acid band and shifted it a few millimicrons higher toward the acid frequency. The alcohol formed from the hydroperoxide increased the intensity of the alcohol absorption and caused the band to shift slightly to a lower wavelength. The carbonyl intensity was decreased, and the band maximum was shifted a little lower, probably because some of the water-soluble aldehydes were washed out. Acid removal with NaHCO₃ also diminished the intensity of the acid-hydroperoxide band but shifted the band maximum a few millimicrons lower, toward the hydroperoxide frequency. Alcohol absorption was unaffected. The carbonyl band was affected exactly as with KI reduction. When the reduced sample was itself washed with NaHCO₃, the acid-hydroperoxide band was further lowered and broadened. Alcohol hydroxyl was little affected. Carbonyl was further decreased, probably because more aldehyde was washed out.

The near infrared, as used here, can have limited use in studying gross changes in autoxidized fats and oils and in distinguishing among their oxygenated products. Small changes and low concentrations would be difficult to detect. If more concentrated solutions are used to increase the absorbancy in slightly oxidized samples, association becomes a strongly disturbing factor. Such association makes the quantitative use of these spectra difficult. Even carbonyls are subject to some degree of association and in solution do not obey Beer's Law (8). However near infrared spectra can be quite useful in determining the components of mixtures of oxygenated compounds and in detecting impurities in reagents.

Summary

The usefulness and limitations of near infrared spectroscopy as applied to the oxygenated products of fat oxidation has been studied. Hydroperoxides, acids, alcohols, esters, aldehydes, and ketones all absorb in the narrow range from 2,700 mμ to 3,000 mμ. Alcohols may be distinguished from hydroperoxides and acids, but the latter are too close together to be resolved. In mixtures all the C=O absorptions attributable to esters, aldehydes, and ketones combine to form one band. In autoxidizing methyl oleate, the increase in alcohol, carbonyl, and combined acid-hydroperoxide can be followed in the near infrared spectra of CCl₄ solutions. In the absence of acid the increase in hydroperoxide absorbance is linear with peroxide value. The changes in the spectra of a reduced and bicarbonate-washed sample of oxidized methyl oleate correlate well with the expected chemical changes.

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Theory and Practice of Resin-Catalyzed Epoxidation[1]

A. F. CHADWICK, D. O. BARLOW, A. A. D'ADDIECO, and J. G. WALLACE

Electrochemicals Department, E. I. du Pont de Nemours and Company
Wilmington, Delaware

IN THE LAST TEN YEARS epoxidation has developed into a major method for making new products from unsaturated fatty esters and similar raw materials. This development was initiated by Swern and his co-workers (3), who discovered a practical method for using peracetic acid in the reaction. They carried out the epoxidation in two steps, first preparing the peracetic acid and then reacting it with the unsaturated compound. Further work by others has led to simplified methods in which the peracid is formed *in situ* rather than as a separate step. These methods use either formic acid (6) or a mixture of acetic and sulfuric acids (4).

In 1954 du Pont (1) announced the development of a new one-step epoxidation procedure in which a polystyrene sulfonic acid was used as the catalyst. It had previously been shown that these resins were effective catalysts for peracid formation (8). This new process made it possible to obtain higher epoxide conversions and a faster reaction.

Since the introduction of resin-catalyzed epoxidation, several adaptations of the original procedures have been proposed. The use of minimal quantities of resin (5) and the dehydration of the resin in a

vacuum oven prior to epoxidation (7) have recently been stressed.

This laboratory has studied methods for continuous operation of the resin-catalyzed epoxidation process because continuous processes usually permit greater operating efficiency. This work, which is described below, has led to the conclusion that a cascade process is the most practical. Pertinent data on the batch process are also included.

Experimental Procedures

Batch Process. A typical batch epoxidation is carried out as follows. A standard, medium-porosity grade of polystyrene sulfonic acid in its hydrogen form is washed in a column with its own volume of acetic acid to replace the water. After removal of the excess acetic acid the quantity remaining on the resin is determined by washing a small weighed portion with water and titrating the aqueous extract.

To a mechanically stirred, round-bottom flask containing 1 mole (based on double-bond content) of an unsaturated ester, such as methyl oleate or soybean oil, are added the desired quantities of resin and acetic acid. With good stirring, 1.1 moles of 50% hydrogen peroxide is added at such a rate that the

temperature rises to 60°C. in about 15 min. Cooling is used to keep the temperature at 60°–65°C. When the exothermic reaction has slowed, heat is applied to keep the temperature in this range until the desired degree of reaction has been reached. The resin is then separated from the cooled reaction mixture by filtration. The oil layer is separated and washed successively with 1% aqueous NaCl, 5% aqueous NaHCO₃, and water. The product is then dried in a vacuum at 100°C. Iodine number and epoxy oxygen content of the product are determined by the Hanus-Wijs and HBr-acetic acid procedures, respectively.

Cascade Process. Figure 1 shows a diagram of the equipment for this process. Three stirred reactors are used in series. All the reactants are fed to the first reactor. The reaction mixture overflows into the other reactors in turn. The product overflows from the third reactor.
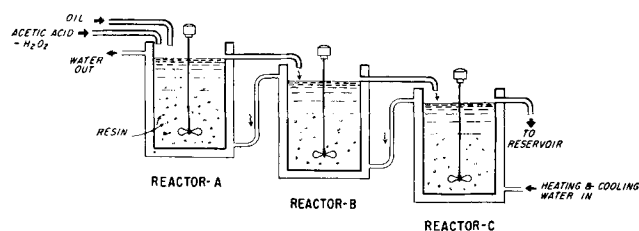

FIG. 1. Schematic drawing of cascade epoxidation.

The liquid reactants are fed through metering pumps. To simplify laboratory operation the 50% H_2O_2 and acetic acid are premixed in the desired ratio and pumped together. As continuous resin addition is impractical on this scale, the desired quantities are added at 10- to 15-minute intervals. The following is an example of a typical procedure.
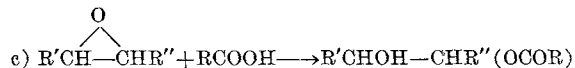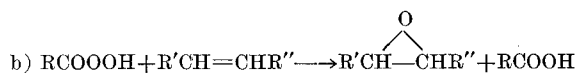
Flask A (210-ml. volume) was charged with 135 g. of technical methyl oleate (I.V. 90), 10.6 g. of glacial acetic acid, and 20.3 g. (12% by weight of oil) of polystyrene sulfonic acid resin (medium porosity) previously treated with acetic acid. The mixture was warmed to 60°C., and 35.9 g. of 50% hydrogen peroxide were added dropwise at 60°C. over a period of about 25 min.

After a hold-up of one hour (timed from the beginning of the addition of hydrogen peroxide) methyl oleate and a mixture of glacial acetic acid and 50% hydrogen peroxide (molar ratio 0.5:1) were added continuously in two separate streams to flask A at a rate of 210 ml./hr. of reactants. The reaction mixture in flask A was allowed to overflow into flask B and finally into flask C at a rate corresponding to the rate of addition of reactants. Resin catalyst (5 g.) was added to flask A every 15 minutes and allowed to overflow into flasks B and C with the reaction mixture. (Resin added in this manner maintained about a 12% proportion of resin in each flask). Stirring and a temperature of 60°C. were maintained in each flask.

The crude reaction mixture was collected in the overflow from flask C and was filtered to remove the resin catalyst. The epoxidized oil was separated from the aqueous phase and purified by the procedure described for batch reaction.

Mechanism of Reaction

The following three consecutive reactions explain the chemistry of epoxidation systems:

a) $RCOOH + H_2O_2 \rightleftharpoons RCOOOH + H_2O$

b) $RCOOOH + R'CH=CHR'' \longrightarrow R'CH\overset{O}{\overbrace{\quad}}CHR'' + RCOOH$

c) $R'CH\overset{O}{\overbrace{\quad}}CHR'' + RCOOH \longrightarrow R'CHOH-CHR''(OCOR)$

Reaction b), the actual epoxidation step, requires no catalyst and is the fastest of the three reactions. Reactions a) and c) are both acid-catalyzed. Although sulfonic acid resins are equivalent to other strong acids in catalyzing peracid formation (reaction a), they do not catalyze by-product formation (reaction c), when relatively high molecular weight raw materials are used. Many of the advantages of the resin catalysts are based on this difference from other strong acids.

The slow rate of by-product formation in resin-catalyzed epoxidation appears to be caused by lack of contact of the epoxidized oil with acid centers in the resin. Supporting this mechanism are data obtained by comparing the effectiveness of polystyrene sulfonic acid resins containing varying quantities of divinyl benzene as a cross-linking agent. The data in Table I show that, with resin containing 2% to

TABLE I
Effect of Resin Cross-Linkage[a]

Divinyl benzene (%)	Double bond removal (%)	Epoxide conversion (%)
2	73	5
4	78	7
8	91	92
12	93	96
16	90	89

[a] Reaction conditions—0.10 mol methyl oleate, 0.11 mol 50% H_2O_2, 0.05 mol acetic acid, 60% resin on oil wt., 1.5 hr. at 60°C.

4% divinyl benzene, the unsaturated compound reacts but is mostly converted to by-products. With resins cross-linked with 8% or more divinyl benzene the yields of epoxide based on the double bonds reacted are essentially quantitative. From these data it is concluded that either the structure of the less cross-linked resins is more porous or that they swell sufficiently to allow contact of the oil with the sulfonic acid groups.

Because resins do not promote by-product formation, relatively large quantities of catalyst can be used without decreasing the yield. This permits shorter reaction times than with other acids. As shown in Table II it was necessary to raise the tem-

TABLE II
Effect of Resin Quantity and Pretreatment[a]

Resin quantity[b] (%)	Type	Time (hr.)	Temperature (°C.)	Epoxide conversion (%)	Double bond removal (%)
2	Acid-wet[c]	7	80	80	90
20	Acid-wet	2.5	60	93	93
60	Acid-wet	1.5	60	93	93
20	Water-wet[d]	3	60	87	91

[a] 0.10 mole methyl oleate, 0.11 mole 50% H_2O_2.
[b] Percentage based on weight of methyl oleate.
[c] Total acetic acid 0.05 mole.
[d] Total acetci acid 0.10 mole.

perature to 80°C. to effect reaction in 7 hrs. with 2% resin. When an excess of resin was used, 60% of the oil weight, better conversions were obtained and reaction time was reduced to 1.5 hr. at 60°C. In contrast, soluble acid catalysts require reaction periods of 6 hrs. or more for best results (4, 6).

A major problem with this process is to obtain a satisfactory life of the resin catalyst. One cause of resin breakdown is oxidation, which is catalyzed by heavy metals. Because of this, reduction of metallic impurities in the epoxidation system will improve resin life. The data in Table III show that purity of

TABLE III
Productivity of resin

Raw material	Grade of resin	Grams epoxidized/ gram resin
Methyl oleate	Regular[a]	130
Soybean oil	Regular[a]	50–60
Soybean oil	Low metal[b]	170

[a] "Amberlite" IR-120, "Chempro" C-20, "Dowex" 50-X-8, "Nalcite" HCR, and "Permutit" Q.
[b] "Dowex" 50 W (low metal).

resin and raw material both affect resin life. In this table resin life is expressed as productivity, i.e., weight of oil processed per unit weight of resin. For these studies the resin was re-used until it was no longer effective in giving a good epoxide yield. With relatively pure methyl oleate, resin productivity was 130 whereas it was only 56–60 with soybean oil which contained about 50 ppm. of iron. When a special resin containing only 10 ppm. iron was used, productivity was three times as good as with regular resin which may contain 300–400 ppm. iron.

A minimal resin process in which 1–2% resin based on oil weight is used and discarded after each bath will give a productivity of 50–100. However the increased temperature and time necessary reduced the epoxide yield. Table IV compares data obtained with

TABLE IV
Batch Soybean Oil Epoxidation[a]

Percent resin[b]	Time (hr.)	Temperature (°C.)	Epoxide conversion[c]	By-product[c] (%)
1	7	80	81	12
2	7	80	84	14
15	4	60	93	3

[a] 10% excess of 50% H₂O₂, 0.5 mol acetic acid/mol H₂O₂.
[b] Based on oil weight.
[c] Based on double-bond content of raw material.

1 and 2% resin with the use of 15% resin. At the same level of reaction of the double bonds in the oil, the epoxide yield is about 10% higher when 15% resin is used.

A more promising method of obtaining good productivity consists of using the optimum quantity of resin and replacing a small portion after each batch. With this technique 21 consecutive batches of soybean oil have been epoxidized without apparent resin degradation. In this experiment 12% of a commercial resin (8% cross-linked) was used in the standard batch procedure outlined above. After each batch 10% of the resin was discarded, and an equal quantity of fresh resin was added. This indicates that productivities approaching 100 can be obtained. This technique can also be applied to continuous processes.

An additional advantage of this procedure is that it will permit the use of water-wet resin for the replacements. The last experiment listed in Table II shows that the use of water-wet resin requires a

longer reaction time and reduces the yield slightly. However, when only 10% of the resin charge is water-wet, this effect is slight.

Continuous Processes

For economy of operation and for product uniformity it is desirable to operate continuously wherever the quantity produced is great enough. Therefore several possible continuous processes have been studied.

Use of Resin Columns. Passing the reactants through a static resin bed in a single pass, the most obvious process, did not prove satisfactory. To obtain the contact time required to complete the reaction, it was necessary either to use an excessively large resin column or to circulate the reactants so slowly that the two phases of the heterogeneous liquid system separated, with resultant poor conversions.

Better results were obtained by recirculating the reactants through a small column until the desired degree of conversion was obtained (2). This process was operated continuously by removing a small fraction of the product as it recirculated. The chief drawback of this system was that resin degradation was concentrated in the first part contacted by the reactants. The result was that this portion of the resin disintegrated after a short period of operation and gradually plugged the column. This problem was especially acute with soybean oil because resin disintegration was faster and the viscosity of the oil increased during epoxidation.

Cascade Process. Laboratory trials indicate that the cascade process is the most promising method of continuous operation. The procedure and equipment have been described above.

The success of a cascade process depends on reaching a steady state in each reactor; the concentration of epoxide is higher in each successive reactor. Conditions must be chosen so that the conversion of reactants to products has reached the desired level in the final reactor. The variables which control the degree of conversion include the number and relative volume of reactors, rate of addition of reactants, and the temperature which is maintained in each reactor. The three reactors of equal volume used in this work were chosen to illustrate the principles involved. In practice any number of reactors can be used, depending on processing requirements.

Mathematical calculations show that when the contents of a reactor have been replaced three times in continuous operation, it will essentially have reached a steady state. With three reactors of equal volume in series, all three should have reached a steady state after the contents of the first reactor have been replaced 6.3 times. The results described below are in essential agreement with this calculation.

TABLE V
Continuous Epoxidation of Methyl Oleate[a]

Time[b] (hr.)	Epoxy O (%)	Residual iodine no.
3.0	3.7	26
4.5	4.0	17
6.5	4.4	11
7.5	4.8	8
8.5	4.7	8
9.5	4.7	8
10.5	4.8	7
11.5	4.8	7

[a] Iodine number of methyl oleate = 90. 1 mole oleate/1.1 mole H₂O₂/ 0.5 mole acetic acid. 12% resin based on oil. Temp. 60°C. Approximately 1-hr. hold-up in each reactor.
[b] Time taken from initial charge to 1st reactor. Initially this was filled. After 1 hr. continuous feed was started.

TABLE VI
Continuous Epoxidation of Soybean Oil[a]

Time (hr.)	Epoxy O (%)	Residual iodine no.
4	5.6	29
6	6.2	19
9	6.4	13
11	6.6	9
12	6.7	9
13	6.7	7
14	6.8	7
15	6.7	6

[a] Iodine No. of oil = 130. 1 mol oil/1.1 mol H_2O_2/0.5 mole acetic acid. 12% resin on oil. Temp. 60° C. in 1st 2 reactors, 70°C. in third. Approximately 80-minute hold-up in each reactor.

Table V shows the results from a typical experiment with methyl oleate, using 12% resin and an average reaction time of about 3 hrs., at 60°C. Equilibrium was reached at an epoxide conversion of about 90%. With 8% resin under these same conditions the product composition levelled out at a conversion of 81%. These results show that, as with batch reactions, about 12% resin should be used for the best results. Increasing the hold-up time however should produce results with 8% resin approaching those obtained with 12%. Economic operation will require re-use of the resin from this process. This can best be done by the partial replacement technique.

Use of a minimal quantity of resin (2% of oil weight) does not appear attractive for this process. With the temperature raised to 80°C. and a one-hour hold-up in each reactor, the conversion to epoxide was only 51%. As 58% of the unsaturation had been removed at this point, lengthening the time to increase conversion would lead to excessive by-product formation.

This process was also demonstrated with soybean oil. Using the same conditions as for methyl oleate with 12% resin, the product levelled off at 6.4%

epoxy content and an iodine number of 14. To reduce the iodine number further the hold-up time for each reactor was increased to 80 min., and the temperature in the third reactor was raised to 70°C. As shown in Table VI, this raised the epoxy content of the product to 6.7% and reduced the iodine number to 1.

Summary

Commercial polystyrene sulfonic acid resins have been shown to be effective in catalyzing epoxidation of unsaturated fatty esters with hydrogen peroxide and acetic acid because they catalyze peracid formation but do not promote by-product formation when used under proper conditions. Special resins with less cross-linkage have been shown to yield mostly by-products.

Best catalyst life has been obtained with a special resin prepared with a low metal content.

A continuous process based on the cascade principle has been demonstrated in the laboratory. The problem of resin re-use for both continuous and batch processes can best be solved by using the optimum 10–15% based on oil weight and by replacing about 10% of the resin after each use.

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Binding of Gossypol Under Conditions of Complete Rupture of the Pigment Glands

W. H. KING, VERNON L. FRAMPTON, and A. M. ALTSCHUL,
Southern Regional Research Laboratory,[1] New Orleans, Louisiana

ATTENTION HAS BEEN FOCUSED on the "free" gossypol in cottonseed meals (as determined by the A.O.C.S. method) since it is felt by poultry investigators that very small quantities of this material in cottonseed meals fed to laying hens induce egg yolk discoloration (3). Previous work (5) has shown the presence in aqueous acetone extracts of cottonseed meal of materials in addition to gossypol, which yield colored reaction products when treated with aniline. Two properties distinguish these materials from gossypol, namely, a) they cannot be extracted from aqueous acetone with benzene, and b) the absorption spectra of the aniline reaction products differ from those of dianilinogossypol. Varying quantities of these materials are found in commercial cottonseed meals, and they may account for one-half to two-thirds of the aggregate of "gossypol and gossypol-like substances" as determined by the A.O.C.S. method for "free" gossypol (1).

Raw cottonseed meats usually contain approximately 1.00% of "free" gossypol. A large proportion of the gossypol originally present in the seed is bound to the meal in the cooking operation. Most of the pigment glands are broken during rolling and cooking, and the liberated gossypol becomes bound under the influence of heat and moisture to meal constituents. The combined residual pigments (the "free" gossypol of the A.O.C.S. method), eluted by aqueous acetone in the analytical procedure, generally range from 0.02 to 0.06% in commercial meals, such as screw-pressed (2) and prepressed solvent-extracted meals, which are produced by processes involving attrition during the pressing operation. Hydraulic meals (2) usually contain approximately 0.10%, and uncooked, direct solvent-extracted meals 0.15% or more (8).

An effort has been directed toward finding a practical mechanical procedure for completely rupturing the glands so that all of the pigments can be bound to the meal in a subsequent cooking operation (6).