the harder shortenings do not become too hard.

Table II shows the results of experiments on various types of commercially manufactured shortenings, including four samples of hydrogenated vegetable oil shortening covering a range of quality.

A portion of each sample was melted and replasticized by the laboratory method, and the remainder was used as received, as a standard.

TABLE II

Comparison of Plant and Laboratory Samples of Various Types of Shortenings

Shortening	Pound-cake volume values	
	Plant-plasticized	Laboratory-plasticized
	ml./100 g.	*ml./100 g.*
1. Hydrogenated vegetable oil shortening, No. 1.	234	244
2. Hydrogenated vegetable oil shortening, No. 2.	257	266
3. Hydrogenated vegetable oil shortening, No. 3.	271	268
4. Hydrogenated vegetable oil shortening, No. 4.	239	243
5. Modified lard-hydrogenated vegetable oil shortening	258	259
6. Emulsifier type, modified lard-hydrogenated vegetable oil shortening	259	261
7. Emulsifier type, hydrogenated vegetable oil shortening	230	234
8. Experimental modified lard blend	269	261
9. Hydrogenated vegetable oil for deep fat frying	277	243
10. Flaked lard	146	151

The results obtained on the plant-plasticized and laboratory-plasticized samples are in good agreement. A statistical analysis of the data shows, with one exception, no significant difference in the pound-cake volume values.

Only in item 9 is a significant discrepancy evident. This was a sample of a deep frying fat, which is not customarily used for baking because of its short plastic range.

If the minimum pound-cake volume value specified for a high quality hydrogenated vegetable oil shortening is 250, it is obvious from the results that samples 1 and 4 plasticized by either method are readily classified as substandard whereas samples 2 and 3 are shown to be above standard in quality.

Table III shows the variation between pound-cake volume values of duplicate laboratory-plasticized samples of hydrogenated vegetable oil shortenings.

Portions of each commercially prepared hydrogenated vegetable oil shortening were melted and replasticized by the laboratory method, and the remainder was used as received, as a standard.

TABLE III

Variation Between Pound-Cake Volume Values of Duplicate Samples of Hydrogenated Vegetable Oil Shortening

	Pound-cake volume values
Sample 1	*ml./100 g.*
Plant-plasticized	240
Laboratory-plasticized	243, 246
Sample 2	
Plant-plasticized	257
Laboratory-plasticized	265, 267
Sample 3	
Plant-plasticized	270
Laboratory-plasticized	264, 272
Sample 4	
Plant-plasticized	238
Laboratory-plasticized	234, 233

Results obtained on the duplicate laboratory-plasticized samples show no significant difference in pound-cake volume values. These results, compared with those for the plant-plasticized sample, are in good agreement.

In addition to the data in Table III many other analyses confirm the conclusions that the laboratory method gives reproducible results comparable to those obtained with plant-plasticized samples.

Summary

A procedure for plasticizing fats in the laboratory, using a Hobart Kitchen Aid Mixer (Model K-4-B), has been described. The data indicate that this procedure is applicable to the common types of baking shortening for determining their pound-cake volume value and gives results in agreement with those obtained on plant-plasticized samples. The apparatus is relatively inexpensive and easy to assemble and operate. The procedure is fast and simple and has proven to be a helpful research tool in evaluating experimental shortenings.

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Recent Advances in in-Situ Epoxidation Reactions with Resin Catalysts[1]

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IN THE LAST SEVERAL YEARS the preparation of epoxy or oxirane compounds by the epoxidation of unsaturated fatty acids or esters with hydrogen peroxide or peracetic acid has assumed the role of a unit operation. Although perbenzoic acid was employed in the original synthesis of epoxides in 1909 (10), this reaction has been carried out with other peracids. The most prominent among these has been peracetic acid (3, 4, 6, 12).

Recently *in-situ* epoxidation procedures have been developed in which hydrogen peroxide is used as the oxidant. This eliminates the necessity of using a preformed peracid. Peracid formation and reaction with the double bond occur simultaneously with approximately stoichiometric amounts of hydrogen peroxide.

