OCCASION

This publication has been made available to the public on the occasion of the 50th anniversary of the United Nations Industrial Development Organisation.

DISCLAIMER

FAIR USE POLICY

CONTACT

Please contact publications@unido.org for further information concerning UNIDO publications.

For more information about UNIDO, please visit us at www.unido.org

UNITED NATIONS INDUSTRIAL DEVELOPMENT ORGANIZATION
Vienna International Centre, P.O. Box 300, 1400 Vienna, Austria
Tel: (+43-1) 26026-0 · www.unido.org · unido@unido.org

D00429

United Nations Industrial Development Organization

[illegible]
[illegible]
[illegible]
ORIGINAL: [illegible]

[illegible] Industries in Developing Countries

[illegible], 21 - [illegible] 19[illegible]

ID/[illegible]/[illegible]0

PRODUCTI[illegible] OF SUR[illegible] [illegible]

[illegible]

by

[illegible]
[illegible] Scientific
Research Institute [illegible]
[illegible]

[illegible]

United Nations Industrial Development Organization

Distr. LIMITED

ID/WG.83/59 SUMMARY
23 July 1969

ORIGINAL: RUSSIAN

International Petrochemical Symposium on the Development of the Petrochemical Industries in Developing Countries

Baku, 20 - 31 October 1969

PET SYMP 8/1

SUMMARY

PRODUCTION OF SURFACE ACTIVE AGENTS ON THE BASE OF SYNTHETIC FATTY ALCOHOLS[1]

by

I.N. Rozhkov
Scientific Research Institute
for Fat Substitutes
USSR

Three trends in the production of higher fatty alcohols on the base of conversion of normal paraffins are being observed in the USSR. One of them is production of alcohols by catalytic reduction of methyl esters of synthetic fatty acids with hydrogen under pressure. The second is recovery of alcohols formed in the process of synthetic fatty acid manufacture and concentration in various fractions [1].

The method of production of secondary alcohols by direct oxidation of normal paraffins with the air oxygen in the presence of boric acid has been worked out and commercialized in the USSR.

1/ The views and opinions expressed in this paper are those of the author and do not necessarily reflect the views of the secretariat of UNIDO. This document has been reproduced without formal editing.

14.69-635

In correspondence with the composition, structure, and properties of the above alcohols a series of methods of converting them into anionic and nonionic surface active agents has been elaborated and introduced.

Primary alcohols are mainly processed to alkylsulfates. Sulfuric acid, oleum, chlorosulfonic acid, gaseous SO_3, sulfamic acid and others are used as sulfating agents. Depending on the sulfating agent applied the degree of conversion of alcohols into alkylsulfates amounts from 80 to 94-96%.

Alcohols from unsaponifiables II and secondary alcohols sulfated with ordinary sulfating agents are converted into alkylsulfates which are subjected to additional extraction refining.

By application of a complex sulfating agent formed from urea and chlorosulfonic acid a more complete conversion of alcohols into alkylsulfates is provided.

Secondary alcohols and alcohols from unsaponifiables II are converted more effectively into surface active salts of sulfosuccinic acid monoesters. In this case the degree of conversion amounts to 90-92%.

On the base of the above alcohols nonionic surface active agents are produced and used in different industry branches.

Low-ethoxylated products are converted into effective anionic surface active agents such as alkylsulfates and sulfosuccinic acid derivatives. The yield of them is high.

On the base of the above mentioned surface active agents formulations have been worked out for the manufacture of liquid, paste and powder synthetic detergents for domestic and industrial use.

During last decade [illegible] surface-active agents (SAA) in various fields of engineering has become one of the essential factors of technical progress. Along with the application of surfactants in domestic and industrial detergents there is ever increasing use for intensifying various processes in mining-and-chemical industry and in the coal industry in oil production and oil refining, in machine building and radio engineering, in light and food industry, in chemistry and heat engineering, in medicine, in power, agriculture and in many other fields.

Due to their universal application and, at the same time, specific action, the world output of SAA is in excess of 3 million tons per year as early as 1965. About one half of SAA was used in detergent applications, while the other half was used for numerous industrial processes.

About two thirds of the world output of SAA is in the form of anion active substances, about one fifth nonionics and the rest-cationic and ampholytic substances.

