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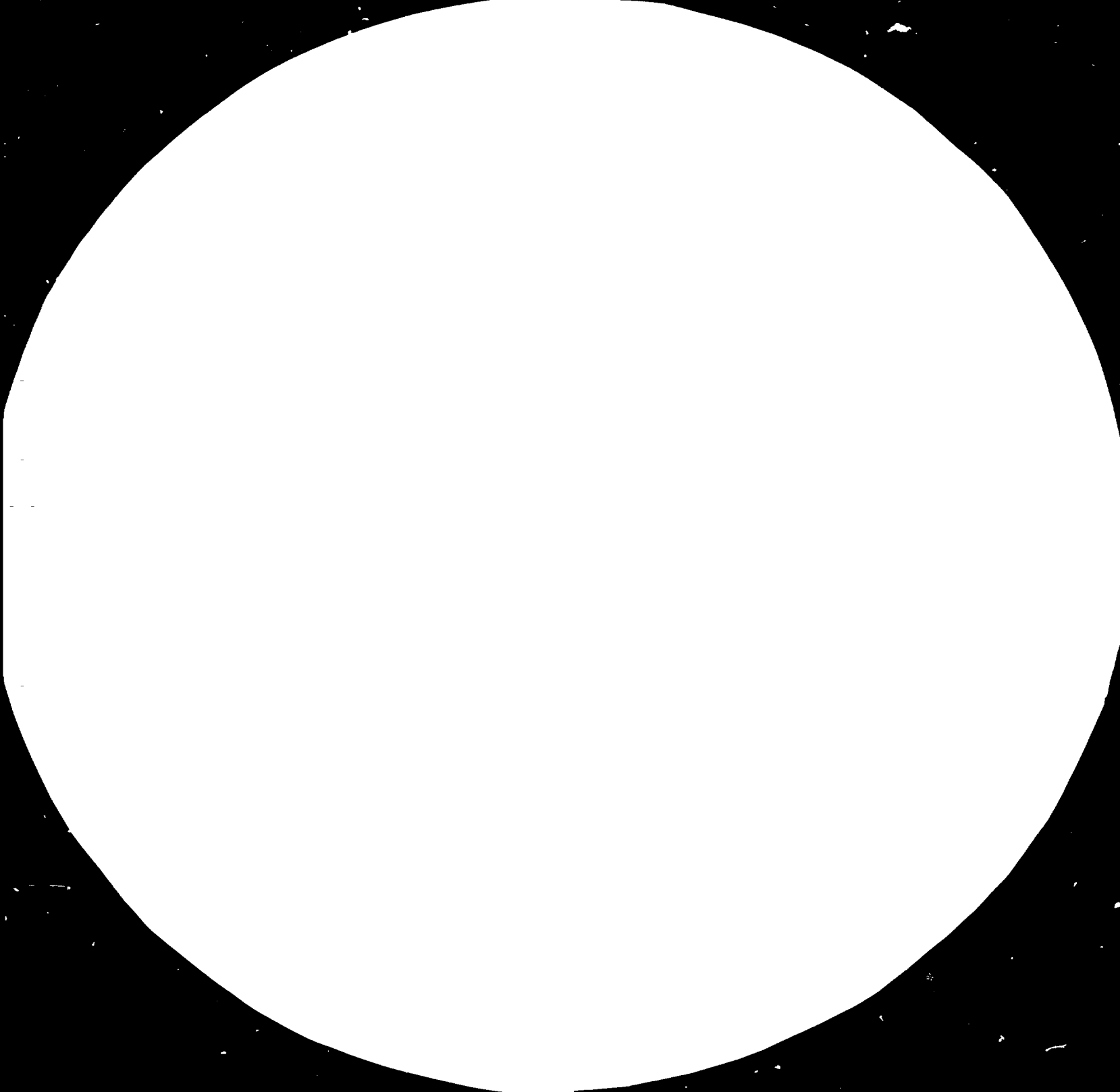
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27 September, 1984

English

Yugoslavia.

DEVELOPMENT OF ENVIRONMENTALLY SAFE  
TECHNOLOGIES FOR THE PRODUCTION OF  
DIVERSIFIED POLYETHERS AND THEIR  
APPLICATION IN COSMETIC PRODUCTS.

