# Synthetic Fatty Acids in Eastern Europe

**KARL T. ZILCH, Emery Industries, Inc., Cincinnati, Ohio**

## Abstract

For over a century various investigators have studied the air oxidation of paraffinic hydrocarbons to produce synthetic fatty acids. Today in the socialistic countries there are six to eight plants manufacturing these acids to replace in soaps tallow fatty acids which are needed as a source of food.

The principal technological advances in air oxidation, prior to World War II, were made by Germany while more recently Russia and its satellite countries have made the major contributions. Although the oxidation involves a multitude of chemical reactions taking place consecutively and simultaneously, it has been fairly well established that the alkylhydroperoxide precursors are converted to alcohols and then further oxidized to carboxylic acids.

The cost of manufacturing synthetic fatty acids in Eastern Europe ranges between 8–12¢ per pound depending upon the raw material, processing costs and by-products.

## Discussion

SYNTHETIC FATTY ACIDS are currently being produced on a large scale in Eastern Europe through air oxidation of paraffinic hydrocarbons. This technique of air oxidation has been studied for over a century and will continue to be investigated because of its complicated reaction mechanisms and the variety of products formed during the reaction. It is interesting to see how world conflicts and world food shortages have brought about the commercial production of synthetic fatty acids.

There is some discrepancy throughout the published literature on paraffinic oxidation, as to who might have carried out the first piece of research in this area. Perhaps Gessner (Gessner, O., *Practical Treatise on Coal, Petroleum and Other Distilled Oils,* 1865) in 1865 was the first to report the results of his preliminary study which was systematically expanded upon by Schaal (Schaal, E., *Verfahren zur Oxydation von Petroleum und Ähnlichen Kohlenwasserstoffen zu Säuren und zur Herstellung von Seifen und Äther dieser Säuren,* 1871, Patent Schrift No. 32: 705) in 1871 who registered the first patent in 1884.

Very little was published on the synthesis of fatty acids until World War I when a shortage of fats and oils developed and prices skyrocketed. At this time both Germany and England initiated major research programs and Professor Francis at Bristol University in England began to develop some important basic knowledge on the oxidation of paraffins. From his work it was concluded that the most efficient and economical method of producing synthetic fatty acids was by means of catalytic air oxidation at high temperatures. The first plant for synthetic fatty acids through the oxidation of mineral oils was built and operated by the Fanto Company in Pardubitz, Czechoslovakia, during the First World War.

After World War I practical interest in synthetic acids declined because natural fats and oils became more plentiful and prices declined. However, in 1921 Badische Anilin and Sodafabrik built a small experimental unit at Oppau, Germany, which processed lignite paraffin. In 1931 I. G. Farben together with Standard Oil of New Jersey built a 90 ton per month installation for processing petroleum paraffins in Baton Rouge, Louisiana.

TABLE I

Replacement of Tallow Fatty Acids with Synthetic Fatty Acids in the Manufacture of Soap

*U.S.S.R. Soap Production 1959*
1,319,000 tons household soap
100,000 tons toilet soap

*U.S.S.R. Seven Year Plan Ending 1965*
40% Replacement of household soap (contains 60% fatty acid)
15% Replacement of toilet soap
335,000 tons of S.F.A. needed
$C_{10}$–$C_{21}$ Soap type acids is 55% yield of production
610,000 tons S.F.A. must be produced

*U.S.S.R. Five Year Plan Ending 1970*
200% Increase or 1,830,000 tons needed

By 1935 the Germans had developed on a commercial scale the Fischer Tropsch process which made available large quantities of a soft-waxy paraffin by-product called "Gatsch" for which uses had to be found. A synthetic fatty acid plant based upon this by-product was built at Witten, Germany, in 1938 by Henkel and Markische Seifen Industries. It processed 44,800 tons of paraffin a year to yield 34,720 tons of fatty acids for the manufacture of soaps. Later I. G. Farben built plants at both Oppau and Heyebreck, Germany, to process 22,400 tons per year at each location.

