has been lacking in the liquid standards. It is believed that a large percentage of the liquid standards that have been in use for a few years will not meet the chromaticity coordinates set forth in Ka 3-58 and should be replaced if accurate color readings are required.

Revision of Method Ka 6-59, Viscosity by Bubble Time, to use numerically marked comparator tubes as standards replacing the Gardner-Holdt letter series has been completed and sent on to the Uniform Methods Committee for final approval and inclusion in the Methods Book.

The Subcommittee is attempting to write a method on "Appearance." Ed Handschumaker presented a method on "Determination of Clarity by Total Nephelos," which employs a nephelometer and would give a quantitative measurement. The Subcommittee decided a qualitative method also is desirable and solicits suggestions.

Polymerized Fatty Acids, Gerald Wilson, Chairman

The Subcommittee has completed collaborative tests on polymerized fatty acids using the following AOCS Methods: L 2b-57, Moisture, Modified Karl Fisher Reagent; L 3a-57, Acid Value; L 4a-57, Unsaponifiable Matter; L 7a-57, Saponification Value; and Ka 3-58, Gardner Color. It was found that all of the methods were applicable to polymerized fatty acids and their adoption for use in the analysis of polymerized fatty acids is recommended to the Uniform Methods Committee.

The Subcommittee decided that none of the common methods of determining unsaturation such as halide addition, high pressure hydrogenation or ozone absorption will work on polymerized fatty acids. The Subcommittee is open to suggestions from members of AOCS and will consider any method proposed if it is accompanied by supporting data.

The following definition was proposed for polymerized fatty acids: "polycarboxylic polymerized fatty acids in essentially free acid form."

Fatty Nitrogen Subcommittee, Gerald Wilson, Chairman

Collaborative work on fatty amido amines showed the following methods in the "N" section of AOCS Methods to be applicable to fatty amido amines: Gardner Color, Moisture by Karl Fisher, Total Amine Value and Iodine Value. It was recommended that fatty amido amines be included in the definition and introduction to the "N" section and that the precisions obtained be included as a part of the methods. Collaborative work is continuing on other methods applicable to fatty amido amines and, also, methodology on dimethyl fatty amines, fatty diamine and fatty amine.

Consolidation of Methods

At the present time, each Subcommittee of the Industrial Oils and Derivatives Committee has its own section of methods: that is, Drying Oils—Section K, Fatty Nitrogen–Section N, Commercial Fatty Acids–Section L, etc. As new Subcommittees are added, such as Polymerized Fatty Acids, the establishment of a new section will be required if the same procedure is to be continued. The Industrial Oils & Derivatives Committee recommend to the Uniform Methods Committee that all of the methods falling under the jurisdiction of the Industrial Oils & Derivatives Committee be consolidated into one section. This will eliminate much duplication in methods that are common to many or all of these compounds such as Color, Iodine Value, Moisture, etc. It is, also, recommended that an introduction be written for each of the classes of compounds to be tested similar to that now appearing in Section N Fatty Nitrogen Compounds. This would give the analyst an idea regarding test methods to be used and assist him in interpreting results obtained.

The Uniform Methods Committee gave tentative approval to this recommendation and requested that a format of introductions and methods be written and submitted prior to the fall meeting of AOCS.

Continuous Deglycerination of Monoglycerides

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Abstract

A relationship was established between the smoke point of a superglycerinated shortening and free glycerol content. A maximum free glycerol content of 0.02% was established for smoke points of 340F or better.

Based on a 6% usage in emulsifier type shortening, commercial monoglycerides should have 0.30% glycerol or less to meet a desirable smoke point. A 2-stage extraction with 5% NaCl solution reduced free glycerol from 5.51% to 0.14%.

A continuous process was developed for removing glycerol from commercial monoglyceride preparations with a thin-film evaporator. Operation at 340F and 6 mm Hg absolute pressure with stripping steam reduced glycerol content to 0.3%. Analysis showed substantially no monoglyceride reversion under process conditions, and considerable improvement in flavor and odor was obtained.

