



TOGETHER
for a sustainable future

OCCASION

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



TOGETHER
for a sustainable future

DISCLAIMER

This document has been produced without formal United Nations editing. The designations employed and the presentation of the material in this document do not imply the expression of any opinion whatsoever on the part of the Secretariat of the United Nations Industrial Development Organization (UNIDO) concerning the legal status of any country, territory, city or area or of its authorities, or concerning the delimitation of its frontiers or boundaries, or its economic system or degree of development. Designations such as “developed”, “industrialized” and “developing” are intended for statistical convenience and do not necessarily express a judgment about the stage reached by a particular country or area in the development process. Mention of firm names or commercial products does not constitute an endorsement by UNIDO.

FAIR USE POLICY

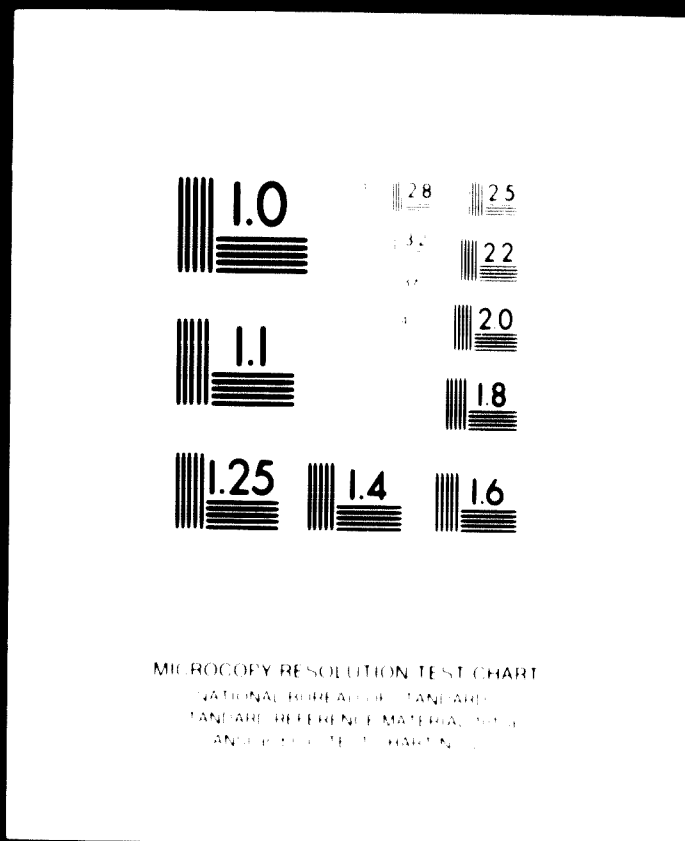
Any part of this publication may be quoted and referenced for educational and research purposes without additional permission from UNIDO. However, those who make use of quoting and referencing this publication are requested to follow the Fair Use Policy of giving due credit to UNIDO.

CONTACT

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

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

1 OF 1



24x
F

CONFIDENTIAL

NATIONAL PETROCHEMICAL COMPANY
PLANNING, ENGINEERING & DEVELOPMENT DEPARTMENT

01066

DETERGENTS FOR AN EXPANDING IRANIAN ECONOMY

Prepared by : W.E. Mydans
United Nations Consultant

Approved by : L. Bahari

December 1971

CONFIDENTIAL

NATIONAL PETROCHEMICAL COMPANY
PLANNING, ENGINEERING & DEVELOPMENT DEPARTMENT

DETERGENTS FOR AN EXPANDING IRANIAN ECONOMY

Prepared by : W.E.Mydans
United Nations Consultant

Approved by : E. Bahari

December 1971

DETERGENTS FOR AN EXPANDING IRANIAN ECONOMY

TABLE OF CONTENTS

	<u>Page</u>
Glossary of Terms and Abbreviations	1a
I. Summary and Conclusions	1
II. Introduction	8
III. Detergents-General	9
A. Soaps	9
B. Synthetic Detergents.	11
IV. Synthetic Detergents to Meet the Future Need of Iran	29
V. Chemistry and Technology of Synthetic Detergents	42
A. General	42
B. Specific Detergents.	47
1. ABS Surfactants	47
2. LAS Surfactants	50
3. SAS Surfactants	56
4. N-Primary Alcohol Sulfates	57
<u>Appendix A:</u> Quality of Water in Iran.	62

GLOSSARY OF TERMS AND ABBREVIATIONS

ABS	: Alkyl benzene sulfonate
Builder	: A material used in conjunction with synthetic detergents to enhance their action.
DDB	: Dodecyl benzene
DDBS	: Dodecyl Benzene sulfonate
Hard water	: Water which contains Ca and Mg ions in excess of 250 PPM. (parts per million)
Hard detergent	: A non-biodegradable detergent; i.e. resistant to bacterial degradation.
Hydrophilic Group	: A strongly polar group, usually rich in oxygen, that is attracted to water and repelled by fatty materials; a lipophilic group.
Hydrophobic Group	: A hydrocarbon group that repels water or is attracted to fatty materials; a lipophilic group.
LAS	: Linear alkyl benzene sulfonate; a soft or biodegradable detergent.
NPC	: National Petrochemical Co.
SAS	: Sodium alkyl sulfonate
Soft Detergent	: A biodegradable detergent; one consumed rapidly by bacteria.

GLOSSARY (Contd.)

Soft water

: Water which contains less than 80 ppm of Ca and Mg ions.

STPP

: Sodium Tripolyphosphate

Surfactant

: A surface active agent useful as a detergent or a wetting or emulsifying agent.

DETERGENTS FOR AN EXPANDING IRANIAN ECONOMY.

7. SUMMARY & CONCLUSIONS

A review has been made of detergents and how they fit into the Iranian industry, economy and useage. It is concluded that in rural areas where water is not too hard, conventional soaps should be continued in use because they are effective, and in order to make economic use of fatty by-products of the slaughtering industry and because they are biodegradable and do not pollute streams and underground waters.

Where waters are hard - as in most of Iran - synthetic detergents are essential, and this need has been met by a 10,000 - 12,000/mta dodecyl benzene (DBB) plant at Abadan. The detergent made from this material, called alkyl benzene sulfonate (ABS), is very effective and efficient, but it is non-biodegradable, which leads to major problems in sewage disposal. Except in a few isolated cases, there are not yet any sewage disposal plants in Iran, with all sewage being disposed by cesspool - soil percolation (as in Iran) or by discharge into rivers, estuaries or the seas. Problems associated with a non-biodegradable detergent have not yet arisen in a serious fashion in Iran.

A study of current and potential markets for detergents in Iran reveals that, on extrapolating the demand growths of the past two or three years, the capacity of the DBB plant at Abadan to supply the combined domestic and export markets with synthetic detergents will be exhausted by 1972; and by 1974-75 for sodium tripolyphosphate (STPP) from the new plant near Shiraz.

This conclusion requires, however, a qualification, as is apparent from this table:

m.tons of compounded detergents containing 30% DDB sulfonate ******

	<u>Consumed in Iran</u>		<u>Exported to USSR</u>		<u>Total</u>
	M.tons	%increase	M.tons	%of total	
1968	15,000	→	10,000	40	25,000
1969	20,500	→	13,500	56.5	34,000
1970	27,500	→	15,000	47	42,500
1971	31,000	→	17,000	39	48,000
1972 (Est.)	40,000	→	20,000	33.3	60,000
1973 (Est.)	52,000	→	25,000	32.5	77,000

This emphasizes with what a very large dependence the health of this industry rests on exports to Russia. Over one third of all the eggs are in a single basket. Although the growth in domestic demand has been very great and steady, the growth in U.S.S.R. exports have been even greater, ranging from one third to over one half of all production. Such a large dependence upon a demand that is totally outside of all Iranian controls can hardly be considered healthy. It is true that these exports have shown a progressive growth during the past five years; but the insecurity of this business is manifest when it is realized that it rests on barter deals that could end abruptly should U.S.S.R. find other detergent sources, or should U.S.S.R. fail to provide compensating exports desirable to Iran, or should unforeseen political obstacles arise.

****** It should be noted that some detergents produced in Iran have as little as 17% DDB sulfonate, but this is not usual. It may, however, influence the date at which current domestic production becomes inadequate.

This factor must be emphasized, because it makes rational planning for the expansion of the Iranian synthetic detergent industry very difficult. If the U.S.S.R. requirements from Iran continue to grow at a rate projected from the immediate past, then our domestic production of DDB and STIP will fail to meet requirements by mid 1972 for DDB and by 1973-74 for STIP. If, however, the U.S.S.R. demand were to end with 1971, our current production would suffice until end 1974-75 for DDB and probably until 1976-77 for STIP.

Further, considering these uncertainties, it becomes all the more important that future expansions in the production of synthetic detergent materials be of a modern type, e.g. linear alkyl benzene sulfonate (LAS) (see below), which, if need be, can be exported to competitive markets that no longer will accept the non-biodegradable old detergents. It is obvious that between the exhaustion of our present productive capacities and the creation of new additional capacities, there will have to intervene a period when the deficiencies must be provided by imports. Modern productive facilities in the chemical field require an immediate output of at least 70% of rated capacity for economical function, so that the new plant expansion must wait on the development of new demand - combined domestic and export - for close to 70% of the new output.

In order to make the planning for the future expansion of this industry as rational as possible, further studies beyond this report are necessary. This study has concerned itself largely with technical aspects and has sought to

direct attention to the specific synthetic detergents that will best meet the future needs of Iran. In this study, also, an attempt has been made to gather and interpret what market data that exists relative to these materials, - but it serves to point up the paucity of the data and its inadequacy relative to our needs. It is recommended, therefore, that a study in depth be initiated to develop greater market knowledge on synthetic detergents, which, while directed primarily toward the domestic market, should extend, so far as is possible, to those export markets which might serve to absorb the Iranian excess production. It is important that any new plant be of such a size that it can enjoy economies of scale, and that appears to be a dubious possibility unless an appreciable export business can contribute to the volume of production. The recommended study should range broadly, but should seek to develop knowledge on the following points:-

- a) An analysis and projection of the domestic demand for synthetic detergents. The projection should extend for ten years, i.e. until 1982, This will require demographic analysis covering both population growth and the rising standards of living which are often measured by the per capita consumption of detergents.
- b) Far more difficult than a) is a similar effort directed toward selected possible export markets. The selection will have to be in large part arbitrary, resting on political and economic factors, and on what the export recipients have in money or commodities with which to

pay for the synthetic detergents. Our exports can be three-fold: linear alkyl benzene, linear alkyl benzene sulfonate, and completely formulated synthetic detergents in bulk and in packaged form.

- c) An analysis with the help of engineering contractors of the system to be used for the production of linear alkyl benzene, and to develop what size production will be economic under Iranian conditions; also what raw materials will be required under the several systems of production with particular reference to the production of the straight-chain, alpha olefin. Only when the optimum production size has been established can we project at what point in our time VS demand curve the approximate time when the demand will absorb 70% of the new production.

Requests to Engineering Contractors for initial order of magnitude offers should be requested without delay in order that this planning may start with proper proportions.

