about the book . . .

Alpha Olefins Applications Handbook assists in identifying the ever-widening and seemingly endless possibilities for applications of alpha olefins.

The first user-oriented book of its type, focusing primarily on applications for higher linear alpha olefins containing 4 to 30 carbon atoms, this indispensable reference covers the basic descriptive chemistry and methods of production of these olefins . . . summarizes physical and toxicological properties for the alpha olefin family . . . reviews pertinent marketing data . . . presents a broad base of historical information and many key references . . . and much more.

Written and edited by recognized experts in the field, working for many of the major companies involved in this area of industrial chemistry including Ethyl, Dow, ICI Chemical, Pennwalt, Monsanto, Hoechst Celanese, and Lion Corporation, this excellent handbook is essential reading for chemical engineers/manufacturers; plastics, petroleum, production, and design engineers; petrochemical producers and chemists; plant/product managers and process designers; purchasing, marketing, production, and sales staff in petrochemical companies; and advanced undergraduate- and graduate-level students in the above disciplines.

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APPLICATIONS HANDBOOK
CHEMICAL INDUSTRIES

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Alpha olefins are extremely versatile chemical intermediates to a wide variety of industrial and consumer products. Through the practice of chemistry and chemical engineering, derivatives of alpha olefins have been developed that touch our lives in many ways. In some applications, only a low concentration of one of the higher olefins means greatly improved properties. In other applications, the alpha olefins represent most of the product. Whether present in small concentrations or large, they are used because they are most effective in a particular application. Sometimes products based on alpha olefins are the only choice, but more often the derivatives are chosen for their particular cost effectiveness as compared to other products.

Over the 25 years that alpha olefins have been commercially available, one new use after another has been developed. For example, the development of biodegradable surfactants for laundry detergents has been facilitated by the availability of alpha olefins. These cost-efficient derivatives mean effective cleaning in their end-use applications with minimal environmental impact on waterways in highly populated areas. Tougher linear low-density polyethylene plastic films containing alpha olefin comonomers mean less damage to goods in shipment and efficient disposal of refuse. Plasticizer esters with improved properties mean polyvinyl chloride
plastics that are usable over a wider temperature range in automobiles, so
they are less likely to crack in winter than were the older plastics. Im­
proved crack resistance in high-density polyethylene bleach bottles
means less breakage, with the accompanying losses and messes for the
grocer and the consumer. Synthetic lubricants made from alpha olefins
mean better automobile fuel economy and longer times between oil
changes. Alpha olefin derivatives are used to produce longer-lasting paper
and rubber seals in the space shuttles; they are also used to help maintain
sanitary conditions in hospitals and to assist in extracting more crude oil
from the ground.

We forecast that many new uses will be developed because of expansion
of the literature and because of industrial and academic scientists’ work
with samples in all parts of the world. We hope that the reader will be
challenged by the successes and ideas presented here to discover and
develop still more uses.

The purposes of this book are to discuss the applications of higher
linear alpha olefins containing 4 to 30 carbon atoms, to describe current
commercial uses of alpha olefins, to indicate potential new uses, to docu­
ment methods of production, and to provide physical property and
general property data on the olefins, but not necessarily on the derivatives.
Within this book, we have concentrated on generally recognized commer­
cial applications for alpha olefins. We exclude the lighter alpha olefins
ethylene and propylene. Butene is discussed since it is a key polyethylene
comonomer and is produced in traditional alpha olefin plants. Some of
the applications discussed can use other olefins such as the nonlinear
olefins or the non-alpha olefins, and the properties of derivatives of these
non-alpha olefins are compared to the properties of the derivatives of
alpha olefins where appropriate. These properties are included for the
benefit of those who work with and understand the physical and tox­
icological properties of olefins.

Chemistry is more interesting when related to applications, so we have
endeavored to illustrate the relative value of the different applications by
presenting some market information. This market information sets the
stage for the applications, with emphasis placed on those applications
that have the most commercial value and on those that are growing
rapidly. Because the book is organized around applications, one reaction
may be discussed in more than one chapter. For example, the oxo reaction
will be discussed in the chapters on basic chemistry, plasticizers, deter­
gents, and synthetic acids.

