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Fatty Alcohols

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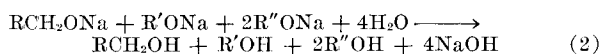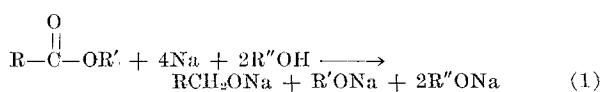
THROUGH an oversight, deliberate or accidental, Nature has left a rather wide gap in the oxidative chain from hydrocarbon to fatty acid. Compared with the almost unlimited quantities of hydrocarbons and fatty acids available, the fatty alcohols are found in rather limited quantities, occurring in the free or combined state only in certain animal, vegetable, and mineral waxes. Even in these, certain members of the homologous series of fatty alcohols are conspicuously absent, or present only in extremely small quantities.

As early as 1883 (1) researchers were attempting to fill these gaps in the homologous series of fatty alcohols by tedious and many-step syntheses, which were complicated by undesirable side reactions and very low yields. The first satisfactory laboratory synthesis of fatty alcohols, starting with readily available raw materials, was discovered in 1903 by Bouveault and Blanc (2). Their procedure utilized the combined reductive action of sodium and ethanol toward an ester grouping, according to Equations 1 and 2.

G. R. Wilson

$$R-\overset{\overset{\text{O}}{\|}}{C}-OR' + 4Na + 2R''OH \longrightarrow$$
$$RCH_2ONa + R'ONa + 2R''ONa \quad (1)$$

$$RCH_2ONa + R'ONa + 2R''ONa + 4H_2O \longrightarrow$$
$$RCH_2OH + R'OH + 2R''OH + 4NaOH \quad (2)$$

Bouveault and Blanc's discovery remained a laboratory procedure for some 30 years. Near the end of this period, in the 1930's, a second and equally important reductive process for the preparation of fatty alcohols was discovered — hydrogenolysis (3). This method involves the high-temperature, high-pressure reduction of fatty acids, esters, or salts with hydrogen in the presence of a catalyst as in Equation 3.

$$R-\overset{\overset{\text{O}}{\|}}{C}-OH + 2H_2 \xrightarrow[\text{catalyst}]{} RCH_2OH + H_2O \quad (3)$$
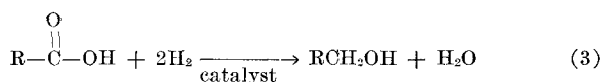
Modified and improved, these two processes constitute the two major industrial methods for the current production of fatty alcohols used in the preparation of synthetic detergents. A third method, not as important tonnagewise, is the alkaline saponification of sperm oil, which yields a mixture of cetyl, stearyl, and oleyl alcohols. Present annual production of fatty alcohols (by sodium reduction and hydrogenolysis) is estimated at 130 million pounds, with the sodium-reduction route accounting for nearly 80% of this total.

Hydrogenolysis versus Sodium Reduction

Since details for the preparation of fatty alcohols by hydrogenolysis or sodium reduction are found in the chemical and patent literature (4, 5), only the basic fundamentals of operation will be presented here, to point out differences, special problems that exist, and their solutions.

The Sodium-Reduction Process. The basic steps of the sodium-reduction process are diagrammed in Figure 1. All operations are conducted at atmospheric
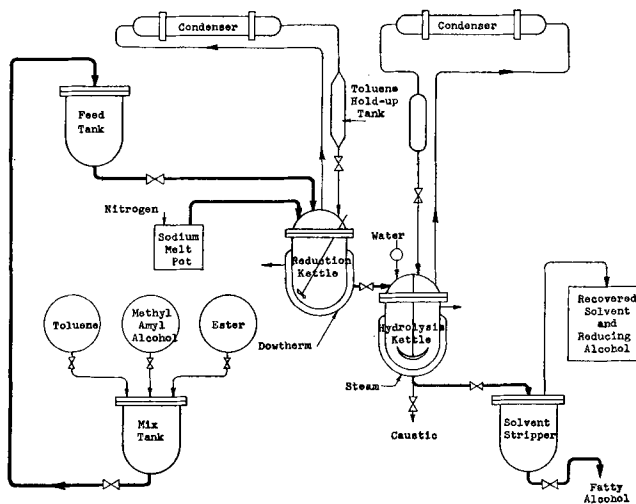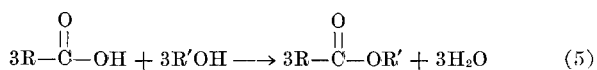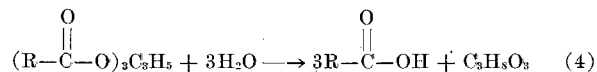
FIG. 1. Process flow sheet ester reduction unit.