- d) The study should seek to gather technical and market information on the newer synthetic detergents that are in the course of development. This information though it has a low immediacy, can be valuable to provide both direction and proportion to planning for a "third generation" production, targeted, perhaps, at 1982. Long before that time is upon us, a clear concept of direction and magnitude should have developed in this field.

An analysis of the vast number of currently developed and developing synthetic detergents leads to the conclusion that:-

- a) The currently produced DDB sulfonate will continue to serve the rural areas well and efficiently and its non-biodegradability will involve such areas in no major problems. The production of this material should not be interrupted, except, that as urban areas grow, efforts should be made to direct the ABS detergents to rural areas, and the newer biodegradable detergents to the urban areas.

- b) With a half million cubic meters of sewage being dumped every day into ^{the} soil under Tehran, and comparable per capita amounts in other larger cities, sewage disposal plants are being planned. These will be necessary to avoid subsoil water pollution and health hazards, and to recover the waste waters for use in irrigation. Such plans compel us to look to a biodegradable detergent for a "second generation" cleansing agent. Adhering to the dictum that at this time Iran wants only well proven processes and products, the choice of a new surfactant centers on linear alkyl benzene sulfonate (LAS). A productive unit is recommended, large enough to gain economies of scale, to supply domestic needs for urban areas and, being biodegradable, can win a possible place in export markets. U.S.S.R. is currently taking one

third of all the ABS detergents produced in Iran, - but this important market is tenuous in view of world reaction against non-biodegradable detergents. The technology for the production of LAS synthetic detergents is readily available from a number of competitive sources.

It is emphasized that an effective synthetic detergent consists basically of two essential components: a surfactant and a "builder". The most effective and economical builder is sodium tri polyphosphate (STPP). A productive facility for this material is now under development at Shiraz Fertilizer Complex, which will utilize soda ash from the plant now nearing completion in the same plant area.

- c) Looking forward to 1978-1980, a "third generation" of synthetic detergent is considered - a linear alkyl sulfate which is a superior surfactant. The manufacture of this material will depend on the production of a C12-C14 straight chain, primary alcohol by polymerizing ethylene in a technique very similar to the process that NPC/Mitsui will employ in the production of high density polyethylene resin. It is important, therefore, to give consideration to this proposal at this time so that the demand for high purity ethylene and plans for a production facility can be coordinated and possibly made a part of the NPC/Mitsui Olefin Complex.

II. INTRODUCTION

Currently, Iran has a detergent industry that supplies the domestic market with soaps and synthetic detergents, the latter based upon 10,000-12,000 m.t./a of dodecyl benzene produced by Abadan Petrochemical Company. Obviously as the Iranian population expands, additional amounts of detergent will be required; and as the Iranian economy grows in affluence and the industry in sophistication, additional types of detergents will be demanded. It is the purpose of this study to look ahead and to recommend to National Petrochemical Company the type or types of detergents that should be developed to supply those growing needs.

III. DETERGENTS GENERAL

A. Soaps: Amongst detergents, the earliest and for many years the only cleansing agent was soap, manufactured from natural vegetable and animal oils and fats. When properly selected and produced, and when used in waters not excessive in hardness, soaps function well, at moderate cost and with considerable versatility, covering the broad spread in uses from personal cleansers, laundry and industrial textile cleansers, industrial wetting, dispersing and emulsifying agents. Much of the raw materials are close at hand and of low costs, e.g. animal tallow and vegetable oils. Further, soaps can be made in widely distributed factories of modest size and capital requirements and until 1935-1940 fulfilled virtually all cleansing, dispersing and emulsifying functions.

The chief defect of soap is the extreme sensitivity to the presence of heavy metal impurities in water, e.g. calcium and magnesium ions, which precipitate the soap as an insoluble curd. This curd, when deposited in small amounts from successive launderings, leads to a yellow or gray coloration and a gummy feel to the fabric. When, however, the water is not excessively hard, the use of an excess of soap can soften the water by precipitating the heavy metal ions. If enough soap is used, it may disperse the precipitated curd. Thus, soaps may function reasonably well, even in moderately hard waters, but the use of soaps to soften water, or in large excess to cleanse in hard waters is very uneconomical and, in addition, leads to yellowed and gummy fabrics.

Summarizing soaps, they are still preferred where soft water is available from natural sources or by water - softening treatment; also for personal cleansing where there is a high soap to water ratio. No synthetic detergents have yet been developed from which good toilet soaps can be made that function as well as good coconut fat soaps. There remains an important economic advantage to the continued use of soaps where water is soft enough and also to provide an outlet for the cheap and abundant tallow which is a by-product of meat production. For example, soaps continue to be used in the emulsion copolymerization of butadiene and styrene to produce SBR synthetic rubber. Since the process is carried out in deionized water, soaps are effective and function at low cost.

In general, water which contains up to 80 ppm (parts per million=mg/liter) of total hardness (calculated as CaCO_3) is considered soft; above 500 ppm the water is too hard for effective use of soap, and between these two limits is a wide area in which soaps may be used, but with increasing difficulty and economic disadvantage as the hardness increases. Unfortunately, in Iran, most waters are hard in varying degrees, and are, in general, too hard for effective use of soaps. Surface waters vary in hardness from place to place and from season to season. In surface waters that drain to the Caspian Sea, total hardness varies from as low as 100 ppm, which is relatively soft and in which soaps may function, to as high as 1300 ppm, in which soaps cannot function at all. For rivers that drain to the Persian Gulf, the average total hardness is somewhat higher,

making the use of soaps even more ineffective. Deep well waters, e.g. in Shiraz and Isfahan, are without exception too hard for effective and economic use of soaps. See Appendix A for water qualities in Iran. Though soap use may be low in unit cost, it is excessive in application cost, since a major portion of the soap is used to soften the water, and the large amount of precipitated soap curds yield off-color and gummy-feeling fabrics.

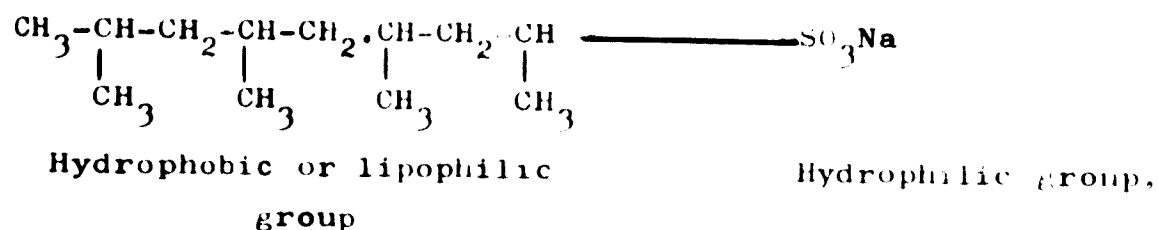
The above resume on soaps has been included in order to point up and emphasize the importance of finding and developing more effective and economical cleansing agents than soap. All over the world, there has been a constantly growing pressure toward the replacement of soap (except for personal cleansing) by synthetic detergents which work with great effectiveness and economy in cold and hard waters.

B. Synthetic Detergents

It was early recognized that calcium and magnesium salts of organic sulfonic acids have relatively high water solubilities as compared with the solubilities of the same salts of carboxylic acids, i.e. soaps. It was natural, therefore, to seek the development of hydrophobic groups (water repelling hydrocarbon chains) attached to sulfonic acid groups (as hydrophilic groups) as replacements for the readily precipitated soaps, --- and such materials were, in fact, the first synthetic detergents. Such compounds can be produced in a number of ways and there has resulted a whole family of such compounds,

each with small differences in properties and with varying economic advantages and disadvantages. The ultimate selection of a suitable synthetic detergent for large scale production depended in large measure on the relative availability of its raw material requirements. Rapidly, soon after 1945, one such compound rose to a dominant position, and dramatically swept across America and Western Europe and in little more than five years (1945-1950) displaced over one half of the soap in use and covered broadly the entire use of detergents from household uses through industrial and laundry applications.

The new synthetic detergents were mostly dodecyl benzene sulfonate (called alkyl benzene sulfonate or ABS) and typically represented by :-



The sulfonic acid group is fixed in its hydrophilic properties, but the hydrophobic hydrocarbon chain can be made longer or shorter at will and so alter its properties. It was found that a chain containing 12-14 carbons gave an optimum balance to the sulfonic acid group and resulted in a very effective detergent. Furthermore, it could be produced by well known

techniques in large quantities at low cost. It was very **effective in cold, hard water** and it was without toxic or allergic effects. The production and use of this detergent grew rapidly.

The **abs detergent**, however, had initially two major defects, and later it was discovered to have a third very serious defect. The two initial defects were: a) a relatively harsh action which made it undesirable for personal cleansing, and b) a marked capacity to lift dirt and soil from fabrics but a poor ability to hold the lifted dirt in suspension, and an important portion of the dirt was redeposited on the fabric, leading to a graying of light colored materials. With time and effort, both of these defects were overcome or minimized:-

- a) The harshness by the incorporation of emollients.
- b) Through the recognition of the importance of "builders" and their development and use as essential components in synthetic detergent compositions.

The builders are colloidal materials which serve to hold the soil lifted off by the abs detergent in stable suspension. The most effective builders are polymeric sodium or potassium phosphates, e.g. tetrasodium pyrophosphate ($\text{Na}_4\text{P}_2\text{O}_7$), sodium tripolyphosphate ($\text{Na}_5\text{P}_3\text{O}_{10}$), and higher phosphate polymers. The one having optimum properties at moderate cost has been the sodium tripolyphosphate. Reasonable stability even in hot water, excellent powers of colloidal suspension, and strong

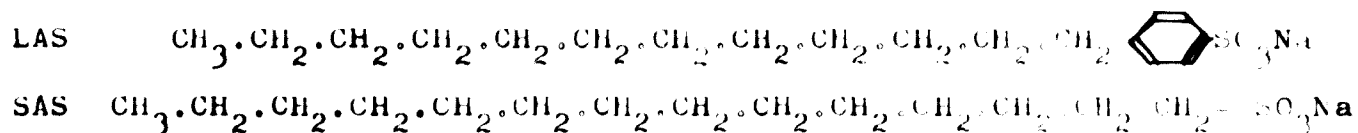
complexing power by which it ties up and renders ineffective heavy metal ions (e.g. ferric ions) which are responsible for many fabric discolorations. These polymeric phosphate builders are used in fairly large proportions, e.g. up to 60% by weight of a synthetic detergent formulation. They are, therefore, of prime importance in the development of a synthetic detergent industry and production facilities for sodium tripolyphosphate must be created to parallel those for the synthetic detergent itself. The use of sodium tripolyphosphate as a synthetic detergent builder now represent the largest non-fertilizer phosphate application.

In addition, it was discovered that the incorporation of small amounts of other colloidal materials (e.g. 1-3% of sodium carboxy methylcellulose) greatly increased the capacity of the polymeric phosphates to hold lifted dirt in suspensions from which little or none was redeposited on the cleaned surfaces.

Thus, the modern synthetic detergent emerged and when built with polymeric phosphates and carboxy methyl cellulose (silicates and other materials serve as alternates, but are not so effective), was very effective and economical. Since much of the world must carry out its cleansing operations in hard waters, this new synthetic detergent rapidly pushed soaps aside, and in so doing resulted in a precipitous drop in the price of tallows. Though intensive research has resulted in the development of many new uses for tallow, the price level still remains considerably below that at which it was as the basic raw material for soaps.

