taken from the various plants at time intervals for analysis to assess the quality. The samples drawn at these stages are checked for iodine value, acid value or GLC, depending on the relevance of the data in relation to the desired product.

At the final stage prior to packaging samples are analyzed for the following: iodine value, titre, acid value, saponification value, unsaponifiable matter, color and FA by GLC. These specifications should conform to published standard specifications.

If the liquid sample is found to be out of specification, measures are taken to rectify the problem. The product may be redistilled to improve the color, for instance, or it may be blended with other fatty acids in a ratio that will meet the required chain length distribution.

When the liquid sample is within the desired specification, it is either bulked, flaked or drummed depending on the titre of the product. Regular monitoring of the heat color stability, ash content, moisture, impurities and nickel content, especially in the case of hydrogenated fatty acids, is important.

REFERENCES

1. PORIM Technology No. 4, p. 1.
2. PORIM Technology No. 6, p. 2, 4.
3. "Coconut Oil Processing," FAO Publication, 1968, Chapter 7.
4. Schwitzer, M.K., An Introduction to the Biotechnology of Oils and Fats, p. 169.

Oleochemicals in the Plastics Industry

H. VERITY SMITH

ABSTRACT

There are opportunities for the producers of natural renewable products to manufacture downstream products of industrial value. The plastics industry is only one of many that offer such opportunities. Palm and coconut are two of the many plants with chemical possibilities.

INTRODUCTION

The northern industrial countries are in the process of transformation from "manufacturing" to "information" societies (1). As they pass from manufacturing economies to service economies (2) it will be the turn of the developing countries to become the industrial and manufacturing centers.

In order to render the transition into manufacturing societies as painless as possible, it is necessary that the developing countries concentrate on using their own natural and renewable resources. They should not follow the lines of development that were pursued in the northern industrial revolution, but should seek their own pathways, using their own resources and without relying upon organized assistance from the "old world." In its modern context, I take this expression to include Europe, North America and Japan.

As examples of new industrial enterprises for developing countries, based on renewable natural resources, it is proposed to consider the opportunities available to the producers of palm, palm kernel and coconut oils in the plastics industry. Similar opportunities exist in many other industries and are open to many other vegetable products in addition to those being studied at this conference.

It is suggested that petroleum must be replaced as the raw material of the chemical and plastics industry because supplies are about to be exhausted. The best estimates are that petroleum supplies will last into the third quarter (3) of the twenty-first century and natural gas into the last quarter (4).

It will indeed be argued that this is not the time for the developments I propose. There is presently a glut of petroleum on the world market, and in real terms, supplies are getting cheaper all the time (5). This is short-term thinking in a long-term context.

The best estimates suggest that, in real terms, petroleum (and therefore petrochemical) prices will start to rise in the mid 1990's (6). Such estimates cannot take into account escalation of the conflict in the Middle East. The programs of development of products for the plastics industry which I am about to suggest could be coming to full fruition in about ten years' time.

REASONS FOR DEVELOPMENT

There are three reasons why downstream products from renewable vegetable resources should be developed now.

Commercial

In some cases, the oleochemical route produces a cheaper product under today's conditions. For example, linear alcohols are used in the plastics industry for the manufacture of stabilizers. At the average price of coconut and palm kernel oils over the last ten years, it has been cheaper to manufacture natural linear alcohols in the C_8-C_{12} range than to make synthetic linear alcohols from ethylene by the Ziegler process.

World natural fatty alcohol production is about 260,000 tons per year, compared with about 420,000 tons of synthetic linear alcohols (7). The competitive position of the natural product will continue to improve with time, assuming that the vegetable oil producers keep up with the demand.

It is encouraging to observe the progress, both in the Philippines and in Malaysia, in the production of natural alcohols. There would appear to be no reason why the developing countries should not take over this market, providing that they remember that competition exists not only from synthetics, but from other natural products. It would not be the first time that a synthetic chemical had been ousted by a natural one. Synthetic glycerine is on its last legs.

Financial

There does not appear to be any sign that the banking community is making, or is likely to make, much contribution to the solution of the debt problem for which it is in large measure responsible (8). Currently, the third world is paying back more interest to the commercial banks than it is receiving in new financing (9).

Most developing countries must import all their petrochemical requirements, including plastics, and must pay for them in dollars. Most developing countries have a balance of payments problem and need to ration dollar foreign exchange. This has a delaying action on the industrial progress of developing countries because the necessary raw materials and equipment for local manufacturing processes cannot be made available.