pressure in conventional mild-steel reactors. A solution of ester, reducing alcohol, and solvent (in the correct proportions) is fed into a reactor containing metallic sodium suspended in a solvent (inert to sodium). An exothermic reaction occurs, yielding a solution of sodium alcoholates. This solution of alcoholates is then fed into a reactor containing water, resulting in hydrolysis of the alcoholates and the formation of a two-phase system—an organic layer (consisting of solvent, reducing alcohol, and fatty alcohol)

and an aqueous caustic layer (containing glycerine or other water-soluble alcohols, depending upon the type of ester used in the raw material). The caustic layer is separated, and the fatty alcohol is recovered from the organic layer by removing the solvent and the reducing alcohol.

In the past there have been several objectionable features to the sodium-reduction process; however these have now been by-passed or overcome. For instance, the recovery of glycerine from caustic solutions (which results from the reduction of glyceride esters) is eliminated by one of the following modifications:

1. Fat-splitting to recover the glycerine and subsequent re-esterification of the free fatty acids with a monohydric alcohol—preferably the same alcohol used as a reducing alcohol, Equations 4 and 5.

$$(R-\overset{\overset{\text{O}}{\|}}{C}-O)_3C_3H_5 + 3H_2O \longrightarrow 3R-\overset{\overset{\text{O}}{\|}}{C}-OH + C_3H_5O_3 \quad (4)$$

$$3R-\overset{\overset{\text{O}}{\|}}{C}-OH + 3R'OH \longrightarrow 3R-\overset{\overset{\text{O}}{\|}}{C}-OR' + 3H_2O \quad (5)$$

2. Transesterification of the glyceride esters with a monohydric alcohol (preferably the reducing alcohol) and recovery of the glycerine prior to the reduction step. An example is the transesterification of tallow with methylisobutyl carbinol. A mixture of one equivalent of tallow, 3.2 equivalents of methylisobutyl carbinol, and 0.2 equivalent of the sodium salt of methylisobutyl carbinol is maintained at the reflux temperature of the carbinol for one hour. At the end of the reflux period the alkoxide catalyst is neutralized with acid and the glycerine washed from the organic layer. Recovery of glycerine is 95-98% of the theoretical yield. The advantage of this modification is that the newly formed ester need not be isolated. The transesterification mixture is reduced directly since it contains excess of reducing alcohol in the correct proportion for reduction.

3. The recovery of glycerine from a neutral solution, following the reduction step, can be effected by utilizing the Emery modification (6). This modification involves the addition of urea to the mixture of sodium alkoxides which results from the reduction of the ester. The urea reacts with the sodium alkoxides to yield alcohols, ammonia, and sodium cyanate, according to Equation 6. This reaction

$$RONa + NH_2-\overset{\overset{\text{O}}{\|}}{C}-NH_2 \longrightarrow ROH + NH_3 + NaOCN \quad (6)$$
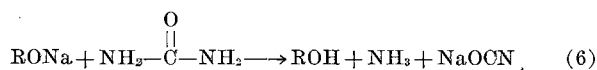
proceeds very slowly however, and this modification has not yet been commercialized, pending the development of a market for sodium cyanate.

A second objectionable feature of the sodium-reduction process has been the formation of rather stable emulsions whenever the solution of alkoxides is hydrolyzed. These emulsions may be broken effectively by various techniques, such as adding methanol or certain phenolic compounds (7) to the emulsions, or by increasing the ratio of reducing alcohol to solvent (8).