Nothing, it seemed, could be more efficient and economical than the new ABS synthetic detergent compositions, and so Iran, in seeking to develop a domestic means to meet its hard-water detergent needs, built at Abadan a facility to produce 10,000-12,000 m.tons per year of dodecyl benzene. This material is sold to a number of ultimate detergent makers who sulfonate and compound it. So far it has met the domestic needs very well and it has given little trouble in Iran, - but elsewhere, particularly in America, Western Europe and Japan the use of enormous quantities of ABS detergents has led to vast mountains of foam which inundated sewage disposal plants and rendered them inoperative. It has filled rivers and lakes with great intractable layers of foam. Earlier in this discussion, it was noted that ABS detergent had three major defects. This was the third defect. It developed slowly at first as the intensive use of the new ABS detergent was growing. In Germany in the Ruhr Valley the situation became intolerable. Intensive investigations revealed that the ABS detergent, unlike soaps, did not precipitate in the presence of hard water metallic ions. Also, unlike soaps which are readily consumed by bacteria, i.e. readily biodegradable, the ABS detergent was very resistant to such biodegradability and therefore persisted in unchanged form until its concentration in the sewage stream built up to such proportions that its strong foaming tendency made it a public nuisance. It took some time for this problem to emerge and more time to study and discover its cause, and still more time to develop ways to overcome it. By 1960 it had become apparent that the hydrophobic hydrocarbon chain in the ABS detergent, being highly branched, was resistant to biologic degradation. If, however, the hydrocarbon chain were

made straight without branches, i.e. linear, it was discovered that it was biodegradable. By 1965, ways had been developed to produce commercially linear hydrocarbon-based detergents that had satisfactory rates of biodegradation while otherwise retaining the excellent detergency of the ABS materials; and since that time these new detergents called LAS (linear alkyl sulfonates in which a straight C12 chain is attached to a benzene ring which is subsequently sulfonated), and SAS (sodium linear alkyl sulfonate), etc., have taken over the applications formerly held by ABS detergents. The detailed chemistry of these compounds will be discussed in IV and V below, but briefly they may be represented:-



The term "biodegradable" needs a bit of clarification. There is no black and white distinction between compounds that are biodegradable and those that are not. It is a matter of rates of destruction. Ultimately all detergents are degradable, but ones in which the process is relatively slow, in which the detergent molecules persist through the sewage treatment and out on to rivers and lakes are said to be non-biodegradable.

For a long time it was believed that hydrocarbons were not subject to attack by micro-organisms. Later it was found that they are subject to attack, but that the rates are low and that the attack is obscured by the more rapid biological

attack on other more reactive compounds. Now, it has been found that in the world of micro-organisms, diligent searching can discover organisms that can attack almost all organic matter, but at greatly different rates. During World War II, a seemingly intractable problem arose in the complex fuel systems of fighter aircraft in which the fuel systems that were kept scrupulously clean became plugged, often with resulting disaster. After much time and effort it was revealed that micro-organisms were, in fact, living and proliferating in the hydrocarbons of the fuel and generating materials that plugged the system. Minute traces of essential nitrogen and phosphorus compounds must have been present. The discovery that the problem was the result of micro-organisms living in and consuming petroleum hydrocarbons as foodstuff was received, at first, incredulously. But the final recognition of the nature of the problem led to its ultimate solution and, of equal or greater importance, opened the door to the development of the modern process whereby selected micro-organisms consume straight chain hydrocarbons in kerosene or gas oil (together with added essential nitrogen and phosphorus compounds) and the accumulated mass of micro-organisms are collected as a new and important source of protein foodstuffs.

It is well known that the aromatic ring is very resistant to degradation. In the ABS detergent, rapid biodegradation proceeds only to a methyl group branch on the hydrocarbon chain, i.e. the chain is shortened by only one or two carbon atoms; then a very slow process of degradation takes over. The molecule, thus remains virtually intact and retains most

of its surface activity and capacity to foam for a long time. In contrast, with an LAS detergent, biodegradation proceeds unhindered along the entire length of the linear (unbranched) hydrocarbon chain all the way to the aromatic ring. The ring is resistant to rapid degradation, but the remaining fragment, which is an aromatic sulfonate and is devoid of any hydrophobic hydrocarbon chain, has, therefore, no longer any surface activity, nor any capacity to present intractable foaming problems in the sewage disposal. Furthermore, here it should be emphasized that problems of biodegradability of synthetic detergents in Iran have scarcely arisen up to this time. With only a few exceptions, sewage is disposed of in Iran by seepage and percolation into the soil, most of which is, in Iran, sand, gravel and detritus which is ideal for that purpose. * Little is known at present of the processes of sewage decomposition in deep soil percolation where temperatures and oxygen concentrations are low. In any case, problems relating to detergent biodegradability do not arise so long as the input of sewage to the cesspools is not greater than the percolation capacity of the soil to carry off the liquid fraction. In a recent incident, a large new hotel in Tehran, in a rush program to get ready for the big October celebration, used much ABS detergents and flushed them to large and seemingly adequate cesspool-percolation pits. There followed extensive foaming that rose and flooded above the covered pits, and presented temporarily a considerable nuisance.

* Mr. R.Veldes-Pinilla, U.N. World Health Organization Tehran & Regional Water Board.

However, soil percolation as a means of sewage disposal has its limits. Tehran, with a population now close on 3.5 million persons, is saturating its subsoil with approximately half a million cubic meters of sewage every day. This presents several problems. Already the percolating sewage is penetrating into the subterranean water table in places, especially to the south of the city where the water table is only 5 to 10 meters below the surface, and is leading to pollution of this valuable asset. Though the soil through which the percolation occurs is an efficient filter for removal of solid materials and acts to some extent as a zeolite adsorbent for some dissolved materials, its capacity to remove these materials is soon exhausted by the constant flow of new sewage. The pollution, now well started, is very serious and ominous for the future. In recognition of this problem, a plan for a sewage system for Tehran is in the making. The construction of a sewage system is to be spread over the next four Five-Year Plans. It will be a very ambitious project with a vast money requirement. The treated and innocuous fluid effluent will be used for irrigation. Though the implementation of this plan is several years in the future, it does raise problems relating to the use of hard or non-biodegradable detergents. There can be little doubt that the use of appreciable amounts of ABS detergents (the kind currently being produced and used in Iran) will render such sewage treatment plants inoperable. In Tehran, the water from the Karaj reservoir is hard enough to foster the replacement of soaps by synthetic

detergents, and if ABS detergents are the only ones available, trouble can be expected when a sewage system comes into operation.

Elsewhere in Iran there are potential trouble spots where the use of non-biodegradable ABS detergent can give trouble. In Isfahan a comprehensive sewage system is being developed containing a modern sewage treatment plant. At present the system serves only an area containing approximately 40,000 persons (out of a total of 650,000 persons). This system is to be expanded as rapidly as funding permits. It appears a good system designed by Israeli engineers and constructed by French contractors. Already, however, the present plant is plagued with extensive foaming problems. This author visited the plant in mid-November and saw the intractable foam rising above the treatment basins and in some cases above the control panels.

In considering and visualizing this problem, it is important to remember that in sewage treatment we are dealing with a foul and septic fluid and that the foam generated from it is similarly foul and septic. The generation of mountains of foam is itself a nuisance, but in overflowing and covering all equipment, control panels, etc, it renders all of it foul and dangerous to operators and maintenance men. It is, indeed a serious problem. The use of the newer non-biodegradable detergents completely eliminates this problem.

The rest of the sewage at Isfahan, i.e., that from 650,000 less 40,000 (sewage treated) persons, is currently being disposed of into cesspool-percolation pits. Already the volume of sewage has risen to a proportion that is polluting the subterranean water table from which the city draws its fresh water. Everywhere in Iran, this is becoming a serious problem and the first step in its solution is to promote general recognition of it. Because of paucity of water in Iran, it is essential that underground waters be preserved from pollution. Obviously easy and inexpensive cesspool-soil percolating will remain the preferred method of sewage disposal in towns, villages and wherever population concentration is low. But in all major population centers, ultimately some kind of sewage disposal systems will be required and the use of ABS detergents will make them inoperable.

In Ahwaz a relatively small portion of the sewage is aerated and chlorinated to render it less noxious and then dumped into the Karun River, thereby creating a nuisance in the river. This author witnessed extensive foaming above and about the sewage aeration chlorination plant. The rest of the sewage is disposed of by cesspool-soil percolation.

In Abadan and Khorramshahr the sewage goes into the Arvand Rud, some of it with aeration and elsewhere along the Persian Gulf, sewage is dumped untreated into estuaries and bays and creates localized nuisances that will require correction as population densities rise. Sewage from

industrial plants is particularly difficult because it usually contains higher concentrations of dissolved materials than does ordinary municipal sewage. The dissolved materials cannot be removed by conventional sewage treatment processes, e.g. sedimentation and activated sludge processing, and remain in the clarified effluent. ABS detergents are in this class, remaining in the clarified effluent as a pollutant to rivers and lakes or to subterranean water reservoirs. Soaps, which are completely precipitated by metallic ions and the soap and suspended precipitate completely degraded in activated trickling fillers, present, therefore, no problems. It is obvious that every effort should be made by careful planning to reduce the amounts of dissolved materials in clarified sewage effluent. The maximum use of soaps where water hardness permits is a step in this direction. In Tehran, it is planned that such clarified effluents will be used for irrigation, -- a use that is very sensitive to the presence of all dissolved materials, especially since evaporation allows such materials to accumulate in the soil and render it sterile.

Other important components of synthetic detergent formulations, besides the organic surfactant include the "builder" usually sodium tripolyphosphate, and a filler, usually sodium sulfate (Glauber salt). Both of these materials are used in appreciable amounts and both are water soluble. The builder is used in widely varying proportions depending upon whether the detergent is a light or heavy duty agent and in amounts up to 60% by weight of the entire composition.

The sodium sulfate functions as a low cost, inert and water-soluble filler to reduce the proportion of active components to practical working concentrations. Actually its proportion in the finished powdered detergent is dictated more by the sulfonation technique employed than by any considerations as a diluent. Where sulfuric acid (100% H_2SO_4) is employed, a considerable excess of acid must be used to push the reaction to completion, and usually the excess acid is neutralized with soda ash or caustic soda when the entire reaction mixture is converted to the sodium salt. Under such conditions, the amount of Glauber Salt ($Na_2SO_4 \cdot 10H_2O$) produced and remaining in the mixture as an inert diluent may exceed 30%. More modern techniques of sulfonation employ sulfur trioxide (SO_3), either directly as such or as a solution in sulfuric acid called oleum. In these systems, not only is the sulfur trioxide a more active sulfonating agent than sulfuric acid, but the SO_3 reacts with the water of reaction and pushes the sulfonation reaction to completion. The final sulfonated mixture, therefore, contains only a slight excess of sulfuric acid, so that when the sulfonation mixture is neutralized, only a little Glauber salt diluent is formed. That is desirable in making concentrated, heavy duty or liquid detergents, but when it is desired to market a product similar to that made by the earlier sulfuric acid techniques, powdered Glauber salt is frequently added to the final composition. It is therefore essential that Iran develop adequate productive facilities to produce SO_3 and oleum from the abundant sulfur.