Replacement of imported petrochemical products by locally-produced vegetable derivatives would therefore make financial sense even if the products so manufactured were more expensive, for the moment, than their imported equivalents. It would also make industrial and social sense, because it might well be a choice between the availability and nonavailability of a material necessary for the production of a useful and profitable product for local industry.

Political

The less a country is dependent upon imports designated in a foreign currency, the greater is its political independence. The more a country can produce from its own renewable resources, the less dependent it becomes upon outside political influence. The risks of overdependence upon either of the world's major power blocks are too obvious to require emphasis here.

THE PLASTICS INDUSTRY (10)

There are at least three common misconceptions about the plastics industry. They concern its age, its size and the provenance of its raw materials.

The plastics industry is, in the economic sense, a mature industry, a number of its products having become commodities.

Celluloid, regarded as the first plastic material, was exhibited at the Second Great Exhibition in London in 1862; it was invented by Alexander Parkes, and the raw material was cotton.

Cellulose acetate was first manufactured by Henri and Camille Dreyfus just before the First World War; it is still produced, and the raw material still cotton.

The first entirely synthetic plastic to be produced on a large scale was *polystyrene* (of which the monomer, curiously enough, exists in nature). It was first produced in Germany, by I.G. Farbenindustrie, in 1930. The basic raw material was benzene derived from coal tar distillation. The size of the plastics industry is widely and wildly underestimated. World production is in excess of 40 million tons a year.

Polyvinyl chloride accounts for about 16 million tons a year. The first patents on PVC were issued in 1912 in Russia to Ostromislenski and in Germany to Klatty. Production commenced in Germany in 1937. The raw material was acetylene derived from coal.

Polyethylene was discovered by Fawcett and Gibson in 1933 and production commenced in England by ICI in 1937. The raw material was ethylene produced by dehydrating ethanol from fermentation of grain.

It is commonly thought that plastics are of necessity derivatives of petroleum. The materials I have mentioned include three of the four most important types on today's market, and in no case was the earliest production dependent upon petroleum. Only the most recent of the four most important types, *polypropylene*, discovered by Prof. Natta and first produced in Italy by Montecatini in 1956, was from the first a petrochemical derivative.

After the Second World War when petroleum became, for a period of about thirty years, the cheapest and most abundant source of raw materials for the chemical industry, there was an immense amount of development of petroleum chemistry. Today, with the exception of the cellulosics and nylon 11, almost all plastics are made from petrochemical feedstocks. The existence of alternative sources is all but forgotten.

Having shown that the plastics industry is not necessarily dependent upon the petrochemical industry, we can proceed to examine the opportunities and limitations for palm- and coconut-based oleochemical products. It is convenient to divide these opportunities into three categories.

- Products currently made from oleochemicals, but which the vegetable oil-producing countries do not produce and market specifically to the requirements of the plastics industry.
- Products currently made from petrochemicals which could be replaced by oleochemicals.
- Products which are not currently manufactured, but which could be derived from palm and coconut oils and which should be able to find a place in the plastics market.

The materials of the plastics industry are:

- *Polymers:* large molecules that give their specific properties to the plastics; relatively low-cost products made on a big scale.
- *Additives:* chemicals that modify the polymer either to make it easier to process into the finished product, or to modify the properties of the finished product itself.

To make clear how some of the products which can interest the plastics industry are derived, Figure 1 explains the chemical relationships of some of the important fatty derivatives.

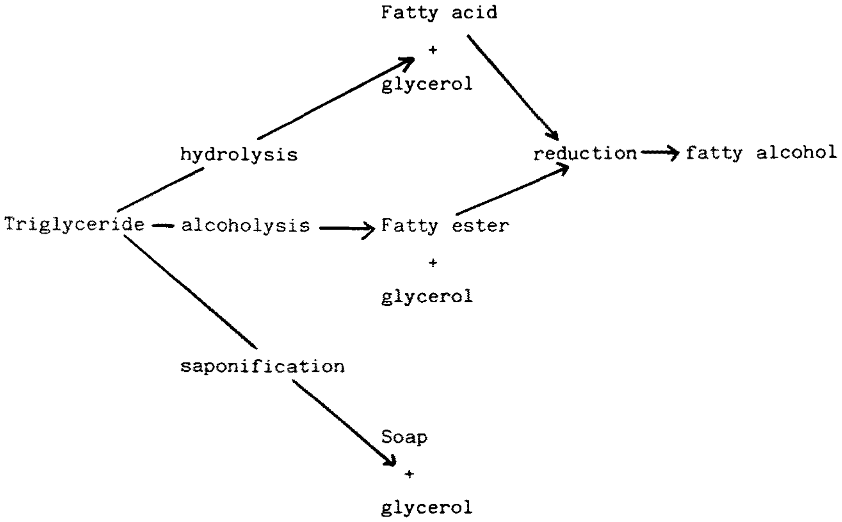

FIG. 1. Some chemicals from fats.