By 1930, many alpha olefin reactions had been discovered. These reac­
tions could not be utilized fully, however, until the alpha olefins were
readily available at economic prices. The higher linear alpha olefins first
became available in commercial quantities in 1962 when Chevron began
production based on cracking C20 and higher waxes. Before 1962, they were produced by dehydration of primary alcohols. Production from alcohols ceased in about 1966. Chevron had expanded their capacity in 1964. Gulf was the first to produce alpha olefins based on ethylene when they started operation in 1966. Widespread availability at a reasonable price resulted in many large volume uses for alpha olefins. Since 1965, alpha olefins has grown from a small, expensive specialty with under 10 million pounds utilized annually to a 2 billion plus pound per year basic petrochemical building block.

Alpha olefin production is possible by many routes. Oligomerization or chain growth of ethylene is the primary source of linear alpha olefins today and is likely to be the basis for such production for many decades. The trend away from production from waxes or paraffins has occurred for reasons of economics and quality. The entry of each additional supplier of linear alpha olefins has been positive for the further growth of alpha olefin markets. Both Ethyl in the United States and Mitsubishi in Japan entered the market in 1970; Shell U.S., in 1978; and Shell U.K., in 1983. Each entry added to the development of new markets: Chevron investigated many applications, Gulf initially supplied olefins for synthesis of tertiary amines, and Ethyl became a large supplier to plasticizer and detergent producers. Both Ethyl and Shell helped alpha olefin sulfonates grow, while Shell and Chevron pioneered efforts in the use of surfactants for enhanced oil recovery.

This book represents the efforts of some of the most experienced people in their industries. Each contributor has been selected either by the editors or by others knowledgeable about their particular segment of the chemical world. Whereas all the contributors are experts in their fields, each in a way represents the efforts of many other workers. The editors can count at least 200 people in Ethyl who have contributed in production or applications development over the last 25 years. Much of the technology goes back to Professor Karl Ziegler's group at the Max Planck Institute for Coal Research, Mulheim, Germany. Some of the key people at Ethyl include M. F. Gautreaux, A. O. Wikman, R. A. Moser, A. E. Harkins, C. W. Lanier, J. R. Zietz, M. E. Tuvell, W. T. Davis, W. D. Taylor, and T. H. Bramfitt.

We hope this book will have widespread appeal for all in the chemical industry, including people in education, research, design, purchasing, production, sales, marketing, and management. Finally, we acknowledge the assistance of family members, friends, and co-workers for their patience with us in this endeavor.

George R. Lappin
Joe D. Sauer
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<td>Organization and Location</td>
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CHAPTER 1

Commercial Aspects

GEORGE R. LAPPIN Ethyl Corporation, Baton Rouge, Louisiana

1 INTRODUCTION

Linear even-carbon-number alpha olefins having four or more carbons are a basic petrochemical building block of over 2 billion pounds, including 790 million pounds per year of captive requirements. In addition, an estimated 400 million pounds per year of butene-1 are produced by non-higher alpha olefin processes. First produced in 1964 in significant commercial quantities at attractive prices, alpha olefins have grown rapidly and are expected to continue to grow as the literature on uses of alpha olefins continues to expand (see Figs. 1 to 3). The general markets are frequently categorized as (1) PVC plasticizers, (2) household detergents, (3) linear low- and high-density polyethylenes (as comonomers), (4) lubricants, and (5) other uses. Significant markets include detergents, sanitizers, plastics, lubricants, paper, metalworking, oil recovery, agriculture, and various specialty applications (see Fig. 4).

This chapter is an overview of the commercial aspects of alpha olefins, including routes for production and major markets. As these areas are explored in more detail in later chapters, the reference chapter is shown after each main heading in this chapter.
**Figure 1** Alpha olefin markets, projected for 1990.

**Figure 2** Alpha olefin market growth, excluding the USSR and its allied countries (billions of pounds per year).
Figure 3  Alpha olefin capacities estimated for 1988 and 1993 (millions of pounds per year).

2 ROUTES TO LINEAR ALPHA OLEFINS (CHAPTER 3)

Alpha olefins are produced in ethylene-based plants operated by Ethyl, Shell, Chevron/Gulf, and Mitsubishi (see Table 1). Enichem Augusta (formerly Liquichimica) in Italy produces odd and even linear internal olefins by extraction from partially dehydrogenated kerosene fractions.