These materials - builders and diluents - are important to our considerations herein, because a) their manufacture must be provided for in any integrated detergent industry and b) being soluble end-products in any detergent use, their effect as pollutants must be considered. Steps have already been taken to provide a domestic production of soda ash used to neutralize the sulfonation mixture and with which to convert phosphoric acid to trisodium phosphate (used in heavy duty, alkaline detergents) and to sodium tripoly phosphate (now virtually the standard synthetic detergent builder).

Because these materials are water soluble their possible effect as pollutants in the percolated effluent into subterranean waters and as sewage treatment effluents into rivers, lakes and coastal waters should be considered. Even when the synthetic detergent compositions are used in vast quantities, it is obvious that these materials become diluted to very low concentrations in their final disposal.

Sodium salts are undesirable in irrigation waters, but sodium sulfate is far less toxic to plants than sodium chloride. Generally, the undesirable sodium component in irrigation waters can be kept within manageable limits to the average crops of cereal grains, vegetables and fruit trees by periodic flooding and run-off. Similar considerations apply to the phosphate builders, but with two differences:-

- a) All polyphosphates gradually hydrolyze to simple orthophosphates which, though they have little colloidal and complexing properties (as compared to the polyphosphates), still have a strong affinity for many soil components, e.g. zeolites, and tend to be adsorbed and retained in the soils. The phosphates, therefore, would seem to pose only a minor problem as a pollutant.

- b) The phosphates are important fertilizer components. In fact, the use of phosphates in fertilizers is the biggest use for phosphates, dwarfing in amount all other uses combined. The use of phosphates in synthetic detergents is the second largest use for these materials, but in aggregate is relatively small as compared to fertilizer uses. The use of phosphates as detergent builders has become complicated, however, because it has been caught up in and indicted as a major water pollutant in the international hysteria that is now gripping the entire world. After a long, long period of apathy toward frequent warnings against the pollution of our atmosphere and aquasphere, there has been a sudden awakening, and with an intensity that borders on hysteria. Unfortunately, many complex technical considerations are involved, most of which are beyond the comprehension of the public at large, and so a vast ignorance, coupled with a deep fear of that which is unknown and ill-comprehended, has gripped the world and has been fanned to greater intensity by leaders of little understanding or

with special interests to foster. This is not to say that the present deep concern relative to the growing pollution of our planet is not a good thing; but that time will be required for the problems to be evaluated and more fully understood and for the confusion-generating hysteria to abate. This concerns us here, because the use of phosphates in synthetic detergents has become charged as one of the major villains in the current hysteria and now the term "eutrophication" is on the tongue of even ill-educated people. That term actually means to make rich in dissolved nutrients. It has been observed in recent years that rivers, irrigation and drainage canals, ponds, lakes, even reservoirs have become choked with dense growths of water hyacinth, algae and fungi. This relatively sudden proliferation has been traced to a greatly increased concentration of plant nutrients in the water of such streams. The two particular nutrients that have greatly increased have been nitrogen (mostly as nitrites and nitrates) and phosphates, and most of this has come from run-off and drainage from heavily fertilized agricultural areas in the new "green revolution" which is to cure or alleviate widespread hunger in the world. In the indictment of fertilizer materials in this problem, phosphates from the sewage disposal of synthetic detergent have been similarly charged, and, in fact, in the intemperate charges that have been thrown about, the part played by fertilizers has been almost forgotten and the role of phosphates from synthetic detergents as a polluter has been greatly magnified. In America, where

this hysteria has become particularly pervasive, the big three detergent makers (Procter and Gamble, Lever Brothers and Colgate Palmolive) rushed to cancel large contracts for sodium tripolyphosphate and initiated crash research programs to find suitable alternatives to the polyphosphate builders. They began a furious merchandising of "New Detergents - Contain No Phosphates". These detergents were heavily loaded with soda ash, sodium silicates, and sodium nitrilotriacetic acid (NTA). They were dangerously alkaline and performed very badly as detergents. In the two years of this hysteria, the crash research programs have uncovered no suitable alternatives to the polyphosphates that perform well and which do not introduce even greater technical, economic and ecological problems than those charged against the phosphates. It is indeed fortunate that legislative machinery is slow and cumbersome, which is the only thing that has prevented the widespread enactment of impulsive laws prohibiting the use of phosphates in synthetic detergents. A few such laws were rushed into being and will require reconsideration, for now that the dust is settling, it is being realized that a) phosphates in detergents are not the major source of eutrophication, and b) there are no suitable alternatives to polyphosphates as synthetic detergent builders, and c) the eutrophication problem is not the ultimate disaster as it was initially portrayed. The popular pendulum swings widely and wildly. Already in U.S. and in Europe, there are strong reactions against bans on the use of phosphates in synthetic detergents. The over-

reaction against eutrophication may well do much harm to reasonable and intelligent efforts to preserve a relatively unpolluted atmosphere and aquasphere.

But for our purposes, it is important to observe that polyphosphates are essential to the production of effective and economical synthetic detergents; and that their deleterious effect on the pollution of our water environment has been grossly exaggerated. There is, therefore, no reason to reconsider the current plans to produce sodium tripolyphosphate in Iran.

IV - SYNTHETIC DETERGENTS TO MEET THE FUTURE NEEDS OF IRAN.

From all that has said above, it is apparent that the selection of a type of detergent for the future expansion of the industry in Iran involves some complex considerations.

For the present and until the major cities of Iran develop sewage collection and treatment systems, — and except for Isfahan, this appears at least ten years in the future — the present production of hard detergents based on branched alkyl benzene sulfonate (ABS) appears to warrant no change. The ABS surfactant has the advantages of a good raw material situation, a modern production facility with capacity for present needs, a well developed know-how and experience ranging all the way from raw materials through to finished marketable detergents, and a market (domestic and in U.S.S.R.) which accepts its excellent performance. All these considerations are strong factors against change.

The dodecyl benzene (DDB) plant at Abadan is currently producing at close to 10,000 m.tons/a and could under pressure increase that output to 12,000 mt/a. The 10,000 mt/a of DDB yields 15,000 mt/a of sodium dodecyl benzene sulfonate (DDBS), which in commercial detergent formulations containing an average 30% surfactant yields 50,000 mt/a of finished detergent. The DDB and compounded detergent consumed and estimated for the period 1966 through 1972 is given in Table No.1.

Table No.1

<u>DDB</u>		<u>Compounded Detergent Containing 30% Surfactant</u>		
<u>Consumed in. tons</u>		<u>Domestic</u>	<u>U.S.R.</u>	<u>Total</u>
1966	1800	8,900	30	8,930
1967	2600	11,300	1,800	13,100
1968	5000	15,000	10,000	25,000
1969	6800	20,500	13,500	34,000
1970	3400	27,500	20,000	42,500
1971	10,000	31,000	20,000	51,000
1972 (Estimated)	12,000	40,000	20,000	60,000
1973 (Estimated)	15,400	52,000	25,000	77,000

NOTE: 1 ton DDB yields 1.5 ton sodium DDB sulfonate (DDBS)
 1 ton DDB Sulfonate yields 3.33 ton compounded detergent
 containing 30% surfactant
 Thus, 1 ton DDB yields 5.0 tons compounded detergent.

From the above, it is apparent that the 1971 production of synthetic detergents (containing an average of 30% of DDBS surfactant = ABS detergent), just consumes in its entirety the 10,000 mt/a production of DDB. Assuming no important changes in U.S.S.R. or other exports in the near future and that the domestic demand continues to grow at a rate comparable to that of the three years preceeding, domestic requirement of synthetic detergents will reach 60,000 mt/a in 1972, which will consume completely the 12,000 mt/a of DDB that can

be available from Abacem Petrochemical Co. We have already noted that 12,000 mt/a of DDB is the maximum that can be produced from that source. It is apparent, therefore, that additional production facilities will be required no later than early 1973, - or alternatively imports of DDB in amounts of the difference between production and requirements.

Equally important in the final compounded detergent is the builder, now almost universally sodium tripolyphosphate ($\text{Na}_5\text{P}_3\text{O}_{10}$) (STPP). The function of the builder is complex, acting as a colloidal suspending agent, as a heavy metal sequestrant, and, doubtless, performing many more subtle functions. It is, therefore, not to be regarded as an optional adjunct to the surfactant, but as an essential component of the compounded detergent. Of all the materials that provide properties of a builder in varying degrees, sodium tripolyphosphate has been found to provide the best combination of properties. Tetra-sodium pyrophosphate also serves as an effective builder, but the detergent industry has pretty much settled on STPP as the preferred builder. For special uses, as in heavy duty industrial detergents, the building action of STPP is frequently augmented with other more alkaline agents such as sodium silicate (Na_2SiO_3) soda ash, trisodium phosphate (Na_3PO_4) and others.

It is important to note, also, that in the usual commercial detergent the amount of STPP used usually exceeds that of the surfactant by a considerable margin. For example in U.S. a widely used household detergent has the following approximate composition:-

LAS Surfactant	20 wt.%
STPP	45 "
Glauber Salt ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$)	25 "
Moisture, enzymes, carboxy methyl cellulose, perfume, etc.	10 "

Without the STPP, the effectiveness of the detergency action falls off rapidly. Without exaggeration, it may be said that without the assistance of an effective builder, the synthetic detergent industry could not have achieved its present success. The STPP is used in synthetic detergent preparations in widely varying amounts depending upon the ultimate function of the detergent, e.g. from 20 to 60 weight percent of the total composition; with about 40% an overall average. For our computations below for Iranian synthetic detergents, an average of 35% STPP has been used.

At present, all the STPP required by the growing domestic detergent industry is imported. It is anticipated that Iran will soon have a production facility for STPP, which must, however, wait on the supply of soda ash to come from the NPC facility near Shiraz. A recent study * estimated the requirements for STPP (based on an average STPP content of 35% in commercial detergents) as follows:-

* A Marketing Plan for Sodium Carbonate, Sodium Bicarbonate And Sodium Tripolyphosphate prepared by P. v. International Management Consultants, Ltd., 28 October 1971 - Tehran.

Table No.2

	<u>NPC Production</u>	<u>Imports</u>	<u>Total Requirement</u>
1971	0	18,000	18,000
1974	18,000	9,000	27,000
1975	24,000	5,000	29,000
1976	30,000	5,000	35,000

It is obvious, therefore, that around 1974 or 1975, when the demand for commercial detergents (combined domestic and exports to U.S.S.R.) already exceeds the domestic productive facilities for DDB, the demand for STPP, will also exceed the domestic productive capacity. Now is none too soon to commence planning for needs that will be manifest in only one year for DDB and in four years for STPP. The determination of what kind of surfactant we should plan to produce to fill the burgeoning needs is a primary and pressing purpose of this study. Equally important is to define the anticipated needs of STPP, so that plans for production of adequate supplies can be developed.