PRODUCTS CURRENTLY MADE FROM OLEOCHEMICALS

Additive Lubricants

Lubricants are used to facilitate the passage of the plastic through the processing equipment and also to modify the surface properties of the product, such as "slip" or "tack" in films. Commonly used lubricants include oleamide, glyceryl monostearate, ethyl palmitate, butyl stearate, methyl oleate, ethylene glycol dipelargonate, all of which obviously can be derived from palm or coconut oils. Fatty acids are also used as lubricants, as are their calcium, magnesium and lithium soaps.

Production of a suitable quality of any of these products does not appear to present much of a problem. Facilities for quality control testing in actual plastics formulations would be necessary. The problem would be marketing. This will be considered in the context of stabilizers, where the problem is more difficult.

Vinyl Stabilizers

Stabilizers for PVC are necessary to protect the thermally unstable polymer from degradation by the heat of processing, and to protect the finished product against the effects of light. Worldwide consumption of vinyl stabilizers is of the order of 400,000 tons per year.

Formulation and application of vinyl stabilizers is as much an art as a science. A comprehensive technical service facility in the market itself is a prerequisite for success in this highly competitive market.

An opportunity to enter this market could, however, be created. A relatively small number of companies dominate the world market for vinyl additives. Some of these companies do not make their own intermediates, and some of these intermediates are oleochemical.

Di-n-octyltin dichloride is one of the stabilizer intermediates which is traded. The octyl portion is oleochemical, because the U.S.F.D.A. toxicity regulation specifies 100% linearity. The tin comes from Malaysia. There appears to be a case for a feasilibility study on the manufacture of organotin intermediates, other stabilizer intermediates and lubricants in Malaysia, to be marketed in close cooperation with one of the international plastics additive marketing companies. The other organotin intermediates are of no oleochemical interest (dibutyltin dichloride and methyltin trichloride), but would logically form part of the program. Other oleochemical stabilizer materials are barium-cadmium laurate, zinc octoate and smaller quantities of a wide range of fatty derivatives.

PRODUCTS CURRENTLY MADE FROM PETROCHEMICALS WHICH COULD BE SUBSTITUTED BY OLEOCHEMICALS

Plasticizer Additives

The function of plasticizers is to reduce the attractive forces between the polymer chains by pushing them apart, thus making the product more flexible. The main use is in vinyl plastics and the worldwide consumption is of the order of 1.8 million tons per year.

The most widely used plasticizer is di 2-ethylhexyl phthalate, commonly known as DOP. The branched chain alcohol from which it is made is a petrochemical derivative which presently has a price advantage over natural n-octanol derived from coconut or PKO. It can confidently be expected to lose this advantage as petroleum prices rise in the 1990's, opening up a very important market for natural alcohols.

The acid used to make DOP is phthalic anhydride, a petrochemical derivative. Alternative oleochemical acids, such as azelaic, obtained by the ozonolysis of oleic acid (11), have advantages in that the octyl ester confers better low-temperature properties on the PVC, but, because of its lower molecular weight, it is at a disadvantage as regards volatility, and hence permanence. The azelates have a place in the market, which means that azelaic acid has a place in the market, but it is limited by the fact that the azelates are not suitable as sole plasticizers and are normally mixed with DOP.

The synthetic branched-chain alcohols used in the manufacture of plasticizers are derived from olefins by the "oxo" process, a hydroformylation reaction involving the use of carbon monoxide and hydrogen. This reaction can also be applied to unsaturated fatty acids or esters, using rhodium or palladium catalysts (12). By this reaction secondary plasticizers of the type methyl 9(10) formyl stearate can be derived from methyl oleate. A more interesting product, which has not been commercialized and which can be derived from oleic acid, is methyl 9,9(10,10) bis acetoxymethyl octadecanoate. This product and some of its analogs (12,13,14) appear to be superior to DOP as a primary plasticizer and economically competitive when the sources of oleic acid are at average price levels.

In view of the growing disquiet, especially in the United States, about pollution of the environment by DOP, it would appear to be worthwhile to investigate the feasibility of producing plasticizers of this entirely vegetable-based type.

