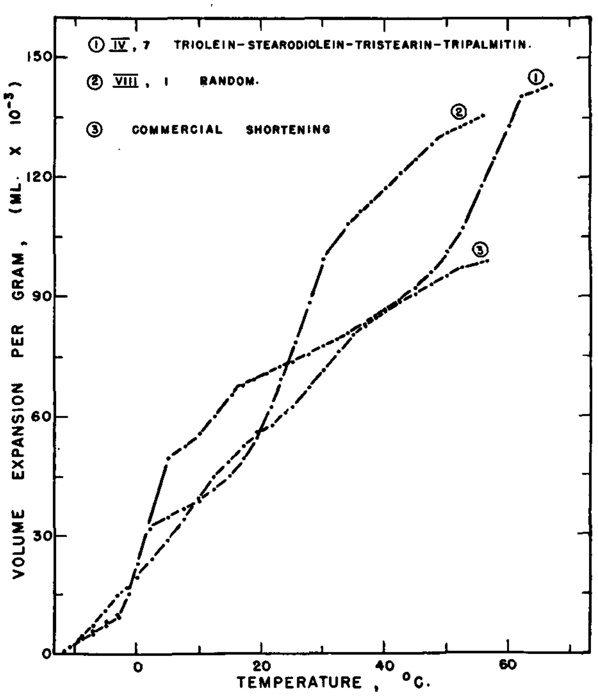

FIG. 10. Volume expansions of glyceride mixtures IV, 7; VIII, 1; and a commercial shortening:

IV, 7 triolein 54.0%; stearodiolein 20.2%; tristearin 13.6%; tripalmitin 12.2%.
VIII, 1 triolein 38.4%; stearodiolein 29.1%; oleodistearin 14.4%; oleodipalmitin 13.5%; palmitodistearin 1.7%; stearodipalmitin 1.7%; tristearin 0.6%; tripalmitin 0.6%.

dilations of the individual triglycerides are known, and on the basis of our observations that in more complex systems the melting ranges are extended, and except in the simplest systems, overlap, we concur in Bailey's conclusion (1) that the calculation of solid-to-liquid ratios from the dilatometric curves of natural fats is not possible with any degree of accuracy unless information from other types of measurements is available.

Summary

The melting dilations and the coefficients of expansion of the solid and liquid states have been reported for five symmetrical mixed triglycerides and three simple triglycerides. The melting dilations were found to decrease with increasing proportions of oleic acid in the triglyceride molecule. In some simple mixtures the melting dilations of the several phases were found to occur discretely, but in the more complex systems there was an extension and overlapping of the melting ranges. In the mixtures of triolein with more saturated triglycerides, the melting point of triolein was found to be generally unaffected, but the melting points of the more saturated glycerides were lowered by the presence of triolein. Calculations of the solid-to-liquid ratios from dilatometric data were found to be impossible in the more complex mixtures due to wide variations in the melting dilations of the several phases and to the overlapping of their melting ranges. Approximate calculations of solid-to-liquid ratios in simple systems in which melting dilations occur discretely can be accomplished if the melting dilations of the individual triglycerides are known.

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Sweetwater Deionization on a Plant Scale[1]

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THE ion exchange phenomena and the basic process have been described in innumerable publications and have been thoroughly discussed at various meetings similar to this over the last decade. The process itself has been applied to water and many other purifications, of which one of the most recent and novel is the treatment of glycerol sweetwaters and crude glycerols.

Kahler (1) described the purification of crude glycerol by ion exchange, and recently Caskey (2) delivered a general treatise covering ion exchange purification of various impure glycerols. Reents and Stromquist (3) lately published a more detailed study of treatment of crude glycerols and glycerol sweetwaters by ion exchange to produce a C.P. product. There are other articles in the literature regarding glycerol purification, but none of them concerned the production of C.P. or U.S.P. glycerol by ion exchange and evaporation. All previous work on the ion-exchanging of glycerols to produce a C.P. product necessitated distillation as a final measure. The production of a chemically pure glycerol by ion exchange and evaporation with the subsequent elimination of distillation has led several firms to purchase and install large scale equipment for the treatment of both glycerol sweetwaters and crude glycerols. The Archer-Daniels-Midland Company plant at Wyandotte, Michigan, treating glycerol sweetwaters obtained by hydrolysis, has been in successful operation for over a year, the operation of which will be discussed in a later portion of this paper. A similar installation on the west coast has been in operation for several months. A soap lye crude ion exchange purification unit has been operating successfully over a period of a few months. This is also located on the west coast, and a discussion of the characteristics of this unit will be presented at this meeting by a member of the company concerned.

