soap stock composition, presence of additives, hardness, and temperature. Representative data obtained by the method are presented, and a theoretical interpretation of the test is given.

REFERENCES

1. Ross, J., and Miles, G. D., Oil & Soap, *18*, 99 (1941).

2. Barnett, G., and Powers, D. H., Proc. Scient. Sect. TGA, No. *24*, 24 (Dec. 1955).

3. Masters, E. B., J. Am. Oil Chemists' Soc., *29*, 412 (1952).

4. Becher, P., J. Am. Oil Chemists' Soc., *33*, 113 (1956).

5. Krahe, F., and Shedlovsky, L., unpublished data.

6. Kolthoff, I. M., and Sandell, E. B., "Textbook of Quantitative Inorganic Analysis," p. 487, New York, Macmillan, 1936.

Epoxidation of Polyesters of Tetrahydrophthalic Acid and Unsaturated Alkyd Resins

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IN THE COURSE of an investigation carried out in our laboratory, directed toward synthesis of molecules containing a large number of epoxide groups, oxidation of unsaturated polyesters to the corresponding epoxide derivatives offered considerable interest. Particularly, epoxidized derivatives of tetrahydrophthalic acid polyesters and unsaturated alkyd resins could be important intermediate compositions from a practical standpoint. We wish to report not only the subject compositions but also processes suitable for their preparation and purification in high yield.

The efficient epoxidation of the olefin bonds of these polyesters offers the opportunity to synthesize molecules containing several epoxide groups. For example, polyesters of tetrahydrophthalic acid can be prepared containing at least 10 to 15 recurring units. Molecules containing this large number of recurring units would contain a significantly larger number of epoxide groups than herebefore commonly known, provided efficient esterification without appreciable loss in olefin and epoxidation was accomplished. Similarly, complex esters of a "medium" to "long oil" alkyd type of resin, likewise epoxidized, would give a structure of analogous character. The reaction of ethylene glycol and tetrahydrophthalic anhydride and oxidation of the resulting polyester to the corresponding polyepoxide illustrates the polyester type.
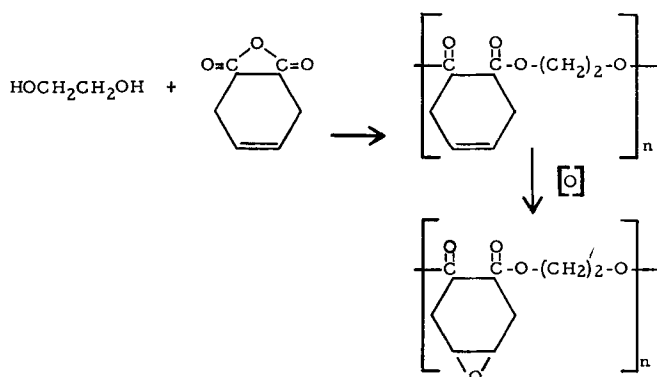
The epoxidation product of a complex ester made from pentaerythritol, phthalic anhydride, and glycerol trioleate demonstrates the oil-modified polyepoxide alkyd type.

In order to obtain polyepoxides, of the type illustrated, basic epoxidation processes already known were evaluated. However epoxidation of these polyester and alkyd type of resin compositions by a preformed peracetic acid process of Findley and
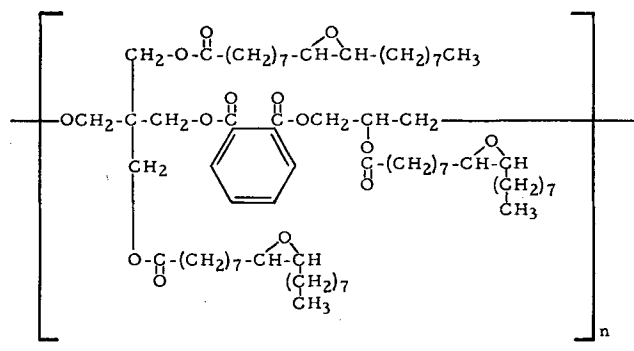