During World War II Hübbe and Fahrenholtz built a plant at Magdeburg, Germany, having a rated input of 22,400 tons paraffin and later in 1948 a similar size plant was built in Eastern Germany at Rodleben which in 1965 converted 43,000 tons of paraffin to fatty acids. The socialistic countries have continued to develop the field of paraffin oxidation while development in Western countries came to a standstill. The principal reason for continued interest in the socialistic block was the shortage of food. It was recognized that the natural fats and oils being consumed for the manufacture of soap could be used in edible products. Russia itself had a seven-year-plan which began in 1959 and ended in 1965 which called for replacing 40% of the natural fatty acids in soap with synthetic fatty acids and 15% of the toilet soap natural fatty acids. As seen in Table I this would mean a yearly production of 335,000 tons of $C_{10}$–$C_{21}$ synthetic fatty acids. Since this fraction represents only 55% of the over-all yield, it would mean that approximately 610,000 tons of synthetic fatty acids would have to be manufactured to satisfy their yearly needs. Recently Russia announced a 200% increase in production to be completed by 1970.

1. $\mathrm{RH} \longrightarrow \mathrm{R}\cdot$
2. $\mathrm{R}\cdot + \mathrm{O_2} \longrightarrow \mathrm{RO_2}\cdot$
3. $\mathrm{RO_2}\cdot + \mathrm{RH} \longrightarrow \mathrm{ROOH} + \mathrm{R}\cdot$
4. $\mathrm{RO_2}\cdot + \mathrm{RO_2}\cdot \longrightarrow \mathrm{ROOR} + \mathrm{O_2}$
5. $\mathrm{RO_2}\cdot + \mathrm{R}\cdot \longrightarrow \mathrm{ROOR}$
6. $\mathrm{ROOH} \longrightarrow \mathrm{RO}\cdot + \cdot\mathrm{OH}$
7. $\mathrm{RO}\cdot + \mathrm{RH} \longrightarrow \mathrm{ROH} + \mathrm{R}\cdot$
8. $\cdot\mathrm{OH} + \mathrm{RH} \longrightarrow \mathrm{R}\cdot + \mathrm{H_2O}$
9. $\mathrm{ROOH} + \mathrm{RH} \longrightarrow 2\mathrm{ROH}$
10. $\mathrm{ROOH} \longrightarrow \mathrm{R_1COR_2} + \mathrm{H_2O}$
11. $\mathrm{ROH} \longrightarrow \mathrm{R_1COR_2}$
12. $\mathrm{ROH} \longrightarrow \mathrm{Acids}$
13. $\mathrm{R_1COR_2} \longrightarrow \mathrm{Acids}$

FIG. 1. Free radical reaction mechanism involved in the oxidation of paraffins to synthetic fatty acids.

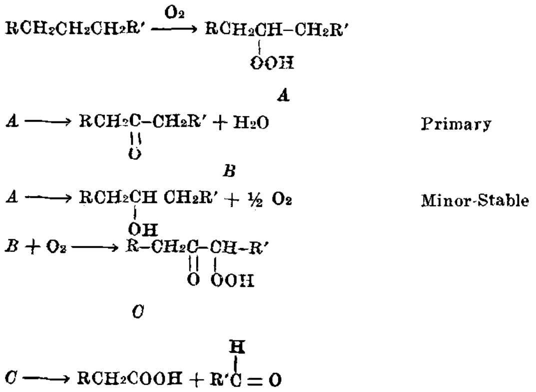

FIG. 2. Pritzkow's explanation of paraffin oxidation to yield carboxylic acids.

Presently there are six to eight plants located in Russia and its neighboring satellite countries.