As far as the volume of production is concerned, the first place among the anionics is occupied by alkyl benzene sulfonates, the second - by alkylsulfates.

Until quite recently the leading place among nonionics was occupied by ethylated alkylphenols.

As the scale of production of SAA and application of them increased, the problem of producing biologically "soft" SAA characterized by sufficiently quick and complete digestion in the process of biological purification of sewage, has become of great importance.

This and a number of other circumstances help to explain the interest shown in anionic and nonionic SAA obtained on the base of natural higher fatty alcohols which are biologically "soft".

For some time the production of SAA on the base of higher fatty alcohols was not developing fast enough due to the limited possibilities of obtaining higher fatty alcohols from natural fats and oils.

The high activity of SAA based on higher fatty alcohols, the demands for replacing biologically "hard" SAA by "soft" ones and the necessity for economical and rational use of world resources of natural fats and oils, contributed to intensifying the efforts to find synthetic methods of

producing higher fatty alcohols.

At present, on a world basis a number of petrochemical routes are known for producing synthetic alcohols.

Among the methods of production of higher fatty alcohols in the USSR are those based on obtaining higher fatty alcohols by oxidation of liquid and solid paraffins by atmospheric oxygen in the presence of certain catalysts.

The successful development of these processes depends first and foremost on the presence of considerable resources of liquid and solid oil paraffins in the USSR.

Considerable influence was exercised on the successful development of the oxidation method for the production of higher fatty alcohols by the research of academician N.N. Semenov and his school in the field of free-radical mechanisms of oxidation of hydrocarbons.

Three general methods for the production of higher fatty alcohols by oxidizing paraffins are developing in the USSR. One of them is the production of alcohols by hydrogen reduction under pressure of synthetic fatty acids obtained by oxidizing paraffins in the presence of manganese catalysts.

As a result a mixture of primary saturated $C_{[illegible]} - C_{18}$ alcohols is obtained. The alcohols thus obtained are of high quality and are subjected to separation into the fractions required for use in various technical fields.

In the process of oxidising paraffins higher fatty alcohols are formed side by side with fatty acids; the former are concentrated in the so-called unsaponifiables-I, i.e. the neutral fraction which is distilled off the main part of the reaction mixture after the thermal treatment unit.

The alcohol mixture contains about [illegible] per cent of primary alcohols and 20 per cent of secondary alcohols. Several methods of isolating and using these alcohols have been suggested.

The industrially applied method is isolating alcohols through their boric acid esters.

The relative simplicity of technology and the fact that the alcohols are obtained in the process of a large-scale manufacture of the synthetic fatty acids, [illegible] favourable technical and economic prospects for alcohols obtained from unsaponifiables-II and good prospects for their production in the future.

In the USSR, there has been developed and realized under production conditions, a method of obtaining secondary alcohols by direct oxidation of normal paraffins in the presence of boric acid. Protecting the alcohols formed against further oxidation, boric acid influences favourably the process of alcohol formation.

Nevertheless, some by-products are formed [illegible] acids with alcohols, the former being [illegible] in the process of subsequent processing of the reaction mixture.

The choice of proper raw material, oxidizing under optimum conditions and additional refining, make it possible to obtain alcohols which can be successfully used in the production of surface active substances.

Depending on the purpose and in accordance with the composition, structure and properties of the three types of named alcohols a number of ways have been developed of converting them into anion- and nonionic surface active substances.

Alkyl sulphates. The main method of treating the primary alcohols obtained by reducing synthetic fatty acids is to convert them into alkyl sulphates.

Under optimum conditions of sulphation a product is obtained which is not inferior to alkyl sulphates based on coconut and other natural oils.

As a result of sulphating various fractions of the primary alcohols alkyl sulphates are obtained. They are valuable raw material for the production of liquid detergents and light and hard detergents with varying foamability. On the basis of these alcohols various plasticizers, depressants, additives and other [illegible] for special application are manufactured.

As sulphating agents, sulphuric acid, oleum, chloro-sulfonic acid, gaseous sulfur trioxide, sulfamic acid, [illegible] and a number of others are used.

