cluding those cases where ion exchange is prohibitive in cost, it is generally not feasible completely to remove all of the ionic material by ion exclusion. Therefore when complete deionization is desired, the bulk of the ionic material can be removed by ion exclusion and the remaining ionic material can be removed by conventional ion exchange.

Ion exclusion is a technique developed by the Dow Chemical Company, which utilizes ion exchange resins to effect the separation of water-soluble ionic salts from non-ionic glycerol material without the use of heat or regenerant chemicals other than water for elution. The polystyrene type ion exchange resins are in the form of small spherical beads. These beads contain a high percentage of water and are quite permeable. Due to the Donnan equilibrium effect, when these resin beads are placed in an aqueous solution of ionic and non-ionic materials, the ionic material tends to be more concentrated around the beads than inside the beads while the non-ionic material tends to have the same concentration within and without the beads. This difference in concentration within and surrounding the beads is the basic scientific fact upon which the ion exclusion process is based.

The simplest operation of the process consists of feeding a volume of an aqueous solution of ionic and non-ionic materials into a column filled with an ion exchange resin, following this with one or more volumes of rinse water. An aqueous solution of the ionic material comes out of the column first, followed by an aqueous solution of the non-ionic material. The separation may or may not be sharp and complete, and the effluent is more dilute than the feed solution when operating at low ionic concentrations, but the non-ionic can be concentrated with a high ionic concentration.

While almost any type of ion exchange resin may be used, Dow Chemical Company exppeimens have shown that the more strongly ionized resins give better results than those slightly ionized. It is also essential that the resin be in the same ionic form as the ionic material being separated. In accord with the principle of ion exclusion the best resin would have the following properties:

The fixed ionic concentration inside the resin particles would be high.

The water content of the resin particles would be high to give a large capacity for the non-ionic component.

The diffusion rate would be high so that equilibrium would be rapidly attained.

The first requirement favors a high cross-linked resin, the second favors a low cross-linked resin, and the third implies either a low cross-linkage or small-particle size or both. Thus a compromise must be made, depending upon the requirements of a particular job.

An ion exclusion pilot plant, using the water-dome technique, has demonstrated that glycerol from soap lye crude can, on a practical basis, be separated from approximately 80% of its dissolved salts. There is an over-all loss of between 1.9% and 4.3% glycerol. The concentration of glycerol in the effluent product is approximately 15%, under average conditions, but varies with other factors, notably the feed concentration and recycle timing.

The product of ion exclusion, when further purified by a three-bed system of ion exchange followed by concentration, compares favorably with the product of both the distillation and ion exchange methods of purification.

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Fatty Alcohols

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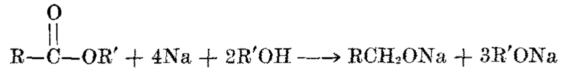
THROUGH AN OVERSIGHT, deliberate or accidental, nature has left a rather wide gap in the oxidative chain from hydrocarbon to fatty acid. Compared with the almost unlimited quantities of hydrocarbons and fatty acids available, the fatty alcohols are found in rather limited quantities, occurring in the 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.

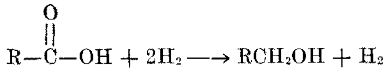
As early as 1883 researchers were attempting to fill these gaps in the homologous series of fatty alcohols by tedious and many-step synthesis, which was complicated by undesirable side-reactions and very low yields. The first satisfactory laboratory synthesis of fatty alcohols, starting with available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



$$R-\overset{\overset{\displaystyle O}{\|}}{C}-OR' + 4Na + 2R'OH \longrightarrow RCH_2ONa + 3R'ONa$$

$$RCH_2ONa + R'ONa + 2R'ONa + 4H_2O \longrightarrow RCH_2OH + 3R'OH + 4NaOH$$

The Bouveault and Blanc 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, namely, the hydrogenolysis process as follows:



$$R-\overset{\overset{\displaystyle O}{\|}}{C}-OH + 2H_2 \longrightarrow RCH_2OH + H_2O$$

This method involves the high temperature, high pressure reduction of fatty acids, esters, or salts with hydrogen in the presence of a copper chromite catalyst.

Modified and improved, these two processes constitute the two major methods for the current production of fatty alcohols. A third method, not as important tonnage-wise, is the alkaline saponification of sperm oil, which yields a mixture of cetyl, stearyl, and oleylalcohols. The present annual production of fatty alcohols (by sodium reduction and hydrogenolysis) is estimated at 150 million pounds with the sodium-reduction route accounting for nearly 50% of this total.