The entire process for the manufacture of fatty acids through oxidation of paraffins involves a multitude of chemical reactions taking place consecutively and simultaneously. The reaction proceeds through a free radical reaction mechanism, as shown in Fig. 1. A number of investigators have studied the oxidation of paraffins without conclusively determining the primary mechanism of reaction. It has been generally accepted that oxygen reacts with the hydrocarbon to yield alkyl radicals and peroxide radicals which lead to the formation of a relatively stable hydroperoxide. Pritzkow [Pritzkow, W., *Fette, Seifen, Anstrichmittel, 67, 399,* (1955)] and co-workers from a study of stable products formed, enunciated the hypothesis that resulted from the breakdown of secondary alkylhydroperoxides which were converted to acids via ketohydroperoxides as shown in Fig. 2. He postulated that the alcohols formed were stable to further oxidation.

Bashkirov [Bashkirov, A. N., Kamzolkin, V. N., *Khim. Tekhnol. Topliva, 4,* 7 (1957)] in 1956 made an important contribution to the understanding of the oxidation mechanism when he showed that it was possible to fix the oxidation of hydrocarbons in one of the initial stages by selectively reacting boric acid with the primary and secondary hydroxyl groups to form borate esters. With this technique he proved that secondary alcohols are formed through the decomposition of hydroperoxides.

Tsyskovskii [Tsyskovskii, V. K., et al., *Khim. Prom.,* No. 3, 21–29 (1959)] using Baskirov's technique showed that low temperature oxidation gave primary alcohols and that high temperature oxidation yielded secondary alcohols. Fig. 3 illustrates the generally accepted decomposition of alkyl hydroperoxides to primary and secondary alcohols depending upon the reaction temperature and subsequent oxidation to fatty acids.

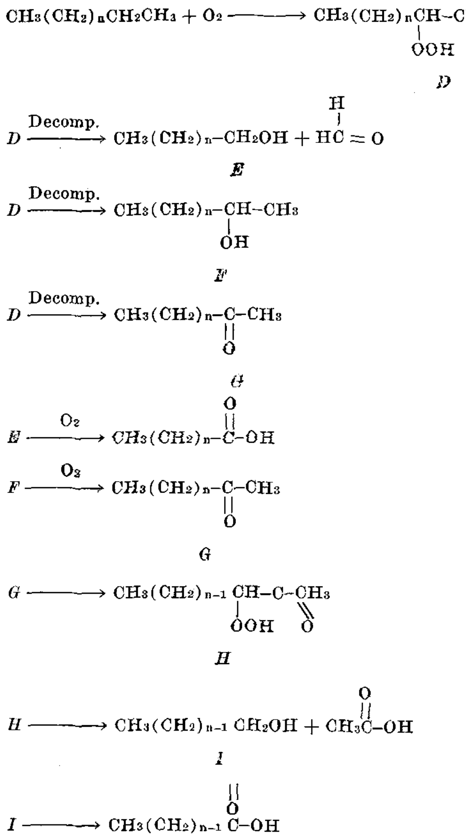

FIG. 3. Tsyskovskii's explanation of reaction mechanism and products.

Most of the commercial plants in Russia and her satellite countries are manufacturing synthetic fatty acids in a continuous operation. Basically, the process consists of partially oxidizing with air a mixture of fresh and recycled paraffins in the oxidation towers at about 100C in the presence of a permanganate catalyst. Oxidation is continued until an acid number of 70 is reached in the oxidate. The oxidation product is then washed with water to remove the low molecular weight oxidation products and saponified with alkali to allow for the mechanical separation of the unsaponifiable constituents from the soap solution. The unsaponifiables which carry along with the soap solution are driven off by means of a complicated thermal process. The soap is acidulated and the recovered fatty acids are fractionally distilled into various fractions. The combined unsaponifiable fractions are recycled back to the oxidation towers.

The type of crude petroleum oil varies from one location to another. Because of this variation the yield of the different synthetic fatty acid fractions produced also vary as shown in Table II. The chain length distribution within the individual fractions also change as illustrated in Table III.

