glycerol from soap lye crude can be separated from at least 80% of the dissolved salts. The concentration of glycerol in the effluent is approximately 15%, and losses are in the range of 2 to 4% glycerol. This product from the ion-exclusion process, when further purified by ion-exchange and concentrated, compares favorably with the product from other methods of purification. The technique affords a means for economies in regeneration costs connected with ion-exchange purification in that the bulk of the ionic material can be removed by this method and the remainder by conventional ion exchange.

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Glycerine: Its Economics and Applications

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THIS HISTORY OF GLYCERINE is quite unlike that of recent developed industrial chemicals, with their planned, rational progress, moving step-by-step from laboratory to pilot plant to market development to full commercial sale. For 150 years glycerine has responded to insight and accident, developing markets along unexpected lines, more influenced by outside forces and discoveries than by glycerine technology itself.

Its discovery first came because lead plasters, formulated with litharge and olive oil, were popular pharmaceutical necessities about the time of the American Revolution. The great Swedish pharmacist, Carl Wilhelm Scheele, brought a true scientific spirit to his routine chores in their manufacture. He became interested in the sweet-tasting liquid resulting from the action of lead oxide on the olive oil, a component of the cooling water as the plaster was stretched and kneaded. Scheele described this substance in his notes in 1779, indicating how its properties differed from sugar syrup. Four years later, in a communication to the Royal Academy of Sweden, he reported that all fats contain this "natural sweet principle."

A full explanation of the relationship between fats, fatty acids, and glycerine was developed later by the French chemist, Michel Chevruel, between 1813 and 1820 and was published in a work still regarded as a chemical classic. Not only did he name glycerine, but he patented the first process intended for its production. This was our old friend, saponification, followed by hydrolyzing the soap with sulfuric acid and recovering glycerol from the water.

In the United States, too, glycerine has had a similar pharmaceutical origin. About 1840 a Philadelphia druggist, Robert Shoemaker, began following Scheele's lead plaster procedure. He found a market for small quantities of glycerine at a price of $4 a pound. From 1840 to 1850 production in the United States remained a few hundred pounds or so a year, all used as a pharmaceutical specialty. Meanwhile glycerine's useful physical properties as a solvent and for viscosity and moisture control were becoming better known.

In the 30 years from 1850 to 1880 the first great period of change took place. In this period the quantities consumed industrially came to be reckoned in millions of pounds per year. At the same time the price of glycerine went from several dollars a pound to about 18¢.

The initial recovery of glycerine from fats came, not in soapmaking, but from the production of stearine candles. A soapmaking treatise of 1869 makes no mention of glycerine recovery. At that time however large amounts of tallow were being saponified with lime, and the resulting calcium soap was acidulated with sulphuric acid to yield fatty acids. Recovery of glycerine from the waste water followed.

The fact is that the big boost to glycerine recovery came from outside these industries: it was the discovery of nitroglycerine and its practical employment in the form of dynamite about 1866. Once the demand for glycerine from this source took on major proportions, fat-splitting methods and soap-making methods were revamped to maximize glycerine recovery and steam distillation was quickly improved. By 1880 the enormous waste of glycerine in the manufacture of soap was recognized, and patents for various types of salting-out evaporators were being issued. Within the next 10 years soap lye crude became the dominant glycerine source. At the same time various methods of hydrolysis before saponification—autoclave-splitting, Twitchell-splitting, and the high-pressure, continuous splitter, followed the course set by the candle-maker. By 1900 world production of glycerine was about 100 million pounds, about one-third of which was made in the United States. With the exception of some textile-softening use, almost all went into dynamite.

Recently The New Yorker ran a series of articles on the life and times of Alfred Nobel that gave a lively concept of the early development of dynamite and blasting gelatin from the 1860's onward. There were dozens of examples, even after the product became commercial, of death and destruction arising from unstable materials and from the processing and handling of nitroglycerine. Today's rocket failures and school-boy experimentation are minor by comparison. But again, by about 1900, the dangers had been brought well under control.