Swern (1) or of Terry and Wheeler (2) could not be advantageously used because of the difficulty of isolation and purification of the epoxidized product in the first case and side reaction of the epoxide as well in the second case. A newer *in situ* process, using a cation exchange resin of the sulfonic acid type (3, 4), has also proved unsatisfactory in yielding desired epoxides. The reduced quantity of acetic acid required by this latter process is a desirable advantage if it could be made operable for the epoxidation of the subject compositions. Schmitz and Wallace have indicated its commercial feasibility (5). We have found that the use of dehydration in vacuum at 80 to 85°C. of a carefully washed acid form of a cation exchange resin of the styrene-divinyl benzene sulfonic acid type permits efficient *in situ* epoxidation of the subject unsaturated polyesters. The dehydrated property of the dry cation exchange resin apparently is essential to their successful epoxidation.

Table I compares the use of a wet and dry cation exchange resin of the sulfonic acid type (Dowex 50-X8, 50-100 mesh). In all cases the use of a dried cation exchange resin resulted in more efficient epoxidation, and clear transparent reaction products were isolated. In the case where the wet ion exchange resin was used, milky turbid reaction products were

TABLE I
A Comparison of the Use of Wet and Dry Cation Exchange Resin

Species epoxidized	Percentage conversion to epoxide	
	Wet ion exchange resin	Dry ion exchange resin
Tetrahydrophthalic-1,5-pentanediol polyester.....	4.3	81.4
Unsaturated alkyd resin.....................................	53.1	71.5
Butyl oleate...	79.0	86.6

isolated from the reactions of the tetrahydrophthalic 1,5-pentanediol polyester and the unsaturated alkyd resin. However epoxidized butyl oleate separated from the water used to carry the hydrogen peroxide into the reaction mixture and the water by-product of the depletion of hydrogen peroxide and peracetic acid from the well known equilibrium:

$$CH_3COOH + H_2O_2 \underset{H^+}{\overset{}{\rightleftarrows}} CH_3COOOH + H_2O$$
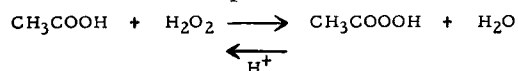
Since a dry cation exchange resin was found requisite in the epoxidation of these compositions and clear transparent products could be obtained directly from the reaction, variations in the reaction conditions were studied in order to determine trends toward optimum.

We have further found that a dehydrated strong base anion exchange resin is very effective in purification of the epoxidation reaction mixtures. Again the dehydrated property of the anion base is advantageous, probably because the water of neutralization of the free acid is tenaciously held to the exchange resin rather than allowed to contaminate and cause turbidity of the product and side reaction of the polyepoxide. Alternatively the free acetic acid may be co-distilled with aromatic solvents at sufficiently reduced temperatures and pressures so that the epoxide again does not enter into undesirable side reactions. These purification techniques are particularly advantageous where conventional purification by water washing cannot be used.

Experimental

A. PREPARATION OF UNSATURATED POLYESTERS

Preparation of Polyesters of Tetrahydrophthalic Acid. Although 1,5-pentanediol, 1,4-butanediol, ethylene glycol, and diethylene glycol were also used in preparing polyesters of tetrahydrophthalic acid, the preparation of the polyester of tetrahydrophthalic acid, and 1,5-pentanediol will illustrate the procedure used. A mixture of 167.4 g. (1.1 moles) tetrahydrophthalic anhydride and 17.8 g. (0.2 mole) n-butanol was placed in a 3-neck flask provided with a thermometer, a nitrogen inlet, a mechanical agitator, and a Dean and Stark moisture trap, to which was attached a reflux condenser. After melting the tetrahydrophthalic anhydride in the presence of the butanol, 104.15 g. (1 mole) of 1,5-pentanediol were added. The reaction mixture was gradually heated with agitation to 225°C., at which point a sufficient amount of xylene was added to give refluxing at esterification temperature. The reaction mixture was then heated with continuous agitation at 225–235°C. until the acid value decreased to 1.8. The resulting polyester had an iodine number of 98.1.