A special class of plasticizer, usually known as "polymerics," is made by reacting a diacid with a dihydroxy compound such as ethylene glycol. These are used where resistance to extraction and a high level of permanence at elevated product service temperature are specified. Azelaic acid is suitable for the manufacture of these plasticizers.

Polyester Polymers

Unsaturated polyesters are versatile products which are used as potting resins for the encapsulation of electronic components, as casting resins for short-run molding operations, and of course, as components of fiber-reinforced plastics. The usual diacid is phthalic anhydride; replacement by azelaic acid gives polyesters improved impact strength and resilience.

Polyethylene

The raw material for the first commercial manufacture of polyethylene was fermentation alcohol dehydrated to ethylene. In Brazil, Dow Chemical is building a polyethylene plant for which the feedstock will be fermentation alcohol derived from cane sugar. There is no particular reason why, in addition to polyethylene, PVC could not be produced from "biomass ethylene." The other raw material is chlorine, derived from the electrolysis of common salt.

Great progress has been made in improving the economics of producing ethanol from biomass (15). A four-stage process is involved: pretreatment to convert the raw material into a hydrolyzable substrate, enzymatic hydrolysis to convert the starches or celluloses into sugars, yeast fermentation of the sugars to ethanol, and purification of the ethanol.

One of the major costs in producing ethanol from biomass is in the collection of the biomass. In Malaysian palm plantations there already exist the means of collection, and it is already paid for. The waste foliage from the palm fruit has to be disposed of by the palm oil mill. Might not this very large quantity of biomass be considered as a source of ethanol? And the ethanol could then be a source of ethylene—the basis for a polymer industry.

It is unlikely that such a production of polyethylene or PVC would, at present, be competitive with the imported petrochemical product. But it would be a domestic product, and would not require foreign exchange. And in the foreseeable future it might well become competitive.

PRODUCTS NOT CURRENTLY MANUFACTURED

A New Nylon Polymer

In 1934, Wallace H. Carothers of Dupont invented a new type of material, the superpolyamide, now universally known as nylon. The first nylon was made by reacting a diacid with a diamine, and as both the components, adipic acid and hexamethylene diamine, have six carbon atoms, it became known as nylon 6,6.

As an alternative to reacting a diacid with a diamine, it is possible to polymerize a compound with an amine group at one end and an acid group at the other. Caprolactum, for example, can be polymerized to yield nylon 6.

In 1955, Aquitaine Organico in France (now part of the ATO-Chimie group), introduced a new nylon, nylon 11, the first thermoplastic for over forty years to be based on a natural raw material, castor oil. The monomer for nylon 11 is 11-amino undecanoic acid. So successful was this material that when suitable supplies of castor oil became unavailable to ATO they were forced to turn to nylon 12, a petrochemical product with similar properties, in order to supply the market. It is apparent that any unsaturated acid would provide the basis for a nylon(16).

The U.S. Department of Agriculture has synthesized nylon 13-13, starting from erucic acid (17,18,19). They have molded it and spun fibers from it. As would be expected, it is quite similar to nylons 11 and 12. The starting material was the oil from Crambe abyssinica. Assuming that they could obtain Crambe oil for $0.30/lb, they calculated that they could produce nylon 13-13 for $0.99/lb. The current selling price of nylon 11 is about $2.50/lb.

From these figures, it would seem reasonable to consider the feasibility of making nylon from the unsaturated acid which is common to palm and coconut. Palm olein is already a commodity, and I understand that coconut olein will shortly be on the market.

Nylon 9 has been prepared in the laboratory (20,21,22). In Figure 2, which is based on one of the routes given by Perkins, Roden and Pryde (22), a synthesis of nylon 9 is shown. The authors estimate processing costs to be between $0.37 and $0.47 per lb (not including raw materials and investment).

Figure 3, based on work by Nieschlag, Rothfus, Sohns and Perkins (19), shows a possible route to nylon 9,9. It