Introduction

GENERAL PURPOSE SHORTENINGS have been and are used in large tonnage by institutions, bakeshops, and housewives for baking. One of the characteristics of good shortenings for this purpose has been a high smoke point. Within the past 30 years we have seen the considerable growth of special all-hydrogenated shortenings with superior emulsifying properties which allow the baker to use a higher ratio of sugar to flour and still obtain light and full-volumed cakes. These shortenings contain more combined glycerol than ordinary fats and oils as a result of adding 6–8% of mono- and diglyceride preparations, and are known in the trade as "superglycerinated," or "emulsifier type" or "high-ratio." They are very popular in cakes and pies and are used substantially by the average household as well as commercial bakeries.

Superglycerinated shortenings are approximately similar to ordinary all-hydrogenated shortenings in

TABLE I

Analysis of Glycerol Monostearate

	%
Glycerol Monostearate	42
Glycerol Distearate	40
Glycerol Tristearate	8.8
Free Fatty Acid (as stearic)	1.2
Glycerol	6.8
Moisture	1.0
Miscellaneous	0.2

appearance, taste, stability, and odor. However, they run higher in free fatty acids, ranging from 0.05–0.20% (1), and are unsuitable for commercial deep-fat frying because of their lower smoke point. Bailey describes the relationship between smoke point and free fatty acid content in edible fats and oils, namely about 450F at a free fatty acid content of 0.01% and about 200F for 100% free fatty acid. However, these data do not apply to superglycerinated shortenings which may contain free glycerol in addition to free fatty acids. Consequently experimental work was carried out to relate smoke point of shortenings with free glycerol content, and to develop a process for obtaining shortenings with a desirable smoke point when a commercial monoglyceride is the added emulsifier.

Experimental

The reaction product obtained from the esterification of fatty acids with glycerol or from the interesterification of fats and oils is commonly called a monoglyceride. A typical composition of commercial glycerol monostearate is shown in Table I. Data were taken from a bulletin issued by the Colgate-Palmolive Co. titled "Mono and Diglycerides," which describes a product made by esterification of stearic and glycerol.

Smoke Point Relationships

The smoke point of fatty material as defined by Bailey (1) is "the temperature at which decomposition products are evolved in sufficient quantity for them to become visible." For the purpose of this study we added 6% of an experimental monoglyceride (at various glycerol levels) to a commercial salad oil which was essentially corn oil with a smoke point of 450F. Smoke points were then run on these mixtures which were considered equivalent to superglycerinated shortenings, and are shown in Figure 1.

The smoke point of a commercial high-ratio shortening was measured as 342F. Figure 1 indicates that very poor smoke points are obtained with shortenings with glycerol levels above 0.07%, and an acceptable value of 340F or higher requires a glycerol content of 0.02% or less. Consequently, commercial monoglycerides used for superglycerinated shortenings should have a corresponding glycerol content of 0.3% or less.

Extraction With Salt Solution

Pohle, Mehlenbacher and Cook (2) mention the use of 20% sodium chloride solution for removing glycerol from samples prior to the determination of monoglycerides by oxidation with periodic acid. As a follow up of this approach, commercial monoglycerides were gently shaken with an added 50% of aqueous salt solution at 194F (90C) in separatory funnels. It was found that 50 parts of a rather dilute (one per cent) solution of sodium chloride would separate from 150 parts of mixture in about 10 min when held in a bath at 194F. When a propeller mixer was substituted for simple shaking, the dilute salt solutions formed emulsions which broke very slowly, and the salt concentrations had to be increased to 5%.