The first published *in-situ* process was described in the patent literature (9) and employed formic acid and hydrogen peroxide.

A procedure, developed in our laboratories, for the *in-situ* epoxidation of unsaturated fatty acid esters, employing acetic acid and hydrogen peroxide, has been described (4). In this process hydrogen peroxide is added to an acetic acid solution of the unsaturated ester in the presence of an acid catalyst

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[1] Presented at the 29th fall meeting of the American Oil Chemists' Society, October 10–12, 1955, Philadelphia, Pa.

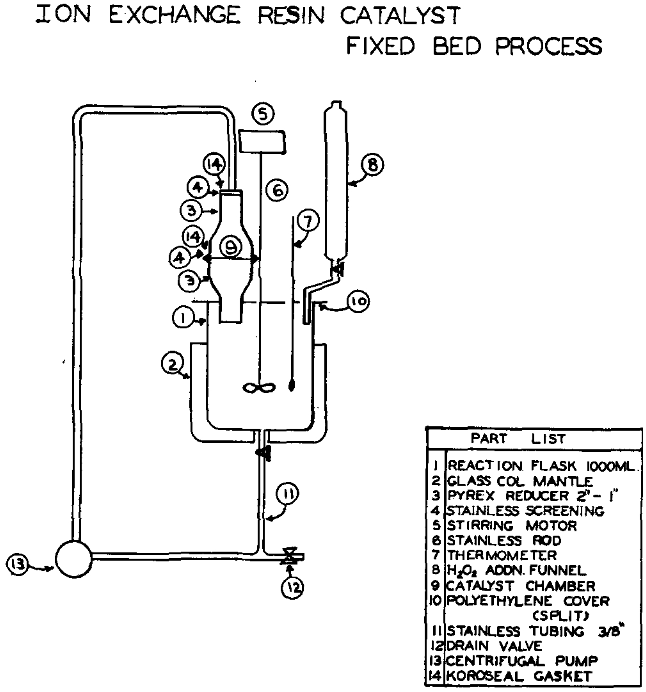
(sulfuric acid, alkane sulfonic acid, or a strong sulfonic-acid type of cation exchange resin) at temperatures of 60–70°C. Optimum yields are obtained at a controlled molar ratio of 0.5 acetic acid to 1.0 of ethylenic unsaturation in 8 to 14 hrs.

The resin catalysts are of particular appeal for the epoxidation of polyunsaturated esters (*e.g.*, soybean oil) giving higher conversions (7) to epoxide than either sulfuric or alkane sulfonic acids. At the optimum catalyst level of 25%, resin catalyst systems are uneconomical because of the high cost of resin. Further work has been undertaken in our laboratories to develop economical and practical processes with resin catalyst. Two procedures have been studied; one included the circulation of reactants through a fixed resin catalyst bed and the other used expendable quantities of ion exchange resin.

Experimental

Continuous Flow—Fixed Bed

Attempts continually to reuse the resin catalyst (7) in batch procedures (25% level) resulted in pronounced fragilation, swelling, and degradation of the resin after several reuses. Filtration of the degraded resin became difficult, and concurrently epoxy yields gradually fell off in successive runs. Thus it was conceived that fixing the catalyst in a bed would minimize mechanical action as a cause of fragilation and reduce resin handling.



ION EXCHANGE RESIN CATALYST
FIXED BED PROCESS

PART LIST	
1	REACTION FLASK 1000ML.
2	GLASS COL MANTLE
3	PYREX REDUCER 2"- 1"
4	STAINLESS SCREENING
5	STIRRING MOTOR
6	STAINLESS ROD
7	THERMOMETER
8	H_2O_2 ADDN. FUNNEL
9	CATALYST CHAMBER
10	POLYETHYLENE COVER (SPLIT)
11	STAINLESS TUBING 3/8"
12	DRAIN VALVE
13	CENTRIFUGAL PUMP
14	KOROSEAL GASKET

FIG. 1.