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[1] Presented at the 25th Annual Fall Meeting, American Oil Chemists' Society, Chicago, Ill., Oct. 8-11, 1951.

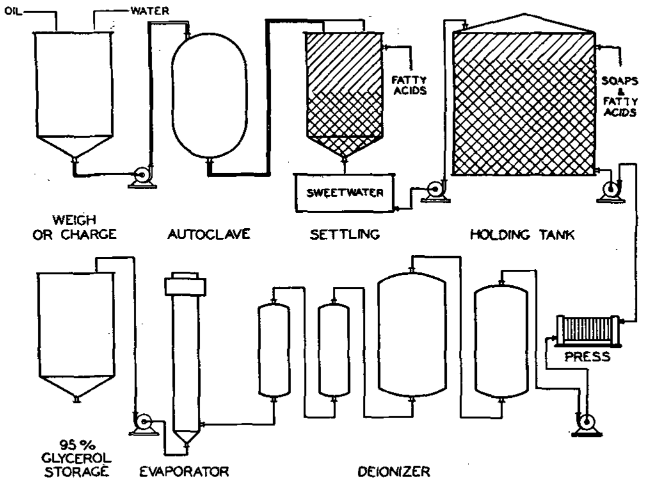

FIG. 1. Flow sheet.

In removing ionized solids from aqueous solutions of non-ionized materials, such as glycerol, the solution involved is generally first passed through a cation exchanger and then an anion exchanger or several combinations of these. Each passage of solution or treatment thereof by a pair of exchange resins, namely, cation and anion resins, removes approximately 90% of the influent ionized solids and slips the remaining 10%. Therefore the concentration of the influent ionized solids and the final concentration of impurities desired determines the number of passes required to purify a particular material. For example, a crude glycerol containining 10% ash would require 3 passes through successive pairs of cation and anion exchangers to produce a C.P. product. A simpler material to treat, such as glycerol sweetwater with an ash of 0.2%, would require a double pass to produce a similar product. An active, regenerable color adsorbent resin can be used appropriately to remove color bodies from glycerol solutions that are heavily colored. The cation exchangers used for this type of work are regenerated with an acid such as sulfuric or hydrochloric, and the anion exchangers are generally regenerated with caustic soda.

When a glycerol-bearing solution containing sodium chloride as the major impurity is percolated through a cation exchanger bed that is operating on the hydrogen cycle, approximately 90% of the sodium ions are exchanged for hydrogen ions to form hydrochloric acid. Any other salts present would similarly exchange their associated cations in a corresponding manner for the hydrogen ion. The resulting acid, hydrochloric acid in this case, or other acids formed are removed by the anion exchanger employed. The chemistry of the removal or exchange in this case of the anion exchanger is somewhat debatable.

Glycerol sweetwaters are produced in a variety of ways, among them being hydrolysis of fats and oils at high temperature and pressure, and/or hydrolysis of the same materials at ordinary pressures with the aid of a catalyst. After separation of the glycerol sweetwater from the fatty acids, further treatment and clarification are generally necessary before exposing the sweetwater to ion exchange. If sulfuric acid is present, as is the case with some sweetwaters, it is considerably cheaper to add lime to precipitate calcium sulfate and, in addition, to clarify the water rather than remove the acid by ion exchange. It is one of the prerequisites of ion exchange that the solution to be treated be clear and free from turbidity as treatment of turbid solutions often leads to fouled exchanger beds. The raw sweetwaters may also be successfully clarified with alum, lime, or ferrous sulfate, depending on the requirements in each particular case.