When sulphating with sulphuric acid in excess of 100 per cent, the degree of alcohol conversion into alkyl sulphates amounts to [illegible] - 92 per cent.

By means of chloro-sulphonic acid 9[illegible] per cent conversion of alcohols into alkyl sulphates is achieved. In such case no excess in consumption of alkali is necessary (the paste obtained contains small amounts of mineral salts).

Sulphating with gaseous sulphur trioxide is more effective: the degree of alcohol conversion reaches 94-9[illegible] per cent.

In case of sulphating the alcohols from unsaponifiables-II and from secondary alcohols by means of sulphuric acid the non-sulphated products remaining are removed from the paste by means of alcohol-petrol extraction.

At present a method has been developed and realized under industrial conditions of sulphating the secondary, primary and other alcohols by means of a complex sulphating agent with increased reactivity. The application of this complex reagent ensures the conversion of all alcohols and other hydroxyl-containing compounds into sulphated products with a yield of 94-9[illegible] per cent of that theoretically possible.

It was found to be most convenient to transform the anhydrous sulphate mass obtained into granulated synthetic detergents by mixing them with additives with subsequent plasticizing and forming into blocks (bars), tablets, "vermicelli", etc.

It is necessary to mention, that alkyl sulphates possess excellent biodegradation thanks to their structure and colloidal-physical properties, and are very valuable raw materials for the production of synthetic detergents. They preserve high detergency even in the presence of limited quantities of useful additives and builders.

Alkyl sulphosuccinates. One of the methods of conversion of higher [illegible] alcohols into surfactants is the production from them of surface active derivatives of sulphosuccinic acid.

The process consists of two simple stages. At first the alcohols react with an equivalent amount of maleic anhydride (maleic acid anhydride). The conditions are selected in such a way that condensation is carried out with the formation of monoesters.

In the second stage monoesters are treated with sulphurous acid salts.

Sulphonation of double bond, the rate of which is near to the rate of ionic reaction, proceeds with almost quantitative yield of monoester salts of sulphosuccinic acid. We call these surfactants "[illegible]" with the suitable prefix, characterising the alcohol used.

The sulphosuccinic acid derivatives are characterized by complete biodegradability and essentially "soft" action on the skin and hair.

Also they possess fungistatic and bacteriostatic properties. Some compounds are "soft" bactericides.

If the production of oleic derivatives is modified and it becomes cheaper, the sulfosuccinic acid derivatives will attract more and more attention.

The surfactants of the SS type can be prepared from alcohols, alkylol amides, alkyl phenols and other hydroxyl-containing compounds.

In all cases the degree of useful conversion reaches 92-94 per cent of theory. The most effective however is the production of surface active derivatives of sulphosuccinic acid from alcohols, the sulphation of which with usual sulphating agents is difficult. This especially relates to the alcohols from unsaponifiables and to secondary alcohols.

The industry of the USSR has long experience of production and application of surface agents of the SS type. The possibility of preparing high concentrated powders under the SS proved its practical importance in the production of synthetic detergents by the method of spraying.

The surfactants will be very valuable when alkylol amides on the base of synthetic fatty acids are used for SS. For the first time in the world the industrial manufacture of SS is being realized in the USSR on the base of spermaceti, which are strictly speaking not petro-chemical products, but nevertheless they are produced on petrochemical enterprises by selective hydrogenation of sperm fat.

SS on the base of sperm alcohols in powder, paste, gel and in other forms, as opposed to other surfactants do not exert irritating action but on the contrary they possess softening effect. That is why SS on the base of sperm alcohols are the best agents for washing wool, silk and other industrial soils.

Sulfoethoxylates, which form products of superficially ethoxylated alcohols are of great interest. They, when surfactants possessing high solubility, soft action, intensive foaming and other properties is required, for example for shampoos, lotions, etc., they are alcohols ethoxylated with 2-3 moles of ethylene oxide per mole and subjected with chloro-

sulphonic acid can be recommended. Also, preliminary limited oxyethylation of primary alcohols contributes to the increase of sulphation depth, reaching 96 - 98 per cent.