The Hydrogenolysis Process. Discovered in the 1930's, the hydrogenolysis of fatty acids, their esters, or their metallic salts to yield fatty alcohols probably has one of the most thorough patent coverages of any commercial processes. The original process employed a simple copper chromite catalyst and relatively fixed conditions of temperature and pressure; the combinations and permutations of catalysts and conditions since developed are too numerous and complex to discuss here (9-18). In general, the conditions vary from 100-200 atmospheres of pressure and 200-350°C. although there are statements in the literature to the

effect that, at above 300°C., hydrocarbon formation takes place (19). The product alcohols from hydrogenolysis are predominantly saturated, regardless of the unsaturation of the raw materials; however, by proper selection of catalysts or catalyst combinations, it is possible to produce fatty alcohols from unsaturated raw materials that retain a portion of their original unsaturation (20).

The current production of fatty alcohols by hydrogenolysis has been limited chiefly to use of the De-Nora Process (21). This process utilizes a copper chromite catalyst and a fatty-acid feed stock containing less than 6% oleic acid. The feed is preheated to 304°C. and fed, together with powdered catalyst and preheated hydrogen, to the bottom of an electrically heated high-pressure reaction chamber. The reaction takes place at 335-338°C. and 3,500 p.s.i. When the hydrogen absorption has slowed, the batch is discharged and filtered to remove the catalyst. The alcohols are purified by distillation.

Although hydrogenolysis can utilize a wider variety of raw materials—fatty acids, their esters, or their metallic salts—than the sodium method (which is restricted to esters), it also has certain limitations and disadvantages. For instance, although glyceride esters are readily reduced to fatty alcohols, the glycerine is lost through formation of propylene glycol, water, etc. (22). For economic reasons therefore glycerine recovery is necessary prior to reduction and is effected by splitting, transesterification, or conversion to soaps. The hydrogenolysis of fatty acids usually yields a considerable quantity of esters, formed by esterification of the fatty acids with the fatty alcohols being produced. This undesirable side reaction is remedied to a certain extent by incorporating special promoters or modifiers in the catalyst. The formation of hydrocarbons (a side reaction of hydrogenolysis) is undesirable if the alcohols are to be used for the preparation of synthetic detergents since a hydrocarbon content greater than 1% adversely affects their performance.

Economics of Sodium Reduction and Hydrogenolysis

The major steps involved in both reduction processes are outlined in Figure 2. Material balances for the two processes are tabulated in Table I, and the
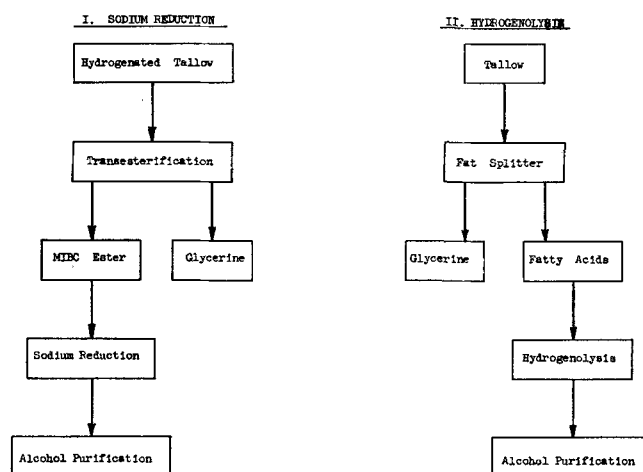

FIG. 2. Comparison of basic steps of sodium reduction and hydrogenolysis.

labor and utility requirements are summarized in Table II.

Availability of equipment, hydrogen, and choice of plant location complicate calculating comparative investment requirements. However it is estimated that a bare hydrogenolysis plant, exclusive of hydrogen generation facilities, probably requires two or two and one-half times the bare plant investment for a sodium reduction plant. A complete 30-million-pound-per-year sodium-reduction plant, including transesterification and all necessary storage facilities, is estimated to cost $2.5 million.