We have already concluded that a hard or non-biodegradable surfactant, such as ABS, will provide major difficulties in the urban centers within the next decade. It is, in fact, a type now considered obsolete, even legally banned in much of the world since 1968-1970. So long as it serves the

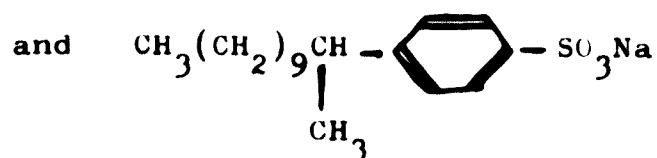
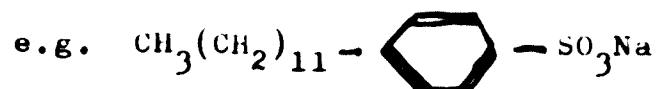
Iranian economy well and efficiently, considerations as to its replacement by newer biodegradable surfactants need not concern us. But the need to create facilities for the production of additional surfactant within the next two or three years (or resort to appreciable and mounting imports), compels us to take an early decision as to the type that will best serve Iran.

At present, some 60% of Iran's population is living in villages and rural areas without plans for sewage disposal. For these people it will continue to be expedient to dispose of sewage by cesspool - soil percolation. To meet the demands for detergents in these areas, ABS detergents will continue to be effective and most economical and their production should not be interrupted.

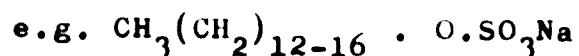
However, to expand the production of ABS detergents to meet the growing needs of urban areas after 1975 would be shortsighted. Such detergents would interfere with and impede the development of essential urban sewage systems. For these areas, it appears quite clearly that the production of some new, effective, economical and biodegradable detergent should be developed. Moreover, with export markets for ABS detergents being closed by growing legal restrictions in much of the world (U.S.S.R. still uses ABS, but we have no knowledge as to future Russian restrictions), we would do well to develop a new synthetic detergent that can serve our growing domestic needs and, at the same time, can be exported.

Today, there are many types of surfactants (detergents, wetting agents, dispersing and emulsifying agents), each with special properties that yield some technical or economic advantage. These various surfactants will be considered more fully under V Chemistry and Technology of Surfactants, but it may be noted here that because of raw material and other economic and performance considerations only a few surfactants have attained large volume production and even fewer will merit our serious consideration for development in Iran. Of these surfactants, only two appear to meet our needs, considering biodegradability, raw material requirements, ease of production and economy and efficiency of function :-

A) LAS (linear alkyl benzene sulfonate)



B) Sodium linear alkyl sulfate

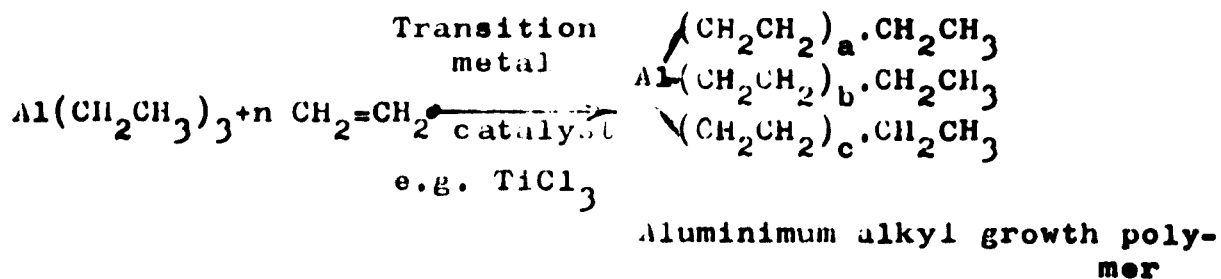


A) is already in large scale production and in use in much of the world. B) is newer, its markets are developing, it is more completely degradable than A), and while, perhaps, slightly more costly to produce than A), has some functional

advantages. The SAS (sodium alkyl sulfonate) surfactants, mentioned earlier in this study, have some very large economic advantages which are counterbalanced by some very imposing disadvantages and are therefore dismissed from our consideration. This is discussed in part IV.

LAS is produced by condensing a linear alpha olefin, e.g. $\text{CH}_3(\text{CH}_2)_9\text{CH}=\text{CH}_2$ with benzene, followed by sulfonation and neutralization. The production techniques are well developed. The only problems are concerned with the production of the linear alpha olefin and the control of the condensation with benzene so that isomerization to branched chain isomers is minimized. The resulting sulfonates are excellent surfactants, foam well, have good calcium and magnesium solubilities, light color, low odor and excellent response to formulation with builders. LAS detergents are now the largest synthetic detergent used in the world where laws require that a surfactant must be at least 80% biodegradable. If made in Iran under efficient conditions, it could enjoy export markets. There are other, still newer synthetic detergents with considerable promise. But if we adhere to the dictum that we want for Iran at this time only processes and products that have been well developed and tested so that all hazards of production, sales and uses are minimum, then we have little choice except to select LAS surfactant for our "second generation" detergent production. In order to gain economies of production and also to permit Iran to participate in the growing export markets for this material, a production facility considerably larger than the DDB plant at Abadan should be planned. The exact size must be defined by a market analysis in depth.

For a "third generation" surfactant to be developed in Iran in perhaps 1980-1982, our choice may well be B) (sodium linear alkyl sulfate). This requires the production of a linear, primary C₁₂-C₁₆ alcohol. As will be explained in Part V, this can be manufactured by the same type of polymerization of ethylene with a Ziegler catalyst as will be used by NPC/Mitsui in the production of high density polyethylene, but with this difference: by control of conditions, the polymerization is stopped when 2 to 11 ethylene molecule have combined to yield a mixture of C₄-C₂₂ aluminum alkyls, e.g.



a, b and c = 2 to 11.

$$\eta = a + b + c$$

Then the Al alkyl growth polymer is blown with dry air to convert the Al alkyls to Al alkoxides, followed by acid hydrolysis to a mixture of straight chain, primary C₆ to C₂₂ alcohols. This is then fractionated, the lower C₄ to C₁₀ alcohols being channeled to the production of plasticizers and foam killers, the C₁₂-C₁₈ to synthetic detergents, the C₂₀-C₂₂ alcohols to developing uses, e.g. special surfactants, emollients, plasticizers, etc. By varying reaction conditions

a preponderance of C₁₂-C₁₈ alcohols can be produced at the expense of lower and higher alcohol fractions. The C₁₂-C₁₈ alcohols are treated with oleum or SO₃ for conversion to sodium linear alkyl sulfates. The products are superior surfactants with remarkable foaming properties, absence of color and odor, compatibility with all anionic surfactants (in fact, used to build foaming properties in low-foam detergents), and if made on a large enough scale their superior properties permit them to compete with lower cost surfactants. Their only defect is a susceptibility to hydrolysis in hot acid solution—a condition rarely encountered in normal detergent operations. These linear primary alcohol sulfates have climbed in U.S. from near zero in 1963 to over 300,000,000 lbs. in 1967 and is still going up.

In summation, considering the present domestic and export requirements for synthetic detergents, the maximum output of DDB from Abadan Petrochemical Co. will suffice only until the end of 1972. Thereafter, there will have to be imports of DDB until new facilities are created for the production of additional surfactants.

The new surfactant should be LAS (linear alkyl benzene sulfonate) which is a good detergent and is at least 80% biodegradable. A sizeable plant should be designed to produce linear alkylbenzene, its size to be determined from a market study which considers both the growing domestic requirements and exports of both linear alkyl benzene and sodium linear alkyl benzene sulfonate and finished compounded detergents.

A study should also be initiated covering the economic and technical parameters of producing n-primary C₁₂-C₁₈ alcohols by Ziegler polymerization of ethylene, followed by air oxidation and hydrolysis of the ethylene growth polymers. Though this product is contemplated as a basis for a "third generation" synthetic detergent, and is therefore not of immediate importance, an early, detailed review should be made in order to coordinate this possible manufacture within the overall scope of the MOC/Nitro Olefin Project.

In addition, the importance of STP in synthetic detergent compositions should not be overlooked. By 1975, domestic production, which is not yet even started, will become inadequate to supply the combined domestic and export requirements for synthetic detergents. If exports to U.S.A. grow beyond the 1971 20,000 m. tons, the inadequacy of domestic STP production will be upon us even before 1975. If U.S.A. exports terminate by the end of 1971, STP production will suffice until, possibly, 1976-1977. Plans for the expansion of STPP production based either on soda ash or caustic soda should be developed without delay.

Furthermore, consideration should be given to the domestic production of other important, but lesser in volume, requirements:-

- a) Trisodium phosphate (Na_3PO_4): This material is used in modest amounts in strongly alkaline industrial and laundry detergents, providing a buffered action which is superior to that of soda ash. Imports are not known, since all phosphates including STP, are grouped together, 90, 00 lb. ton (127, 00). It could be produced readily in the same plant producing STPP, - or, since its replacement may be easiest, could be left to the private sector for production from purchased phosphoric acid (aluminum) and soda ash or caustic soda.
- b) Tetra sodium pyrophosphate ($\text{Na}_4\text{P}_2\text{O}_7$): The availability of this material would be desirable, but, with adequate supplies of TPI, is not considered essential.
- c) Sodium silicates (Na_2SiO_3 and polymers): used in moderate amounts, like a) above in alkaline industrial cleaners; also in box-board adhesives. In 1970, 47,500 tons of sodium silicates were imported.

It would be highly desirable to foster a domestic production of this material because its availability to a growing industrial country is important. Sodium silicates is written in the plural because it is actually a whole family of compounds, varying both in the ratio of Na_2O to SiO_2 and in the degree of polymerization. Manufacture is neither complex nor difficult: finely powdered, high purity silica sand

is fused with soda ash and/or caustic soda and the product is powdered or dissolved in water. It is offered to industry in a series of 8 to 10 ratios of $\text{Na}_2\text{O} : \text{SiO}_2$. Besides its use as a buffered alkaline builder in industrial synthetic detergents (along with STPP), it is used extensively as a builder in laundry and industrial soaps. The high silica ratio material is used largely as a low cost adhesive in the manufacture of corrugated box-board. Although imports of only 4750 m/tons in 1970 would suggest a small volume specialty product, it is probable that demand for these materials would expand greatly and rapidly if it became readily available at low cost from a domestic source. The raw material requirements should present no problems. This manufacture should be recommended to chemical producers in the private sector.

- d) Most other components used in synthetic detergent compositions are used in too small quantities to justify domestic manufacture at this time. Sodium carboxy methyl cellulose is important in high grade synthetic detergents, but its use at levels of only 0.5-2.0% would hardly justify a local production, and its production is relatively complex. Perfume materials, though used in relatively small proportions, are high cost components. They are used in many consumer oriented products and the production of even limited variety should be recommended to private sector industry.