Preparation of a Typical Alkyd Resin. A typical alkyd resin was prepared as follows. To a one-liter flask provided with a condenser, a nitrogen inlet, mechanical stirrer, and thermometer were added 290 g. of white refined soybean oil. While bubbling a continuous stream of nitrogen through this oil, the temperature was raised to 250°C., at which temperature 0.23 g. of litharge was added, and the temperature was held at 250°C. for 5 min. While holding the temperature above 218°C., 68.0 g. (0.5 mole) of pentaerythritol was added, after which the temperature was raised to 238°C. and held until a mixture of

one part of the product and 2½ parts of methyl alcohol showed no insolubility (about 15 min.). At this point 136 g. (0.92 mole) of phthalic anhydride were added, and the temperature was gradually raised to 250°C. and held for 30 min.

The condenser was then removed from the flask, and the pressure was reduced somewhat by attaching a water aspirator evacuating system. With continuous agitation the mixture was then held at 250°C. until the acid value had reached 10.5. The iodine number was 78.9.

Preparation of Butyl Oleate. To a one-liter, three-neck flask equipped with thermometer, mechanical stirrer, water trap, and reflux condenser were charged 565.0 g. (2 moles) of oleic acid, technical grade, and 296.5 g. of n-butanol. The reaction was heated to reflux, and refluxing continued for 16 hrs. until the acid number was reduced to 11.2. The reaction mixture was vacuum-distilled. A fraction, weighing 392 g. and boiling at 195–201°C. at 1 mm., was collected which had an acid number of 2.2 and an iodine number of 67.2.

B. PREPARATION OF DEHYDRATED CATION EXCHANGE RESIN

The dehydrated acid form of a cation exchange resin of the sulfonated styrene-divinyl benzene type was prepared by reacting the sodium salt with excess amounts of 4 N HCl a minimum of 6 times. The acid form of the resin was then slurried with distilled water and filtered on a Buchner funnel until the filtrate was free of chlorides. The resin was pressed as dry as possible on the filter, using a rubber membrane to cover the filtering solids. The filtered resin was removed to a Pyrex tray and dried at 60–80 mm. pressure for 16 hrs. at 80–85°C.

C. EPOXIDATION

Epoxidation of tetrahydrophthalic-1,5-pentanediol polyester will illustrate the procedure used.

Some 100 g. of the acid form of the dehydrated cation exchange resin were placed in a one-liter, 4-necked Pyrex fluted resin flask equipped with Pyrex stirrer, thermometer well, addition tube, and reflux condenser. Then 30 g. (0.5 mole) of glacial acetic acid were added to the cation exchange resin so that the resin was wetted as completely as possible by the acid. A solution of 258.8 g. (one olefin equivalent calculated from the iodine number) of tetrahydrophthalic-1,5-pentanediol polyester, prepared above in 258.8 g. of xylene, was added to the reaction flask at room temperature, and the mixture was stirred. The reaction flask was provided with a water bath for heating or cooling. During 45 to 60 min. 74.8 g. (1.1 moles) of 50% H₂O₂ were added and the temperature of the reaction was increased to 48°C. After the H₂O₂ had been added, the temperature was slowly increased to 60°C. and held there for a period of 2 hrs. At this point a one-ml. sample of the solution required 0.80 ml. of 0.1 N Na₂S₂O₃ in an iodometric titration for peroxide. The reaction was filtered, using a Nylon filter membrane in a Buchner funnel, and 474 g. of resin solution (56.88% non-volatile) were isolated. The acid number of the solution was 30.4, and the epoxide equivalent of the polyester was 322.0.