Some fascinating economic interrelationships between glycerine and world history came about *via* dynamite. The tremendous surge in mining after the turn of the century: gold, copper, iron, and all the rest, was a direct consequence of this convenient, controllable, low-cost explosive. The whole economic development of South Africa has been ascribed to this glycerine-derived starting point. By the time of World War I glycerine had moved from a waste product to a world commodity of highest essentiality. It had important military uses, particularly in the form of cordite, a standard propellant of the British Navy. But it was even more vital as the basis of industrial explosives underlying the industries behind the military machines. In Germany the fat shortage was such that production of glycerine by fermentation from sugar beets was carried on despite low yields and difficult purification problems.

From 1910 onward great improvements took place in the technology of soapmaking. Still the United States remained a glycerine-importing nation until during World War I, when both soapmaking and glycerine production grew apace.

Crude glycerine was 50¢ a pound in 1917, but 10¢ a pound in 1919. For, once a soap plant had been equipped for glycerine recovery, there was no economic advantage in discarding spent lye-glycerine solution, even with glycerine at an unatttractive price.

The "Roaring Twenties" did not roar for glycerine. Even so, its production in the United States and in Europe kept moving upward as soap sales grew. In 1929 U. S. production was 112 million pounds, and another 17 million were imported. This importation came despite the fact that crude glycerine then sold at 7¢ a pound and refined glycerine of dynamite grade at 11¢. At the depth of the Depression crude was 4¢ a pound. Its producers sought new and enlarged markets, and for the first time a deliberate research effort on glycerine usage began. The first major outcome of this campaign was the introduction of glycerine solution, with corrosion inhibitors added, as a permanent anti-freeze for automobiles. For several years this was a substantial and expanding market for glycerine. From the long-range standpoint however it served principally to open the door for the first large-scale production of ethylene glycol. Prestone and its companion brands, it turned out, could undersell the glycerine product and give equal protection at slightly lower concentrations. Since 1935 the anti-freeze properties of glycerine have been applied to specialty uses where factors such as nontoxicity are important, but virtually no glycerine has been used for permanent anti-freeze for cars.

Here again, at the critical point when an ever-increasing excess of glycerine might have been expected, another of its properties found it a new field of usefulness. Polymeric esters, produced by various combinations of glycerine, a dibasic acid, and fatty acids, opened a whole new market area. To a certain extent this was another lucky accident, for R. H. Kienle was really looking for electrical insulation but found instead the most widely useful, protective-coating vehicle, the alkyd resin. This was in the late '20's, but it took five or six more years before the alkyd resin business became an important factor on glycerine demand. Its effects may be noted particularly in the 1937–38 period, when glycerine usage for the first time rose to a level of 150,000,000 lbs. a year. Imports of crude glycerine were high as well. The alkyd resin business began to move toward its position as the largest single application for glycerine that it has maintained right up to today.

There is an impression, created no doubt by the allocation restrictions of World War II, that glycerine in the United States had to meet a tremendous surge of military demand. If U. S. production of explosives, rocket propellants, and the like is meant, this is a misconception. Actually the alkyd resin demand kept growing faster, in the United States at least, than the nitroglycerine demand throughout the World War II period. Alkyds, as an industrial protective coating for ships, tanks, and military equipment were the major user.

Glycerine was under price control from November 1941 to November 1946, and under strict allocation from 1942 to 1944. This greatly distorted the normal marketing pattern and created many of the latter problems of substitution and competition from other polyols. Tobacco usage for example, was cut to one-quarter of its pre-war level. In 1943 more than 80 million pounds of glycerine were exported, primarily to the United Kingdom, under Lend-Lease. Meanwhile, because of the strict allocation policies, stocks of glycerine rose to new highs of more than 80 million pounds. So-called nonessential markets had to remain unfulfilled even though there was plenty of glycerine to go around.

