Isostearic and Other Branched Acids

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ABSTRACT

Raw materials selection and method of synthesis determine the type of branching in a commercial branched fatty acid. The type of branching plus the isomer distribution, the normal chain/branched chain ratio, the chain length distribution, and the purity of the acid determine the physical properties of commercial branched acids. The latter four characteristics are affected by postsynthesis processing of the crude branched acids using such standard manufacturing or finishing techniques as distillation, solvent separation, hydrogenation, and bleaching. The generally lower titers or pour points of branched acids and their derivatives combined with their different (relative to *n*-chain materials) solubilities and their generally good heat and oxidative stabilities make them useful in applications in such diverse areas as soaps, cosmetics, lubricants, plastics, and coatings among others. The physical and usage properties which branched acids effect in products in such areas are often very different from the physical and usage properties which straight chain acids (which are also used in the same areas) effect. Thus, the use of branched acids gives an increased range of formulation possibilities and greater flexibility to product developers and formulators.

INTRODUCTION

Commercial branched acids are not naturally occurring materials. They are products of specific synthetic routes or else arise as byproducts of manufacturing processes. They have properties distinctly different from normal chain acids, and they extend the range of materials available for formulating end products with desirable characteristics in a diverse group of applications areas.

Manufacturing or Synthesis

Isostearic acid is a byproduct of the processing of naturally occurring unsaturated C_{18} fatty acids to produce dimer/trimer acid (1). Heating the unsaturated fatty acids in the presence of certain catalysts produces dimeric (C_{36}) and trimeric products (C_{54}), but instead of polymerizing, a portion of the acid rearranges to give a branched monomeric (C_{18}) product which can be isolated by distillation. This crude acid can be distilled, solvent-separated, bleached, or hydrogenated to produce a final commercial isostearic acid of desirable iodine value (IV), titer, and saponification value. The complete structure of isostearic acid has not been fully elucidated, but the main components seem to be a complex mixture of methyl branched isomers.

Other branched acids are produced by direct synthetic routes largely from hydrocarbon sources. Some major processes (2) are illustrated in Figure 1. Paraffins, olefins, and hydrocarbon-derived alcohols and aldehydes can serve as starting materials or intermediates in these processes.

Factors Affecting Physical Properties

There are a number of factors which affect the physical properties of a commercial branched acid.

The *type of branching* affects the physical properties. Figure 2 illustrates some common types of branching. Raw material choice obviously affects the type of branching obtained and so does the synthetic process used. The Koch process leads specifically to neo-branching while straight paraffin oxidation leads to mixed alkyl branching as would be expected of a free radical process. Oxo processing of terminal olefins favors α-methyl branching while Oxo processing of internal olefins would favor α-higher alkyl branching.

The *ratio of normal chain to branched chain* acids also affects physical properties. Raw material choice, synthetic method, and reaction conditions influence this ratio. For example, Oxo processing of a linear terminal olefin will lead to an equilibrium mixture of normal chain and branched chain acids, and the equilibrium ratio is a function of reaction conditions and catalyst choice. On the other hand, Koch processing of terminal olefins will give all neo-type acids. Subsequent distillation or solvent separation can sometimes separate isomers, thereby altering this ratio.

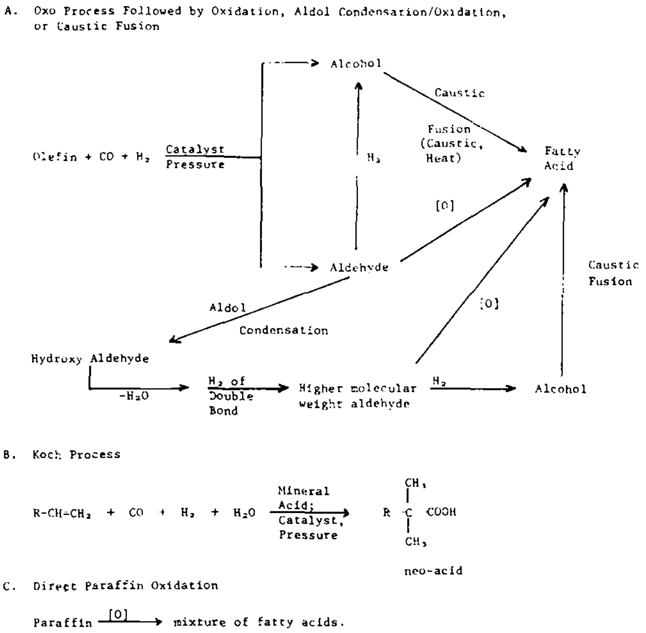


FIG. 1. Synthesis of branched chain fatty acids.