TABLE I
Estimated Raw Material Consumption
(Millions of Pounds Per Year)

Sodium Reduction [a]		Hydrogenolysis [b]	
To Transesterification		To Fat Splitter	
Hydrogenated tallow	37.5	Tallow	38.5
Methylisobutyl carbinol	83.4	Water	16
Toluene	37.5		
Sodium catalyst	0.3		
Hydrochloric acid	0.45		
From Transesterification		From Fat Splitting	
Methylisobutyl		Fatty acids	35
carbinol ester	45.5	Glycerine	4
Glycerine	3.5	Water	15.5
Methylisobutyl carbinol	55.6		
Toluene	37.5		
Feed to Reduction		Feed to Hydrogenolysis Unit	
Methylisobutyl carbinol	55.6	Fatty acids	35
Toluene	37.5	Hydrogen	0.9
Sodium	12.6	Catalyst	0.6
Methylisobutyl			
carbinol ester	45.5		
End Products		End Products	
Hydrogenated		Hydrogenated	
tallow alcohols	30	tallow alcohols	30
Sodium hydroxide	21.6	Spent catalyst	0.6
Residues and Losses		Residues and Losses	
Methylisobutyl carbinol	0.3	Hydrocarbons, etc.	4.0
Toluene	0.3		
Residues	3.4		

[a] In the sodium reduction process, a conversion of 98% for transesterification with 90% glycerine recovery, and a 92% yield of fatty alcohols are assumed—an over-all yield of 90%.

[b] The yield of fatty acids and glycerine by fat splitting is assumed to be 96%, and the yield upon hydrogenolysis is 90%, resulting in an over-all yield of 86.5%.

TABLE II
Labor and Utility Requirements
Est. Labor Requirements for 30 MM. lbs. Alcohols/Year

Sodium Reduction		Hydrogenolysis
Operating labor	10 men/shift	6 men/shift
Repair labor	15 men total	20 men total
Supervision	6 men total	6 men total

Utilities per 1,000 pounds of Alcohols		
Steam	6,000 pounds	1,000 pounds
Water	63,000 gallons	2,000 gallons
Electricity	20 KWH	1,000 KWH

The raw material cost for tallow alcohols is slightly higher for the sodium-reduction process for two reasons: a) the higher cost of sodium as compared to hydrogen; and b) the higher cost of hydrogenated tallow as compared to tallow. The cost difference is partially offset by the cost of hydrogen—if purchased —and by the cost of the hydrogenolysis catalyst. The economic data for hydrogenolysis estimates (Tables I and II) are based upon the description of the De-Nora process published by the Lummus Company (21).

From Table II it is apparent that actual differences in production costs for the two processes are small, and, assuming that a product of proper quality can be produced by both processes, the ultimate choice will depend upon the chosen rate of pay-out. High tax rates and short pay-out times favor the sodium-reduction process. Lower tax rates and longer pay-out times favor hydrogenolysis. The advantages of each process are summarized in Table III. It seems rea-

sonable to conclude that both processes will continue to find their place in the future development of the detergent industry.

TABLE III
Principal Features of Fatty Alcohol Processes

Advantages of Sodium Reduction	Advantages of Hydrogenolysis
1. Can produce both saturated and unsaturated alcohols	1. Uses cheaper raw materials
2. Lower initial investment	2. Has a wider choice of suitable feedstocks
3. Simpler operation and maintenance	3. Has a wider choice of suitable locations
4. Superior quality products	

The Fatty Alcohols, Properties, and Uses

Properties. The fatty alcohols resemble their fatty-acid analogs in many physical aspects, ranging from liquids to solids at room temperature. Being less associated than the corresponding fatty acids, the fatty alcohols possess slightly lower boiling points, as illustrated in Figure 3.
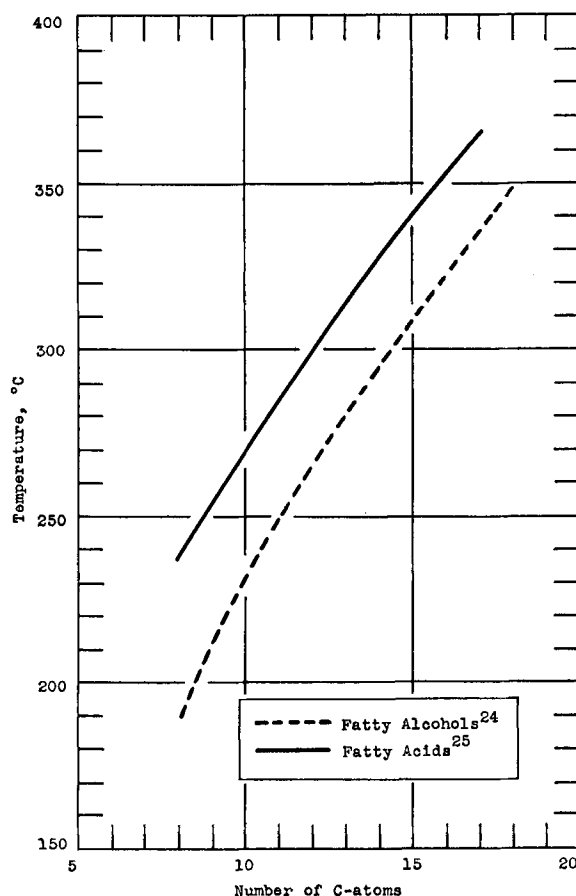

