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Synthetic Fatty Alcohol and Acids—New Additions to the Raw Material Pool for Soaps and Detergents

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Abstract

The United States capacity for synthetic fatty alcohols and their derivatives has been greatly expanded. More recent additions to this alcohol pool have received wide acceptance in the marketplace. In fact, because they bring new features, mainly in the areas of economics and performance, their continued growth both in volume and in the number of applications is assured. With regards to synthetic fatty acids, over the past 30 years many potential candidate acid systems have been examined. A wealth of process technology has been accumulated. The marketplace has been tested with several new tailor-made acids, and therefore now we believe the stage is set, the opportunities are at hand and we should see some large scale development in the United States in the near future.

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Introduction of Commercial Scale Facilities for Producing Synthetic Primary Alcohols

Synthetic primary fatty alcohols in the detergent range have become a commercial reality only in the past five years. By this we mean they are now freely available at competitive prices. Detergent range is taken to include C_{12}–C_{18} although small amounts of alcohols outside this range are utilized as surfactant intermediates. This paper focuses on alcohol mixtures which are characterized by a primary hydroxyl group and high normal alcohol content. Prior to about 1963, demand for this type of material was served for the most part by alcohols derived from natural fats and oils, mainly tallow and coconut oil.

Today, some five commercial and large scale facilities are operating in the free world to produce synthetic primary alcohols as defined above. Three of these are of the ethylene polymerization type employing basically Ziegler chemistry and produce a range as broad as C_2–C_{20} of essentially all normal, primary alcohols, all of which contain an even-number of carbon atoms. Two of these units are located in the United States, one is located in Europe. The other two facilities, both located in the United States, produce primary alcohols in the C_{12}–C_{15} range utilizing a Shell patented process. Of these alcohols, trademarked Neodol Alcohols, about 80% are normal and the remainder is primarily methyl branched in the 2-position.

Apart from the above mentioned five commercial facilities, several pilot units are now producing or have produced relatively insignificant amounts of primary alcohols, we believe via conventional or modified oxo chemistry feeding on alpha olefins. These alcohols with a normal content of about 60% and, of both odd and even numbered carbon chains, have not achieved a market position and therefore cannot be considered a commercial success.

In viewing synthetic competitors to natural fatty alcohols, recognition must also be given to other new

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materials. These include the expanded role of normal alpha olefins which in some cases can displace alcohols as intermediates. Alpha olefins have been utilized for many years in Europe, but large-scale commercial production in the United States has been a commercial reality only since the early 60's. These olefins are produced either by cracking high paraffinic content wax or by ethylene polymerization employing Ziegler chemistry. The former route yields a broad range of odd and even numbered predominately terminal olefins while the ethylene route yields only even numbered olefins. We are also aware of the availability of ethylene oxide adducts and ether sulfate derivatives of C_{11}–C_{15} random secondary alcohols. Here, to the best of our knowledge, the alcohols per se are not commercially available. To date, non-surfactant uses for these alcohols have not evolved for a variety of reasons.

Synthetic primary alcohol production in the C_{12}–C_{18} range, as defined above is estimated at about 175 million pounds in 1967 including production of the alcohol facility in Europe.

Current Status of Synthetic Detergent Range Alcohols

Considering the magnitude of the above mentioned 1967 supply of synthetic alcohols, it is appropriate to review the status of these materials in the marketplace. Our experience indicates that synthetics are acceptable in essentially all of the markets previously served by naturals; and they have, in addition, opened up new markets where the higher prices of natural alcohols prohibited their utilization. Most quality aspects are on par with natural alcohols and in some cases even better. It is quite apparent and remarkable that producers are still demonstrating quality improvements as required to meet specific end-uses.

In considering the progress made by synthetic fatty alcohols, it must be emphasized that the bulk of this progress has been made in extremely performance-oriented markets where product evaluations are very lengthy, expensive and drawn-out. It is not uncommon for commercial offtake to occur 1–2 years after product introduction at a particular account. The acceptance of synthetics can be attributed to many reasons such as: (a) an acceptable high degree of biodegradability, characteristic of natural alcohols—with the case of linear alkyl benzene, however, synthetic alcohols have not received a value premium over the materials displaced due to this biodegradability; (b) lower cost of synthetic alcohols or derivatives as compared to their natural alcohol counterparts; (c) a more favorable price/performance relationship over that of the natural alcohols; (d) the desire to protect future alcohol supply in the event of the abandonment of natural alcohol production facilities.