Hydrogenolysis Versus Sodium Production

The sodium reduction process equipment is shown in Figure 1. All operations are carried out at atmospheric pressures 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 properly suspended in solvent, preferably the same solvent used to dissolve the ester feed mixture. The sodium solvent suspension is heated to reflux, and upon addition of the ester feed mixture an exothermic reaction occurs and should be maintained for the duration of the feed mixture, which is approximately 1 hr. This reaction yields a solution of sodium alcoholates. The 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 as 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 by suitable distillation.

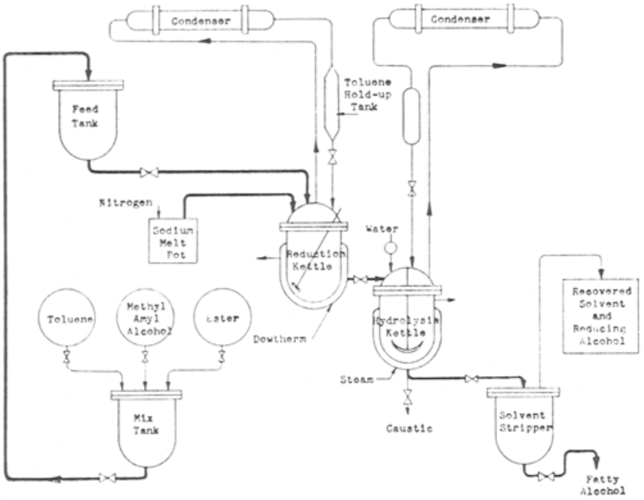


FIG. 1. Process flow sheet ester reduction unit.

As can be readily concluded, the sodium process, of course, is limited to esters of fatty acids as raw materials but not necessarily glyceride esters. Furthermore these esters must be neutral and should not contain more than ½% free fatty acid. The reduction of glyceride esters yields by-product glycerol in the form of a caustic-glycerol solution. Fortunately other esters are suitable for reduction, and they can be prepared readily from glyceride; thus glycerol recovery is possible prior to reduction.

To accomplish a glycerol recovery prior to the reduction, one of two methods may be resorted to:

The fats can be split by a suitable method to obtain free fatty acids and glycerol, and the fatty acids may be re-esterified with a suitable alcohol. The recovery of materials is simplified if the esterifying alcohol ($R'OH$) is the same as the reducing alcohol, which is preferably methyl isobutyl carbinol. Tallow fatty acids can be esterified almost completely within 2 hrs. with methyl isobutyl carbinol, and the resulting ester can be reduced in high yield.

The alternative method for recovery of glycerol is *trans*-esterification, preferably with the reducing alcohol. The MIBC esters of tallow are prepared by contacting one equivalent of tallow with 3.2 to 4 moles of MIBC (a slight excess over that required for *trans*-esterification plus reduction) in the presence of 0.1 to 0.2 moles of sodium alkoxide, preferably the sodium salt of MIBC at temperatures of 160°C. to 200°C. and moderate pressures (to maintain the MIBC in the liquid phase) for a contact time of 5 to 15 min. Glycerol is recovered in 90 to 95% yield by water-washing, and the recovery of ester is essentially quantitative.

By a unique modification of the ester reduction process, glycerol can be recovered from a neutral solution. In this instance the reduction step is carried out as usual, but, instead of proceeding with the hydrolysis step, urea is added directly to the reduction mass in stoichiometric quantities that react with the sodium alcoholates to form the corresponding alcohols plus sodium cyanate and ammonia. The precipitated sodium cyanate is removed by filtration, and the glycerol is recovered from a neutral organic solution.

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 had one of the most thorough patent coverages of any comcercial process. 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. 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. 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.

The current production of fatty alcohols by hydrogenolysis has been limited chiefly to the use of the DeNora Process. 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 the 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 proylene glycol, carbon dioxide, water, etc. For economic reasons therefore, glycerine recovery is necessary prior to reduction and must be effected by splitting, *trans*-esterification, 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 characteristic 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.

I. Sodium Reduction	II. Hydrogenolysis
Hydrogenated Tallow	Tallow
Trans-esterification	Fat Splitter
MIDC Ester Glycerine	Glycerine Fatty Acids
Sodium Reduction	Hydrogenolysis
Alcohol Purification	Alcohol Purification

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

Labor and utility requirements are summarized in Figure 3.