In this system (Figure 1) 300.0 g. of soybean oil (iodine value 135, equivalent to 1.59 moles of ethylenic unsaturation) were dissolved in 49.5 g. of acetic acid (0.82 mole) and heated to 50°C. The mixture was circulated through the resin bed, containing 42.0 g. of sulfonic-acid type of cation exchange resin[2] (dry weight basis). To this 119.0 g. of 50% hydrogen peroxide (1.75 moles) were added over a two-hour period. The temperature was then raised to 60°C. and controlled between 60° and 65°C. until the reaction was completed (6–7 hrs.), as indicated by periodic titration of the reaction mixture for residual hydrogen peroxide. The recycle rate (240 cc. per min.) was measured after the hydrogen peroxide addition and at the end of the reaction. Repeated runs were made in this system to determine the maximum number of cycles possible. A typical isolated product contained 6.5% oxirane oxygen and had an iodine value of 6.0.

After 8 to 10 runs resin fragilation and degradation were encountered, and the flow was reduced to about one-half of the initial rate. Some degraded resin was observed as an insoluble resin film on the inside wall of the reactor. Screen plugging also occurred. However, in spite of these diffculties, the bulk of the resin remained active, as determined by removal of the resin from the catalyst chamber and subsequent evaluation in a batch type of preparation.

Continued work in our laboratories has shown that the resin attack is closely associated with metallic contamination of the resin. This may initially result from the resin, reactants, or reaction vessel. Resin life has been greatly prolonged when care was taken to eliminate contamination. These studies will be reported in a later paper.

Expendable Resin Process

The use of minor amounts of resin catalyst (4) was also further investigated.

A simple, practical, and economical process, utilizing expendable amounts of resin catalyst, has now been developed. In essence it is a modification of the previously described *in-situ* process (4), employing higher temperatures. Typical epoxidations of mono- and polyunsaturated fatty acid esters by this process follow:

Epoxidation of Butyl Oleate. Some 100.0 g. of butyl oleate (iodine value 76, equivalent to 0.299 mole of ethylenic unsaturation) were weighed into a three-neck flask equipped with a reflux condenser, thermometer, and mechanical stirrer. To this 9.0 g. of glacial acetic acid (0.150 mole) and 0.62 g. of sulfonic-acid type of cation exchange resin[2] (dry weight basis) were added, and the mixture was warmed to 60°C. Then 22.36 g. of 50% hydrogen peroxide (0.329 mole) were added over a two-hour period. The temperature was raised to 75°C. and controlled between 75° and 80°C. until the reaction was completed, usually 8 to 9 hrs. The mixture was poured into a separatory funnel, and the aqueous layer and resin were drawn off. The oil layer was washed with successive portions of warm water (40–50°C.) until free of acetic acid, dried with anhydrous magnesium sulfate, and filtered. The resultant product showed the following analysis:

% oxirane oxygen	3.8
Iodine value	3.6

Epoxidation of Soybean Oil. The 100.0 g. of soybean oil (iodine value 135, equivalent to 0.532 mole of ethylenic unsaturation) were dissolved in 16.0 g. of glacial acetic acid (0.266 mole) and reacted (as in the above example) with 39.8 g. of 50% hydrogen peroxide (0.585 mole) in the presence of 1.12 g. of sulfonic-acid type of cation exchange resin[2] (dry

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[2] The catalyst concentration was calculated on the combined weight of acetic acid and hydrogen peroxide and on the dry weight of resin. The acid form of Amberlite IR-120, Chempro C-20, Dowex 50X, Nalcite HCR, Permutit Q, and other equivalent resins may be used interchangeably.

weight basis). The reaction was complete in 7 to 8 hrs., and the product was isolated as previously described. The resultant epoxy soybean oil showed the following analysis:

% oxirane oxygen	6.3
Iodine value	3.4

Analytical. The hydrogen peroxide was analyzed by the ceric sulfate method (8). The % oxirane oxygen was determined by both the ether-HCl method (11) and the direct potentiometric titration with acetic acid and HCl (2). The Wijs Method (1) was used for the determination of the iodine value.