At this writing, it is our view that synthetic alcohols, collectively, are performance equivalent and price superior to natural alcohols and will undoubtedly continue to cause the demise of natural fatty alcohols. While our market development experience is limited, we are optimistic that new applications for synthetic alcohols can be developed because of this price advantage. Construction of new fatty alcohol plants based on natural fats and oils is most unlikely, and we are confident that some existing facilities have or will be shut down in the short term.

Outlook for Synthetic Primary Alcohols

Currently the capacity for producing synthetic detergent range alcohols is ample, particularly since Shell's new facility at Geismar, Louisiana, is now on-stream. This unit brings Shell's capacity to over 150 MM pounds per year or about that of the total United States synthetic production in 1967. While several United States firms are reportedly considering an expansion of existing facilities or the construction of new plants, definite announcements have not been made.

Outside of the United States, the next significant increase in synthetic primary alcohol capacity may be at Shell's alcohol complex in England of which the initial units will come on-stream in early 1969. This facility will be producing 2-ethylhexanol, *n*-butanol, and C_7–C_9 and C_{11} plasticizer range primary alcohols in 1969 and it is planned to follow with the detergent range alcohols. We are also aware that three or four firms are in various stages of construction planning in Japan. A number of these appear to be deferring construction such that significant capacity is not likely for several years.

Impact to Date of Synthetic Alcohols on Coconut/Tallow Situation

Using the previously mentioned production figure of 175 million pounds of C_{12}–C_{18} alcohols in 1967, we estimate that this was roughly equivalent to about 240 million pounds of coconut oil or around 5% of the world production. This volume of oil, 240 MM pounds, is quite small on a relative basis, even smaller than the yearly variation in total production caused by differences in annual rainfall; therefore, we believe the reduction in demand for oil to make alcohol will have a very minor effect on the world coconut price situation. Of course, under the present circumstances, with crude coconut oil price at an all time average annual high of 20–21¢/lb, and world production down about 20% from previous yearly averages, a United States demand of another 240 MM pounds would further aggravate present oil prices. But it is thought, and most would agree, that coconut oil price will eventually retreat to its historical mean level of about 12¢/lb. Nevertheless, the majority of consumers will prefer synthetic equivalents which offer protection against widely fluctuating prices which are characteristic of the coconut oil derived products.

The production of synthetic tallow range alcohols in 1967 was very small and merits little comment except to say that no synthetic producer really desires to make these materials. This is because they are produced quite cheaply from tallow, merchant demand for this range of alcohol is quite small, and shorter chain alcohols are usually preferred.

Outlook for the Conversion of Synthetic Alcohols to Fatty Acids

Before we leave the subject of synthetic alcohols, let us look briefly at the possibility of these alcohols serving as starting materials for the synthesis of fatty acids. Prior to the advent of totally synthetic fatty alcohols, fatty acids were abundant, relatively inexpensive and easily converted by catalytic hydrogenation to the corresponding alcohols. Now with already large and increasing capacity for synthetic alcohols established, the reverse procedure, namely the oxidation of primary alcohols to acids justifiably merits attention.

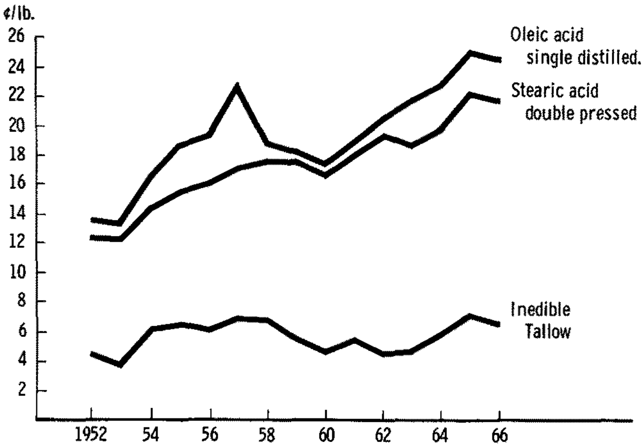

FIG. 1. Price margin, raw material vs finished fatty acid.