Petrochemical operations during the past 20 years show a trend away from wax- or paraffin-based plants and toward ethylene-based plants. For economic reasons, Chevron's wax-cracking plant in California was shut down in September 1984. For several reasons, including economic ones, Shell has curtailed its wax-cracking operation in Europe. Wax-cracking plants yield lower-quality olefins and some undesirable fractions. For example, it is estimated that Shell fed 3 pounds of wax and produced 2 pounds of olefins per pound they sold or used as a primary alpha olefin before they started up their more efficient Shell Higher Olefin Process (SHOP) plant based on ethylene in 1983. Shell restarted their paraffin chlorination-dehydrochlorination (CDC) plant in the United States in mid-1985, apparently because it was a low-cost investment and a readily
available source of capacity. This CDC unit, which had been started up in 1967, was shut down in 1981 when Shell's U.S. SHOP unit was adequate for demands.

Chevron and Gulf pioneered large-volume commercial production of alpha olefins, with plants initially operating in 1962 and 1966, respectively. In a friendly merger aimed at defeating an unfriendly takeover bid by an investment group, Chevron bought Gulf Oil in 1984. This move resulted in merging the initial suppliers of alpha olefins.* Chevron's wax-cracked olefins plant at Richmond, California, had a capacity of about 90 million pounds per year and was operated from 1964 through September 1984. Chevron had a smaller unit in operation in 1962. Gulf's Cedar Bayou, Texas, plant began operation in 1966 with a capacity of 120 million pounds per year, expanding to 200 million pounds per year in 1981 and then to 250 million pounds per year in 1986. Chevron is building a new

* The original Gulf ethylene-based alpha olefin plant will be referred to as the Chevron plant or the Chevron/Gulf plant, but the Ziegler process first developed by Gulf will be called either the Gulf or Chevron/Gulf process.
### Table 1  Estimated 1987 Alpha Olefin Capacity

**Total capacity (million pounds per year)**

<table>
<thead>
<tr>
<th>Producer</th>
<th>Base capacity</th>
<th>Captive demand</th>
<th>Net merchant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethyl U.S.</td>
<td>950</td>
<td>100</td>
<td>850</td>
</tr>
<tr>
<td>Chevron/Gulf U.S.</td>
<td>250</td>
<td>30</td>
<td>220</td>
</tr>
<tr>
<td>Shell U.S.</td>
<td>650</td>
<td>350</td>
<td>300</td>
</tr>
<tr>
<td>Shell U.K.</td>
<td>450</td>
<td>300</td>
<td>150</td>
</tr>
<tr>
<td>Mitsubishi Japan</td>
<td>66</td>
<td>10</td>
<td>56</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>2366</strong></td>
<td><strong>790</strong></td>
<td><strong>1576</strong></td>
</tr>
</tbody>
</table>

**Percent of capacity in C₆-C₁₈ range**

<table>
<thead>
<tr>
<th>Producer</th>
<th>Base</th>
<th>Captive</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethyl U.S.</td>
<td>84</td>
<td>93</td>
</tr>
<tr>
<td>Chevron/Gulf U.S.</td>
<td>71</td>
<td>90</td>
</tr>
<tr>
<td>Shell U.S.</td>
<td>65</td>
<td>65</td>
</tr>
<tr>
<td>Shell U.K.</td>
<td>65</td>
<td>65</td>
</tr>
<tr>
<td>Mitsubishi Japan</td>
<td>71</td>
<td>100</td>
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**C₆-C₁₈ capacity (million pounds per year)**

<table>
<thead>
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<th>Producer</th>
<th>Base capacity</th>
<th>Captive demand</th>
<th>Net merchant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethyl U.S.</td>
<td>798</td>
<td>93</td>
<td>705</td>
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<td>Chevron/Gulf U.S.</td>
<td>178</td>
<td>27</td>
<td>151</td>
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<td>Shell U.S.</td>
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<td>Shell U.K.</td>
<td>293</td>
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<td>98</td>
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<td>Mitsubishi Japan</td>
<td>47</td>
<td>10</td>
<td>37</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>1737</strong></td>
<td><strong>553</strong></td>
<td><strong>1185</strong></td>
</tr>
</tbody>
</table>
LAPPIN