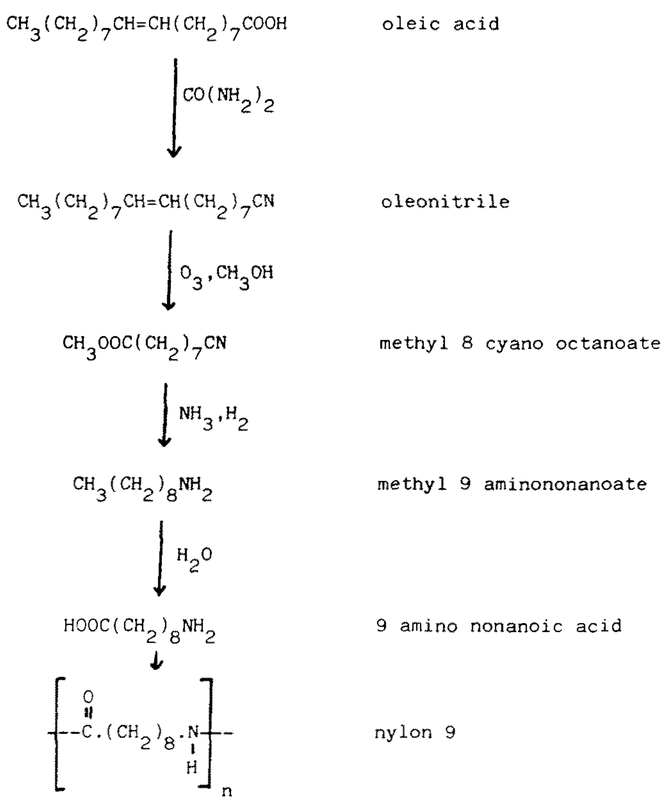

FIG. 2. A possible route to nylon 9.

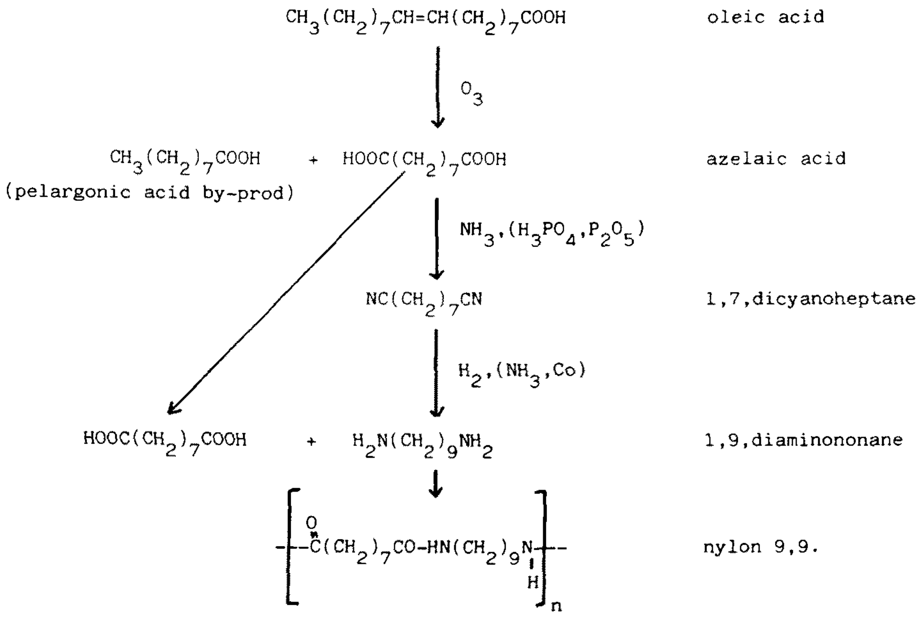

FIG. 3. A possible route to nylon 9,9.

should be pointed out that Figure 2 represents a route which has been tried successfully, and Figure 3 is merely an analog of work successfully carried out on brassylic acid as a source of nylon 13,13.