V - CHEMISTRY AND TECHNOLOGY OF SYNTHETIC DETERGENTS

A. General: All detergents, whether soaps or synthetic detergents, consist of polar molecules with very strong dipole moments, one of which is lipophilic (or hydrophobic), the other hydrophilic (or lipophobic). In use this dipole extends across a lipid-water interface or a gas-water interface and strongly reduces the surface tension, leading to foaming and the suspension of dirt or soil or the emulsification of two or more diverse phases. The art of constructing a good detergent consists in joining in a single, stable molecule a lipophilic group (a hydrocarbon group whose character is determined by the length of the chain), and a hydrophilic group (e.g. - COONa, - SO₄Na, - SO₃Na, - PO₃Na₂). These two dissimilar groups must be carefully balanced so as to yield a molecule with about equal attraction to each of the two phases. In soaps, with a - COONa hydrophilic group of constant polarity, the lipophilic hydrocarbon chain can be varied by the choice of fatty acid raw material to yield molecules with optimum properties. For cold water, full foaming toilet soaps, the optimum lipophilic group has been found to be a C12-C14 hydrocarbon chain derived from coconut fat. With beef or mutton tallow, a C16-C18 chain results, whose hydrophobic strength is a little too great to balance the - COONa hydrophilic pull, resulting in a soap useful only in hot water.

All calcium and magnesium and heavy metal salts of fatty acids are insoluble in water. Soaps are useful therefore, in the presence of such metallic ions only when used in

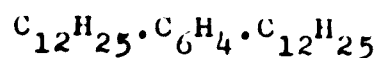
quantities such that there is an excess of soap after all the metallic ions have been precipitated. Furthermore, all soaps, being composed of straight chain fatty acids, are easily attacked by micro-organisms and are readily biodegradable.

Most synthetic detergents employ sulfonate ($-\text{SO}_3\text{Na}$) or sulfate ($-\text{O}-\text{SO}_3\text{Na}$) hydrophilic groups which are somewhat stronger in hydrophilic properties than the carboxyl ($-\text{COONa}$) group in soaps. Moreover, the sulfonic and sulfuric acids are strong acids, yielding as the sodium salts neutral solutions, in contrast to the relatively strongly alkaline solutions produced by fatty acid soaps. The calcium and magnesium salts of the alkyl sulfonates and alkyl sulfates have appreciable water solubilities and so can function advantageously in hard water. In non-ionic synthetic detergents, the hydrophilic group consists of an alternating aggregation of oxygen-containing ethers or esters in hydrogen-bonding chains, and the strength of the hydrophile can be nicely adjusted by the number of ether or ester units incorporated into the surfactant molecule. In cationic surfactants, (fatty amine salts and quaternary ammonium salts), the hydrophilic group is based on nitrogen. The cationic surfactants are all small volume, high cost speciality materials.

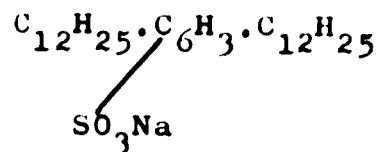
The lipophilic group is a hydrocarbon chain whose length or number of carbon atoms is varied to increase or decrease the lipophilic moment. The molecular configuration of the hydro-

carbon chain is important. The best detergents have the hydrophilic group attached to one end of the hydrocarbon chain; in the best wetting agents the attachment is at or near the middle of the chain. Where very strong lipophilic properties are desired, as, for example, in oil soluble detergents for use in internal combustion engine lubricating oils, very long hydrocarbon chains or two hydrocarbon groups are joined via a benzene ring to one sulfonic acid group.

In the manufacture of dodecyl benzene (DDB) by alkylating benzene with dodecene (tetra propylene polymer), some disubstitution always occurs despite efforts to prevent it. Disubstitution is usually minimized by carrying out the alkylation with a large excess of benzene. In the final distillation of the DDB, the high boiling "heavy ends" fraction is essentially di-dodecyl benzene,



which if sulfonated yields an oil soluble, water insoluble product



At present this heavy-ends fraction constitutes between 5 and 6% of the DDB production, i.e. about 500 mt/a. At present this is not recovered and is disposed of in fuel oil. The di-dodecyl benzene sulfonate has considerable value outside of Iran, being used as oil-soluble detergents in internal

combustion lubricating oils. It may, therefore, be worth saving the heavy-ends fraction, even in crude form, for sulfonation and use in lubricating oils.

All detergents are classified into three categories, only the first of which is important to us in this study.-

- a) Anionic surfactants, e.g. $R.SO_3^- Na^+$, which include soaps, ABS, LAS, SAS, alkyl sulfates, etc. About 75-80% of all synthetic detergents fall into this class. These are the only large volume, low cost commercial surfactants. This group also contains the largest number of variations in molecular structure, but the great commercial bulk of these surfactants is provided by only a few types. The LAS detergent couples the lipophilic linear hydrocarbon group to the $-SO_3^- Na^+$ hydrophile through a readily sulfonatable benzene ring. In others, e.g. SAS type, the lipophilic and hydrophilic groups are coupled directly.

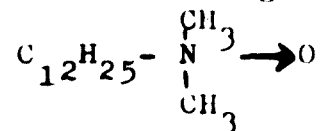
- b) The non-ionic surfactants in which the hydrophilic tendency is due to alternating oxygen atoms in ethers or esters which are hydrated through hydrogen bonding. Usually a long chain lipophilic alcohol or phenol is condensed with ethylene oxide in the presence of an alkaline catalyst to form hydrophilic polyethylene oxide groups containing 6 to 20 ethylene oxide ether units. Thus, in this class of surfactant, the strength of the hydrophilic group can also be modified to provide a nice bipole balance.

This class of surfactant is second in importance, constituting about 18-20% of all synthetic detergents and emulsifying agents. These materials do not ionize and are compatible with both anionic and cationic surfactants. This group of surfactants has a strong potential interest to NPC because of the planned production of ethylene oxide from the NPC/Mitsui Olefin Complex. The production of these surfactants can consume very large amounts of ethylene oxide and could yield valuable products for both the domestic and export markets. In general, these nonionics are more costly than the anionics and are used conservatively only in applications for which they provide some special advantage, e.g. in insecticide spray emulsions and in admixtures with other surfactants to enhance their detergency properties.

- c) Cationic surfactants constitute less than five percent of all synthetic surfactants. They are expensive to produce and have specialized uses, one of which is that the quaternary ammonium salts are powerful bactericides and disinfectants. For example, ROCCAL^(R) which is a 1% solution in water of dodecyl trimethyl ammonium chloride



There is a relatively new surfactant of this class with unexcelled foaming capacity, the amine oxides, e.g.



This group of cationic surfactants has no immediate interest in this study.

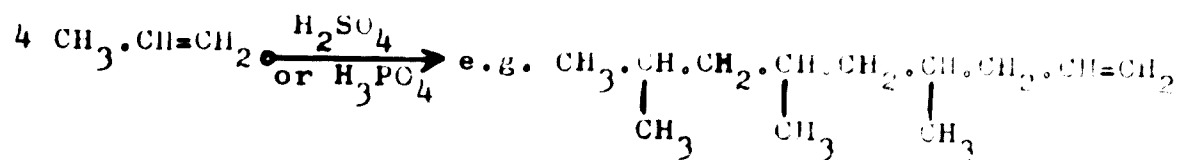
(R) Sterling Products Div. of Anthrop.

B. Specific Surfactants: The number of types of surfactants is already very large and only those which appear relevant to this study are included herein:-

1. ABS (Alkyl benzene sulfonate): This was the first large volume, low cost and highly successful synthetic detergent. In U.S. and in Western Europe within a short period it replaced one half of all soap consumption. It is still unexcelled in function, but has been replaced in much of the world because of its non biodegradability.

ABS is made in three successive steps:-

- a) Production of dodecene: Chemical grade propylene is polymerized in the presence of sulfuric or phosphoric acids to the tetramer (dodecene - 1):

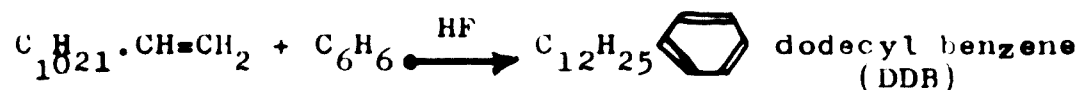


(dodecene - 1)

Actually, the product is a mixture of several isomers. Also the polymerization of the propylene cannot be limited to the formation only of dodecene (C12), but there is obtained a mixture of polymers ranging from 2x propylene up to perhaps, 10x propylene. By careful control of the reaction, a polymer mixture can be obtained in which 4x propylene (i.e. dodecene) predominates, and fractionation yields a relatively pure

dodecene. The lower and higher polymers (i.e. light and heavy ends) have potential uses, but in the process as practiced at Abadan, the light ends constituting approximately 15% of the polymerization product go to the petrol-pool, and the heavy ends, approximately 5%, go into fuel oil. Because the hydrocarbon chain in dodecene has several methyl group branches, a synthetic detergent produced from it is non-biodegradable.

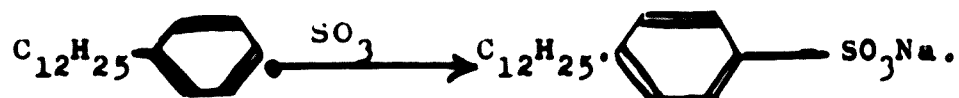
- b) Production of dodecyl benzene (DDB): The dodecene from a) above is condensed with benzene in the presence of anhydrous HF catalyst.



This is the product from Abadan Petrochemical Co. which is produced currently at 10,000 m tons/a, soon to be increased to 12,000 m tons/a. Here, also, close control is essential. The HF catalyst is anhydrous, is expensive, is recycled, and in the presence of any moisture is very corrosive and hazardous to personnel. In the production of DDB, one mol of dodecene condenses with one mol of benzene, but it is difficult to prevent two or more molecules of dodecene from condensing with one benzene to yield varying amounts of unwanted di- and tri-dodecyl benzene. In order to minimize the formation of di- and tri-substituted products, a large excess of benzene is used (10-15 mols C_6H_6), and the

excess of benzene and HF catalyst are recovered and recycled. Despite the large excess of benzene used, 5.5-6.0% of the product is a heavy-ends fraction which is mostly di-dodecyl benzene. When the product is distilled, the heavy-ends fraction which amounts to 550-600 mt/a is disposed, mostly to fuel, with a minor proportion being used as a heat transfer agent. This material is valuable and should be saved since it can be sulfonated to yield valuable oil soluble detergents for use in internal combustion engine lubricants.