plant at Cedar Bayou, Texas, at a cost of $87.5 million. It will raise production to 450 million pounds a year by early 1990 and is designed to be easily expandable to 750 million pounds a year, depending on market conditions. Gulf licensed the original technology from Ziegler in Germany. The process uses catalytic amounts of triethylaluminum to chain-grow ethylene and simultaneously displace the olefins in situ. The product contains 1.4% paraffins because the aluminum alkyl is hydrolyzed at the end of the reaction. The alpha olefins are of good quality, containing some vinylidene olefins and essentially no internal olefins. Gulf’s process has limited flexibility with regard to carbon number distribution, and Gulf has used inventory control to handle excess olefins. Approximately 71% of the population is in the C_6–C_{18} main alpha olefin product range with about 15% each of C_{4} and C_{20–C_{40}} constituting the remainder. Chevron/Gulf is strong in ethylene supply, which is a key to their alpha olefin position. Captive requirements include polylalpha olefins and comonomers for high-density polyethylene.

Mitsubishi is a Gulf licensee with a plant in Japan producing 66 million pounds per year and a market limited to Japan. Approximately half the olefins used in Japan were imported from the United States in the years 1978–1987. Idemitsu has announced plans to build an olefin plant in Japan with a capacity of 110 million pounds per year. In the last 10 years, ethylene has been more expensive in Japan than in the United States, which is one reason the United States has expanded alpha olefin production faster than Japan; other reasons are the faster growth in U.S. requirements and the fact that U.S. plants have been larger and therefore more economical.

Ethyl Corporation began production of alpha olefins in December 1970 by adding to its primary alcohols complex. Like Gulf, Ethyl licensed the original technology from Ziegler in Germany. As was necessary with the alcohol process technology, Ethyl extensively modified the Ziegler olefin technology. The Ethyl process is similar to that of Gulf, as both use triethylaluminum. However, the Ethyl process is reported to use separate growth and olefin elimination steps. Ethyl reports ability to peak carbon numbers of both the alcohols and the olefins, selectively creating the most desired products. Approximately 82% of the production is in the C_{6–C_{18}} main alpha olefin product area, with about 15% as C_{4} and under 2% as C_{20–C_{40}}. The exact distribution varies almost daily as market demands for olefins and alcohols change. Ethyl’s capacity in million pounds per year grew from 200 in 1971 to 400 in 1974, 450 in 1976, 500 in 1980, over 800 in 1981, and over 950 in 1987. Captive requirements include alkyldimethylamines, lubricants, aluminum alkyls, primary alcohols, and alkenylsuccinic anhydride.

Shell’s captive demands for higher olefins include oxo alcohols in the
COMMERCIAL ASPECTS

United States, United Kingdom, and France and linear alkylbenzene (LAB) in Europe, Australia, and South Africa. Feedstocks for these have included SHOP olefins, wax-cracked olefins, and paraffin dehydrochlorination olefins. The two SHOP plants produce over 1 billion pounds of alpha olefins annually, of which an estimated 650 million pounds per year are used internally, leaving an estimated 400 million or more pounds for sales to the alpha olefin merchant market. Shell has 160 million pounds per year of linear odd and even internal olefin capacity in the United States based on their CDC unit. Shell had perhaps 600 million pounds per year of wax-cracked olefin capacity in Europe, most or all of which, as noted earlier, is currently unused. Shell's position in ethylene oxide is a key to their strength in detergents in the United States. Shell is a large-volume producer of ethylene. Since 1980, various portions of Shell have announced plans to build SHOP plants in the United States, Canada, and other parts of the world. Shell is building a new SHOP plant at Geismar, Louisiana, which is scheduled to begin operation in 1989, with 535 million pounds per year of capacity.

Enichem Augusta (formerly Liquichimica) in Italy produces odd and even linear internal olefins by dehydrogenation of normal paraffins extracted from kerosene. These are satisfactory as feedstock to linear alkylbenzene plants and to oxo alcohol plants. They produce linear alkylbenzene and alcohols in their complex.

Butene-1 from alpha olefin production is sold or used by Gulf, Mitsubishi, and Ethyl. Shell can recycle their butene-1 to their disproportionation reactors and use it in polybutylene production. Exxon, Texas Petrochemicals, DuPont of Canada, Huels in Germany, Shell in Europe, and other companies produce butene-1 via separation from various butylene streams. A recently developed system involves feeding ethylene plant butane-butene (B-B) streams into methyl t-butyl ether (MTBE) plants, with the butene-1 being a coproduct of the unit. Adding butene-1 as a coproduct may double the cost of an MTBE plant. Economics appear to favor nonethylene-based routes, so alpha olefin producers sell the butene-1 at generally lower prices than other alpha olefins. Butene-1 must be produced along with all other alpha olefins, and it would appear that the alpha olefin producers will always price their butene-1 to sell in competition with butene-1 from refinery or ethylene plant streams.