Discussion

The effect of molar ratio of acetic acid to unsaturated ester was studied. The procedure followed was as described in the two examples above, except for the variations noted. High molar ratios of acetic acid to ethylenic unsaturation resulted in complete epoxy ring-opening while good yields of epoxy ester were obtained at molar ratios from 0.5 to 1.5 acetic acid to 1.0 of ethylenic unsaturation (Table I). Reaction times were decreased as the molar ratio was increased.

TABLE I

The Effect of Various Molar Ratios of Acetic Acid to Unsaturated Ester on Epoxy Ester Yields

(Soybean oil [1.0 mole of ethylenic unsaturation] dissolved in glacial acetic acid was epoxidized with H_2O_2—50% [1.1 moles] at 50-65°C. in the presence of a 5% cation exchange resin catalyst [a])

Molar ratio acetic acid—unsaturated ester	Reaction time	Oxirane oxygen	Yield [b] epoxy ester	Iodine value	Reacted [c]
	hrs.	%	%		%
0.5 : 1.0	8.3	6.5	83.5	2.3	98.3
1.0 : 1.0	5.6	6.3	80.8	5.7	95.8
1.5 : 1.0	5.2	5.9	75.7	5.0	96.3
5.0 : 1.0	4.0	0.0	0.0	3.0	97.8

[a] Catalyst concentration calculated on the combined weight of H_2O_2 + acetic acid and on the dry weight of the resin.

[b] Calculated from the % theoretical epoxy based on original iodine value.

[c] Calculated from the double bonds reacted.

The influence of temperature on reaction efficiency is noted in Table II. Epoxy ester yields and reaction rates increased as the temperature was raised from 60–65° to 75–80°C.

TABLE II

The Influence of Temperature on Reaction Efficiency

(Soybean oil [1.0 mole of ethylenic unsaturation] dissolved in glacial acetic acid [0.5 mole] was epoxidized with H_2O_2—50% [1.1 moles] in the presence of a 2% cation exchange resin catalyst [a])

Temp. range	Reaction time	Oxirane oxygen	Yield [b] epoxy ester	Iodine value	Reacted [c]
°C.	*hrs.*	%	%		%
60°-65°	23.0	5.9	75.7	3.1	97.7
70°-75°	8.3	6.1	78.3	5.0	96.3
75°-80°	7.2	6.3	80.8	3.4	97.5

[a] Catalyst concentration calculated on the combined weight of H_2O_2 + acetic acid and on the dry weight of the resin.

[b] Calculated from the % theoretical epoxy based on original iodine value.

[c] Calculated from the double bonds reacted.

The effect of catalyst concentration on epoxy ester yield is given in Table III. Maximum epoxy ester yields were obtained at the 2–5% catalyst level.

TABLE III

The Effect of Resin Catalyst Concentration on Epoxy Ester Yield (Soybean oil [1.0 mole of ethylenic unsaturation] dissolved in glacial acetic acid [0.5 mole] was epoxidized with H_2O_2 50% [1.1 moles] at 75°-80°C. in the presence of a cation exchange resin catalyst [a])

Resin catalyst	Reaction time	Oxirane oxygen	Yield [b] epoxy ester	Iodine value	Reacted [c]
%	*hrs.*	%	%		%
0.5 [d]	12.0	5.0	64.2	6.1	95.5
1.0	11.5	5.9	75.7	1.8	98.7
2.0	7.2	6.3	80.8	3.4	97.5
5.0	6.5	6.5	83.5	3.1	97.7

[a] Catalyst concentrations calculated on the combined weight of H_2O_2+ acetic acid and on the dry weight of the resin.

[b] Calculated from the % theoretical epoxy based on original iodine value.

[c] Calculated from the double bonds reacted.

[d] 80°-85°C.