The post-war period brings still other examples of the impact of external forces in changing the orderly economic growth of glycerine. The end of war-time price control coincided with a world-wide shortage of fats and of glycerine, and foreign crude sold up to five times the controlled domestic price. When price control ended, glycerine users in the United States had to make an adjustment to the world market situation, at a level somewhere between the two. In 1947 and 1948 the production of glycerine from fats reached its all-time high, at or above 200 million pounds, and consumption was at about the same level. But new forces were at work. In 1945 synthetic detergents had represented but 5% of cleanliness product volume. By 1950 they represented 30%, compared to soap's 70%. Glycerine from fats began to turn downward, though at a slower rate than the decline in soapmaking, thanks to the fatty acid and fatty alcohol business.

Meanwhile a proposal going back to the time of Berthelot, a plan that would have been laughable in the '30's, found its economic and technological place in the sun. The production of glycerine by synthesis from propylene was begun by the Shell Chemical Corporation. Starting in 1949, the plant soon filled the gap created by lowered soap production. Its expansion, along with that of Dow Chemical, has made it possible and necessary to look at glycerine as a growth chemical. A domestic market for refined glycerine in the range of 240 million pounds, with a long-range growth curve of 2% per year has been conservatively cited as the outcome. Today more than one-third of U. S. glycerine comes from propylene.

One good economic reason why growth is to be expected, provided application technology is kept up to the mark, is the consumer advantages coming out of this dual source of supply. The old concern over shortages and the speculative buying to anticipate them are out of the picture. At the same time dependence on the operation of one or two particular plants is far less acute than would be the case were there no glycerine from fats.

The soapmaker who produces or refines glycerine, even in reduced amount, finds greater acceptance for his glycerine, and glycerine in general, than if it were a product on the downgrade in its volume and range of applications. This would certainly be the case if glycerine from propylene, or from some other source, had not been introduced.

So long as a soapmaker is producing soap in any volume, he must remain interested in glycerine. If he has installed refining capacity in excess of his current crude production, he will probably find that it is good economics to purchase enough crude to keep his refining plant at a stable level of operation. In the production of fatty acids and alcohols he may even have an increasing concern for the value of the glycerine. It has frequently been the key factor in the profitability of fatty acid operations or in the choice between a fat-based and petroleum-based detergent.

Today's Glycerine Usage

No actual figures as to distribution of glycerine sales among its hundreds of specific end-uses have been compiled in recent years. However certain established ratios with published figuress for resin production, cigarette production, and the like make it possible to estimate some fields of use.

Alkyd resins, for example, were estimated last year to take some 70,000,000 lbs. of glycerine. This year the total will undoubtedly be somewhat less. As the ''old reliable'' polyol in alkyd resins, glycerine has been a whipping boy for every new polyol capable of supplying the needed hydroxyl radicals. Pentaerythritol, a 4-hydroxyl polyol made from formaldehyde, has expanded its penetration into the resin business to more than 50,000,000 lbs. However it has substituted for glycerine mainly in specific areas of the long-oil alkyd field and is not a ''general replacement.'' There are those who believe that glycerine still has definite advantages in formulation, because of structure, for most alkyd resin formulations. Given the specialized promotion and novelty value of some newer polyols, it would be the ''growth chemical'' of the field. Our more difficult problem is competition arising from water-base systems that use acrylic, vinyl or other emulsions, to which the entire field of alkyds is now exposed. The compatibility of glycerine-based alkyds as co-polymers in some of these systems is now under serious study.

On a world-wide basis nitroglycerine for explosives is no doubt still the largest market for glycerine. But it is not a ''growth'' market in the United States, having stabilized at somewhere around 25,000,000 lbs. of glycerine. The problem is that glycols and other polyols have been incorporated in the formulations which still are reported in government statistics as ''nitroglycerine.'' Also ammonium nitrate is doing some chores previously performed with glycerine-based products.