Many indirect types of competition exist for the alpha olefin products, including coconuts, leather, glass, and paper. The oil from coconuts can be made into primary alcohols. Leather, glass, and paper are alternatives to plastics. Derivatives of alpha olefins have been replacing many of these in specific end-use areas.
3 POLYETHYLENE (CHAPTER 4)

Alpha olefins are used in both high-density and linear low-density polyethylene as comonomers to improve their properties. In high-density polyethylene (HDPE) the olefins are used at up to the 2% level to impart stress-crack resistance, particularly for household bleach bottles. There are many grades of polyethylene, and comonomers provide one of the key differences. Many HDPE grades use no comonomer, resulting in an average comonomer usage level under 1% of the total HDPE usage.

Linear low-density polyethylene (LLDPE) is the largest volume end use of C₆-C₁₈ alpha olefins today. To a large degree, the near-term future of alpha olefins depends on the rate of LLDPE growth, the amount of comonomer used, and which of the three—butene, hexene, or octene—will be most useful. Various forecasters predict that LLDPE will penetrate to between 30 and 50% of the combined global market for LLDPE and the conventional high-pressure low-density-pressure polyethylene (LDPE). It has been estimated that LLDPE’s share was about 18% in 1985. The analysis in Table 2 is based on LLDPE penetrating to 30% by 1990, which would require 890 million pounds of alpha olefins. If it reaches 50%, much new comonomer capacity will have to be added, as comonomer demand would reach 1.5 billion pounds.

Table 2  Global Demand for LLDPE, LDPE, and HDPE

<table>
<thead>
<tr>
<th></th>
<th>1985</th>
<th>1990</th>
</tr>
</thead>
<tbody>
<tr>
<td>Penetration of LLDPE into LDPE (%)</td>
<td>18</td>
<td>30</td>
</tr>
<tr>
<td>Combined demand LDPE/LLDPE (billion pounds per year)</td>
<td>30</td>
<td>36</td>
</tr>
<tr>
<td>Estimated amount of LLDPE (billion pounds per year)</td>
<td>5.4</td>
<td>10.8</td>
</tr>
<tr>
<td>Total comonomer at 8% of LLDPE (million pounds per year)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>LLDPE butene-1</td>
<td>260</td>
<td>435</td>
</tr>
<tr>
<td>LLDPE hexene-1</td>
<td>65</td>
<td>260</td>
</tr>
<tr>
<td>LLDPE octene-1</td>
<td>100</td>
<td>155</td>
</tr>
<tr>
<td>LLDPE 4-methyl-1-pentene</td>
<td>5</td>
<td>40</td>
</tr>
<tr>
<td>Total</td>
<td>425</td>
<td>890</td>
</tr>
<tr>
<td>HDPE demand estimate (million pounds per year)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HDPE butene-1</td>
<td>100</td>
<td>120</td>
</tr>
<tr>
<td>HDPE hexene-1</td>
<td>55</td>
<td>85</td>
</tr>
<tr>
<td>Total LLDPE/HDPE comonomer</td>
<td>580</td>
<td>1090</td>
</tr>
</tbody>
</table>
4 PLASTICIZERS (CHAPTER 5)

Plasticizers for poly(vinyl chloride) (PVC) may be produced starting with an oxo reaction of C_6, C_8, and C_10 alpha olefins with carbon monoxide and hydrogen to produce a semilinear alcohol. The alcohol is then reacted with phthalic anhydride or other acid to produce a C_7-C_9-C_11 phthalic ester or other ester. The ester is used as a plasticizing agent in flexible PVC, a market of several billion pounds per year for esters of this nature.

The C_6-C_10 olefin requirements for plasticizers vary greatly with economic cycles and peaked in the United States at about 200 million pounds per year in 1979. U.S. demand correlates with housing starts and automobile sales although, on a direct basis, these represent only one-third of the market for the flexible PVC. The linear esters provide more permanence at high temperatures and make the PVC less likely to crack at low temperatures. These desirable properties may also be obtained by using more expensive, less available acids such as azaleic with less expensive 2-ethylhexanol. The semilinear ester values are set by the price of dioctyl phthalate (DOP). Rationalization of the ester supply has been occurring for 15 years and is likely to continue. Monsanto was the largest overall supplier until they sold their Texas City plant to the Sterling group in a leveraged buyout in mid-1986. BASF acquired the plasticizer business portion of the Texas City plant from Monsanto and has alpha olefins tolled by Sterling to plasticizer alcohols and esters. Monsanto remained in the butyl phthalate ester business. Other U.S. suppliers include Exxon, Tenneco, and USS Chemicals, which offer various linear, semilinear, and branched esters.