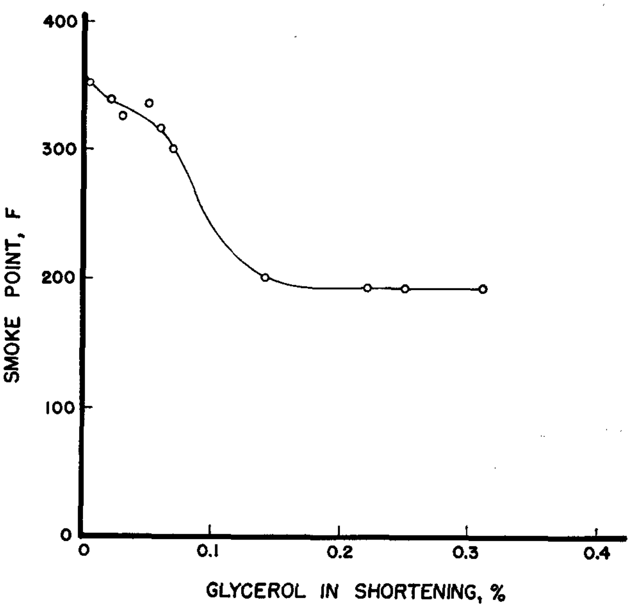

FIG. 1. Effect of free glycerol in shortening on the smoke point.

Pilot plant experiments were carried out in a one-hundred gallon tank using a propeller mixer for agitation. The mixing time was held to 15 sec to minimize emulsification. The batch consisted of 500 lb of commercial monoglyceride at 194F and 250 lb of 5% sodium chloride solution. Analytical results on the product before and after extraction are presented in Table II.

A 2-stage experiment was made using two 125 lb charges of 5% salt solution.

Table III indicates the superior results of a 2-stage extraction which reduces the final glycerol content to 0.14%. Since multistage operation is the conventional way to obtain maximum removal of a component in a liquid stream, a counter current continuous extraction was carried out. A commercial monoglyceride at 194F was fed to the botton of a packed extraction tower at 500 ml/hr. About 200 ml/hr of 5% salt solution was fed at the top. Extracted product taken off the top was found to contain only 0.15% glycerol.

Although the extraction process was found to be adequate for glycerol removal, it had many undesirable aspects such as leaving salt and moisture in the product and having recovered glycerol in the form of a dilute solution containing sodium chloride.

TABLE II

Glycerol Removal by Salt Solution—1 Stage

	Initial Monoglyceride	After Extraction
Glycerol, %	6.05	0.54
Water, %	0.59	1.64
Sodium Chloride, %	0	0.17

TABLE III

Glycerol Removal by Salt Solution—2 Stage

	Initial Monoglyceride	1st Stage	2nd Stage
Glycerol, %	5.51	0.78	0.14
Water, %	0.68	3.85	3.65
Sodium Chloride, %	0	0.04	0.05

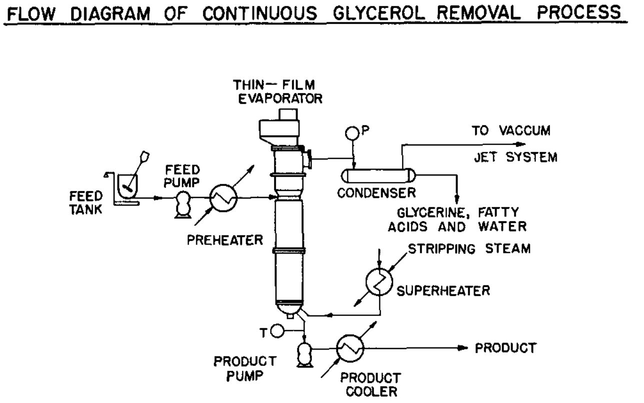

FIG. 2. Flow diagram of continuous glycerol removal process.

Continuous Evaporation

Previous work by Kuhrt, Welch, and Kovarik (3) on molecular distillation of monoglycerides has shown that the bulk of glycerol and fatty acids present in commercial partial glycerides were removed in the forepart (first 10%) of their distillation. Consequently, experimental work was conducted in a continuous film-type evaporator under conditions which would essentially remove glycerol.

The starting material was a commercial product which was made by reacting prime steam lard with glycerol in the presence of a caustic catalyst, and shall be hence known as Lard Monoglyceride. One drum of this material was kept molten, and sufficient 85% phosphoric acid was added to neutralize the alkali catalyst. This was done to prevent reversion of mono- and diglycerides during the glycerol removal process.

Experimental equipment consisted of a stainless steel thin-film evaporator with rotating internal vanes and a heat transfer area of one square foot, as described in a previous article by the author (4). The internal vanes rotated at 3600 rpm and threw liquid against the hot wall. Fillets of liquid formed along the leading edge of the rotor blade and came into intimate contact with a 1/32" to 1/16" thin film. Stripping steam in superheated form was introduced into the bottom of the film evaporator at the rate of 1.5 lb/hr.