Since it is Russia's objective to replace the tallow fatty acids used in the manufacture of household and toilet soaps with synthetic fatty acids, those raw materials which are readily available and give the highest yield of $C_{10}$–$C_{20}$ chain length fatty acids are used as feedstocks to the various plants. However, the market price for the co-products and by-products produced must also be taken into consideration. The actual market prices for the three principal fatty acid fractions produced are as follows: $C_5$–$C_9$—\$322 per ton (short), $C_{10}$–$C_{20}$ \$564 per ton and $C_{21+}$ \$42 per ton. The market prices for these fractions are dictated by the supply and demand as well as their end use applications.

According to Lubbe [Lubbe, E., *Freiberger Forschungsh., A221,* 7–21 (1962)] the $C_5$–$C_9$ fraction

TABLE II
Variation in Composition of Synthetic Fatty Acids Produced from Different Raw Materials

| Boiling range of paraffin | Yield, % $C_5$–$C_9$ | Yield, % $C_{10}$–$C_{20}$ | Yield, % $C_{21+}$ |
|---|---|---|---|
| 240–350C | 25.0 | 54.5 | 20.5 |
| 300–400 | 14.5 | 79.5 | 6.0 |
| 350–420 | 10.5 | 75.0 | 14.5 |
| 420–500 | 4.0 | 60.0 | 36.0 |

TABLE III
Variation in Composition of $C_{10}$–$C_{20}$ Fraction Produced from Different Feedstocks

| Type of raw material | Composition, % | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | $C_{10}$ | $C_{11}$ | $C_{12}$ | $C_{13}$ | $C_{14}$ | $C_{15}$ | $C_{16}$ | $C_{16+}$ |
| Solid paraffin | 6 | 9 | 10 | 4 | 10 | 13 | 7 | 41 |
| Liquid paraffin | 12 | 16 | 16 | 11 | 12 | 10 | 6 | 17 |

is mostly converted to alcohols for manufacturing plasticizers similar to dioctyl phthalate. The $C_{10}$–$C_{20}$ fraction is primarily used in the production of soaps with an expected increase in their conversion to alcohols for use in detergents. A part of this fraction also finds its way into the manufacture of Buna rubber. The $C_{21+}$ fraction has served as a core binder and through chemical reactions has been converted into products that can be utilized as paints and impregnating agents.

Krumstein and Klimenko [Krumstein, B. A., Klimenko, V. L., *Khimicheskaya Promyshlennost*, No. 9, 662–665, (1963)] have published cost data on synthetic fatty acids produced in Russian plants taking into consideration raw material costs, processing costs and pricing of finished goods. Table IV give the cost of producing one ton of $C_5$–$C_{20}$ acids from various raw material feedstocks. Using the actual market price for the various fractions, as stated above, the cost of producing the desired $C_{10}$–$C_{20}$ fraction from the different raw materials is shown in Table V.

It is reported in the literature that plants which are presently using the higher boiling waxes cannot readily be converted to liquid paraffins (240–350C). However, some of the lower boiling material is being blended into the higher boiling waxes to realize a lower cost operation.

Dr. Sonntag: We appreciate the great detail you have provided in this presentation. I frankly did not realize that you had this much new material on this development. A question occurs to me about the pricing. Let us say that the Russians load these acids on a freighter, ship it through the Black Sea, and dump it at a Brooklyn dockside. What is it going to cost, USA?

Dr. Zilch: I'm sorry, Norm, I have my figures on a New York dockside, not Brooklyn.

Dr. Sonntag: That's close enough.