To illustrate the treatment of a typical sweetwater produced by high temperature and high pressure hydrolysis the following data are presented. Figure 1 is a flow sheet representing a typical plant layout to show the production and treatment of such sweetwaters. Particular attention is called to the large storage tank which collects the sweetwaters from various sections of the plant. This tank has a dual purpose. It serves as a settling basin for the finely divided, suspended, fatty acids and insoluble soaps which would foul the resin beds. These are inevitably present and extremely difficult to filter. It also serves to dissipate heat from the sweetwaters which would damage the resin beds. The temperature of the waters entering is approximately 180°F.; they leave at below 95°F., even in the summer months. Retention time in the holding tank is about 15 days. The effluent is relatively free of turbidity. While the tank serves the purpose for which it was designed, its introduction into the flow pattern caused some unforeseen complications. After a few months of operation air-borne micro-organisms contaminated the sweetwaters. These are predominantly gram-negative bacilli, 0.4 to 0.8 microns in size, and a yellowish-brown mold belonging to the *Penicillia genus.* They produced reaction products of the glycerol present.

The result has been a loss of glycerol and a dark-colored finished material. The color is due to iron compounds picked up in the evaporator (whose materials are cast iron and brass). Concentration of the same deionized sweetwaters, in glass, in the laboratory, yielded water white 96% glycerol, indicating that bacterial action had produced materials capable of combining with iron, but not removed by the resins. This phase of the problem is now under investigation. At present, fairly frequent chlorination of the sweetwater in the holding tank keeps the micro-organisms in check although it is known that chlorination is not the final solution to the problem. While the plant has produced C.P. glycerol, all data subsequently presented have been taken from runs using the contaminated sweetwaters.

Figure 2 is a separate outline of the deionizer itself. The materials of construction are largely rubber-

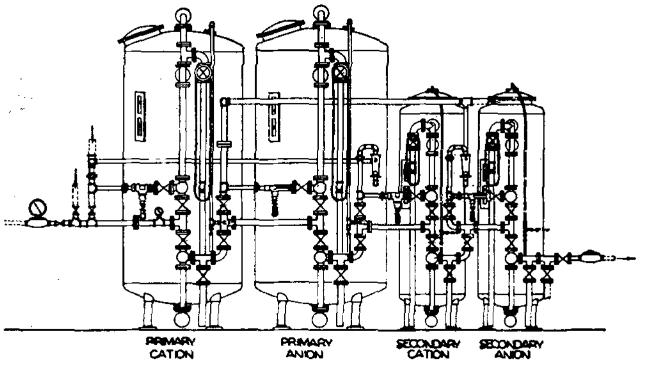

FIG. 2.

lined steel, Saran piping, and hard rubber injectors. The resins are supported on quartz filter beds which rest upon a false perforated bottom located near the lower tangent line of the vessels. The primary cation holds 78 cu. ft. of resin, the primary anion 103 cu. ft. of resin, and the secondaries 15 cu. ft. each. Regeneration tanks are not shown. A complete cycle through this equipment requires about 24 hours. Roughly 13 to 15 hours are necessary to deionize an average of 16,000 gallons of sweetwater. The remaining time is used to "sweeten off," regenerate, and to "sweeten on."

From the size of the equipment and the data following, it will be seen that it is imperative to operate at high efficiency, that is, high gallonage throughout. High gallonage reduces the percentage dilution due to sweetening on.

Liming of the raw sweetwaters does place some additional load on the primary cation exchanger and thereby reduces the total gallonage available per cycle. In this particular case liming of the raw sweetwaters and subsequent ion-exchange produced a glycerol which was inferior to that produced without the liming step. However liming for clarification is not to be condemned for this experience alone because it is being used successfully in another plant where side-effects from bacterial action are not in evidence.

Care must be exercised in backwashing the primary anion after regeneration. These anion resins are of such a nature that they tend to pack in the vessel, thus causing channeling of flow through the bed and reduction of exchange efficiency. Proper backwashing causes sufficient agitation to expand the bed. It should be mentioned that too high a flow rate during washing will cause the resins to escape through the overflow piping and become lost. Such an occurrence could be rather expensive but can be easily prevented with proper operation. Difficulty with packing and clumping is believed to be due in part to the turbid nature of the raw sweetwaters treated by the ion-exchangers.