DP/YUG/82/005/11-02

YUGOSLAVIA

Final report

Prepared for the Government of Yugoslavia  
by the United Nation Industrial Development Organization,  
acting as executing agency for the United Nations Development Programme

Based on the work of Rolf Staniński,  
Consultant

United Nations Industrial Development Organization  
Vienna

This report has not been cleared with the United Nations Industrial  
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the views presented.

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## 1. PREFACE

The present report is based on the experts first mission of 15 days duration accomplished to the SBS-group in Sarajevo in September 1984.

The project DP/YUG/82/005, "Assistance to the Institute of Chemical Engineering in Research and Development of Polyurethane Technology for Industrial Applications" has started in October 1983.

It has been decided to acquire knowledge in polyether production and applications in other industrial fields than polyurethanes. One of the outputs of the projects is the investigation of the polyether applications in cosmetics and lubricants.

The purpose of the subproject DP/YUG/82/005/11.02 is to assist in developing environmentally safe technologies for the production of diversified polyethers and their applications in cosmetic products. It has to be stressed that polyethers for polyurethanes and polyethers for cosmetics and other applications are different by chemical constitutions and in their production procedures.

Furthermore it has to be mentioned that the partners in the mutual project are of different organisations and locations.

Therefore this report requires a some more extensive presentation of the chemical background and the participants in the project.

## 2. ABSTRACT

Was given assistance in analysing the situation of development and production of diversified polyethers, have been conducted lectures and rendered assistance in the selection of polyethers and their applications in cosmetics.

In straight collaboration with the project management the feasibility of development and of production of polyethers was analysed and evaluated.

It has clearly shown, that there exists a unique chance to realize within relatively short time a successful substitution of imported polyethers and to acquire knowledge in R&D and in production of polyethers respectively ethoxylates for the further industrial development.

As the economical situation in Yugoslavia demands an immediate reaction it was searched to present a pragmatic solution to obtain countable results.

It was established a project strategy with the main objective to substitute imported polyethers for other applications than in polyurethanes by identical products.

It was searched for the utilization of existing equipments and the available professional skills as well as teh enlarged utilization of biodegradable raw materials based on domestic fats and oils.

It has shown that major investments probably are not indispensable for the initial production of diversified polyethers/ethoxylates.

The scheduled duration of the mission was not sufficient to investigate and evaluate the parameters for the implementation of the project. This refers specially to figures of the market and figures for further investments.