Dr. Zilch: Most manufacturers of fatty acids have been aware that small amounts of synthetic fatty acids from Europe have been imported into the United States. Three types of products are being offered; namely a $C_5$–$C_9$ product, a $C_5$–$C_6$ fraction and a $C_7$–$C_9$ fraction. The latter products are obtained by fractional distillation of the $C_5$–$C_9$ material. Informed sources tell us the $C_5$–$C_9$ product is coming into Western Europe from behind the Iron Curtain for approximately 5¢ per pound. The acids are then distilled and marketed in the United States for approximately 10–13¢ per pound. It has also been reported that the $C_5$–$C_6$ and $C_7$–$C_9$ acids are being offered for about 13–16¢ per pound. Since Russia and her satellite countries are primarily consuming all the $C_{10}$–$C_{20}$ for household soaps, there is a surplus of the shorter chain acids which are being marketed under distressed prices to whatever country that can utilize them. One drawback to these shorter chain acids is their poor quality with particular reference to odor and color. Whether we will ever see large imports of $C_{10}$–$C_{20}$ acids equivalent to the quality of acids presently being produced in this country is rather doubtful. The Fatty Acid Producer's Council, who represent domestic fatty acid producers, is seeking tariff protection from these acids. I am sure petrochemical companies who are investigating the synthesis of fatty acids should be interested in knowing that tariff protection is being sought.

TABLE IV
Cost of Producing One Ton of $C_5$–$C_{20}$ Acids
Paraffin Raw Material

| | Boiling Range °C | | | |
|---|---|---|---|---|
| | 240–350 | 300–400 | 350–420 | 420–500 |
| Paraffin consumed to yield 1 ton SFA | 1.7 tons | 1.44 tons | 1.3 tons | 1.2 tons |
| Cost paraffin per ton | $ 29 | $ 64 | $ 42 | $ 40 |
| Paraffin costs | 49 | 93 | 55 | 48 |
| Processing costs | 86 | 118 | 107 | 98 |
| Cost per ton SFA | 135 | 211 | 162 | 146 |
| Cost per pound SFA | 6.8¢ | 10.6¢ | 8.1¢ | 7.3¢ |

TABLE V
Cost of Manufacturing $C_{10}$–$C_{20}$ Fraction from Different Raw Materials

| Raw material | Cost of producing 1 ton of $C_{10}$–$C_{20}$ SFA. Corrected for market values of $C_5$–$C_9$ and $C_{21+}$ fractions | |
|---|---|---|
| | ¢/Pound | $/Ton |
| 240–350C | 7.8 | 156 |
| 300–400C | 12.0 | 239 |
| 350–420C | 10.1 | 201 |
| 420–500C | 11.2 | 224 |

Dr. Sonntag: Thank you very much for a very illuminating presentation of the international situation regarding synthetic fatty acids by hydrocarbon oxidation. Now, let us talk about domestic synthetic fatty acids. Dr. Zilch just told us that eastern European countries have developed synthetic fatty acids for soap use, primarily because they do not have enough fats and oils for edible use, and secondarily because they prefer to divert fatty acids they do make from natural sources to industrial uses. American petroleum organizations, in the face of plentiful supplies of vegetable and animal fats and oils, and even a developing marine fat raw material situation, have not yet found it necessary to resort to hydrocarbon oxidation for synthetic fatty acids. When they have researched hydrocarbon oxidation, it has generally been for the purpose of synthesis of dibasic acids, not monobasic acids. Two examples come to my mind: the large effort expended in this area by Tide Water Associated Oil Company, reported in 1956, [Zellner, C. N., and F. Lister, *Ind. Eng. Chem. 48*, 1938–1948 (1956)] involving the air oxidation of paraffin wax to mixed dibasic acids with air and manganese naphthenates as catalyst, and Texaco's two-step process [Patterson, J. A., and S. M. Pier (Texaco Inc.) U.S. Pat. 2,918,487 (Dec. 22, 1959)] for oxidation of paraffins, first with air and potassium permanganate catalyst, followed by a gentle nitric acid oxidation. But, if American petrochemical manufacturers do not feel that hydrocarbon oxidation is the complete answer for feasible or economical synthetic fatty acid production, what kind of raw materials and technology do they feel might be better suited for the production of saturated or unsaturated straight-chain synthetic fatty acids?

Mr. Reck: Dr. Sonntag, would you like to tell us about some of the developments on the American scene with respect to synthetic fatty acids from alcohols, olefins and Ziegler intermediates?