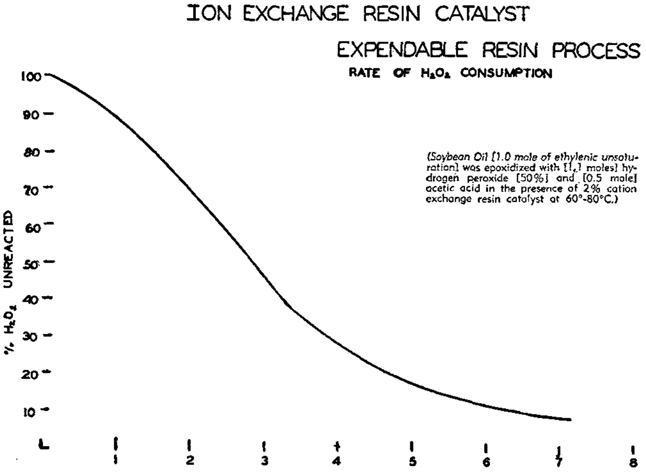

FIG. 2.

The reaction rate is shown in Figure 2. The percentage yield of epoxy ester is calculated from the percentage theoretical epoxy, based on original iodine value. The percentage reacted refers to the percentage of the total double bonds reacted.

Optimum yields of epoxy esetr were obtained in the Becco *in situ* epoxidation process with expendable resin catalyst at a ratio of 0.5 mole acetic acid to 1.0 mole of ethylenic unsaturation at 75–80°C. in the presence of a 2% strong sulfonic-acid type of cation exchange resin catalyst.

Summary

Two new resin catalyst systems for *in-situ* epoxidation have been described. One technique features the continuous circulation of the reaction mixture through a fixed resin catalyst bed. The other, a simple, practical and economical process, employs expendable amounts of resin catalyst.

Yields of 75–85% epoxy ester with very little residual unsaturation were readily obtained.

Acknowledgment

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REFERENCES

1. American Oil Chemists' Society, "Official and Tentative Methods," Cd—1-25.
2. Durbetaki, A. J., J. Am. Oil Chemists' Soc., *33*, 221 (1956).
3. Findley, T. W., Swern, Daniel, and Scanlan, J. T., J. Am. Chem. Soc., *67*, 412 (1945).
4. Gall, R. J., and Greenspan, F. P., Ind. Eng. Chem., *47*, 147 (1955).
5. Greenspan, F. P., J. Am. Chem. Soc., *68*, 907 (1946).

6. Greenspan, F. P., and Gall, R. J. (Becco), U. S. Patent 2,692,271 (1954).
7. Greenspan, F. P., and Gall, R. J., J. Am. Oil Chemists' Soc., *33*, 391 (1956).
8. Greenspan, F. P., and MacKellar, D. G., Anal. Chem., *20*, 1061 (1948).
9. Niederhauser, W. D., and Koroly, J. E. (Rohm and Haas), U. S. Patent 2,485,160 (1949).
10. Prileschajew, N., Ber., *42*, 4811 (1909).
11. Swern, Daniel, Findley, T. W., Billen, G. N., and Scanlan, J. T., Anal. Chem., *19*, 414 (1947).
12. Terry D. E., and Wheeler, D. H. (General Mills), U. S. Patent 2,458,484 (1949).

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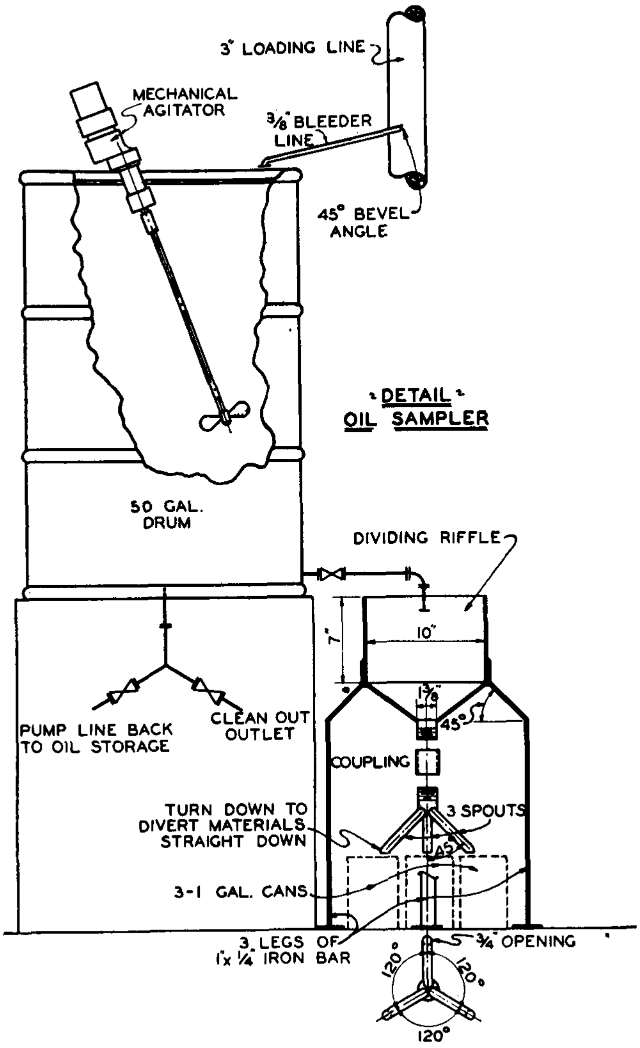
Interim Report of A.O.C.S. Subcommittee on Continuous Flow Sampling of Oils—1956