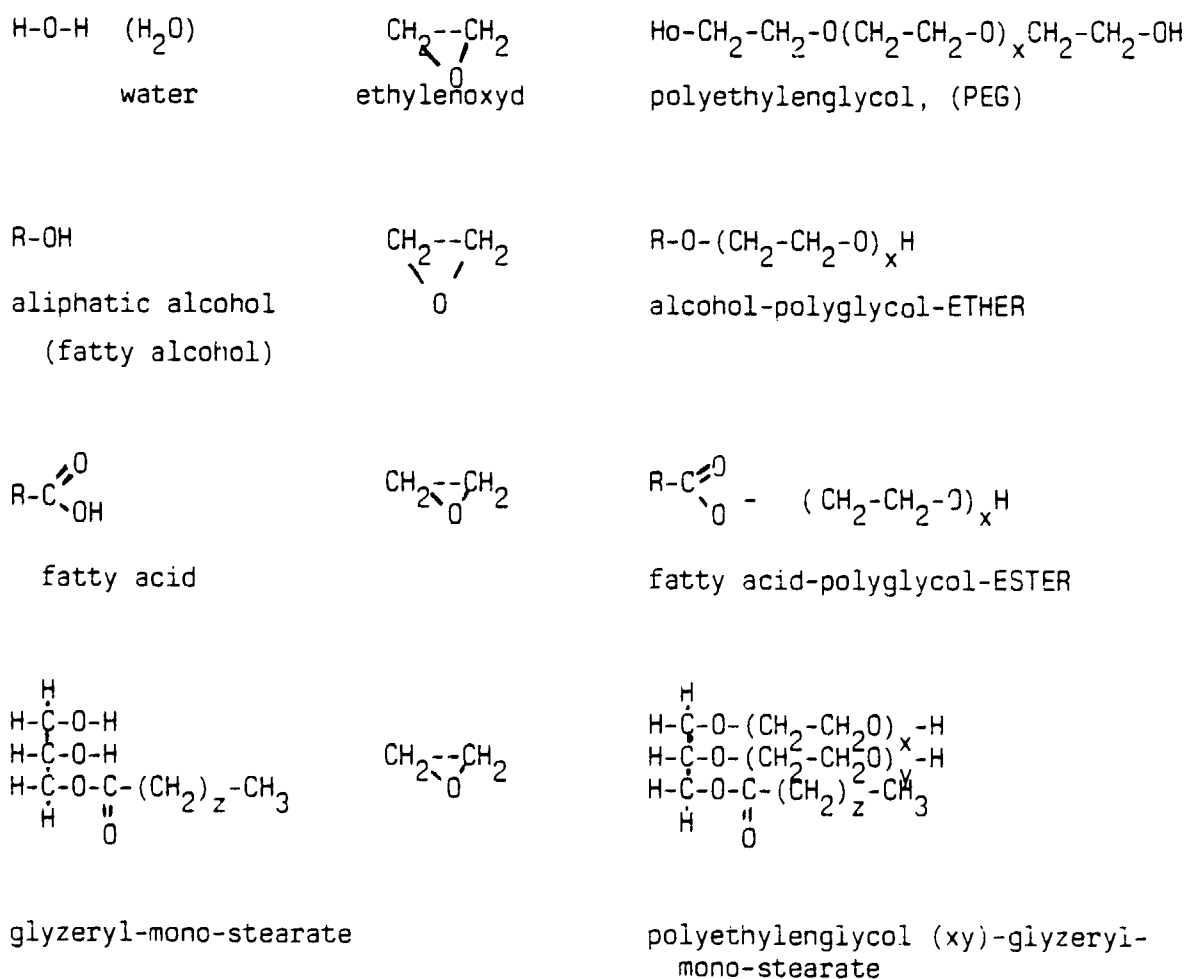
Therefore only guidelines could be established and first recommendations given. It was agreed that the expert should render further assistance in the selection of products and procedures.

### 3. INTRODUCTION

#### A 1. Polyethers, their chemistry and their denominations

One of the components for "Polyurethanes" are the so-called polyols or polyethers. These are condensation products of different chain-lengths of propylenoxyd and ethylenoxyd. These higher molecular polyethers are produced in the installations of SODASO in Tuzla.

The ethylenoxyd, a liquid with an evaporation point of 11°C, is very reactive and reacts with free hydrogen atoms in organic components, forming chains of different molecular weights of "oxyethylen", the polyoxyethylen- or polyethylen-glycol- adducts, resp. the PEG's.





By the addition of ethylenoxyd, the ethoxylation, the normally water-insoluble components become more watersoluble and, depending on the introduced number of ethylenoxyd- (EO)-groups, they develop dispersing or/and emulsifying properties. The resulting products are known under the general denomination "Nonionics" or "ethoxylates". Their production technique is well known and the basic patents have expired.

The commercialized products have a very broad field of applications and are well introduced in the trade. Sometimes one product is sold under double denominations for various applications.

The best known among the nonionics are the nonyl phenol ethoxylates. They are widely used washing- and wetting agents. This type of commodity-product already is produced in Yugoslavia. For several reasons the nonyl phenol ethoxylates are not subject of the project. Normally they are not used in cosmetic formulations.

In cosmetic formulations only ethylenoxyd-adducts of natural fatty acid derivatives can be used as basic raw materials. These are:

- fatty acids
- fatty alcohols
- homologous fatty acid derivatives.

The chemical industry also offers synthetic fatty alcohols, mostly secondary alcohols, but for reasons of smell and biodegradability they are not suitable and not acceptable for cosmetic formulations.

Many other fatty acid based derivatives can be ethoxylated, like the fatty amines or fatty acid ethanolamines. This is another group of well introduced products for cosmetic applications and other applications. At this stage this ethoxylated amines or amides are not subject of the project.