FIG. 3. Boiling points at 760 mm.

The even-numbered homologous series of fatty alcohols are readily separated from each other by fractional distillation at reduced pressures. However, like their fatty-acid analogs, the separation of saturated and unsaturated fatty alcohols of equal chain length, by fractional distillation, is not feasible. Other techniques such as pressing, fractional crystallization, and urea-complex formation (23) must be resorted to for satisfactory separations.

Like their lower-molecular weight homologs, the fatty alcohols undergo all the reactions typical of the aliphatic hydroxyl group.

Uses of Fatty Alcohols. The fatty alcohols *per se* have many desirable properties that find applications

in numerous fields. For example, the fruity odors of the C_8-C_{12} alcohols make them valuable as perfume and cosmetic additives. (26, 27).

The emollient properties of the C_{16} and C_{18} alcohols are utilized in the formulations of shaving creams, ointments, and cosmetics (28-39). The ability of fatty alcohols to reduce stickiness and tackiness in many oily and waxy formulations, necessary for the preparation of carbon papers, cutting oils, hydraulic fluids, and lubricating oils, provides other markets (40). The fatty alcohols are also used as flotation and antifoaming agents.
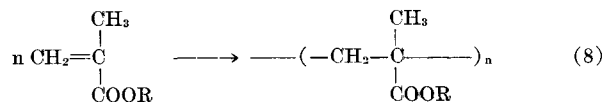
Currently, the most important of the fatty-alcohol derivatives are the sodium alkyl sulfates, a basis for many of the popular household detergents. The sodium·alkyl sulfates derived from the C_{12}-C_{18} fatty alcohols exhibit excellent detergency properties—the water solubilities decreasing with increasing chain length (with the exception of sodium oleyl sulfate).

Initially, the C_{12} and C_{14} alcohols (derived from the reduction of expensive coconut oil) were considered the most desirable for maximum detergency. Now however the expensive coconut oil fatty alcohols have been replaced, in part, by the C_{16} and C_{18} saturated fatty alcohols (derived from the reduction of relatively inexpensive tallow). Stirton and coworkers (41) have shown that sodium oleyl sulfate is a superior detergent. The high oleyl alcohol content (45-50%) of unhydrogenated tallow alcohols represents a great potential raw-material source for the detergent field, provided that a satisfactory and economically acceptable method for sulfating the unsaturated alcohols develops.
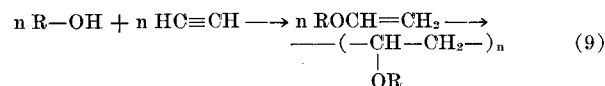
The fatty alcohols also provide a great potential in the field of non-ionics—especially the polyoxyethylene derivatives (42, 43), prepared by the addition of ethylene oxide to the fatty·alcohols according to Equation 7.

$$R\text{---}OH + n\ \overset{O}{\overset{\diagup\diagdown}{CH_2\text{---}CH_2}} \longrightarrow R\text{---}(OCH_2CH_2)_nOH \qquad (7)$$
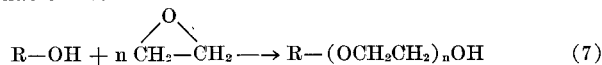
Certain high-molecular weight esters of fatty alcohols, for example, the polymethacrylate esters (Equation 8) show promise as good pour-point depressants and viscosity-index improvers in the field of lubricating oil additives (44).