- c) The DDB is sold by APC to be processed further in the private sector. The DDB is sulfonated with concentrated sulfuric acid, or, better, with SO_3 or oleum (SO_3 in H_2SO_4) :



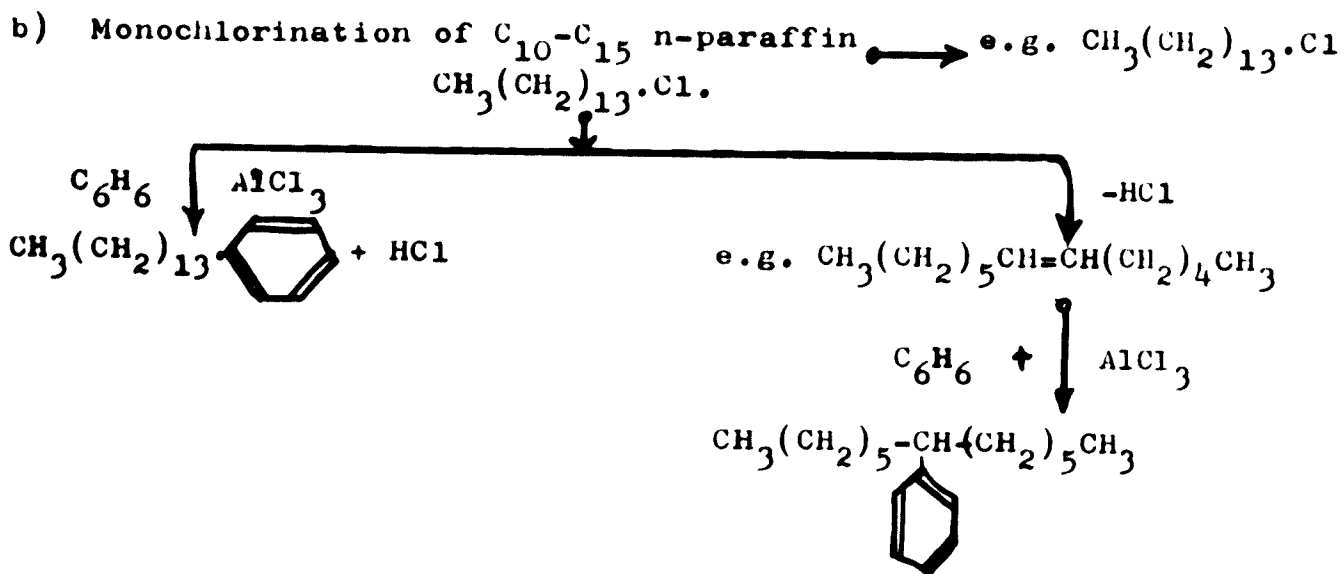
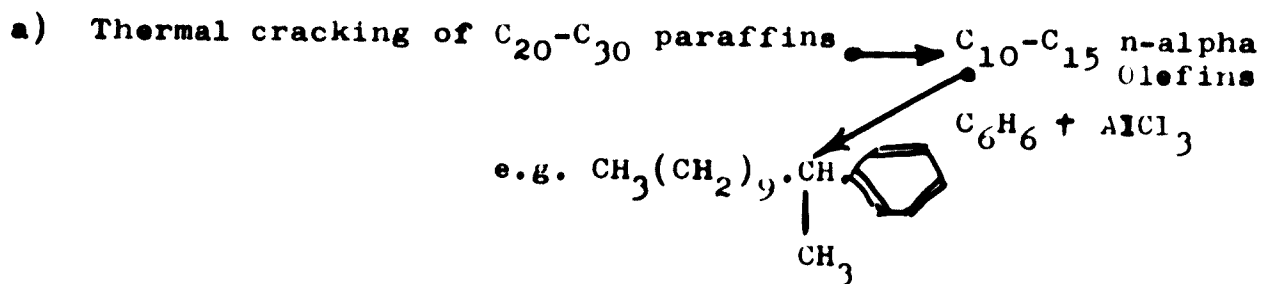
Sulfuric acid is little used anymore because it requires a large excess of acid to push the reaction to completion, and when the reaction mixture is finally neutralized the excess acid leads to the formation of a large proportion of sodium sulfate (Glauber Salt $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$). For liquid and for heavy duty detergents, this high proportion of sodium sulfate, which is an inert diluent, is undesirable. When SO_3 or oleum (40-60% SO_3) is used, the reaction does not require a large excess of sulfonating agent, and the product does not, therefore,

contain so large a proportion of sodium sulfate. The sulfonation is usually carried out in stainless steel equipment in order to minimize the development of color in the product. The surfactant product is then compounded with STPP and other components in varying proportions to make the finished light, medium or heavy duty commercial detergents.

Cost figures on capital, materials and operating requirements on the production of dodecyl benzene for ABS manufacture are well known to N.P.C. from Abadan Petrochemical Co. and no effort is made herein to develop them.

2. Linear alkyl benzene sulfonates (LAS); This is the large volume, successful "second generation" synthetic detergent and the one herein recommended for development in Iran. Depending on the character of the lipophilic hydrocarbon group and its method of manufacture, its biodegradability may vary upwards from 80% to over 90%. In a brief time around 1965, this type of detergent largely replaced non-biodegradable ABS detergents in America, Western Europe, and by 1969 in Japan.

There are a number of techniques for the production of LAS surfactants, but essentially they may be reduced to two routes:-



Many companies are operating in this area and all have developed processes which differ in raw materials and in conditions and techniques of processing, and which yield linear alkyl benzenes which, after sulfonation, provide surfactants which differ somewhatⁱⁿ functionality and in biodegradability. To attempt to cover all of these processes in detail would require a considerable effort to survey and appraise the large number of patents and the published literature. This study attempts only to provide a broad survey and to establish basic values. A detailed study of all processes and their variables should be undertaken as a first step toward entering this activity.

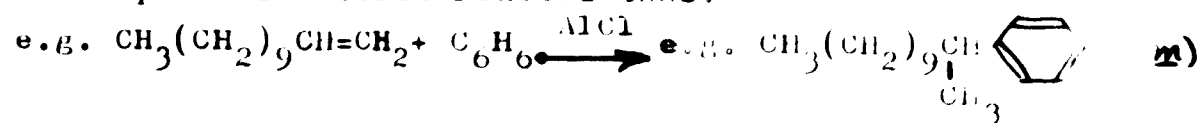
Considering first the raw materials, the first successful process to produce an LAS detergent involved the thermal cracking of a high molecular weight ($C_{20}-C_{30}$) paraffin wax to yield a $C_{10}-C_{15}$ straight chain olefin fraction with a high proportion of the unsaturation between the first and second carbons, i.e. alpha olefins. This technique was developed by Shell at Pernis, Netherlands. This alpha olefin fraction, when converted into a linear alkyl benzene sulfonate detergent was much superior to ABS detergents in biodegradability, but it suffered from several defects:-

- a) The cracking operation gave a mixture with a wide range of olefin chain lengths. After the desired $C_{10}-C_{15}$ fraction was separated, the fractions below and above this range constituted a significant part of the product and for which adequate markets have not been found. This resulted in relatively high costs for the $C_{10}-C_{15}$ olefin fraction. For example Chevron (Standard Oil Co. of California) in 1969 cracked 100,000,000 lbs of a wax fraction and collected the product in narrow fractions from C_5 to C_{20} , with only 60% of it $C_{10}-C_{15}$ going into LAS detergents. The $C_{10}-C_{15}$ fraction typically contained:-

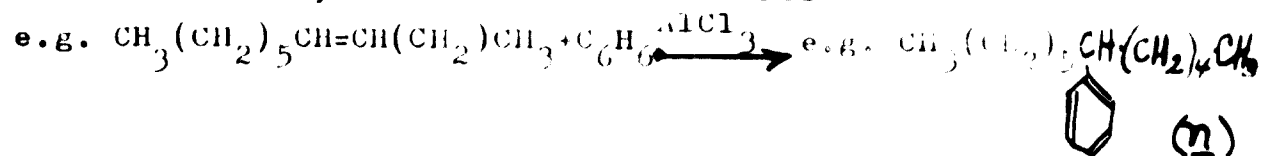
Alpha olefins	85%
Internal olefins	85%
Diolefins	3%
Saturated hydrocarbon	3%
Aromatics	0.5%

- b) The C₁₀-C₁₅ olefin mixture, while containing much alpha unsaturation, contained also considerable unsaturation distributed in a random fashion along the hydrocarbon chain. Then when benzene was alkylated with this mixture of olefins (e.g. with C-12 olefins):-

The alpha C-12 olefin reacted thus:-



and an internally unsaturated olefin thus:-



Both of these derivatives may be biodegradable, provided the chains are unbranched down to the carbon connected to the aromatic ring. In that case, the molecule becomes degraded to a benzene sulfonate with only at most one or two carbons attached to the ring, and such product is water soluble and without surface activity or capacity to foam however, (m) with a long hydrocarbon chain attached at its end to an aromatic ring yields a surfactant which is an excellent detergent with good foaming properties, while (n) with an attachment near the center of the hydrocarbon chain is a much poorer detergent, a better wetting agent, and a poor foamer. In fact, these detergents because of a considerable proportion of (n) type, foamed so poorly that the addition of foam builders was required.

- c) The selected paraffin wax fractions for cracking to alpha olefins have not been plentiful and have imposed additional costs on this path to LAS detergents.

With the development of molecular sieve adsorbents (aluminosilicate zeolites) a practical means became available for separating n-paraffins from paraffinic kerosenes, and provided a relatively cheap and abundant supply of n-paraffins. A number of highly successful processes have been developed to exploit this technique, e.g. ISO-SIV by Linde-Union Carbide, Molex by U.O.P., British Petroleum process and Ensoarb by ESSO. All these processes are relatively similar. A large plant feeding a kerosene containing 25% C₁₀-C₁₈ n-paraffins can yield a product containing over 95% n-paraffins and which can be fractionated to give 90% of the C₁₀-C₁₅ paraffins present. The economics of the process is helped by the removal of the n-paraffins which leaves an extracted kerosene which is a superior jet fuel.

Still another process for separating n-paraffins from kerosene is the urea-clathration system developed by Shell and Deutsche Erdöl A.G. This process is highly selective but very little about its economics has been published.

As above, with paraffin wax fractions, the n-paraffins separated from kerosene can be cracked to yield olefins rich in alpha unsaturation and suitable for the manufacture of n-alkyl benzene for detergent production. These materials are rather better in function than the products from wax cracking, but they have been difficult to rid from a kerosene odor.

Alternatively, a technique has evolved in which the C_{10} - C_{15} n-paraffin fraction is chlorinated to yield a C_{10} - C_{15} mono alkyl chloride. In order to minimize di chloro-substitution, only one third as much chlorine is introduced as would be required for a complete conversion to mono alkyl chloride. The economics of this process is much improved if there is a use for the by-product HCl evolved, which contains one half of all chlorine introduced. The product, a C_{10} - C_{15} mono alkyl chloride, is frequently referred to as keryl chloride. It is used in one of two ways:-

- m) It may be dehydrochlorinated over an aluminosilicate catalyst to C_{10} - C_{15} olefin, which is then condensed with benzene in the presence of $AlCl_3$ or HF catalyst to yield the linear alkyl benzene.
- n) It may be condensed directly with benzene in the presence of $AlCl_3$ using the large excess of unchlorinated C_{10} - C_{15} n-paraffin that is present in the mixture as a reaction medium. The excess of n-paraffin is recovered and recycled.

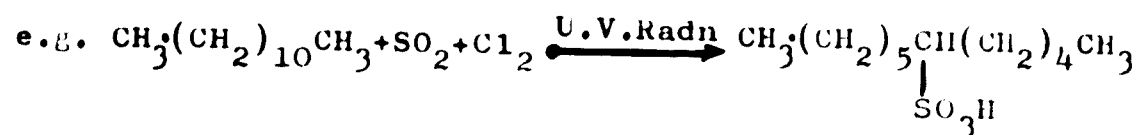
All these systems give linear alkyl benzenes, i.e. the hydrocarbon chain attached to the aromatic ring is without branching beyond the carbon attachment to the ring, and therefore, yields products with a relatively high biodegradability factor. However, it must be noted that the chlorination of the n-paraffins produces chlorine substitution that is random along the hydrocarbon chain (and with very little substitution on the terminal carbons). So, like with the olefins in which

there was an appreciable amount of the unsaturation distributed randomly along the chain, alkylation of benzene with alkylchlorides in which the mono chloro substitution is also random, yields an alkylate in which the aromatic ring is attached at or near to the middle of the hydrocarbon chain. Such molecules yield surfactants which are serviceable but inferior to those in which the ring attachment is to the end of the chain. The resulting LAS detergents have excellent wetting properties and poor foaming which is usually enhanced by additions of alkyl sulfates, or alkanolamine or alkyl amine oxide foam boosters.