Besides of the mentioned ethoxylates of fatty acid components, many other components can be ethoxylated and are used in the industry, as e.g. thiodiglycol,  $S = (CH_2-CH_2O)_2$ .

The expert is in the position to assist in the selection of such products.

In fact, at this early stage of the project, the mutual efforts should concentrate on the ethoxylates of the straight derivatives of fats and oils, available at this time and of domestic origin and with less sophisticated processes of production and problems of reproduction. This procedure will, obviously, lead within short time to acceptable results with environmentally safe products.

A 2 Biodegradability

The referred ethoxylates of derivatives of natural fats and oils show an excellent primary biodegradability (almost 100%) within a very short time. Also they don't show fish toxicity in effluent systems.

Most of the products have been tested and corresponding literature is available.

Ethoxylates of synthetic alcohols (secondary alcohols) show a significant minor biodegradability.

A 3 Toxicity

Under application conditions the referred ethoxylates are not toxic. Products within the established specifications, under application conditions, do not show irritations of the human skin. Corresponding literature is available.

A 4 Applications of ethoxylated products in cosmetic formulations.

Besides of fatty alcohols and fatty alcohol sulfates as the basic ingredients of cosmetic products they are used as

cream bases	glyceryl-and glycol-esters and their ethoxylates
oily components	mainly fatty acids esters, also polyglycol-esters
emulsifiers (also for pharmaceutical formulations)	mainly fatty alcohol ethoxylates based on natural fatty alcohol
foam- and viscosity stabilizer	fatty acid alkanolamides and their ethoxylates
viscosity regulator	polyethylenglycols of different molecular weight

and as

intermediates for anionic  
tensioactive components

n-fatty-alcohol-polyglycol-ethers

B PARTNERS IN THE PROJECT DP/YUD/82/005/11-02

UNDP/Governmental liaison to the Socialistic Republic of Bosnia  
and Herzegovina:

Republican office for technical co-operation,  
Sarajevo

discussed with:

Dr. Panjeta, Vice Director

Mrs. T. Vidorić

B 1 Project management

Dr. Vahid Sendijarević

project director  
director of the development  
department in WO HAK I of SODASO;  
Tuzla

Dr. Duško Lazrević

president of the council of  
of the project  
president of the Institute of  
Chemical Engineering (ICE), Tuzla

Dr. Danilo Božanić

director of the WO R&D-Institute  
of the SBS-group, Sarajevo  
Co-ordinator of activities within  
the SBS-group

The activities within the project are divided between

Institute of Chemical Engineering (ICE), Tuzla

R&D-activities for the ethoxylation

Chloralkali complex WO HAK I of SODASO, Tuzla

pilot plant for ethoxylations  
production plant ethoxylation



B 3 ASTRO Cosmetic industry, Sarajevo

Director Mr. Krvavac Asim

Originally an old soap manufacturer and nowadays with a soap market share of about 10%, the working unit Astro has developed to a well known manufacturer of cosmetic products. Formerly working in licences since 2 years Astro has developed their own brands of cosmetics, as e.g. decorative and care products, shampoos, household cleaners and perfumes. The cosmetic market share is estimated at about 3%.

Detergents in powder are not in their programme. Detergents are produced by the WO DITA, belonging to SODASO in Tuzla.

In 1984 a new factory and new development laboratories will be constructed, the production will be improved by the acquisition of more advanced equipments.

Mrs. Fisca Merdzana is Deputy director of the development laboratories.

B 4 AFS

In this new production unit many of the formerly imported raw materials and intermediates for pharmaceutical products are now produced locally, under licence of Astra/Sweden.

The production unit is well equipped with reactors and distillation columns, vacuum pumps etc. Also exist modern multipurpose glass reactors with columns etc.

B 5 Quality control laboratories

The laboratories are well equipped and are responsible for the quality control of Astro-, TPF-, and AFS-products.

B 6 The WO Scientific Research and Development Institute deals with organic synthesis, formulation of pharmaceutical products, analytical research, market research etc. Actually the institute is in reorganisation in view of product development and market research.

Available in the Institute is a laboratory for preparative organic research and a pilot plant with an appropriate pilot reactor of 25 liter capacity.