Solid propellants for rockets, incorporating nitroglycerine, do not appear to have moved up from small rockets into the missile area. However one British news item suggests such use in a ground-to-air device.

It is interesting to calculate, in the U. S. consumption picture, that perhaps one-half of the glycerine used depends on its physical rather than its chemical properties. These are uses as a cellophane plasticizer, a tobacco humectant, many adhesive formulations, textile-treating chemicals, pharmaceuticals, and toilet goods.

Sometime ago a list of more than 1,000 specific uses for glycerine was compiled. Unfortunately those that were the most interesting often require very small quantities, such as the preservation of living tissue, blood cells, and sperm cells by freezing in glycerine solutions.

Perhaps the best way to grasp the areas of use is from the combination of properties glycerine offers. On any one of these properties it may be equalled or surpassed by some other material. But there is no other product with the same combination of properties suitable for formulation work: humectant and plasticizing action, low vapor pressure, viscosity, chemical stability and compatibility, solvent power, lubricity, nontoxicity, and sweet taste.

The use of glycerine in toothpaste, shaving creams, skin lotions, and the like are probably the most familiar markets. Other pharmaceutical uses range from cough syrups to contraceptive jellies.

Glycerine, as such, is not an emulsifier, but the mono- and diglyceride emulsifiers are among the most widely used derivatives, particularly in shortening and in foods, such as bread and ice cream, where Federal Standards of Identity apply. Because these partial esters are actually found in the body when fats are consumed, they have been ruled acceptable as additives whereas products based on ethylene oxide, for example, have not been accepted. Mono- and diglycerides can be made either by esterification of fatty acids or by alcoholysis of a fat by glycerine.

Recently further fields of applications have been opened up by the introduction of acetylated monoglycerides, that is, glycerides in which one or more of the long-chain fatty acids have been replaced with acetic acid. A bright future in various plasticizing and food-coating applications has been predicted for these interesting materials.

One of the problems that arises for any product which has been around as long as glycerine is the tendency to regard it as having been ''researched out.'' The newer, so-called miracle chemicals are applied in the effort to meet new problems, but because glycerine has no ''new product development'' department behind it, it may be left on the shelf.

The Association is trying to overcome this tendency by suggesting that glycerine is going into many products and fields of use as new as tomorrow. Another related problem is the tendency of each new generation of technical men to move into industry with a rather sketchy knowledge of well-established materials. There is an effort to get glycerine's good properties recognized at the academic level as a prelude to tomorrow's purchasing decisions. This is one objective of the annual Glycerine Research Awards, now in their sixth year.

Some persons expect to spend their future in the detergents business. With more than 70% of the cleanliness product business now synthetic detergents and less than 30% in soap, they may say, what's glycerine to me?

Let's get things in perspective. Although the amount of recoverable glycerine in 100 lbs. of tallow may be 8 or 9 lbs., and higher for coconut oil, the value of the glycerine has sometimes been one-third of the total value. The value of the crude glycerine, figured as a credit against the cost of fat, has had a significant bearing on the manufacturing cost of soap and on the particular production processes used in soap-making and fat-splitting.

Currently the economic balance for detergents based on fatty alcohols and fatty acid derivatives for wetting agents, emulsifiers, and the like must also include the value of glycerine as an important factor. There is a strong likelihood that the decline in glycerine recovered from fats has about run its course.

Of course, glycerine remains a product having world-wide ramifications on both the supply and demand side. In England and on the Continent there is the same tendency to shift from fats to synthetic detergents going on, but with a time lag of three to five years. On the other hand, a great growth-potential for soap, including good-old-fashioned bar soap, still exists in populous countries where *per capita* soap consumption is still low. In a country like India, for example, soap usage seems likely to grow for many years, and at a faster rate than the local glycerine demand. Japan is another example. Running water in the home is limited to less than 30% of the population. American exporters of tallow are actively cooperating on a program to encourage soapmaking and soap consumption in Japan. An estimated 10% increase in soap production in 1958 in Japan is expected to add to its glycerine-exporting tendency.