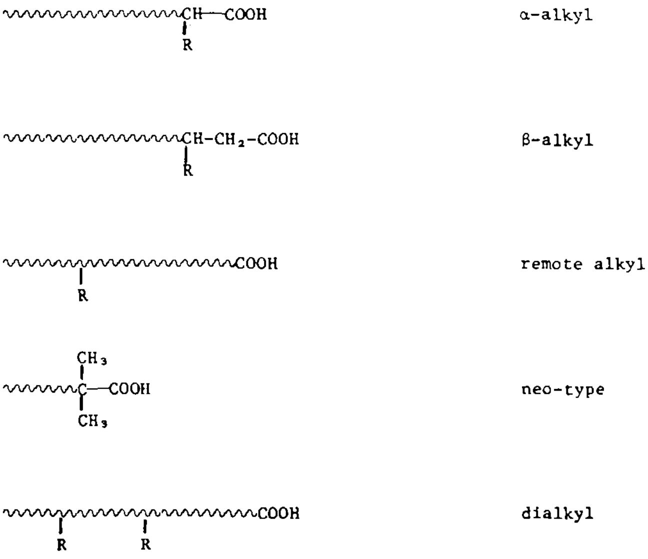
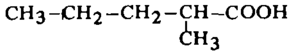
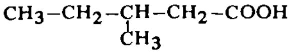
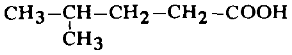
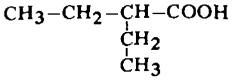
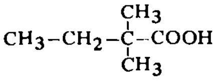
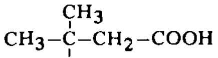
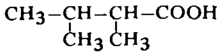


FIG. 2. Common types of branching found in commercial branched acids.

TABLE I

Variation of Melting Point of C_6-Branched Acids with Branched Position and with Branching Type

Acid	Melting point, °C[a]
$CH_3-CH_2-CH_2-CH_2-CH_2-COOH$	-3.9
 $CH_3-CH_2-CH_2-\underset{\underset{CH_3}{\vert}}{CH}-COOH$	below -85
 $CH_3-CH_2-\underset{\underset{CH_3}{\vert}}{CH}-CH_2-COOH$	-41.6
 $CH_3-\underset{\underset{CH_3}{\vert}}{CH}-CH_2-CH_2-COOH$	-33
 $CH_3-CH_2-\underset{\underset{\underset{CH_3}{\vert}}{CH_2}}{\underset{\vert}{CH}}-COOH$	-31.8
 $CH_3-CH_2-\overset{\overset{CH_3}{\vert}}{\underset{\underset{CH_3}{\vert}}{C}}-COOH$	-15
 $CH_3-\overset{\overset{CH_3}{\vert}}{\underset{\underset{CH_3}{\vert}}{C}}-CH_2-COOH$	+6.7
 $CH_3-\underset{\underset{CH_3}{\vert}}{CH}-\underset{\underset{CH_3}{\vert}}{CH}-COOH$	-1.5

[a] Sources: "CRC Handbook of Tables for Organic Compound Identification," and "The Condensed Chemical Dictionary."

TABLE II

Titers of Various Commercial Branched Chain Fatty Acids and Their Commercial Straight Chain Analogs

Acid	Titer, °C[a,b]
Isostearic (Emersol 875)[c]	10 max.
Isostearic (Emersol 871)[c]	10 max.
Stearic acid (Emersol 153, 95% C_{18})	67-69
Stearic acid (Emersol 132, ~45% C_{18})	54.5-55.5
Oleic acid (Emersol 221, low titer)	5 max.
Caprylic acid (Emersol 657, 99% C_8)	14-16
2-Ethylhexoic acid	-118.4 (freezing point)

[a] All values except for 2-ethylhexoic acid were taken from Emery bulletin "Emery Fatty and Dibasic Specifications and Characteristics." Emersols are products of Emery Industries, Inc.

[b] Value for 2-ethylhexoic acid was taken from Union Carbide Product Information Bulletin, December, 1967.

[c] These isostearic acids contain saturated, linear fatty acids of C_{16} and C_{18} chain length.

Vigorous processes like the dimerization process from which isostearic is derived or the paraffin oxidation process lead to mixtures of branched isomers as does Oxo processing of mixtures of olefin isomers. The *isomer distribution* obtained will affect physical properties. Subsequent distillation or solvent separation can alter this distribution.