THE FOLLOWING REPORT constitutes the recommendation of the Subcommittee on Continuous Sampling as a revision of the Petcock sampling method, paragraph D(a) of Method C 1-47. This method was rejected by the Uniform Methods Committee as being too cumbersome. However the subcommittee feels that this is an excellent method of sampling and accuracy should not be sacrificed for simplicity. The proposed procedure is intended as a replacement for the Petcock method only (C 1-47, d) and has no bearing on other sampling procedures such as the Core, Bomb, Trier, or Thief procedures. Although the proposed continuous method does not have A.O.C.S. official sanction, the procedure is being published as a matter of information for those who might be interested. However the subcommittee is being continued to further its search for something more simple.



Sampling

D. Procedure:

a) Continuous Flow Method for Sampling Tank or Tank Cars During Loading or Unloading.

1. If the conditions are suitable, this is a very satisfactory method of sampling. This method is applicable only if the product is completely liquid and free-flowing and does not contain any material that may plug the bleeder line.
2. A bleeder line, ⅜ in. minimum inside diameter, with a slight downward slope is located in a vertical section of the pumping line through which the product is continuously flowing upward to the individual tank or tank car being sampled. The sample line should be located as far away from elbows or tees as possible, should penetrate to the center of the pumping line, should be cut beveled at the end looking downward, and should discharge into a sample tank or drum as illustrated in the accompanying sketch. The sample line should not have a petcock.
3. The metal sample tank or drum is of approximately 50-gal. capacity. Just above the bottom a ⅜ in., draw-off line equipped with petcock is installed, and leads into a dividing riffle, which discharges through separate lines into three 1-gal. sample cans. At the center of the tank bottom a wye is installed to facilitate emptying the sample tank; the two emptying lines are each equipped with a petcock, one line serving to pump or drain unused oil back to storage or to the tank car, the other to act as a clean-out line. To prevent loss of solvent by evaporation, a suitable metal cover, with slots or holes to permit insertion of sampling pipe and mixer shaft, should be placed over the sample tank or drum during the sampling and mixing operation.
4. Prior to the start of the pumping period, the sampling equipment should be examined and the draw-off lines closed. During the pumping period it should be made certain that a continuous flow of oil is being obtained. When the filling of the tank or tank car has been completed, the mechanical mixer is started, and the gross sample is mixed thoroughly in order to obtain uniform distribution of moisture, meal, and impurities. After thorough mixing, with the agitator still running, the draw-off line is opened, and three 1-gal. samples withdrawn through the dividing riffle into new and dry 1-gal. containers to a level about 2 in. from the top. The sample containers are immediately closed and properly labeled.
5. The unused oil remaining in the sample tank is returned to oil storage or to the tank car if the official weight were obtained prior to sampling, and the tank is thoroughly cleaned by flushing, washing, and drying, or other suitable means, depending upon conditions. The cleaning procedure should be such however that there will be no contamination of the next sample drawn.

NOTE: Where multiple loading or unloading facilities are in use, a separate sample tank should be available for each unit although individual agitators and dividing riffles are not required.

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