	Sodium Reduction	Hydrogenolysis
Operating Labor	10 man/shift	6-man/shift
Repair Labor	15-man total	20-man total
Supervision	6-man total	6-man total
Utility per 1,000 lbs. of Alcohols		
Steam	6,000 lbs.	1,000 lbs.
Water	63,000 gal.	2,000 gal.
Electricity	20 KWH	1,000 KWH

FIG. 3. Labor and utility requirements.
Est. labor requirements for 30 million lbs. alcohols per year.

Comparative investment requirements are less easy to calculate since the available equipment, location, and availability of hydrogen affect the total investments required. A bare hydrogenolysis plant, not including 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 *trans*-esterification and all necessary storage facilities, can be built for an estimated $2.5 milion. The raw material cost for tallow alcohols is higher for the sodium-reduction process because of the higher cost of hydrogenated tallow compared to tallow and because of the cost of sodium. These costs are only partially off-set by the cost of hydrogen—if hydrogen is purchased—and by the catalyst cost. The net difference is perhaps 4–5c per pound of alcohols in favor of the hydrogenolysis process.

Since actual production costs are not greatly different for the two processes (Figure 3), the ultimate choice of a process, assuming that product of proper quality can be produced by both processes, will depend upon the plant investment and the chosen rate of pay-out. If tax rates are high and the pay-out time required is three to five years, the sodium-reduction process will be favored. Lower tax rates, hydrogen availability, and long pay-out times favor hydrogenolysis.

The advantages of each process are summarized in Figure 4.

Advantages of Sodium Reduction	Advantages of Hydrogenolysis
1. Production of both saturated and unsaturated alcohols	1. Use of cheaper raw material
2. Lower initial investment	2. Wider choice of suitable feed stocks
3. Simpler operation and maintenance	3. Wider choice of suitable location
4. Superior quality products	

FIG. 4. Principal features of fatty alcohols processes.

It seems reasonable to conclude that both processes will continue to find their place in the future development of the fatty alcohol industry.

Description of Some of the Sodium Reduction Process Equipment

The heart of the process (Figure 1) is the reactor. In this unit two different functions must be included: a) an efficient dispersion of the sodium in an inert solvent must be effected in this unit, or, if the sodium is made in another vessel, this dispersion must be maintained; and b) intimate mixing of the other feed materials, namely, the fatty acid ester to be reduced must be carried out. Both of these are essentially agitation problems, and careful attention must be paid to the agitator design. In very small reactors this problem will not be too serious, but in large vessels excessive splashing and other factors must be taken into account. In addition, provision must be made for heating the vessel before the reaction starts so that the sodium will not freeze. The sodium reduction reaction is quite exothermic, and the only feasible method of removing the heat of reaction is to vaporize the solvent, condense it, and reflux the solvent, using the latent heat of vaporization of the solvent as the heat carrier.

If a water condenser is used special precaution must be taken that will make it impossible for water to get into the reactor, no matter what part of the unit or system may fail. This can be done by using double tube sheets, whereby the tubes are rolled into two tube sheets at each end of the heat exchanger. This eliminates the possibility of having water leak through the tube sheet into the process side. The only other possible way that water can get into the process side otherwise is for a tube to rupture. In order to protect against this possibility, however remote, it is possible to install dielectric probes which can distinguish between organic solvents and water. These should be located in a trap in the return system from the condenser to the reactor so that the heavier water will settle out and change the dielectric in the area of the instrument. Signals from this instrument can then be used to operate shut-off valves or other safety features. Another hazard which must be guarded against because of the high exothermic nature of the reaction is the build-up of unreacted sodium and fat in the unit. This could happen, for example, if for some reason the agitator were to stop running and the feed should continue to enter the reactor. The agitator might then be started, and a terrific quantity of heat would be liberated in a very short time, overloading the system. It is therefore necessary that interlocks be provided between the agitator and the feed stream.