The adaptability of surplus fats to tomorrow's chemical processes and products is likely to be wider *via* fatty acids rather than as glycerides. This also suggests the fact that glycerine from fats will continue to be an important market factor for the foreseeable future.

A few hundred tons of foreign crude glycerine are a highly negotiable commodity with which a country like Argentina can get badly needed dollars. Existing refining capacity, not only in soap plants but in independent or user companies, is available to prepare it for market.

The producers of glycerine from propylene are keenly aware that they face a problem of building new markets, rather than simply "filling a hole" caused by the decline of domestic soapmaking. Their continuing investment in facilities confirms their belief that glycerine has the properties that make it a growth chemical potentially as well as historically.

It will be interesting to see if glycerine's growth pattern finally does fall into the rational, well-researched development pattern of the chemical marketing specialist or if, as so often in the past, some fortuitous discovery or unexpected factor in the world economy opens new horizons now unforeseen.

Dermatologic Aspects of Soaps and Detergents[1]

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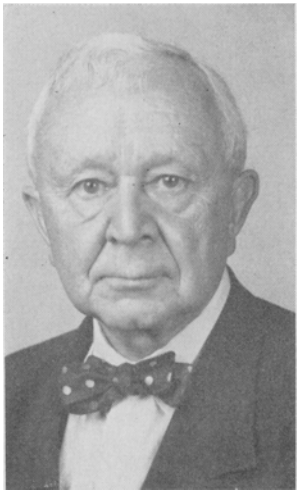
SOAP has been safely used as a cleansing agent by millions of people for hundreds of years. Practically everybody in the civilized world today uses soaps or other detergents, and the incidence of dermatitis is low indeed. However within the last few years it seems that dermatologists see more cases of dermatitis from cleansers than formerly. There may be a number of reasons for this. The importance of cleanliness as a hygienic and prophylactic measure is being more and more emphasized, consequently more and more people use cleansers more and more frequently. Cleansing compositions are now more complex than they formerly were. Where previously only soaps were used, now the syndets are coming into use; mixtures of soaps, syndets, and water-softening agents are sold on the market, especially as household cleansers. In recent years domestic help has become more and more difficult to obtain, and the lady of the house must do an increasing amount of domestic work. She washes dishes and clothes, scrubs floors, sinks, and toilets. Hence, despite the automatic dishwashers, clothes washers, and floor cleaners, a greater number of people have more contact with stronger cleansers than ever before.


Louis Schwartz

Most cases of dermatitis attributed to cleansers are not caused as much by actual allergy to the cleanser as they are by the fact that certain people have such anatomical or physiological defects of the skin that it cannot rapidly regenerate the epithelium and the secretions removed by cleansers. Drying and chapping of the skin result, especially if the skin is excessively exposed to these detergents, as in the case of domestics, housewives, washwomen, kitchen workers, soda fountain attendants, etc.

Soaps constitute the large percentage of skin-cleansing materials. The soaps used for skin cleansing are sodium or potassium salts of long-chain fatty acids. There is a difference in the skin irritant potential of soaps. The long-chain fatty acid soaps are less irritant than the short-chain, and soap solutions having a high pH are more irritant than those having a low pH. Soaps containing a high amount of free alkali are more irritating than those having a low amount. Rosin soaps are more apt to be irritant than fatty acid soaps. A rosin short-chain fatty acid soap with a high pH and a high amount of free alkali would be one with a high skin-irritant potential.

Cleansing Action of Soaps

The soap molecule is both hydrophilic and lipophilic. Hence soap can combine with both oil- and water-soluble substances and make a stable emulsion

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[1] Dinner lecture.