5 SURFACTANTS (CHAPTERS 6–9)

Detergents as a class are less subject to economic cycles than plastics are. But detergents have shown slower growth than plastics. Growth is occurring as alpha olefin derivatives replace other less biodegradable surfactants.

In the United States, Shell is the key producer of oxo alcohols for detergents, for which an estimated 350 million pounds per year of alpha olefins are consumed. Oxo alcohols in Europe represent a market of 400 million pounds per year for alpha olefins in the European detergent alcohol market. The resulting alcohols are sold as oxo alcohol ethoxylates. Shell is the largest producer, and this accounts for perhaps 100 million pounds per year of their internal demands for C_10–C_14 olefins. ICI is the next largest producer in Europe. BASF and Exxon-CdF Chimie consume the remainder. The total market is growing at 2% per year, and
ethoxylates are penetrating at another 1% per year, for a total growth rate of 3% per year.

Linear alkylbenzene (LAB) is increasing in importance as a market for alpha olefins as developing countries switch to biodegradable detergents. One large potential is in Latin and South America, where a switch from propylene tetramer to C_{10}-C_{18} alpha olefins is occurring for a portion of the requirements. For the longer term, companies in these regions may build paraffin-based plants, which tend to be more economical to operate but require significant investment to build. If all this region were to convert their entire alkylbenzene production to LAB, the total olefin demand might well be more than 200 million pounds per year.

Alpha olefin use in alpha olefin sulfonates (AOS) reached 74 million pounds per year in 1985 and is expected to grow to 105 million pounds per year in 1990. AOS provides superior performance in cold, hard water and works with alcohol ether sulfates in light-duty detergent applications. It is used in heavy-duty laundry powders in Japan. There are plans for using AOS in India, China, and other parts of the world. Concern about skin sensitivity has been resolved by the avoidance of bleaching of AOS with hypochlorite.

6 TERTIARY AMINES (CHAPTER 9)

The tertiary amine market represents a requirement for 50 million pounds per year of alpha olefins, with growth to 60 million pounds per year projected by 1990. Uses for the tertiary amines include light-duty liquid detergents, disinfectants, sanitizers, and oil recovery. These olefin derivatives, in the form of quaternary salts, play an important role in the battle against infectious diseases. They kill bacteria, fungi, and viruses involved in pneumonia, gonorrhea, diphtheria, influenza, polio, and many other contagious diseases.

7 ENHANCED OIL RECOVERY (CHAPTER 10)

Steam was used in California to recover heavy crude oil when crude oil was $3 per barrel. Thermal recovery of heavy oil continues during high and low crude oil prices. Enthusiasm for thermal recovery methods necessarily decreased as crude oil prices fell. C_{16}-C_{18} AOS, C_{16}-C_{18} dimer AOS, and C_{16}-C_{18} alkylaryl sulfonate have all been shown to increase oil recovery in individual tests of their use as foam-diverting agents by Shell, Texaco, Chevron, Stanford University, the University of Southern California, and the U.S. Department of Energy. The foams are used to divert the steam into oil-rich portions of the formation that the steam might otherwise bypass. Testing continues, aimed at identifying the overall effective-
ness of the foam procedure and the best surfactant for this application. Although use of alpha olefins in foam-diverting agents is small today, the maximum potential for alpha olefins could be of the order of 100 million pounds per year. Development will probably be slow as significant investment in materials and personnel are required to implement the use of the foam. Heavy oils are also recovered by thermal methods in Canada, Venezuela, and Indonesia, and these could greatly increase the potential for alpha olefins.

Alpha olefin derivatives may eventually play a role in various other enhanced oil recovery (EOR) activities, including carbon dioxide and micellar-polymer. It is difficult to attempt to forecast demands for alpha olefins in these areas because these uses lack either or both the economic incentives and the technical indications of potential success.