If the starting raw material is composed of a mixture of homologs, the branched acid obtained is obviously going to be a mixture of acids of different chain lengths. The *chain length distribution* will affect physical properties. Subsequent distillation or solvent separation can alter this distribution.

For any acid, branched or normal, the *purity of the acid* affects both physical and usage properties. The inclusion in branched acids of unreacted olefin, aldehyde, alcohol, paraffin, or other material can have a decided effect on the physical and usage properties of the branched acids. Purity of the acid is a function of purity of starting material and subsequent processing which could include distillation, bleaching, solvent separation, and hydrogenation.

General Physical Properties of Branched Acids

In general, branched acids have lower titers than their straight chain analogs. Cason has synthesized all the methyl isomers of octadecanoic acid (3) and found that branching at the 10- or 11-position gave the minimum melting points for the series. The other isomers had higher melting points, but all were lower than n-C_{19} acid.

Table I illustrates the variation of melting point of a 6-carbon system with: (a) positional variation of methyl

TABLE III

Pour Points of Esters of Commercial Isostearic Acids and Their Straight Chain Analogs

Ester	Emersol 871 Isostearate[a]	Stearate	Oleate	Emersol 875 Isostearate[a]
Methyl	-26 F	+ 80 F	- 4 F	
Ethyl	-22 F			
n-Propyl	-25 F			-72 F
n-Butyl	-25 F	+ 65 F	-14 F	
Isotridecyl	-42 F	+ 30 F	-46 F	
Glyceryl (mono)	+6 F	+133 F	+34 F	-22 F
Glyceryl (tri)	-12 F	+127 F	- 4 F	

[a] Emersol isostearic acids are products of Emery Industries, Inc.

TABLE IV

Solubilities in Organic Solvents of Zinc and Lead Soaps of Isostearic, Stearic, and Oleic Acids

Solvent	Zinc isostearate	Zinc oleate	Zinc stearate	Lead isostearate	Lead oleate	Lead stearate
Acetone	Sl.S.[a]	Sl.S.	I			
Chloroform	S	S	Sl.S.			
Ethyl acetate	S		I	S		I
Ethyl ether	S	S	I	S	S	I

[a] S=Soluble; Sl.S.=slightly soluble; I=Insoluble. Solubilities listed for room temperature.

TABLE V

Heat Stability Test Results

Acid	Initial color, % transmission at 440/550 nm[a]	Color, % transmission at 440/550 nm, after 2 hr at 205 C with 100-ml/min. Subsurface Air Flow[a,b]
Triple-pressed stearic (Emersol 132)[c]	93.5/98	70.5/96
Oleic acid (Emersol 233)[c]	83/98	16/71
Isostearic (Emersol 875)[c]	83/98.5	30/87
Isostearic (Emersol 871)[c]	45/96.5	6/61
Isooctanoic[d]	99.5/100	60/98
Isohexadecanoic[d]	98/100	89/98
Isooctadecanoic[d]	92/99	85/98
Isotridecanoic[d]	94/99	44/95
Isononanoic[d]	97/99	66/96
Versatic 10[e]	85/98	41/92

[a] Most initial colors and color stabilities can be improved, some greatly, by distillation of the acid.

[b] This test is called the Emery heat stability test and is a variation of the AOCS test which uses N_2 instead of air.

[c] Product of Emery Industries, Inc.

[d] Product of American Hoechst.

[e] Product of Shell, a neo-type acid of about 10 carbons.

branching; (b) ethyl branching vs. methyl branching; and (c) dimethyl branching vs. ethyl branching. Table II contrasts titers for certain commercial branched acids and their straight chain analogs.

Table III illustrates that this effect carries over to the pour points of branched acids' derivatives, these derivatives having lower pour points than derivatives of analogous normal chain acids. Derivatives of the two isostearics differ considerably in pour point.

Solubilities of branched acids also differ from those of normal chain analogs. Sodium isostearates are soluble in distilled water to the extent of ca. 15%, approximating the solubility of sodium oleate, as compared to 1% or less for sodium stearate. Table IV illustrates that heavy metal soaps of isostearic acids also tend to have solubilities in organic solvents more similar to analogous straight chain unsaturates than to straight chain saturates.

Branched acids and their derivatives generally have good thermal and oxidative stability properties (Tables V and VI).

Applications of Branched Acids

The physical properties which differentiate branched acids from straight chain acids also make them uniquely suitable for applications in diverse areas. In soaps, branching can alter the foam structure of normal chain soaps to produce creamy lather or inhibit crystallization to produce transparent soaps (4,5).