$$n\ \underset{\underset{COOR}{|}}{\overset{\overset{CH_3}{|}}{CH_2{=}C}} \quad\longrightarrow\quad \text{---}(\text{---}CH_2\text{---}\underset{\underset{COOR}{|}}{\overset{\overset{CH_3}{|}}{C}}\text{---}\text{---})_n \qquad (8)$$
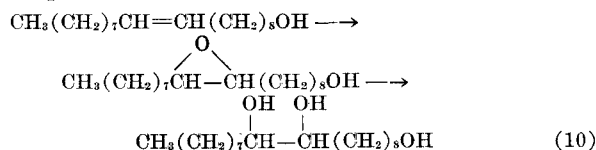
The addition of fatty alcohols to acetylene (Equation 9) yields vinyl ethers that can be polymerized to polyvinyl ethers (45). These polyvinyl ethers offer certain properties that make them desirable as lubricating-oil additives.

$$n\ R\text{---}OH + n\ HC{\equiv}CH \longrightarrow n\ ROCH{=}CH_2 \longrightarrow$$
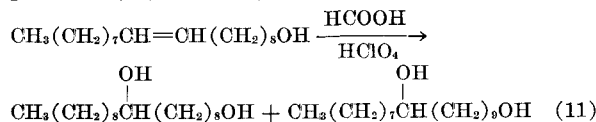$$\text{---}(\text{---}\underset{\underset{OR}{|}}{CH}\text{---}CH_2\text{---})_n \qquad (9)$$

The unsaturated fatty alcohols, such as oleyl, linoleyl, and linolenyl, are readily prepared by sodium reduction. The bifunctional nature of these unsaturated alcohols provides a basis for synthesizing polyfunctional hydrocarbons, as the following examples illustrate.

1. The epoxidation of oleyl alcohol with per acids (46) followed by ring opening (Equation 10) provides a con-
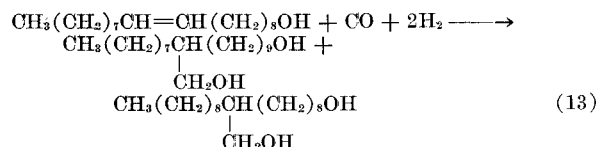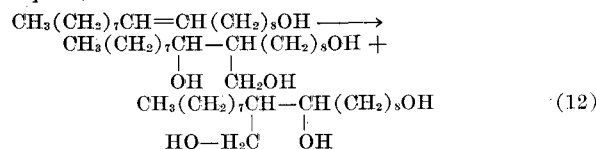
venient method for the preparation of polyhydroxy compounds.

$$CH_3(CH_2)_7CH{=}CH(CH_2)_8OH \longrightarrow$$
$$CH_3(CH_2)_7\overset{\diagup\diagdown}{\overset{O}{CH\text{---}CH}}(CH_2)_8OH \longrightarrow$$
$$CH_3(CH_2)_7\underset{\underset{OH}{|}}{CH}\text{---}\underset{\underset{OH}{|}}{CH}(CH_2)_8OH \qquad (10)$$

2. Dihydroxy compounds are readily prepared by the formylation of oleyl alcohol with formic acid, catalyzed by per acids (47) according to Equation 11.

$$CH_3(CH_2)_7CH{=}CH(CH_2)_8OH \xrightarrow[\text{HClO}_4]{\text{HCOOH}}$$
$$CH_3(CH_2)_8\underset{\underset{OH}{|}}{CH}(CH_2)_8OH + CH_3(CH_2)_7\underset{\underset{OH}{|}}{CH}(CH_2)_9OH \quad (11)$$

3. Branched-chain, polyhydroxy compounds are possibilities by application of the Prins reaction (48), according to Equation 12 and the Oxo reaction (49), according to Equation 13.