The preliminary oxyethylation of secondary alcohols however is especially effective. On directly sulphating secondary alcohols with chlorosulphonic acid, the degree of useful conversion of alcohols into alkyl sulphates because of side reactions, does not exceed 50 per cent. When secondary alcohols are preliminary oxyethylated with 3-5 moles of ethylene oxide, subsequent sulphation with chlorosulphonic acid the yield approaches the sulphation depth of primary saturated alcohols.

Ethoxysulphosuccinates. The preliminary oxyethylation of alcohols with 2 - 3 moles of ethylene oxide in preparing surface active compounds of sulphosuccinic acid is effective too. In this case not only the weight yield of surfactants, but also their surface activity and detergency are increased. The most effective surfactants of DOS type are produced from secondary alcohols $C_{12} - C_{18}$.

When heavier alcohols are used the solubility of surfactants sharply decreases and the detergency falls too. The preliminary oxyethylation of alcohols increases the solubility of surfactants and makes possible the application of alcohols with higher molecular weight.

Nonionic surfactants. As was shown by laboratory and experiments, primary alcohols and alcohols from transesterification-II undergo oxyethylation without any complications and yield highly active nonionic surfactants which may be successfully used as auxiliary textile substances and the base of synthetic detergents.

The oxyethylation of secondary alcohols requires somewhat more complicated conditions, but they also yield very effective surfactants which are of value for use as washing and auxiliary textile substances, emulsifiers and so on.

Low-ethoxylated alcohols were discussed earlier.

The manufacture of anionic surfactants on the base of low-ethoxylated alcohols becomes of special value in case of limited resources of ethylene oxide.

All the above mentioned surfactants are produced on a commercial scale. Besides the above mentioned, other surfactants prepared from higher fatty alcohols should be referred to. Among them are esters of acrylic acid and

polyacrylates, vinylation products, derivatives of phosphoric and polyphosphoric acids, dialkyl sulphosuccinic acid salts, phosphosuccinic acid derivatives and others.

In principle, such surfactants can be obtained [illegible] of higher fatty alcohol derivatives. These surfactants possess various valuable properties. They [illegible] be emulsifiers, demulsifiers, wetting agents, dispersants, foamers, defoamers, [illegible] and have many other uses.

On the base of alkyl sulphates, alkyl sulphosuccinates, sulphoethoxylates, ethoxysulphosuccinates and other surfactants, the formulae of various washing agents for domestic and industrial use have been worked out and produced. These surfactants have been recommended for use in the compounding various washing agents for cotton, linen, silk, woollen and synthetic cloths.

Extensive research [illegible] is being carried out in numerous specialized research institutions with respect to application of the above mentioned [illegible] for speeding-up drilling, in the composition of coolants, in processes for emulsion polymerisation and production of latices, for emulsifying pesticides; in the textile industry, in civil engineering and in many other fields.

Summary and Conclusion

[illegible] program for the development of a wide assortment of surfactants of various kinds has been planned and is being carried out in the USSR. A considerable part in this program is assigned to surfactants based on higher fatty alcohols.

In the USSR a wide assortment of surfactants is being produced based on primary and secondary saturated alcohols and on alcohols [illegible] together with [illegible] and unsaturated alcohols, by selective hydrogenation of fats of marine animals.

Depending on the [illegible], structure and properties of the above mentioned alcohols, a number of [illegible] have been developed of converting them into anionic and [illegible] surfactants.

The primary alcohols [illegible] predominantly into alkyl sulphates. [illegible] sulphating [illegible] of sulfuric acid, oleum, chlorosulphonic acid, gaseous sulfur trioxide, sulphamic acid and others.

Depending on the sulphating agent used, the degree of alcohol conversion into alkyl sulphates amounts to 80 - 95 per cent.