The condensation reaction of the C_{10} - C_{15} olefin or C_{10} - C_{15} alkyl halide with benzene is very similar in technique to the condensation of dodecene and benzene as is now practiced at Abadan Petrochemical Co. With similar throughputs, capital and operating costs would be virtually identical for the C_{10} - C_{15} olefins. With the C_{10} - C_{15} alkylchloride a means of disposing of the evolved HCl must be added.

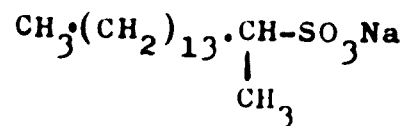
3. Sodium alkyl sulfonate (SAS): These products made from C_{10} - C_{15} straight chained paraffins have received intensive study and because of low raw material costs, presented great promise - a promise, which, unfortunately, has not been borne out because of poor functional properties. This class of detergent has now dropped out of serious development and is included herein only because its potential is so great that it may yet be successfully developed. Dupont (Duponol), I.G. Farben (Mersolate), ESSO and Hoechst all worked this field intensively and all have ultimately backed away from it. Essential a straight chain

paraffin hydrocarbon is treated with a mixture of SO_2 and Cl_2 while exposed to actinic radiation:



As with the limited chlorination of n-paraffins (See B2 above) the sulfonation substitution is random, giving a complex mixture of products that are better wetting agents than detergents.

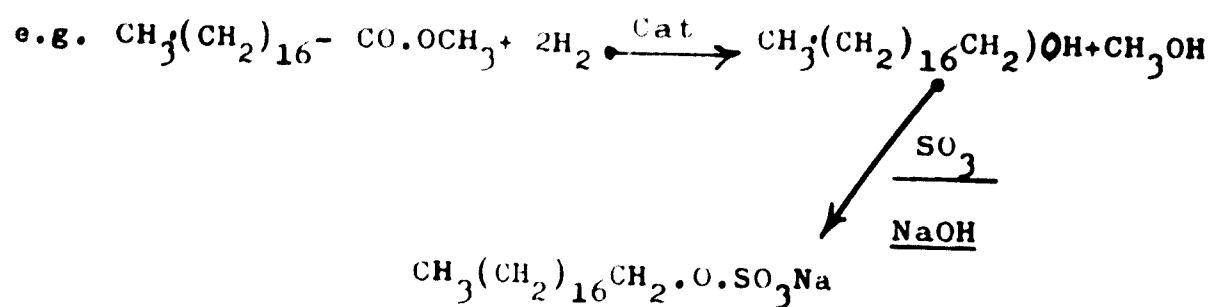
Similarly, efforts have been made to treat alpha olefins directly with oleum or SO_3 to get



The products, however, are complex, containing beside the desired linear sulfonate, appreciable amounts of polymers, sulfones, sultones, etc. Efforts to commercialize these products have been disappointing to this point.

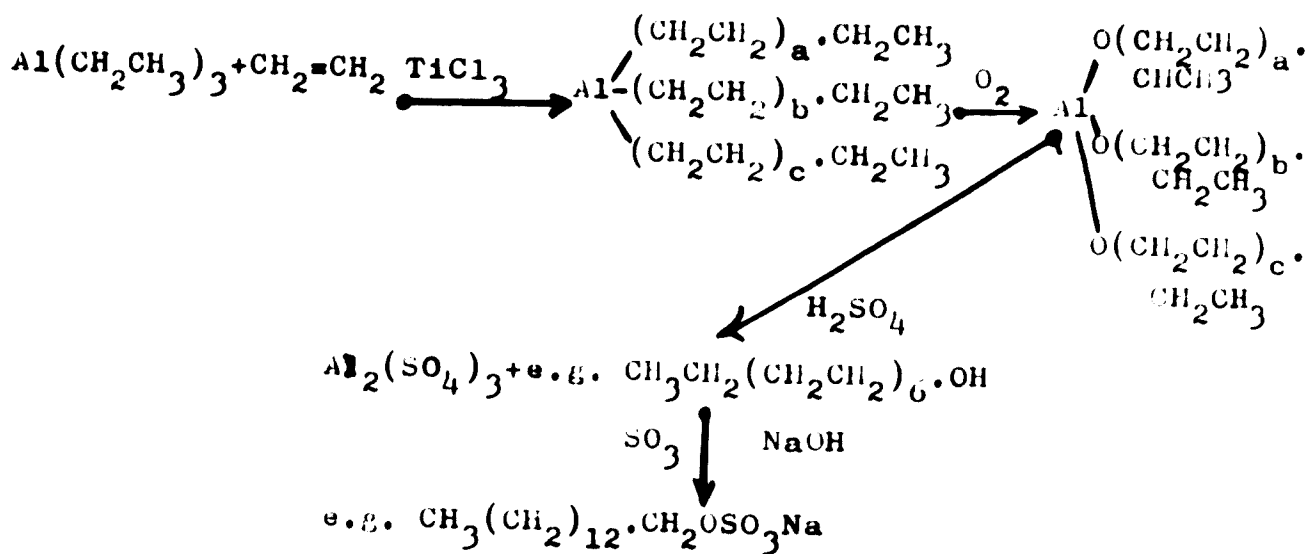
4. N-primary alcohol sulfates: e.g. $\text{CH}_3(\text{CH}_2)_{13}\text{O}\cdot\text{SO}_3\text{Na}$

Detergents of this category have been around for a long time as a class of superior, but relatively costly materials. Initially, they were made by sulfating n-primary alcohols with SO_3 or oleum. The primary alcohols were made by reducing fatty acids from natural fats with metallic sodium and alcohol and later by catalytic reduction of fatty acids with hydrogen:



Because of the relatively high cost of these materials, their use were sharply limited, mostly to applications in personal cleansing, cosmetics etc., and where their unexcelled foaming action was important. So long as these materials (e.g. du Pont: Gardinols) were made by the above technique, they remained a small volume, specialty detergent. Being straight chained, they were, of course, completely biodegradable. A major use has been to admix minor quantities with LAS detergents to enhance the foaming properties of the latter.

With the development of the polymerization of ethylene to long, unbranched hydrocarbon chains under the influence of Ziegler Catalysts (e.g. $\text{Al}(\text{C}_2\text{H}_5)_3$ + a transition group halide such as Ti Cl_3), a means to the low-cost volume production of $\text{CH}_3(\text{CH}_2)_n\text{CH}_2\text{OH}$ alcohols became available, where $n=8$ to 14. At first this process was used to make macromolecules: i.e. high density polyethylene resins. Later means was found by which the polymerization of ethylene under the same catalyst system could be stopped after 2-20 molecules had condensed and a mixture of moderate sized ethylene polymers could be obtained. The so-called growth polymer, an aluminium trialkyl could then be oxidized to an alkoxide and acid hydrolyzed to alcohols with chain lengths suitable for detergent manufactures:-



In this polymerization of ethylene, it is possible to control the reaction so that the product consists of a mixture of $\text{CH}_3\text{CH}_2(\text{CH}_2\text{CH}_2)_n\text{OH}$ alcohols where $n=1$ to 7 with the preponderance at $n=4-7$ (desirable for detergents manufacture). The product mixture of alcohols is fractionated, and the alcohols below and above the desired $\text{C}_{10}-\text{C}_{16}$ range is directed to the manufacture of plasticizers and related products. This technique has been highly successful. Developed initially by Continental Oil Co. in U.S., it has built a unit to produce 500,000,000 lbs/a.

Patent and literature sources indicate that 0.990 ton ethylene plus 0.214 ton $\text{Al}(\text{C}_2\text{H}_5)_3$ yield 1.0 ton of C_4-C_{20} normal, primary alcohols. The consumption of $\text{Al}(\text{C}_2\text{H}_5)_3$ in this process is necessarily higher than in the polymerization of ethylene to high density polyethylene because the growth polymers are stopped at an early stage. In an effort to reduce the consumption of Al-triethyl, which is expensive, recent work has developed a technique

whereby the low molecular weight ethylene polymer is displaced from the aluminium growth polymer as an olefin and the $\text{Al}(\text{H})_3$ that is set free is recycled to repeat the process. The process, when perfected, could be an excellent source of unbranched alpha olefins which would yield highly biodegradable detergents and ones in which because the unsaturation is entirely alpha, would have a very high detergency factor.

These techniques, starting with low cost ethylene and building the hydrocarbon groups to the exact specification desired, appear to have the greatest promise and is, therefore, recommended to NPC for continuous study for ultimately a "third generation" production of detergent. This same process will generate, as a co-product, vast amounts of straight chain, primary alcohols for the manufacture of plasticizers for the expanding polyvinyl chloride and related industries. These plasticizers, because they will be based on straight chain alcohols, will permit the plasticized PVC compositions to be functional at temperatures much lower than those based on branched chain alcohols, e.g. 2-ethylhexanol, or alcohols made from olefins via an oxo-synthesis, which always yield a mixture of straight and branched chain products. This operation, based on ethylene as raw material, should be carried out on a big scale in which exports would be the primary market, and supplies to the Iranian domestic market only incidental.

At this time the entire process in its several modifications is still too new to have developed much literature outside of the flow of patents. At this point, also, the Companies who are developing the processes are too concerned with exploiting these new and exciting markets themselves to be much interested in selling the know-how or in joint-ventures. In, perhaps, five years, the techniques will become better known and major engineering contractors will be able to secure the necessary rights by which they can offer complete plants. By studying intensively these new developments based upon the polymerization of ethylene we shall be in a position to move securely into this area when the developed and tested technology becomes available.

APPENDIX A

INSTITUTE OF HYDROSCIENCES

AND

WATER RESOURCES TECHNOLOGY

QUALITY OF WATERS IN IRAN

(Calcium, Magnesium, Total Hardness, Dissolved
Solids).

Short record of the selected data

BY

Ch.J.FINTAJSL

UNESCO: WATER QUALITY EXPERT.

Tehran, November 1977.

APPENDIX A

1. Sources of information

The following reports have been evaluated:

- 1) Ministry of Water and Power, Surface Hydrology Department, QUALITY OF SURFACE WATERS OF IRAN; Report No.17:
 - a) Vol. 1, Caspian Sea Basin, (1969).
 - b) Vol. 2, Persian Gulf Basin, (1970).
 - c) Vol. 3, Lake Rezayeh Basins and Closed Basins of the Central Iran (1970).
- 2) Analyses of drinking water performed by the Laboratories of the Ministry of Health (unpublished, available in sheets).

The sheets contain the data from the years 1968-1969. The analyses of waters have been carried out during the total period of about 18 months.

2. Evaluation of data

The available data have been evaluated with respect to the following criteria of water quality: