process using the new Hermetic Vegetable Oil Separator. The crude oil and lye are proportioned together, mixed continuously and separated, all under pressure.

The refined oil leaves the primary Hermetic Separator, water is added to the oil to wash out the small amount of soap remaining and is separated in the Hermetic Water-Wash Separator, all under pressure. The washed oil flows on through the vacuum drier, through a cooler, and to storage.

A novel feature in refining, easily accomplished by the use of the Hermetic Separator, is to substitute soda ash for caustic soda as the reagent and then refine. The refining efficiency will be comparable to the older soda ash system, but look at the advantages:

1. No dehydration.
2. No rehydration soda ash dosage.
3. No difficulty in discharging viscous soda ash soap.

When operating under pressure, the soda ash will not release carbon dioxide and cause frothing in the oil. The carbon dioxide and bicarbonate formed are soluble in the soap phase.

In fields related to caustic and soda ash refining there are obvious advantages for the Hermetic Separator in degumming and miscella refining.

In degumming, it has been possible to produce gums analyzing over 80% acetone-insoluble content on a dry basis. These highly concentrated viscous gums are readily discharged by the Hermetic Separator, operating under moderate pressure.

The use of the Hermetic Separator for refining miscella is logical when it is realized that a closed pressure system is necessary on account of the hexane present with the vegetable oil. With pressure within the bowl of the centrifuge the system may be operated at higher temperatures which give better separation efficiency, both in refining and water washing.

Also in connection with new processes the latest Refining Unincorporated process, the ammonia refining system, should be mentioned. In this, ammonia is used as the reagent to remove the fatty acids and gums. The thick soapstock is easily discharged with the Hermetic Separator under pressure. Also, due to the closed pressure system, there is no escape of ammonia during processing.

The model VO-194 De Laval Hermetic Separator has been thoroughly tested in the new vegetable oil pilot plant of the manufacturer before being introduced to the industry. Here, exhaustive tests on the efficiency of separation of the machine were made, and the machine was studied in actual operation on various types of vegetable oil refining. The pilot plant was built to duplicate field conditions, and oil was actually refined at the rate of half a tank car per day. The pilot plant is shown in Figure 5.

As a result of these tests, and the experience of the Swedish affiliates with their Short Mix Refining Process, it is felt that all conditions that will be en-
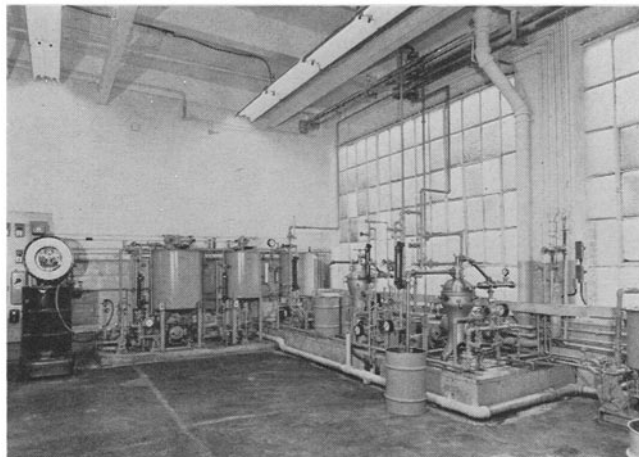

FIG. 5

countered in the field with this machine have been anticipated.

The new De Laval Hermetic Vegetable Oil Separator will have many advantages in refining. Among them are the following:

1. Discharges drier soap.
2. Separates soapstock from oil more efficiently.
3. Improves the quality of the oil.
4. Improves the refining yields.
5. Simplifies operational procedure.
6. Reduces handling costs in treating soapstock. The drier soapstock reduces the problem of water handling, always present in wet, soft soapstock.
7. Permits easier control of variations in the discharge of the soapstock or the refined oil.
8. Permits adjustment of the neutral zone while it is in operation.
9. Can be cleaned without dismantling the bowl. All meal and soap may be removed from the bowl while the centrifuge is running.

Taken together, these points add up to higher oil yields, a better product, and more profits for the processor.

Epoxidation of Methyl Oleate With Hydrogen Peroxide [1]

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ORGANIC peracids, which are conveniently formed from hydrogen peroxide and organic acids, were first used in the epoxidation of unsaturated compounds by Prileschajew (9). The epoxidation reaction however has remained a laboratory curiosity until recent years. At present there is con-

siderable interest in the epoxidation of natural fats and oils as a means of utilizing these surplus materials in the manufacture of chemical products and intermediates.
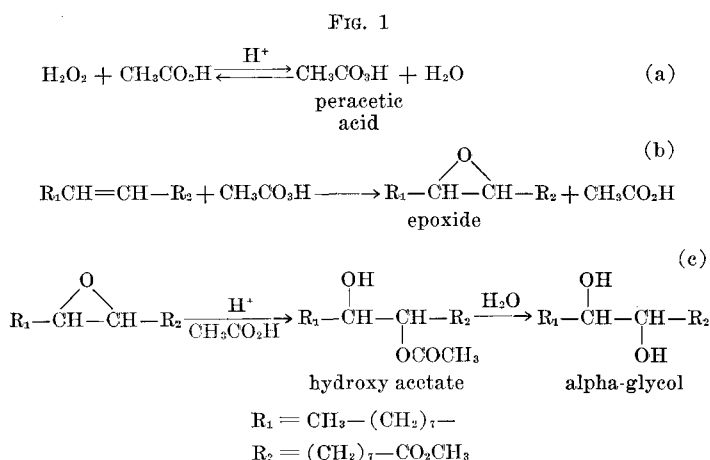
To take advantage of the great number of actual and potential uses (2) for epoxy derivatives, the chemical manufacturer should have available an efficient and economical epoxidation process. An in-

vestigation has been made in this laboratory on the epoxidation of methyl oleate with the aim of utilizing the active oxygen of hydrogen peroxide as effectively as possible. For practical reasons the suitability of some common materials of construction for these reactions has also been determined.

Improved Hydrogen Peroxide Efficiency

High conversion of hydrogen peroxide to peracetic acid and nearly quantitative reaction of the peracid with methyl oleate are both essential for maximum hydrogen peroxide efficiency. These reactions, illustrating the main product as well as further oxidation products, are given in Figure 1.

FIG. 1

$$H_2O_2 + CH_3CO_2H \underset{}{\overset{H^+}{\rightleftharpoons}} CH_3CO_3H + H_2O \quad (a)$$

peracetic
acid

$$(b)$$

$$R_1CH{=}CH{-}R_2 + CH_3CO_3H \longrightarrow R_1{-}\overset{O}{\overset{/\backslash}{CH{-}CH}}{-}R_2 + CH_3CO_2H$$

epoxide

$$(c)$$

$$R_1{-}\overset{O}{\overset{/\backslash}{CH{-}CH}}{-}R_2 \xrightarrow[CH_3CO_2H]{H^+} R_1{-}\overset{OH}{\underset{OCOCH_3}{\overset{|}{CH}}}{-}\overset{|}{CH}{-}R_2 \xrightarrow{H_2O} R_1{-}\overset{OH}{\overset{|}{CH}}{-}\overset{OH}{\overset{|}{CH}}{-}R_2$$

hydroxy acetate   alpha-glycol

$$R_1 = CH_3{-}(CH_2)_7{-}$$

$$R_2 = (CH_2)_7{-}CO_2CH_3$$

As shown in Figure 1, hydrogen peroxide and glacial acetic acid react to give an equilibrium mixture of peracetic acid, acetic acid, hydrogen peroxide, and water. The equilibrium constant (K) for this reaction at room temperature is about 2.5 (1, 6, 8). If equimolar quantities of 50% hydrogen peroxide and acetic acid are used, this value for K shows that only a 40% conversion to peracetic acid can be expected. Increasing the ratio of acetic acid to hydrogen peroxide to 10:1 should result in about a 90% conversion to peracetic acid. In fact, 90% conversion to peracetic acid is actually obtained in 16 to 20 hours at room temperature, using sulfuric acid (1%) as catalyst. Use of high ratios of acetic acid to hydrogen peroxide also results in higher yields of epoxy oxygen (4.51%) since a greater amount of hydrogen peroxide is being converted to the active peracid.

A potential saving in the manufacture of epoxides has been obtained by reducing the ratio of peracetic acid to methyl oleate. Published procedures (3, 10, 12) for epoxidation of unsaturated fatty acids or esters generally recommend at least equimolar and often a 10-20% molar excess of peracid per mole of unsaturation. Unexpectedly, it has been found that essentially the same amount of methyl 9,10-epoxystearate is obtained whether a 1.1:1, 1.0:1 or 0.9:1 molar ratio of peracetic acid to methyl oleate is employed. In each case the yield of epoxide based on methyl oleate was 87-88%. The yield based upon the hydrogen peroxide initially used to make the peracetic acid however increased from 70% to 85% when the ratio of peracetic acid to methyl oleate was decreased from 1.1:1 to 0.9:1. Practically all of the peracetic acid was used in forming the epoxide. The

amount of epoxide obtained corresponded very closely to that expected from the peracetic acid initially present. The reaction product contained a small amount of unreacted methyl oleate. An excess of peracetic acid apparently permits additional by-product formation with a corresponding reduction in unreacted methyl oleate at the expense of additional hydrogen peroxide consumption. To eliminate the variation due to different conversions of hydrogen peroxide to peracetic acid, comparative experiments were made with the same peracetic acid solution. The results of these experiments are summarized in Table I.

TABLE I
Efficiency of H_2O_2 in Epoxidation of Methyl Oleate With Preformed Peracetic Acid

| Molar Ration of Peracetic Acid to Methyl Oleate | Yield of Methyl Epoxystearate Based Upon | | Unreacted Methyl Oleate | By-Products or Loss (Calcd. by Difference) |
	Methyl Oleate	H_2O_2 Init. Used		
	%	%	%	%
0.9:1	87.6	85.0	9.8	2.6
1.0:1	88.6	77.0	6.4	5.0
1.1:1	88.2	69.7	3.9	7.9

Under ordinary conditions it is necessary to neutralize or destroy the strong acids used to catalyze peracetic acid formation prior to epoxidation with the preformed peracetic acid solutions. Failure to remove the catalyst causes cleavage of the epoxy ring (Equation c) to form the corresponding hydroxy acetate. A sulfonic acid ion-exchange resin is of interest as a catalyst since the resin can be separated easily from the peracid solution and used repeatedly. The danger of leaving traces of unneutralized acid catalyst in the peracetic acid solution is also eliminated. Table II shows that a 10% concentration of solid acid resin was about equal to 1.5% sulfuric acid in catalyzing the formation of peracetic acid.

TABLE II
Formation [a] of Peracetic Acid With a Sulfonic Acid Resin [b]

Catalyst	Time	Peracetic Acid	UnreactedH_2O_2
	(Hrs.)	(%)	(%)
1.5% sulfuric acid	3	83.3	14.8
3% resin [b]	4½	79.5	17.2
10% resin [b]	3	82.7	15.6

[a] Using 6.66:1 molar ratio of glacial acetic acid to "Albone" 50 hydrogen peroxide at 40°-45°C.
[b] "Amberlite" IR-120 (Rohm and Haas Company) sulfonic acid resin.

Experimental Procedure

Preparation of Paracetic Acid. A solution containing 300 g. of glacial acetic acid, 3 g. of concentrated sulfuric acid, and 34 g. (0.5 moles) of 50% aqueous H_2O_2 was held at room temperature for 20 hours. At the end of that time, analyses by the ceric sulfatesodium thiosulfate procedure (4) showed that the solution contained 3.16 g. (9.6%) of unreacted H_2O_2 and 33.1 g. (87.2% conversion) of peracetic acid.

Epoxidation of Methyl Oleate. In a 200-ml., threenecked flask equipped with a mechanical stirrer, thermometer, and dropping funnel was placed 69.8 g. of peracid solution containing 6.84 g. (0.09 moles) of peracetic acid. This corresponds to 7.05 g. (0.103 moles) of 50% H_2O_2 initially required to form the

TABLE III

Effect of Materials of Construction on Peracetic Acid Formation and Epoxidation of Methyl Oleate

Material	Peracetic Acid Formation		Yield of Methyl Epoxystearate Based Upon		Unreacted Methyl Oleate	By-Products or Loss (Calcd. by (Difference))
	Peracetic Acid	H_2O_2	Methyl Oleate	H_2O_2 Init. Added		
	%	%	%	%	%	%
S. S. 304, 316, 321, 329, 430.. All coupons in same solution and reaction mixture (av. of 4 expts.)	79.6	13.6	80.0	69.7	9.8	10.2
S. S. 316 only.. (av. of 6 expts.)	81.3	13.6	81.6	73.7	8.4	10.0
None .... (av. of 2 expts.)	80.1	13.2	80.9	72.0	8.3	10.9

peracetic acid. After 3.5 g. of sodium acetate trihydrate had been added to neutralize the sulfuric acid catalyst, 29.6 g. (0.19 moles) of technical methyl oleate (iodine number = 85.5) were added dropwise during 22 minutes at 28-31°C. Occasional cooling of the reaction flask with ice water was necessary to maintain this temperature range. The temperature of the reaction mixture was then allowed to rise to about 45°C. for one hour. The mixture was diluted with water, and an oily layer separated. The oil was washed with a sodium bicarbonate solution, water, and dried under reduced pressure for one hour on a steam bath. There were obtained 31 g. of light yellow oil which, according to the hydrogen chloride-ether procedure (11), had an epoxy oxygen content of 4.51% (theory = 5.12%). An iodine number of 8.4 was obtained by the iodobromide method (5). The yield of epoxide was 87.6% based on methyl oleate employed.

NOTE: In epoxidation, the heat of reaction is more easily assimilated by the surroundings when the peracid solution is added to the fatty oil. Therefore, for larger quantities, the latter method of addition is suggested.

Materials of Construction

An important aspect of commercial epoxidation is the type of material required for the equipment. Preliminary tests indicate that several of the stainless steels are quite satisfactory from the standpoints of both corrosion resistance and effect on the reaction. Duplicate coupons of Stainless Steels 304, 316, 321, 329, and 430 and a single coupon of 2S Aluminum were suspended half-way in a solution containing glacial acetic acid, sulfuric acid, and 50% hydrogen peroxide at 40-45°C. After three hours, sodium acetate trihydrate was added to neutralize the sulfuric acid catalyst; then methyl oleate was added slowly. Epoxidation was conducted at about 45°C. Approximately five hours were required for each cycle of peracid formation and epoxidation. The metal coupons were weighed after each exposure to determine the loss of weight, then exposed again to peracid formation and to the epoxidation reaction. Analyses of the products from each experiment showed that the metals exerted no adverse effect on yield of epoxide (Table III).

Mild steel (1020) was exposed separately to peracid formation, but the coupons were attacked severely (4% loss in weight) and caused rapid and exothermic decomposition of hydrogen peroxide and peracetic acid. The 2S aluminum coupon showed considerable etching and staining while none of the stainless steel coupons showed any visible change over the surface area. The corrosion rates, calculated on a continuous basis, are given in Table IV.

TABLE IV

Rate of Corrosion of Various Metals of Construction During Peracetic Acid Formation and Epoxidation Reaction

Metal	Loss of Wt., g. (W)	Exposure Hours (T)	Surface Area, cm.² (A)	Density g./cm.³ (S)	Continuous Corrosion Rate, mils/yr. (C)
S. S. 316	0.0020	68	34.6	8.03	0.37
S. S. 316	0.0015	68	34.6	8.03	0.27
S. S. 304	0.0005	43	34.7	7.90	0.15
S. S. 304	0.0007	43	34.7	7.90	0.21
S. S. 321	0.0004	43	22.6	7.98	0.18
S. S. 321	0.0004	43	24.1	7.98	0.17
S. S. 329	0.0009	43	41.4	7.69	0.23
S. S. 329	0.0010	43	41.6	7.69	0.25
S. S. 430	0.0008	43	30.7	7.71	0.27
S. S. 430	0.0010	43	28.4	7.71	0.37
2S Aluminum	0.0142	21	32.0	2.71	26.90

$$C = \frac{3,450,000 \ W}{(S) \ (A) \ (T)} \ mils/year$$

Precautions in the Use of Hydrogen Peroxide

Mixtures of organic materials and hydrogen peroxide (especially high strength) are sometimes explosive. Most of the reaction mixtures are easily handled (2) if the inherent hazards are recognized beforehand. In general, systems containing more than 5% active oxygen should be handled carefully.

Summary

Simple addition of hydrogen peroxide to a 10 molar excess of glacial acetic acid in the presence of sulfuric acid catalyst gave about 90% conversion to peracetic acid in the peracid preforming step.

Improved hydrogen peroxide efficiency in the epoxidation step was obtained by using a 0.9 :1 molar ratio of preformed peracetic acid to methyl oleate. Under these conditions most of the peracetic acid was used in forming the epoxide.

Stainless Steels 304, 316, 321, 329, and 430 are satisfactory as materials of construction from the standpoint of both corrosion resistance and effect on the reaction.

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