Figure 3 shows the ionic progress of sweetwaters through the deionizer during a typical plant run. The line A is the pH of the effluent from the primary cation exchanger. The high acidity illustrates the activity of the bed and indicates the quantity of metallic ions replaced. Line B represents the effluent from the primary anion exchanger. The basicity shown at the beginning is probably due to free alkali not washed cleanly from the regenerative cycle. Line C, that of the secondary cation, shows more acidity than B, indicating further metallic exchange. The final effluent (from the secondary anion exchanger), shown as Line D, is nearly neutral throughout the cycle. The last 800 gallons show a sudden change of from nearly zero ppm. to 30 ppm. solids (calculated as sodium chloride) as the resin becomes spent. The feed sweetwater had a nearly constant pH of 4.2.

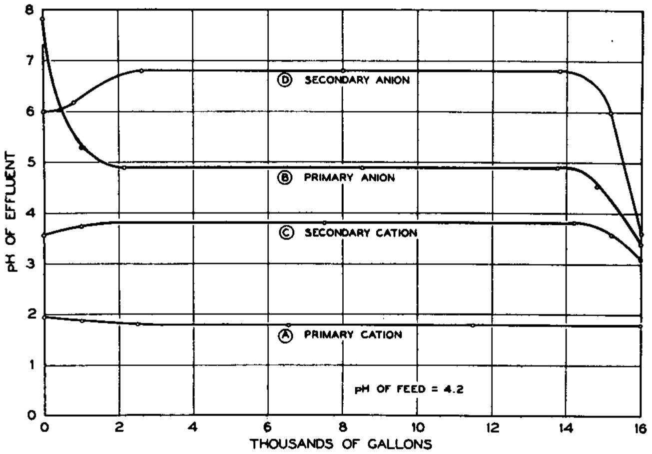

Fig. 3. pH of sweetwaters.

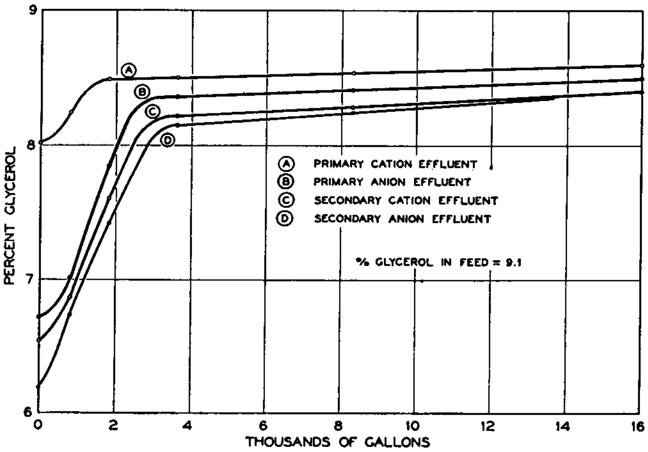

Fig. 4. Dilution of sweetwaters.

Figure 4 is the same type of diagram, illustrating the drop in glycerol content through the system. The drop is due to dilution with the water formed during the cation-anion exchange. The lower concentration of the final effluent at the start of the run is due to the "sweetening on" process.

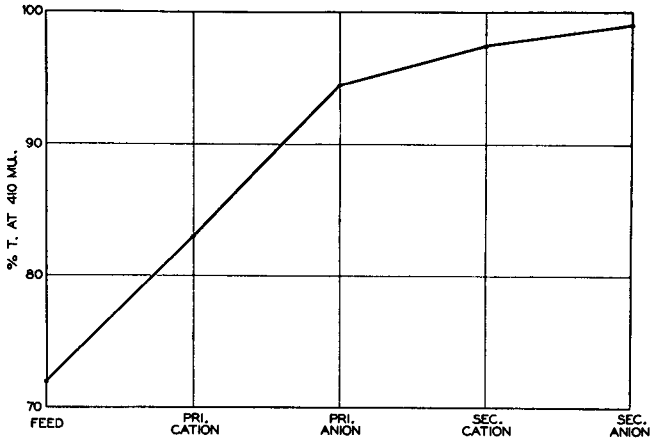

Fig. 5. Clarity of sweetwaters.

Figure 5 illustrates the color improvement over the feed through the four stages of deionization. The samples were selected at random from the middle portion of the run and represent a fair average. Since the sweetwaters are yellowish, the blue portion (410 mμ) of the spectrum was selected to give a maximum spread in the data. Compared with distilled water the improvement is very noticeable: from the

72% transmittancy of the feed to 99% T. of the final effluent.