The epoxide equivalents were determined by refluxing for 30 min. a 2-g. sample in 50 ml. of pyridine hydrochloride (6) in excess pyridine. After

cooling to room temperature, the sample is back-titrated with standard alcoholic sodium hydroxide to a phenolphthalein end-point. One epoxide group is considered to be equivalent to one HCl molecule. Saponification as a possible side reaction of this method of analysis was found to be insignificant. When the unepoxidized esters were refluxed under the same conditions used in the analysis for epoxide, the sample compared with a blank within 1%.

D. PREPARATION OF DEHYDRATED ANION EXCHANGE RESIN BASE

A commercially available strong base type anion exchange resin (Dowex 1), obtained as the salt, was treated with excess amounts of 4 N NaOH a minimum of 6 times at room temperature, allowing a minimum of 2 hrs. of contact time for each treatment, and the last basic treatment was allowed to stand over-night. The exchange resin was then filtered and washed with distilled water and filtered until the filtrate was no longer basic. The resin was pressed as free of water as possible on the filter and then placed in a vacuum oven at 80°C. for 16 hrs.

E. PURIFICATION

1. First, 100 g. of the epoxified reaction product of Part C were treated with 19.8 g. of the dehydrated anion exchange resin base, prepared according to Part D. The reaction was stirred 3 hours and filtered. The filter cake was washed with two 30-ml. portions of acetone. The filtrate had a non-volatile content of 61.5%, weighed 92.3 g., and had an epoxide equivalent of 314.3. The acid number, based on non-volatile content, was 3.7.

2. Then 100 g. of the same product were placed in a 500-ml. round bottom distilling flask and distilled in a suitable apparatus at a maximum pressure of 4 mm. and to a maximum pot temperature of 60°C. The resultant product was 92.63% non-volatile, had an epoxide equivalent of 321.2, and had an acid number of 7.8 based on non-volatile.

Results and Discussion

Since the use of a dehydrated cation exchange resin is important to the successful epoxidation of the polyester compositions described, the amount of dehydrated ion exchange resin present in a reaction was varied. Table II summarizes the results obtained. In this case a tetrahydrophthalic-ethylene glycol polyester, having an olefin equivalent of 242.4, was epoxidized, using 1.1 moles of H_2O_2 and 0.5 mole of acetic acid per olefin equivalent.

TABLE II
The Influence of Quantity and Particle Size of the Cation Resin on Epoxidation [a]

Condition of resin product	Grams dry Dowex 50-X8 / Olefin equivalent	% Net resin product recovered	Acid value	Epoxide/ 100 g.	Epoxide eq.	% Conversion to epoxide
Dry	100[b]	102.5	32.4	.4314	231.8	104.6
Dry	50[b]	76.8	23.7	.3579	279.4	86.8
Wet		17.5	73.8	....	....	0.0
Dry	25[b]	40.6	30.6	.3792	263.72	91.9
Wet		40.9	94.8	....	....	0.0
Dry	100[c]	38.9	21.1	.4155	240.7	100.7
Wet		25.2	68.3	.0107	9345.7	2.6
Dry	200[c]	77.3	27.5	.4292	233.1	104.0

[a] Tetrahydrophthalic-ethylene glycol polyester used.
[b] Dehydrated cation exchange resin 50–100 mesh used.
[c] Dehydrated cation exchange resin 20–50 mesh used.

Table II indicates the trend observed when the amount of dehydrated cation exchange resin, particle size 50–100 mesh, was reduced below 100 g. per olefin equivalent. Below this level the amount of cloudy, wet product separated which contains less than appreciable epoxide increases significantly. However the clear, relatively dry fraction contains a product which has been efficiently epoxidized. In addition, the wet fraction possesses a higher acid number, indicating an expected favorable extraction of acid to the wet phase and favoring conditions for oxirane ring destruction (7). The data further indicate the difficulty of isolating the wet reaction product, with an increasing amount of wet fraction. The total theoretical percentage of epoxidized product isolated diminishes with increasing wet fraction.