8 FATTY ACIDS (CHAPTER 11)

Fatty acids (C7 and C9) were first produced commercially in the United States from alpha olefins (C6 and C8) in 1980 by Celanese (now Hoechst Celanese). Celanese’s synthetic acid plant, the only one in the United States at present, produces 40 million pounds per year. These acids are used in the same areas as the other fatty acids in the C7 and C8 range, although the synthetics are preferred for some end uses because of their consistent quality and availability. They are used in plasticizers, synthetic lubricants, metal salts for grease thickeners and paint driers, surfactants and cosmetics, alkyd resins for coatings, high-water-based cutting fluids, and many other products. Total demand for the C6 and C8 alpha olefin raw material is estimated to be of the order of 20 million pounds per year, with growth of 3 to 4% expected in current areas and with additional growth likely but difficult to predict for developing areas.

9 LUBRICANTS (CHAPTER 12)

The current market for olefins in lube oil detergents is estimated to be 120 millions pounds per year. Shell, Ethyl, and Chevron have captive demands estimated to be 70% of the total. This market continues to grow faster than the total lube oil market as detergent concentrations increase and as “natural” supplies decrease. The natural lube oil sulfonates were coproducts from treatment of oils with sulfuric acid to remove unsaturates and produce white oils. For environmental reasons, hydrogenation is replacing sulfuric acid, and the result is fewer natural sulfonate supplies.
10 SYNTHETIC LUBRICANTS (CHAPTER 13)

Total demand for alpha olefins in synthetic lubricants grew from 65 million pounds per year in 1980 to 100 million pounds per year in 1985. The market is projected to grow at 10 to 15% per year to 200 million pounds per year in 1990. It could grow faster, based on the renewed emphasis in Detroit on 5W30 crankcase oils and their use in transmission fluids.

11 MERCAPTANS (CHAPTER 14)

Key mercaptans produced from the higher alpha olefins are based on butene, hexene, octene, decene, and dodecene. The butyl mercaptans are used to produce cotton defoliants, the octyl mercaptans are used to produce a water repellent, and the dodecyl mercaptans are used in rubber and detergents.

12 PAPER, FABRIC, AND LEATHER (CHAPTER 15)

Alkenylsuccinic anhydride (ASA) based on C_{16}-C_{20} alpha olefins is growing rapidly worldwide as fine-quality paper and gypsum board paper mills switch to alkaline sizing for economic reasons. The fine-quality area is divided into uncoated free sheet and coated free sheet. Growth occurred first in coated free sheet. Growth spread to the gypsum boards next, and now growth appears to be occurring in uncoated free sheet. Alpha olefin usage is forecast to increase from 12 million pounds per year in 1985 to 21 million pounds per year in 1990. The market potential for alpha olefins may be as large as 100 million pounds per year worldwide, but it is too early to predict the maximum. Small amounts of alpha olefins are used to produce other ASAs of various carbon numbers, which are used in petroleum additives, food additives, and other applications. Literature sources list over 20 uses for ASAs of various types.

Alpha olefins may be converted to leather tanning agents by reacting them with sulfonating agents. To be effective, only partial conversion on the order of 20% is achieved, as the unreacted portion acts as an oil and the converted portion acts as a detergent during the removal of the hair from the animal skin. U.S. demand for alpha olefins and olefin-paraffins is of the order of 3 million pounds per year. Many other materials have been used, such as methyl esters and fish and vegetable oils. Growth is unlikely in this area.
13 MISCELLANEOUS USES (CHAPTER 16)

Miscellaneous uses for higher alpha olefins include various small outlets, such as epoxides, chlorinated paraffins, waxes, fuel additives, and drag flow improvers. Total alpha olefin volume in this category is on the order of 30 million pounds per year, and this could grow significantly.

14 TOXICOLOGY (CHAPTER 17)

Alpha olefins are practically nontoxic by oral and dermal routes of exposure. They are expected to be only minimally irritating to the skin and eyes. The lower members, including ethylene, propylene, and butene, are characterized as simple asphyxiants or weak anesthetics.

15 STORAGE AND HANDLING (CHAPTER 18)

Proper storage and handling is essential to assure maintenance of the excellent quality of the olefins. Exposure to air will result in absorption of oxygen and water, with resulting problems when these interfere in various reactions. Peroxides will develop with time after exposure to air.
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Chevron (Gulf) Process


Shell Process


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Applications


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