To obtain the most efficient reaction it is important that the quantities of materials be carefully measured, and this is most readily accomplished in a batch operation by weighing all of the feed streams which enter into the reaction. The inert solvent may be measured volumetrically as small variations in the concentration of this material will not affect the reaction for any particular oil. However it is necessary to vary the amount of inert solvent used for different oils so that fluidity is maintained in the reactor. The sodium is weighed in its own tank in the liquid state, being transferred from storage tanks where it is also maintained as liquid. This transfer is effected by pulling a vacuum on the weight tank and lifting the sodium up from the storage tanks. The sodium is handled in jacketed pipe or electrically heated pipe and is never exposed to the atmosphere or handled directly by the operator. This insures a tight system which can be adequately blanketed and eliminates, to a large extent, the hazards involved in handling metallic sodium. The beam of the sodium weight tank scale can be so connected that it will stop the flow of sodium when the right weight has entered the weigh tank. The fat and the secondary alcohol required for the reaction may both be weighed in the same tank. As these materials may not have been properly purified before reaching the weigh tank or may have come in contact with water subsequent to purification, it is advisable to provide a safety instrument in this vessel as well, which will detect the presence of water and prevent this material from being fed into the reactor. In all cases it is advisable to keep steam heating and water cooling as remote as possible from this unit, and wherever their use is essential, special thought and consideration should be given to the possibility of steam or water entering the process system. It is important to realize that while very small quantities of water may not necessarily cause a fire or an explosion, very small percentages of moisture reacting with the sodium to form sodium hydroxide will saponify the fat or oil being fed to the unit, forming a soap that will not be reduced or significantly decrease the yield and possibly cause processing trouble because of emulsion formation in subsequent operations. After all of the feed has entered the reactor, the agitator should be run for a short time to make certain that the reaction has become as complete as possible.

The batch is now ready for quenching. If a gravity system is used for dropping the sodium from the weigh tank into the reactor and then dropping the reaction mix from the reactor to the quench tank, it is obviously possible to drop sodium directly from the weigh tank through the reactor and into the quench tank. This must be avoided at all costs. A satisfactory system of interlocked valves can be provided which will prevent the operator from consciously or unconsciously dropping sodium into the quench tank. Prior to the quenching operation, the material of construction used on all equipment may be carbon steel. During the quench operation, sodium hydroxide is formed. If iron free caustic is desired as a by-product from this process, it is then advisable to make the quench tank out of nickel-clad steel. This unit should also be provided with an agitator, a cooling jacket, and a condenser. While there is little heat liberated during the quenching operation because of the conversion of sodium alcolates to fatty alcohols and sodium hydroxide, there is always the possibility that some unreacted sodium will enter the quench tank. The jacket and condenser are necessary for removing the heat of reaction of the unreacted sodium with water. After the entire batch has been dumped into the quench tank, it is only necessary to continue agitation for a few minutes as this reaction goes quickly into completion. The agitator in this vessel should be mild in order to minimize possibility of emulsion formation. The agitation is then stopped, and the liquid is permitted to settle. It is possible to begin with drawing the lower caustic layer almost immediately as there is an appreciable specific gravity difference between the water and oil phases.

A sizeable "look box" should be provided so that the inter-face between the water and oil layers is easily observed. It is then only necessary for the operator to switch valves so that his caustic stream goes to caustic storage while the organic layer is pumped to distillation feed storage. The organic layer is then processed by fractionating the reducing alcohol and inert solvent from the production alcohols. The reducing alcohol and inert solvent are taken as overheads and the crude fatty alcohols as bottoms. The alcohols thus produced may be used as is or may be further distilled or fractionated into component cuts as required.

Sulfonation and Sulfation of Oils

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IT WAS JUST 125 years ago, in 1831, that Fremy discussed the reaction of sulfuric acid and olive oil. In 1870 castor oil was first used in the preparation of a sulfated oil and called "Turkey Red Oil" since for the first time the textile industry was able to obtain a bright red color in the dye bath, a color which had been impossible with the soaps available up to that time. Since then practically every known oil and fat has been sulfated. Twitchell (12) in 1899 mixed oleic acid with members of the aromatic series which, after sulfonation, gave products with much greater resistance to breakdown in solution. Up to about 1930 there were few developments of importance as most efforts were directed to improving the products and aimed at overcoming the presence of the water of reaction. Also numerous studies were being made as to the constituents of sulfated oils and the mechanism of the reactions involved.

Over the years there has been considerable confusion in the literature in regard to sulfonated and sulfated products. It is generally agreed however that a sulfated product is one in which the linkage is carbon to oxygen to sulfur while a true sulfonate is one in which the sulfur is directly linked to the