$$CH_3(CH_2)_7CH{=}CH(CH_2)_8OH \longrightarrow$$
$$CH_3(CH_2)_7\underset{\underset{OH}{|}}{CH}\text{---}\underset{\underset{CH_2OH}{|}}{CH}(CH_2)_8OH +$$
$$CH_3(CH_2)_7\underset{\underset{HO\text{---}H_2C}{|}}{CH}\text{---}\underset{\underset{OH}{|}}{CH}(CH_2)_8OH \qquad (12)$$

$$CH_3(CH_2)_7CH{=}CH(CH_2)_8OH + CO + 2H_2 \longrightarrow$$
$$CH_3(CH_2)_7\underset{\underset{CH_2OH}{|}}{CH}(CH_2)_8OH +$$
$$CH_3(CH_2)_8\underset{\underset{CH_2OH}{|}}{CH}(CH_2)_8OH \qquad (13)$$

4. Conjugated, polyunsaturated alcohols are also possibilities. For example, Pryde demonstrated that the sodium reduction of menhaden oil (a polyunsaturated oil) yielded polyunsaturated alcohols containing a high percentage of conjugated double bonds (50).

These are but a few examples of actual and proposed uses for fatty alcohol derivatives. The availability of a wide variety of fatty alcohols (saturated and unsaturated) provides an excellent field for application research and product development.

Summary

The two commercially important processes for the production of fatty alcohols (sodium reduction and hydrogenolysis) have been reviewed with respect to operations, types of alcohols obtainable, relative economics, properties and uses of the fatty alcohols.

The sodium-reduction process is applicable to the reduction of saturated as well as unsaturated esters, and in the latter case the unsaturation of the raw materials is preserved in the product alcohols. Hydrogenolysis, on the other hand, produces predominantly saturated alcohols, regardless of the unsaturation of the raw materials, except in instances where special catalysts are used.

Hydrogenolysis has the advantages of cheaper raw materials, wider choice of feed stocks, and wider choice of locations whereas sodium reduction is more flexible (permits production of both saturated and unsaturated fatty alcohols), requires a lower initial investment, involves simpler operation and maintenance, and yields products of superior quality for detergent uses.

The physical and chemical properties of fatty alcohols have been reviewed briefly.

While the largest current market for fatty alcohols lies in the field of detergent preparation, the unsaturated fatty alcohols and their derivatives also have

many potential uses in the manufacture of such other products as lubricant additives, waxes, and wetting and emulsifying agents. Markets for these fatty alcohols depend upon the results of application research and product development.

Acknowledgment

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Dibasic Acids

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IN CONSIDERING fats and oils as raw material for chemical processing, we find that the production of dibasic acids is an important part of this subject. Sebacic acid, a straight-chain 10-carbon acid, was the first dibasic acid produced from a fat or oil source to become commercially significant. The treatment of castor oil with alkali now accounts for the production of about 20 million lb. of sebacic acid per year. More recently azelaic acid, a straight-chain 9-carbon acid, went into commercial production. Azelaic acid is produced by the oxidative cleavage of oleic acid at its double bond by means of chromic acid or ozone. The third dibasic acid produced commercially from a fat or oil source is di-linoleic acid. This is produced by thermal dimerization, utilizing the linoleic acid content of vegetable fatty acids such as soya and cottonseed acids.

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Numerous other syntheses of dibasic acids from fatty sources have been described in the literature.

This review will emphasize the chemistry of these dibasic acids. Other dibasic acids, particularly the aliphatic ones, will be included also for comparison.

Carboxylic acids are versatile materials, partly by virtue of the variety of chemical reactions of which the carboxyl group is capable. The dibasic acids are unusually versatile because of their two carboxyl groups. This enables many additional types of useful reactions, particularly the building of polymeric structures. The biggest uses today are the simple esters for plasticizers and lubricants, the polyesters for coatings and fibers, and the polyamides for coatings, fibers, and plastics.

The aliphatic dibasic acids vary considerably in their physical properties. The lower members are crystalline solids, very water-soluble and limited in solubility in organic solvents. As the chain length increases through the 6 to 10 carbon range, water-solubility decreases (still soluble in hot water), and solvent solubility increases. Di-linoleic acid represents an extreme in being a viscous oil.

Occurrence

The lower aliphatic dibasic acids (C_2-C_6) occur more abundantly in nature than the higher aliphatic dibasic acids. Oxalic acid occurs as the potassium or calcium salt in several plants. Malonic, glutaric, and adipic acids occur in sugar beet. Succinic acid has been found in amber, turpentine oils, and various