The oxidation of primary alcohols cleanly to aldehyde and on to acid by chemical methods is easily done in the laboratory. But like many laboratory processes, these methods are far too expensive to be considered seriously for large scale manufacturing purposes even if alcohol prices were to drop significantly. One chemical method not often used in the laboratory but developed as a practical commercial process is oxidation by reaction with an alkali metal hydroxide such as sodium hydroxide. In this process the reaction conditions are fairly severe, nevertheless, both the selectivity and conversion to the sodium salt of the acid is high. Fatty acid is obtained by acidification and is subsequently purified by distillation. Several patents have been issued on certain improvements to this process, to Standard Oil of Indiana (1) and to Imperial Chemical Industries Ltd. (2) and more recently to Ethyl Corporation (3) and Gulf Research and Development Company (4). In the Ethyl patent, it is further claimed that this dehydrogenation process can be made still more selective such as to dehydrogenate the straight-chain members only in a mixture of straight and branched-chain alcohols. Of all the chemical methods reported to date for the conversion of fatty alcohol to acid, this caustic fusion process would appear to be best suited for commercial exploitation.

In the past, considerable effort has been directed towards perfecting a catalytic air oxidation process to convert fatty alcohols cleanly and economically to acids. By and large, such a scheme to our knowledge has yet to be reported. We believe the reasons for this lack of success to be threefold; the first of which is the lack of incentive. Only recently have synthetic straight-chain alcohols become available in large volume. Secondly, most alcohol oxidation processes generate an aldehyde intermediate which is sensitive to polymerization and other side-reactions. And finally, the industrial applications today for saturated fatty acids, including toilet bar soap, require acids of very high quality such that any oxidation process must completely avoid the side production of hydroxy and other oxy-acids.

The outlook for the oxidation of synthetic primary alcohols to acids can be summed up as follows. Large volumes of alcohols are available today and also at least one good chemical process for their oxidation. Among these alcohols, which can be classified as either oxo or the linear primary type, it is reasonable to expect the oxidation of the less expensive oxo-alcohols to be commercialized first, particularly that molecular weight range alcohol yielding the more valuable medium chain and coconut range acids. In the United Kingdom, in fact, Imperial Chemical Industries Ltd. for several years have offered Acid 810, a synthetic mixture of C_8–C_9–C_{10} acids which is produced by chemical oxidation of the corresponding oxo-alcohols. Should the price of coconut and palm kernel oils remain at a level somewhat above their long range median of about 12¢/lb crude, and if at the same time newer catalytic oxidation processes be developed, then the chances that some portion of the available straight-chain alcohol would be oxidized are greatly improved.

Fatty Acids, an Expanding Market

Before discussing further the future possibilities for synthetic fatty acids, let us briefly look at the fatty acids market itself.

Current total production for the United States of all grades of fatty acids is about 1.2 billion pounds per year and is growing at a healthy rate of about 7% per year. Of this production, about 90% has as its source tall oil and inedible tallow and grease and, therefore, is of the C_{16}–C_{18} range predominantly. Further, of this 1.2 billion pounds, about 350 MM pounds is classified as saturated fatty acids, spanning the carbon range C_8–C_{18}, and growing in volume at around 5% per year. It is this group of saturated acids which represents the most likely target towards which synthetic interests will develop.

These saturated acids are derived mainly from inedible tallow and coconut oil. Vegetable foots also contribute as a source, but the volume of this raw material available for fatty acid production is declining. It is interesting to examine the price margin, for example, between tallow and its component stearic acid (Fig. 1). This margin is the difference in price between the crude tallow and the finished acid. In the last 10 years, this price margin has increased steadily from 10.1 to 15.3¢/lb. This uptrend in the price margin has occurred with other acids as well (5), both with oleic and the coconut acids. This trend has occurred in spite of the increases in capacity and production of these acids and the very slight, if any, increase in the cost of the crude fat and oil raw material from which they are made. The reasons for this uptrend in the margin are not clear but should it continue, the economic advantages of natural fats and oils as raw material for acids relative to petroleum based synthetic acids could disappear.