In the fabric softener area quaternary ammonium salts of branched acids, or detergent-compatible nonquaternary derivatives, give softening plus improved rewetting properties (6-9). This effect is probably related to structural effects noted in the area of cosmetics and illustrated in Figure 3. The branching prohibits the layer-type film formation characterizing films from normal chain acids. Spaces or holes are created by the branching allowing moisture transpiration through the film (26,27).

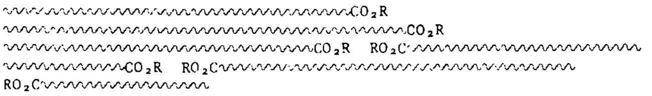
Low pour points, oil compatibility or solubility, good lubricity, and good heat and oxidation stability make branched acids desirable materials for preparing engine lubricant additives or base stocks or extended temperature

TABLE VI

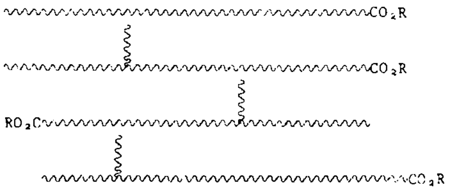
Oxygen Absorption Tests

Product	Time required to absorb 10 ml oxygen at 60 C
Emersol 875	> 100 days
Emersol 871 Isostearic Acid	100 days
Commercial oleic acid (93 I.V.)	1-7 days
Double pressed stearic acid (5.0 I.V.)	25 days
Glyceryl triisostearate	110 hr
Glyceryl trioleate	5 hr

Test Method: A 25 g sample of test product is held at 60 C in a sealed 250 ml flask (fitted with a mercury-filled manometer) under an air blanket. The test is arbitrarily concluded when 10 ml of oxygen (STP) are absorbed by the sample.



Layer Structure Achieved with Straight-Chain Acid Derivatives



"Open" Structure Achieved with Branched-Chain Acid Derivatives

FIG. 3. Structure of fatty films in cosmetic applications (26,27).

TABLE VII

Applications of Branched Acids

General usage area	Properties or effects achieved
Soaps	1. Soaps of branched acids in combination with *n*-chain soaps produce creamy lather (4). 2. Crystallization inhibition leading to transparent soaps (5).
Fabric softeners	1. Quaternaries with isostearic giving softening with improved rewetting (6). 2. Preparation of high concentration fabric softeners possible using quaternaries of branched acids (7). 3. Alkanolamine condensate of isostearic acid as detergent-compatible softener (8). 4. Alkali metal soaps of isostearic acid as detergent-compatible softeners (9).
Coatings	1. Isostearic acid as a deleafing inhibitor in aerosol metallic coating (stearic won't work) (10). 2. Copolymers of vinyl esters of branched acids give pore-free electrodeposition coatings (11). 3. Heavy metal soaps of 2-ethylhexoic acid work well as driers (12). 4. Driers from branched acids prevent "loss-of-dry" (13).
Engine and gear lubricants	1. Ca(isostearate)$_2$ as detergent and anticorrosive (14). 2. Branched acid TEPA condensates as pour point depressing ashless detergents (15). 3. Isostearic aminoamide as jet engine lube oxidation inhibitor (16). 4. Antiwear, anticorrosion additive from branched acid polyamide (17). 5. Isostearic acid and a diamine derivative as antisquawk and rust prevention in transmission fluids (18). 6. Isostearic polyol esters for high temperature (jet engine) usage (19). 7. Isostearic in extended-temperature range greases (20).
Textile lubricant	Isostearic as a Spandex lubricant (21).
Recording tape lubricant	Isostearic as a lubricant for magnetic recording tape (22).
Cosmetics[a]	1. Good emolliency and spreading properties with branched-acid derivatives (23,24). 2. Conditioning effect in shampoo with isostearic acid (25). 3. Improved moisture transpiration (26,27).
Food[a]	Improved surface dryness of O/W emulsion frozen confection mixed with glycerol and propylene glycol monoisostearate (28).
Medical, biological[a]	1. Certain isostearic benzylamides reduce blood cholesterol (29). 2. Quaternaries with branched-acid anions have microbiocidal properties effective in presence of soap (30).
Plastics	Isopropyl triisostearic titanate as a coupling agent for filled polymers improves various physical properties of the plastics (31). The ester "ties together" the plastic and inorganic layers.

[a] These uses are subject to the Food, Drug, and Cosmetic Act and regulations.

range greases (14-20). For similar reasons, these materials have been found useful in lubricants for textiles and magnetic recording tapes (21,22).