Figure 2 is a flow diagram of the process which shows entry points for feed and stripping steam, and exit ports for treated product and dilute glycerol.

A total of 10 pilot plant runs were made with internal temperature, absolute pressure and feed rate as the variables. Molten Lard Monoglyceride was fed into the thin-film evaporator, then the steam rate, product rate, temperature of the liquid film, and absolute pressure were adjusted to steady conditions, and samples were taken for analysis. Table IV gives process and analytical data for all experimental runs.

TABLE IV

Data Summary for Film Evaporator Runs

Run No.	Temperature C	Temperature F	Rate Lb./Hr	Abs Press. mm of Hg	Monoglyceride %	Glycerol %
Start	......	......	....	....	46.3	5.1
1	172	342	16	16	47.1	2.4
2	170	338	12	6.5	48.7	0.49
3	178	352	34	9	49.1	0.76
4	154	309	25	7	47.6	3.6
5	154	309	40	8	47.0	4.2
6	170	338	24	10	48.5	1.2
7	170	338	28	9	48.5	0.97
8	185	365	26	13	50.2	1.0
9	170	338	26	8	44.8	0.29
10	171	340	....[a]	....[a]	47.2	0.10

[a] No data taken due to malfunction of instruments.

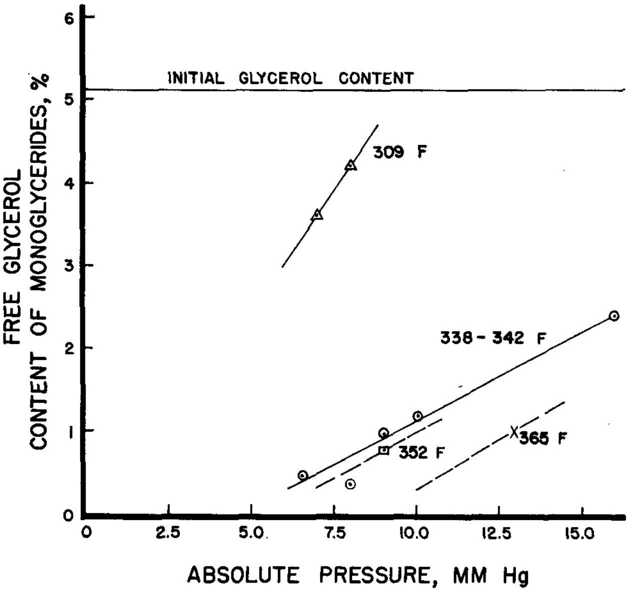

FIG. 3. Effect of temperature and pressure on glycerol removal from monoglycerides.

Residence time in the evaporator varied between 11 and 26 sec. Two layers, fatty and aqueous, were obtained from the vapor condenser with an average analysis of 4.0% fatty matter, 39% glycerol and 56% water. After skimming off the fatty layer which was a mixture of fatty acids and monoglycerides, the bottom layer can be used as feed for glycerol purification. It was noticed that deglycerinated product was considerably improved in flavor and odor over the starting material.

Results and Discussion

To correlate the experimental pilot plant data, Figure 3 is a plot which shows the effect of low absolute pressure in a film evaporator on free glycerol content of a processed commercial monoglyceride. The liquid film temperature was used as a parameter, and it was assumed that variations in feed rate from run to run did not have too great an effect on glycerol removal. Previous work on reaction kinetics in this equipment had established that residence times of 10 sec or more were adequate to complete chemical reactions which are associated with vaporization of a volatile component.

Hence, it is concluded from the plotted data that commercial monoglycerides can be processed continuously through a continuous film evaporator to a reduced glycerol content of 0.3% or less. Operation at 340F would require about 6 mm Hg absolute pressure, about 7 mm Hg at 350F, and increasing the vaporization temperature would allow a correspondingly higher operating pressure.

The final monoglyceride content showed substantially no reversion under process conditions, and the product was considerably improved in flavor and odor.

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