream 8), followed by filtration of the purified precipitate (Fig. 1, block V). The filtrate after repeated washing of the precipitate (Fig. 4.1, stream 9), as well as the filtrate after the primary filtration (Fig. 1, stream 10) are collected and evaporated to constant weight (Fig. 1, block IV). The result is a brown oily liquid (Fig. 1, stream 11).

Thus, in the course of this technology, 2 target products are obtained: crystalline (Fig. 1, stream 8), as well as a liquid mixture of maleic anhydride and oleic acid products and starting reagents (Fig. 1, stream 11).

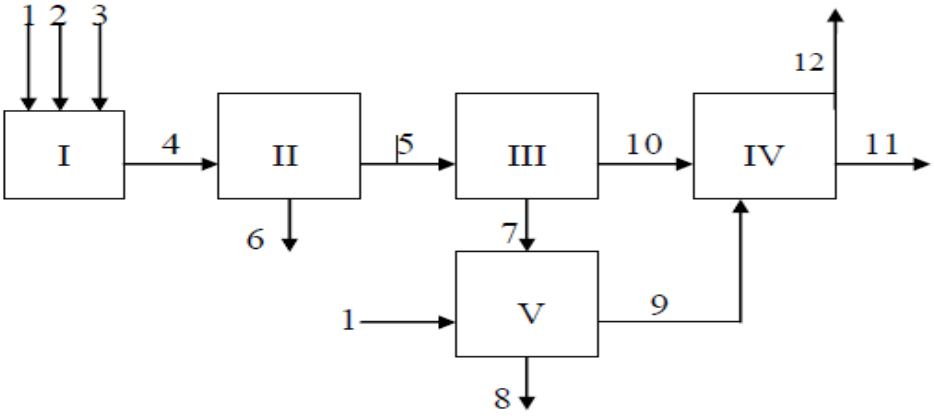

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Fig. 1. Block diagram of the technology for obtaining the products of the interaction of oleic acid and maleic anhydride: I - block of the main stage of the process - synthesis of substances; II - block of primary filtration of hot reaction mass; III - primary filtration filtrate cooling unit and secondary filtration; IV - block for evaporation of the solvent from all filtrates; V - block for re-dissolving the precipitate with subsequent filtration; 1 - perchlorethylene, 2-oleic acid, 3 - maleic anhydride, 4 - hot reaction mass, 5 - filtrate after hot filtration, 6 - precipitate formed during synthesis, 7 - precipitate formed upon cooling, 8 - purified precipitate by redissolution , 9 - filtrate after repeated purification of the precipitate, 10 - filtrate after filtration of the cooled reaction mass, 11 - brown viscous product (a mixture of maleic anhydride and oleic acid products), 12 - evaporated perchlorethylene.

RESULTS AND DISCUSSION

Calculations per ton of the first target product

To confirm the economic feasibility of obtaining a new surfactant from maleic anhydride and oleic acid, it is necessary to carry out preliminary material and technological calculations of the synthesis.

In addition, it is worth noting the features of the technological process.

Oleic acid is a rather viscous liquid, which affects the time of its loading into the apparatus, and also leads to the deposition of its residues on the surface of the pipeline and on the bottom of the measuring vessel. It should be borne in mind that the melting point of oleic acid is 16 ºC. Thus, when the temperature in the production room decreases, oleic acid will crystallize in the measuring vessel and the pipeline, which will affect its loading. Therefore, the line for supplying oleic acid to the reactor should provide for the possibility of heating it during the cold season.

Maleic anhydride is fed in portions within an hour from a heated measuring tank, through a heated feed line, into a reactor preheated to 60 ºC. When melted, Maleic Anhydride is a viscous liquid that crystallizes rapidly at temperatures below 52.5 ° C. Therefore, taking into account the viscosity and temperature conditions, the excess loading of Maleic Anhydride into the reactor should also be about 15% of the calculated one.

Since, in the course of the proposed technology, two target products are obtained, the total output of the technological process is determined by adding the total outputs for each product. Considering each product as a separate technology, we will compile a list of stages for them (Table 1) and indicate the outputs for each.

Technology stages of target products

Table 1.

Stage	First product (crystal) Output, %	Second product (product mix) Output, %
1	2,2	3,1
Reaction between maleic anhydride and oleic acid in a reactor	57	45
Filtration in a different filter from the reaction sludge	54	44
Cooling the reaction mass in an intermediate tank	54,7	42,7
First filtration in a vacuum funnel	55	45
Dissolution of the crystalline precipitate in the second intermediate vessel	56	-
Formation of a crystalline precipitate in the crystallizer	55	-
Second filtration in a vacuum funnel	52,5	-
Evaporation of solvent	53,4	42,2
Drying	52	-
Total yield by product	49,18	37
Total production output	43,09	

Thus, the total technological yield is 43.09%, which makes it feasible.

To determine the consumption of raw materials and auxiliary substances for the production of one ton of the first target product, then for calculations we use the total yield of this product by technology - 49.18%.

The calculation results are presented in table. 2. In this case, the amount of perchlorethylene is indicated taking into account that this solvent is used in two stages: the interaction of the reagents and the re-dissolution of the crystalline product.

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Consumption of raw materials and auxiliary substances per ton of the first target product

Table 2.

Substance	Quantity, kg
Oleic acid	2295,3
Maleic anhydride	797,4
Perchlorethylene	4500,0

The technology provides for the return of perchlorethylene to the system after evaporation. The return rate can be estimated at 80-85%. This allows you to significantly reduce the cost of the product by almost 3 times. The approximate cost of the product for raw materials is about 300 hryvnia per 1 kg. Taking into account the return of the solvent - about UAH 100. Since the target product is recommended to be used as a surfactant, its amount added to the formulation is, as a rule, 0.1-0.3%, which makes it an affordable raw material for various industries. The cost of the acid is also reduced due to the production of the second product by 25%.

CONCLUSIONS

An important scientific and technical problem has been solved - the technological bases for the production and use of the products of interaction of maleic anhydride with oleic acid have been developed. So, maleinization of unsaturated fatty acids is recommended to be carried out at the boiling point of the reaction mixture (120-121 ° C) in an aprotic organic non-polar solvent - perchlorethylene, with a ratio of reagents oleic acid: maleic anhydride = 1: 1.2. This temperature regime is much lower than the known one (200-250 ° C). As a result, a mixture of maleation products is formed with a total yield of 98-99%. The use of a solvent helped to distribute the maleation products, so one crystalline product was isolated, which is a mixture of isomers of maleic anhydride and oleic acid products, and exhibits surfactant properties. The yield of the crystalline product reaches 54-56%.

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