One other group in this category of saturated fatty acids which merits special attention is the medium chain acids. At the present time, the bulk of this group is made up of: C_8 and C_{10}, 20–25 MM lb. from coconut oil; C_9, produced by Emery Industries; and C_7, 8–10 MM lb., imported from France.

In the past, the major use for the C_8 and C_{10} acid was for conversion to plasticizer alcohols, but new applications for medium chain acids, such as synthetic lubricants, are being developed which offer great promise for this range of acid.

Synthetic Fatty Acids, Historical Perspective and the Present Challenge

The subject of synthetic fatty acids, both in the United States and in Europe, has a long history of development. The earliest research on the most basic process, the oxidation of paraffin, began in the late 1800's and this field has been under continuous investigation ever since. At the same time, many attempts have been made to move from research into commercial production. Some have met with success, others have not.

In the early 1930's, Standard Oil of New Jersey had in operation a rather large pilot plant for the production of fatty acids by the direct oxidation of paraffin wax (6). This operation did not lead to the full plant scale manufacture of these acids in the United States, but soon thereafter, by 1936, a similar process led to the large scale production of synthetic acids in Germany and was continued and promoted until the end of the war in Europe in 1945. The feed for these German plants was Fischer-Tropsch hydrocarbon wax and the product acids were consumed in soap-making and also for making industrial and edible fats.

Since 1945, in East Germany, Russia and in other East European Countries, some six to eight plants for the oxidation of both solid and liquid paraffins have been put into operation with a current combined total capacity for synthetic fatty acids approaching 1 billion pounds per year. This process is not selective and, as a consequence, every possible acid is made from C_1 on up, depending on the paraffin feed and severity of oxidation, Table I. In these plants, the raw material is a high quality linear paraffin of petroleum origin. The basic economic reason for the continued success of these plants is twofold: 1. Petroleum is plentiful and this, coupled with their necessity to produce diesel and fuel oils of low pour-point, gives rise to large quantities of paraffin at low by-product prices; and 2. Natural fats are in short supply in that part of the world and therefore cannot be spared for inedible industrial markets.

These conditions are quite the opposite in the United States and in many countries of Western Europe.

Today, in the United States, the successful commercial activity has been confined to the production of several higher valued specialty synthetic fatty acids in relatively modest volumes. These acids include 2-ethylhexanoic, pelargonic, isostearic, phenyl stearic and the trialkylacetic or so-called acids of the neo-configuration. Of these five acids, the last three are composed of a mixture of isomers, a feature which in addition to their chemical structure, contributes to the low melting points characteristic of these acids (Table II).

To date, in the United States, the economics associated with the production of the conventional fatty acids from natural fats and oils have overwhelmed all attempts by would-be synthetic acid producers to gain a foothold in this industry.

Synthetic Acids, Tailor-Made for the Application

The successful ventures in synthetic acids in the United States as we have noted all involve specialty acids. It would appear then, that any further entries in this area in the near future will probably be with acids bearing unique properties and tailor-made to provide performance features unobtainable from the natural fatty acids. After all, the natural fatty acids with their rigid backbones and monotonous homologous structure do not offer the exciting new properties potentially available through the facility of total synthesis.

During the past several years, Shell Chemical Company has had under development a family of synthetic acids in the C_{12}–C_{15} range which offered properties beyond those which are available from the coconut oil derived lauric and myristic acids. This family of acids consisted of three distinct groups of acids:

1. A C_{12}–C_{15} mixture of straight-chain acids, quite similar to a lauric-myristic blend.
2. A C_{12}–C_{15} mixture of 2-alkyl branched-chain acids.
3. A blend of the two mixtures in a ratio of about 3:1, n-acids to 2-alkyl acids.

TABLE I

Paraffin Oxidation, Typical Acid Distribution

Liquid paraffin, boiling range 256–358 C			
	Yield, %		
C_5–C_{20}	80		
C_{21}+	20		
Composition of C_5–C_{20} fraction, %			
C_5	......	C_{13}	12.0
C_6	0.1	C_{14}	10.7
C_7	2.5	C_{15}	7.4
C_8	5.6	C_{16}	5.1
C_9	10.0	C_{17}	3.8
C_{10}	11.1	C_{18}	1.9
C_{11}	14.0	C_{19}	0.7
C_{12}	15.1	C_{20}	......