C SODASO ORGANISATION IN TUZLA

The SODASO organisation is a big chemical complex in Tuzla. Relevant for the products of the project polyethers for cosmetics is the WO HAK I, the Chloralkali Complex I.

Dr. Vahid Sendijarević is director of the R&D department of WO HAK I. A 3 liter reactor for the ethoxylation will be made available in the pilot plant department.

Part of the WO HAK I is the production plant of polyols resp. polyethers for "polyurethanes". The necessary propylenoxyd is produced in a separate plant, the necessary ethylenoxyd comes from abroad in rail tankers and is stored in watercooled big storage tanks.

The synthesis of polyols is an automatically controlled chemical process. For the production of the referred ethoxylates a 500 liter reactor will be adapted. This reactor actually is incorporated into the polyol installation.

The estimated time for the modification of this 500 liter reactor is approximately 3 months.

Actually, for the referred ethoxylation no other raw materials than the ethylenoxyd are available in WO HAK I.

Another working organisation within SODASO in Tuzla is WO DITA. In a spray tower they produce detergents. For detergents also exists a demand of Nonionics/ethoxylates products similar to these for cosmetics.

Within the macroproject DP/YUG/82/005 exists a microproject for the application of nonionics in detergents.

D INSTITUTE OF CHEMICAL ENGINEERING (ICE) IN TUZLA

Dr. Duško Lazarević is president of the Institute. Members of the Institute and of the R&D department of WO HAK I will operate the pilot plant for the ethoxylation.

## I IMPLEMENTATION OF THE MISSION

The expert has given assistance in analysing the situation concerning the production of diversified polyethers and their applications in cosmetics.

The expert has conducted several lectures about the application of ethoxylates in cosmetic formulations in the Cosmetic Industry ASTRO in Sarajevo.

It would be very useful to improve the applicational experiences in ASTRO, specially in view of the future enlarged disposability of domestic ethoxylates for new formulations and the new processing equipments. This abroad training programme is already scheduled in the project DP/YUG/82/005.

The feasibility of the subproject "polyether for cosmetics" was studied, particularly in view of the actual economical situation in Yugoslavia. Unfortunately there were not yet available market figures about the markets in question.

As previously layed down in this paper, there exists a unique chance to realize the substitution of imported ethoxylates by utilizing the domestic resources of environmental safe raw materials, utilizing existing R&D-know how and facilities and disposable production facilities. It is obvious, that greater investments are not indispensable in the initial stage and that the first savings in imported goods can be materialized within short time.

As a result of the investigations and discussions with the project management the following strategies were summarized and agreed to propose as guidelines in this report:

- Substitution of imported ethoxylates by products with identical specifications,
- utilization of domestic raw materials or such of countries with nonconvertible currencies
- utilization of existing equipments or their adaption with a minimum of investments,
- criterions for the selection of the products to be substituted:
  - not yet produced in the desired import-quality
  - products of high performance/price ratio

- homologous products based on a limited number of raw materials
- products based on biodegradable raw materials
- products which could be used for further refinement
- products with applications in several industrial areas
- products suitable for export
- products which could be promoted for increasing consumption in the cosmetic industry.

Only in a later stage of the project and in possession of the required applicational know how and customer service facilities modified or improved ethoxylates should be offered to the market.

## II REMARKS

The actual economical situation asks for an immediate reaction and a pragmatic overcoming.

The only promising solution is the substitution of the imported products without any attempts to improve their performance.

The users of the products only will accept substitutes of domestic origin when they fall exactly into the used specifications!

The production processes of fatty acid derivatives and ethoxylates are known and available, the adaption of the existing pilot plants and production equipments can be done by own personnel and without greater investments and within acceptable time.

The production staffs are experienced in the handling of the ethyleneoxyd and in the synthesis of chemicals of pharmaceutical quality.

The independent quality control laboratories in Sarajevo are experienced in the quality control of products like pharmaceutical specialties.

The marketing of the ethoxylates does not require a specialized organisation. The ethoxylates have to be delivered to several application areas, but marketing is limited to a surveyable number of consumers. For the different areas the roughly estimated



consumption of the referred ethoxylates based on natural raw materials is as follows: (in %)

Cosmetics 15, textiles/leather/fabrics 40, detergents 10, emulsifier for various applications 20, additives 10, others 5.