Table I summarizes the entire process. The analyses are a fair average over many runs and do not indicate finished stocks from the particular sweetwater shown. It should be noted however that with very highly colored sweetwaters from the splitting of poor crude oils or foots somewhat less spectacular results would be obtained. Dilution of such sweetwaters with better grade stock minimizes a low throughput and a dark finished glycerol. Addition of another cation-anion exchanger and/or a decolorizing resin bed would be recommended to process such materials for the production of C.P. glycerol.

TABLE I

Note: Analyses shown are averages.

	Sweetwater	Crude Glycerol	Deionized Glycerol
% Glycerol	9.1	94.5	95.02
R. I. at 25°C	1.3435	……..	1.4662
% Ash	0.2	1.4	0.006
Color	……..	Dark Brown	2.5Y-0.2R

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Annual Review of Literature on Fats, Oils, and Soaps. Part I

Report of the Literature Review Committee *

M. M. PISKUR, Swift and Company, Chicago, Illinois

Introduction

STATISTICS AND OUTLOOK. The immediately following economic information on fats and oils was compiled from late 1951 issues of the publication "Fats and Oils Situation" which was issued by the Bureau of Agricultural Economics of the United States Department of Agriculture.

Production of fats and oils in the year which began October 1, 1951, probably will total over 12.5 billion pounds, 0.2 billion above the record of a year earlier, which in 1950-51 was 3% more than the year before and 42% above the 1937-41 average.

During the 1950-51 year imports of fats and oils and production from imported materials was slightly larger than that of the year before; exports were 19% more than in the previous year.

Domestic disappearance of fats and oils in 1950-51 was 125 million pounds greater than the year before and almost 700 million more than two years ago. Owing to population increase, however, at a per capita basis of 68.6 pounds it was slightly less than the year before but still more than two pounds greater than in 1948-49. Food uses at 43.3 pounds were down 1.3 pounds, while non-food uses at 25.3 pounds increased 0.9 pound per person.

Prices of the major edible vegetable oils have declined in recent months as supplies have been large in relation to demand. The index number of wholesale prices of 26 major fats and oils, excluding butter, in the first half of January, 1952, was 170% of the 1935-39 average compared to 176 in December and 241 in January, 1951.

The economic treatises on fats and oils that appeared during the year were on current domestic and world economic situations as related to fats and oils (Prichard—*J. Am. Oil Chemists' Soc. 28,* 453-5); possibilities for improving the economic status of animal fats through research (Lundberg—*Proc. 2nd Conference on Research Am. Meat Inst. Mar. 23-4,* 112); trade, production and source information on 30 vegetable oils (Shearon—*Chem. Eng. News 29,* 4065); world fats and oils supplies and American soybeans (Quintus—*Oil Mill Gaz. 56,* No. 3, 13); drying oils trade (Andrews—*Oil & Chem. Rev. 114,* No. 8, 10); the fat supply of France (Ferrara—*Olearia 4,* 407); and import and production in Japan (Toyama—*Fette u. Seifen 53,* 65). Because of increasing production of synthetic detergents (syndets) there appeared several treatises on the economics of soaps versus the syndets (Snell—*Chem. & Eng. News 29,* 36; *30,* 30; *Brit. Silk Rayon J. 27,* No. 315, 45; Snell & Kimball—*Soap Sanit. Chemicals 27,* No. 6, 27; Killeffer—*Chemistry & Industry 1951,* 350; Flett—*Soap Sanit. Chemicals 27,* No. 3, 35). Solid soap and syndet productions, respectively for 1951, were 2,780 and 1,500 million pounds as compared to 2,955 and 1,250 million pounds during 1950. The great bulk of syndet production was from petroleum-base alkyl aryl sulfonates. The production was hampered by shortages of the supply of sulfur and benzene for manufacture, and of tripolyphosphate and tetra sodium pyrophosphate for building. These situations should be considerably eased by 1953. The economics and future of the German soap and syndet industry were also reviewed (Harz—*Seifen-Öle-Fette-Wachse 76,* 572).

General papers of economic interest were written on the cultivation of oleagenous plants in Italy (Baldacci & Fischetti—*Olearia 4,* 371); the vegetable oils of Java (Meijer—*Oliën, Vetten en Oliezaden 30,* 187, 198, 210); and inedible oils for technical uses of India (Dutt *et al.*—*Indian Soap J. 16,* 71).

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