For reasons discussed above and illustrated in Figure 3, cosmetic creams and lotions prepared with branched acids and their derivatives give films with improved moisture transpiration properties. Lubricity properties are also excellent and unique in feel (23-27).

In plastics, isostearyl titanate esters have been found to be effective coupling agents for plastics made with inorganic fillers. Flexibility, strength, and other properties are reputedly improved. It has been theorized that these effects are due to partitioning of the esters between the organic and inorganic components, an effect related to the solubility properties of the isostearic moiety (31).

Miscellaneous uses specified in Table VII include medical, biological, and food uses (28-30). The use of branched acids in these areas and in the area of cosmetics is subject, of course, to the Food, Drug, and Cosmetic Act and regulation.

Table VII enumerates uses where branched acids are preferred over straight chain acids. In many other areas branched acids are substitutable for straight chain acids with effects that may be considered desirable by the individual formulator.

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Soap and Fat-Based Detergents

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ABSTRACT

Many materials made from fats and oils derive their importance from their ability to modify the surface behavior of the liquid in which they are dissolved. These compounds are grouped under the broad classification of surface active agents or surfactants. Depending on their use, they are classified as detergents, wetting agents, emulsifiers, dispersing agents, etc. The oldest, and still one of the most important surfactants, is ordinary soap; twenty-three percent of all the tallow produced in the United States goes into soap. This paper covers the present state of the art of soap technology, and the most important classes of fat-based surfactants.

TOILET SOAPS

Soap is the oldest known surface active agent with a long history of acceptability. It is especially useful in toilet bars and in applications where soft water detergency is required. It has, however, two disadvantages: poor performance in hard water due to precipitation of insoluble calcium and magnesium soaps, and instability on the acid side. Soap was the only important surface active agent until the first half of the 20th century. Wartime fat shortages during World War I and World War II stimulated the search for substitutes. This gave rise to the development of synthetic detergents based either on fats or petrochemicals. During the last thirty years, synthetic surfactants have gradually replaced soap in most cleaning applications, except bar soaps, where fatty acid soaps still are the major factor today.

The basic reaction of soap making consists of heating fats with an alkali to yield soap and glycerine. While this seems simple, the technology of soap making is involved and borders on an art due to the extraordinary complex physical nature of soap and its aqueous systems. After saponification, soap passes through a series of phase changes, followed by removal of impurities, the recovery of glycerine, and the reduction of the moisture to relatively low levels. The complete series of operations in the production of a "settled" soap kettle is: (a.) reaction of fat with alkali until it is largely saponified; (b.) graining the soap from solution with salt and recovery of the glycerine; (c.) boiling with excess alkali to complete saponification; (d.) separation of the batch into two immiscible phases: neat soap and "niger." This is the "fitting" operation.

The successive operations to produce a straight kettle soap are called changes. The traditional soap-boiling process is done in huge kettles, often four stories high with capacities of 80,000 to 100,000 lbs. Saponification and the various changes take between five and seven days. These traditional soap-boiling procedures, though they seem old fashioned, are still used widely all over the world today, though at a declining rate.

The reasons for this decline are twofold. First, since the early 1950s, there occurred the rapid replacement of soap by synthetic detergents in most laundry products. Second, during World War II many European soap plants were destroyed and had to be replaced. This encouraged the development of new, more efficient continuous processes to replace the old kettle-boiling process. European firms, particularly in Italy, Sweden, and Germany, developed a number of new, often ingenious processes that have become the method of choice whenever new soap plants are built today.

Continuous processes fall into two categories. First, there are processes based on the continuous saponification of fats. Most important of these are the DeLaval, Sharples, Mechaniche Moderne, and the Mazzoni processes. The second group is based on the continuous splitting of fats into fatty acids, followed by distillation and neutralization of the fatty acids. The most important examples in this category are the Mills, the Mazzoni SB, and the Armour processes.

Sharples Process

Steps in the Sharples continuous process are based on the traditional kettle soap process, i.e., saponification, washing, fitting. At each step high speed centrifuges are used to achieve rapid and continuous saponification of (a) soap and lye, and (b) neat soap and nigers. The time required to convert the feed stock to neat soap is less than 2 hr. Fresh fat is mixed with wash lye with a high glycerine content. This wash lye has come up through several stages of the process in the presence of recycling masses of already saponified materials. The neat soap from the Sharples process is light and clean, since the fat is heated only for one or two min before saponification. Saponification is rapid, and the soap is clarified four times under a high centrifugal force. The use of automatic flow control and interlocking proportioning pumps accurately controls the entire process. Standard plants have capacities up to 13,000 lb./hr.