Exports of the ethoxylates can facilitate the import conditions for absolute necessary raw materials from abroad.

### III. IMPACTS FOR THE REALIZATION OF THE PROJECT

Together with the project management the starting position was defined and it was agreed in the initial actions of the development programme.

### IV. SITUATION OF THE RAW MATERIALS AND PRODUCTION FACILITIES

#### IV.1 Ethylenoxyd

This raw material already is used in the production plant of WO HAK I in Tuzla. The personnel is experienced in the handling of the ethylenoxyd.

Probably because of the great consumption of the ethylenoxyd in WO HAK I there could exist advantages in price and availability of the product.

#### IV.2 Raw materials of natural origin

Except of the ethylenoxyd most of the other raw materials are based on derivatives of natural fats and oils. They are either purified and distilled fatty acids and glycerin or fatty alcohols, produced by hydrogenation of fatty acids.

##### IV.2.1 Fatty acids

A first market investigation has shown that several of the required fatty acids are available in the country. The WO Radeljewić in Dubrovnik was visited on 10.09.1984. This WO is the only manufacturer of hydrogenated fatty acids and of distilled oleic acid. The saturated fatty acids were based on tallow and the insaturated oleic acid based on olive-oil.

The WO Radeljević is in position to supply the fatty acids within the required specifications. Actually several samples were tested in the R&D Institute in Sarajevo.

#### IV.2.2 Fatty alcohols

Fatty alcohols of natural origin, the primary alcohols/n-alcohols, are not produced in the country. They have to be imported and paid in convertible currency.

WO Radeljević has an annual production of 2800 tons of stearic acid and 1100 tons of oleic acid. The General Director, Dr. Jacov Mandun informed that the WO has projected to diversify the fatty acid based production into the field of natural fatty alcohols. The technology of the hydrogenation of the fatty acid is known, but the project cannot be realized because of the known economical situation.

The experts proposal is to investigate the market situation of natural fatty alcohols, specially in view of the import situation, and to screen a project of the national production of natural fatty alcohols.

#### IV.2.3 Glycerin

Glycerin is produced in the working unit ASTRO in Sarajevo, but not in the required waterfree quality. The rectification of glycerin is under investigations in the working unit AFS, Sarajevo.

#### IV.2.4 Derivatives of fatty acids

These derivatives are not yet available within the required specifications. The R&D Institute, Sarajevo, already has initiated a programme of market research and of product development.

Market research will investigate the availability of homologous products of domestic origin, as well as the types, quantity and price situation of imported homologous products. Also they will investigate the supply position of the corresponding raw materials of domestic origin. It is advisable to extend this investigation

to goods from other countries with nonconvertible currency. The synthesis of the required derivatives of fatty acids already has started in the laboratories of the R&D Institute in Sarajevo. The expert has handed over several operating procedures and it was agreed, that he will continue to render assistance to the R&D Institute. The pilot plant, a 25 liter multi-purpose reactor, will be reconditioned within 4 weeks.

It was recommended to start with the esterification of polyalcohols with fatty acids, as e.g. to glyceryl-mono-oleate, glyceryl-mono-stearate and homologous products.

The resulting products will be used as raw materials for further ethoxylations in Tuzla. They also can be used as components for cosmetic formulations. In the same multi-purpose-reactor many other components for cosmetics can be produced, as e.g. diesters, triesters etc. The corresponding products have been discussed.

In the production plant of the working unit AFS, Sarajevo, in which actually the raw materials for pharmaceutical products are synthesised, on principle, the before mentioned products also can be synthesised.

On the other hand there is a good chance, that probable with slide adaptations, other equipments existing in AFS could be made appropriate for the proposed synthesis.

Regarding the favorite availability of equipments and professional skills in the AFS plant, it is advisable to consider the possible production of this type of products just before making up the budget for 1985.

The expert is disposed to render assistance in the denomination of suitable products and procedures.