REFERENCES

1. Naisbitt, J. Megatrends, Macdonald & Co., London, 1984.
2. Weiner, M.J., English Culture and the Decline of the Industrial Spirit, 1850-1950, Cambridge University Press, 1981.
3. Odell, J.R., Oil and gas resources and the supply/demand pattern beyond 2000, Proceedings, Chemrawn III, 1984.
4. Li, C.Y., The oil and gas situation in the Far East and its role in the global context, Proceedings, Chemrawn III, 1984.
5. Anon., The Economist, London, Aug. 5th 1984, p. 15.
6. Schwartz, P., Planning in Shell, energy in the global economy in the Long Term, Proceedings, Chemrawn III, 1984.
7. Richtler, H.J., and J. Knaut, JAOCS 61:160 (1984).
8. Sampson, A., The Moneylenders, Hodder and Stoughton, London, 1981.
9. Clausen, A.W., (president, World Bank), quoted in The Observer, London, July 15th, 1984.
10. Kaufmann, M., The First Century of Plastics, The Plastics Institute, London, 1963.
11. Kadesh, R.G., JAOCS 56:845A (1979).
12. Miller, W.R., E.H. Pryde, and G.R. Riser, JAOCS 55:469 (1978).
13. Miller, W.R., and E.H. Pryde, JAOCS 54:882A (1977).
14. Frankel, E.N., JAOCS 48:248 (1971).
15. Alcohol Fuels: Options for Developing Countries, National Academy of Sciences, Washington DC, 1983.
16. Watowich, A-M.V., and E.B. Shultz, Polymers from Novel Oilseeds in the South Eastern United States, in E.B. Shultz and R.P. Morgan, Fuels and Chemicals from Oilseeds, American Association for the Advancement of Science, Washington DC, 1984.
17. Greene, J.L., R.E. Burks, and I.A. Wolff, Ind. Eng. Chem. Prod. R & D., 8:171 (1979).
18. Carlson, K.D., V.F. Sohns, R.B. Perkins, and E.L. Huffman, Ind. Eng. Chem. Prod. R & D, 16:95 (1977).
19. Nieschlag, H.J., J.A. Rothfus, V.E. Sohns, and R.B. Perkins, Ind. Eng. Chem. Prod. R & D, 16:101 (1977).
20. Kohlase, W.L., E.H. Pryde and J.C. Cowan, JAOCS 47:183 (1970).
21. Miller, W.R., E.H. Pryde, R.A. Awl, and W.L. Kohlase, Ind. Eng. Chem. Prod. R & D., 10:442 (1971).
22. Perkins, R.B., J.J. Roden, and E.H. Pryde, JAOCS 52:473 (1975).

Industrial Uses of Palm, Palm Kernel and Coconut Oils: Nitrogen Derivatives

RICHARD A. RECK, AKZO Chemie America—Armak, 300 S. Wacker Drive, Chicago, IL

ABSTRACT

Palm, palm kernel and coconut oils are sources of fatty acids that can be converted to other oleochemicals that have many applications. This paper describes manufacturing procedures, product characteristics and uses for many fatty acids, alcohols, primary amides, monosubstituted amides, diamides, disubstituted amides, nitrites, primary amines, secondary amines, tertiary amines, diamines, quaternary ammonium compounds, amphoterics, amine oxides and polyoxyalkylene alkylamines.

INTRODUCTION

Palm oil, palm kernel oil and coconut oil are excellent sources for fatty acids, alcohols and nitrogen derivatives of 8-18 carbon atoms, when the alkyl moiety is saturated or when the carbon chain is unsaturated with one double bond, as in the eighteen-carbon chain length.

TABLE I

Chain Length Composition of Coconut, Palm Kernel and Palm Oil (%)

Oil	C_6	C_8	C_{10}	C_{12}	C_{14}	C_{16}	C_{18}	C_{18}=
Palm					1	43.5	4.5	40
Coconut	0.5	7.0	6.0	48.0	19.0	9.0	3.0	6.0
Palm kernel		3.5	3.5	48.5	16.5	8.5	2.5	14.5

TABLE II

Chain Length Composition of Tallow (%)

C_{14}	C_{14}=	C_{15}	C_{16}	C_{16}=	C_{17}	C_{18}	C_{18}=	C_{18}==
3.5	1.0	0.5	25.5	4.0	2.5	19.5	41.0	3.0

Table I contains the chain length distribution as it exists in these oils. In the C_{8-14} chain lengths palm kernel and coconut oil have no natural competition in the acid or amine category of derivatives, but there are competitive feedstocks available from petroleum-drived synthetic alcohols and acids. In the C_{16-18} acids and derivatives, there is no significant competition from synthetics. However, in this range competition from tallow is very significant. Table II contains the chain length distribution in tallow, which is the least expensive source for C_{16-18} fatty acids worldwide. In all cases, the end use requirements and economics will dictate the feedstock.

The production of fatty acids worldwide has grown rapidly since World War II. The estimated production is now close to 1.7 million metric tons (MT). Table III shows a breakdown by percentages of the various fields of application. A general overview of the fat and oil industry was presented at Montreaux last year (1).

TABLE III

U.S. Consumption of Fatty Acids by Market Area

Market area	% of total
Personal care products	19.7
Industrial lubricants, corrosion inhibitors, oil additives	18.1
Coatings	13.0
Household cleaners, laundry soaps, fabric softeners	8.0
Plastics	7.6
Textiles	6.7
Emulsion polymerization	5.5
Rubber compounding	5.0
Asphalt	3.4
Mining	1.7
Miscellaneous	11.3