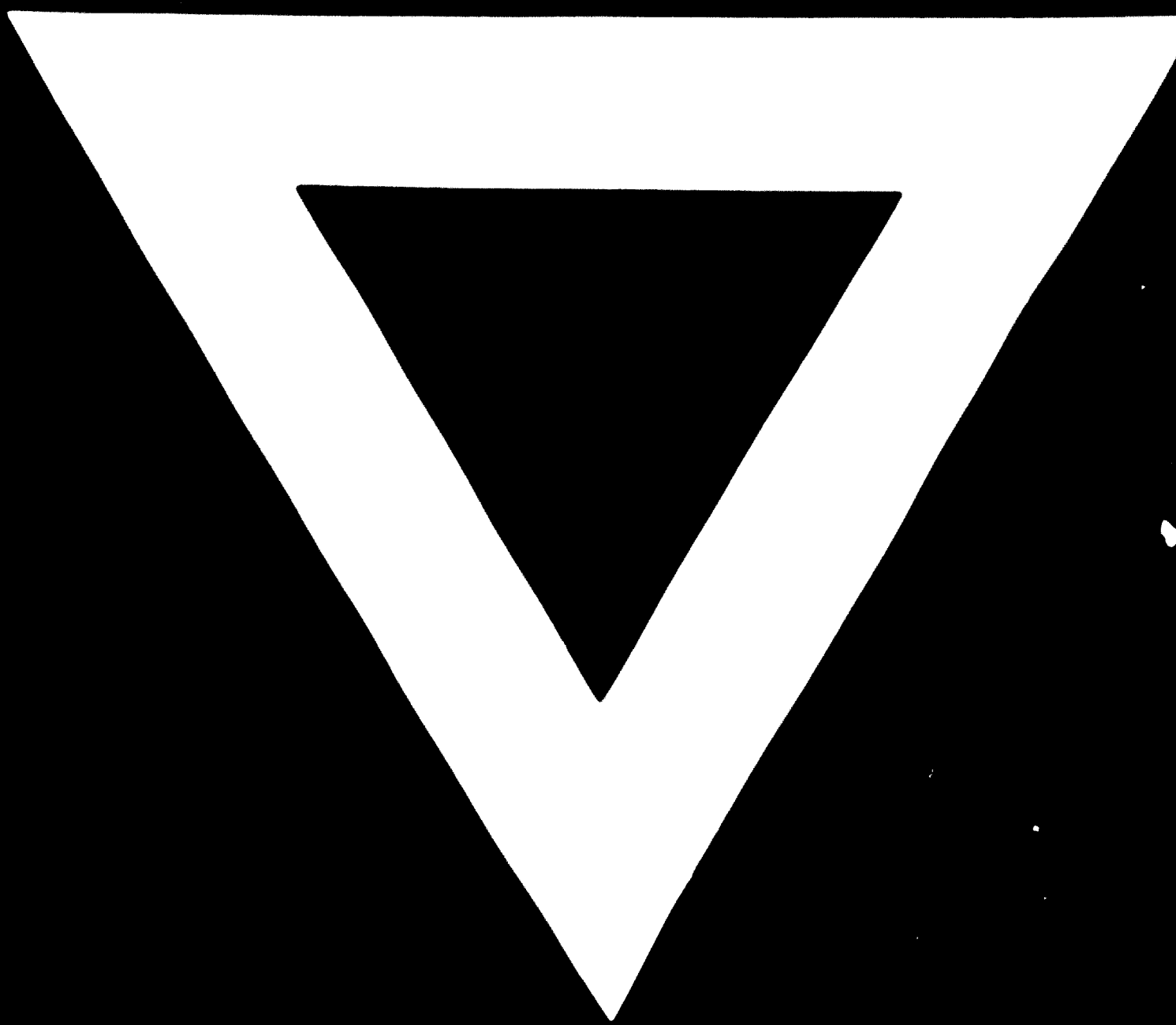
When sulphating the alcohols from [illegible]-II and the alkyl sulphates which [illegible] subjected to additional [illegible]. [illegible] made of a complex sulphating agent, the alcohol conversion into alkyl sulphates approaches 100 %.

For alcohols from [illegible]-II and secondary alcohols, the conversion into [illegible] of [illegible] acid turned out to be most effective. In this case the degree of alcohol conversion reaches 92 - 94 per cent.

On the basis of the above mentioned alcohols, anionic surfactants are obtained which are used in various fields of [illegible].

Low-ethoxylated products are transformed with high yield into effective anionic surfactants of the type of alkyl [illegible] and derivatives of sulphosuccinic acid.

On the basis of the above mentioned and other surfactants, the formulas of liquid, [illegible] and powder synthetic detergents for domestic and industrial use have been worked out and their production organized.



15. 3. 72