## V. PRODUCT DEVELOPMENT PROGRAMME

### V.1 Ethoxylation

The project management has agreed to initiate the ethoxylation programme with the following reactions:

Stearic acid	plus 8 mol EO (Ethylenoxyd)
	plus 20 mol EO
Cetyl/Stearyl-alcohol	plus 12 mol EO
	plus 20 mol EO
	plus 30 mol EO
Glyceryl-mono-oleate	plus 6 mol EO
Glyceryl-mono-stearate	plus 24 mol EO

The specifications of the fatty acid derivatives are well established. The fatty alcohol, for the time being, has to be imported. The fatty alcohol has been selected under consideration of a later domestic production based on domestic tallow.

The specifications and reference samples of the imported ethoxylates are available.

The imported ethoxylates are produced in specially designed equipments. In Tuzla an adapted reactor will be used. Special attention will be paid to the color of the ethoxylates for cosmetics.

The expert is in position to render technical assistance in ethoxylation.

V.2 Esterfication see IV 2.4 derivatives of fatty acids

## VI. MARKETING DEVELOPMENT PROGRAMME

Several of the mentioned ethoxylates or homologous are used in many other areas of applications, mostly under double denomination.

Consequently the consumption of identical or homologous ethoxylates has to be evaluated in the following industrial areas:

Textile industry	as components in textile auxiliaries for the manufacturing and finishing of textile, as wetting-, washing-, dispersing- emulsifying and levelling agents,
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Synthetic fibre industry	as washing and emulsifying agents as lubricants and antistatic agents for man made fabrics
Leather industry	same as textile industry
Detergent industry	as emulsifying-, wetting-, washing- agent in household and industrial cleaners
Petroleum industry	as emulsifier and foaming agents for oil perforations
Mineral oil industry	as antifriction agent and lubricant as additive in metal finishing oils
Agrochemicals industry	as emulsifier for insectizides
Paint and printing ink industry	as dispersing agent for pigments
Plastic industry	as lubricant and slipping agent
Mineral industry	as floating agent for ores and minerals
Building material industry	as wetting agent for concret and dust precipitater
Food industry	as emulsifier for oils and fats
Pharmaceutical industry and	as emulsifier and solubilizer
Cosmetic industry	see A 4 page 7

Market research of the R&D Institute in Sarajevo will establish contacts to key consumers in several areas, also to other consumers in the cosmetic industry.

The expert is in position to render assistance in the selection and substitution of the appropriate ethoxylates in the named areas.

RECOMMENDATIONS

The initiated development-works in Sarajevo and Tuzla will require a further follow-up.

UNDP/WHO/UNIDO is requested:

1. In view of the realistic feasibility of the substitution of imported ethoxylates the experts assistance should be extended to min. 4-5 m/m, spread in intervals over the next 12 months.

2. The activities of a special expert in polyether applications for lubricants should be postponed, because of eventual overlapping in development and production with similar types of polyethers. The expert, with experience in the chemistry of lubricants, can disclose the chemical constitutions and procedures for production, and can assist in setting priorities.

Requested duration of the appointment 0,5 m/m

3. Provision of a fund in convertible currency for acquisition of indispensable literature, books and periodical journals about ethoxylation and the application of ethoxylates.

Requested min. 1000 US \$

Urgently is needed: Surface Active Ethylen Oxide Adducts by Schonfeldt, Pergamon Press, London 1970, (0-08-012819-x) price 55,00 pound sterling.

Please inform Dr. Božanić, Sarajevo, about eventual actions by UNIDO.

4. Screening of a project about the national production of biodegradable fatty alcohols based on domestic fats and oils, eventually jointly with Radeljević in Dubrovnik.

Assistance by the expert, duration 1 m/m

5. Provision of a fund in convertible currency for ad-hoc-acquisition of locally not available raw materials, intermediates or reference

samples and accessories for laboratory and pilot plant.  
Requested approx. 2000 US \$.

ACKNOWLEDGEMENTS

Sincere thanks are expressed for all the assistance and generous hospitality to Mr. Milan Milanović, President of WO Bosnalijek, Sarajevo, and Dr. Danilo Božanić, Director of the R&D-Institute, Sarajevo, and to Dr. Vahid Sendijarević and Dr. Duško Lazarević for their colleguel co-operation.