[a] See Reference 7.
[b] Per cent.

These neat branched-chain acids greatly extended the "liquidus range" over that observed with the coconut acids and in mixtures with the straight-chain acids imparted unusual fluidity properties to the blends. These same properties could also be observed in many of the derivatives to which these mixtures were converted. In particular, ordinary milled sodium bar soaps containing a small fraction of these branched-chain acids demonstrated polymorphic phase behavior quite different from that observed in soaps of ordinary straight-chain acids.

Separate from the motivation of producing a synthetic acid mixture to obtain new and unique physical properties, a situation could arise whereby a new application for certain naturally occurring acids is discovered requiring a large volume of just one or two component acids present in a wide range natural blend. In this case, the necessity to maintain an economic balance over all components of the natural acid blend could favor a synthetic approach for these one or two specific component acids. For example, if some of the unique health and nutritional benefits recently reported (8,9) for the glycerides of the medium chain C_8 and C_{10} acids are substantiated and a very large potential market identified, then only synthesis would be the practical means to produce these large volumes. Of course, there is the alternative remote possibility that a hybrid coconut species could be developed which yielded an oil very rich in C_8 and C_{10} acids.

Process Technology Available for Synthesizing Acids

Separate from the technical merits of a tailor-made synthetic acid, there are practical commercial incentives which favor a synthetic course over that of complete reliance on natural fats and oils. For instance, synthesis offers a constant supply year after year, unaffected by the vagaries of weather and major political turmoil; synthesis offers uniform and pre-

TABLE II

Fluidity: Synthetic vs Natural Fatty Acids

Titer°C			
Stearic	68	Isostearic	10
Oleic	5	Phenylstearic	−26 (Pour point)
n–C_{12}	43	2-Alkyl C_{12}	< 0
n–C_{13}	41	2-Alkyl C_{13}	< 0
n–C_{14}	54	2-Alkyl C_{14}	< 0
n–C_{15}	52	2-Alkyl C_{15}	12

TABLE III

Synthetic Fatty Acids, Processes

Straight-chain, even or odd carbon numbered
- Ziegler, direct to acid or oxidation of Ziegler alcohol
- Telomerization

Straight-chain, mixture of even and odd
- Paraffin oxidation (linear paraffin)
- Olefin oxidation (linear olefin), catalytic air or ozonization
- Oxo-process (linear olefin), physical separation from branched-chain isomers

2-Alkyl branched-chain
- Oxidation oxo alcohols
- Direct oxo-process (mixture with straight-chain isomers)

2,2-Dialkyl branched-chain
- Koch reaction

Random mid-chain branched C_{18}
- Isomerization
- Alkylation

dictable quality, a specification chemical at best; synthesis may provide acids capable of satisfying both industrial and edible product areas as well, in the manner of synthetic glycerine for example; synthesis offers, but does not guarantee, freedom from the balance problem inherent in the products obtained from fats and oils; and, finally, synthesis offers the potential of a more economic source of acids.

The major factors to consider in the establishment of a viable synthetic acid venture are first and foremost the market or markets for which the acids are targeted and secondly, the proper combination of process technology and raw material position. The markets selected to be served will define the performance features required of the acids, and this in turn establishes the chemical composition and structure of the product acids. At this point, it is important to note that the technology for making acids which has accumulated to date is such that of the many processes available (Table III), each gives rise to a different and unique acid or mixture of acids. For example, if the marketing goal is to supply an acid mixture identical to and a replacement for straight-chain even numbered natural acids, then one is restricted by today's technology to a Ziegler-Type process. In finer detail, this process may involve oxidation of existing Ziegler alcohols or the direct oxidation or carbonation of a Ziegler intermediate.

If the marketing goal were less rigid and demanded only that the synthetic acids be straight-chain, so that both even and odd numbered acids qualify, then other technology is available. In this case, the oxidation of pure linear paraffins or the oxidation of linear alpha-olefins would yield the desired product. Should the market demand still greater deviations in performance properties from natural acids, other technologies, the Oxo process, the Koch process, are practical and available for exploitation.

The one area in the synthesis of acids wherein a bonafide technology gap is apparent is the lack of a practical specific process for making the polyunsaturated or essential fatty acids.

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