Table II further indicates that the particle size of the ion exchange resin can be an important contribution. While both resins have the same degree of cross-linkage, the coarser resin was less efficient in yield of polyepoxide under the same reaction conditions although an appreciable fraction of efficiently epoxidized polyepoxide was isolated. When the quantity of the dehydrated coarser resin per olefin equivalent was increased to 200 g., no wet poorly epoxidized fraction was isolated. However the increased ratio of cation resin also tends to reduce product isolation efficiency.

TABLE III
The Influence of Acetic Acid Concentration on Epoxidation [a]

Acid value of reaction mixture	Epoxide gp./ 100 g.	Epoxide equivalent	Mole AcOH / Olefine equivalent	% Conversion to epoxide
8.1	.1549	645.8	.125	43.1
8.8	.2255	443.0	.250	62.8
32.1	.2758	362.6	.500	76.8
49.7	.2932	341.0	1.000	81.6
84.2	.2864	357.3	2.000	79.7
215.0	.2843	351.7	4.000	79.2

[a] Tetrahydrophthalic-diethylene glycol polyester used.

Table III indicates the trend observed when the dehydrated resin is treated with 0.125 to 4.0 moles of glacial acetic acid per olefin equivalent prior to its use in an *in situ* epoxidation. A tetrahydrophthalic-diethylene glycol polyester was epoxidized, using maximum temperatures of 60°C. and 100 g. per olefin equivalent of a dehydrated styrene-divinyl benzene sulfonic acid exchange resin, 12% cross-linked. These data indicate that at least 0.5 to 1.0 mole of acetic acid is necessary to attain efficient epoxidation. We have chosen to use the former value in order to reduce the purification problem indicated by the increasing acid value of the reaction product with increased initial acetic acid.

Table IV indicates the trend observed for various maximum temperatures of reaction mixtures. Here a tetrahydrophthalic-1,5-pentanediol polyester was

TABLE IV
The Influence of Temperature on Epoxidation [a]

Maximum temp. C.	Epoxide gp./ 100 g.	Epoxide equivalent	% Conversion to epoxide
25	.1611	621.3	44.3
40	.2365	422.3	64.9
50	.2565	390.0	70.5
60	.2572	388.8	70.7

[a] Tetrahydrophthalic-1,5-pentanediol polyester used.

TABLE V
Purification of Epoxidation Reaction Products

Reactant		Epoxidation product		Dehydrated anion exchange resin purification			Distillation purification	
Species	Acid value	Acid value	Epoxide equivalent	Acid value	Epoxide equivalent	% Product recovery[a]	Acid value	Epoxide equivalent
THPA[b]-1,5-pentanediol	1.8	53.4	322.0	3.7	314.3	99.8	7.8	321.2
THPA-ethylene glycol	0.0	40.0	231.8	5.8	243.0	......	10.3	255.3
							3.4[c]	251.8[c]
Unsaturated alkyd	10.5	59.0	499.8	13.0	497.5	92.8	......	......
Unsaturated alkyd	10.5	71.0	473.1	10.0	474.8	93.1	......	......
Butyl oleate	8.5	49.6		9.6	358.0	96.0	11.0	413.2
Butyl oleate	7.5	68.0	390.0	2.6	408.6	......	9.8	492.6

[a] Combined cation and anion treatment.   [b] Tetrahydrophthalic acid.   [c] Redistilled with xylene.

epoxidized, using 100 g. of a dehydrated sulfonic acid exchange resin 8% cross-linked per olefin equivalent and 0.5 mole of acetic acid per epoxide equivalent. These data tend to indicate that temperatures of 50–60°C. are necessary in order to attain the most efficient conversion to the epoxide.

Table V indicates the comparable proficiency of free acid removal from the polyepoxide products by the use of the dehydrated basic form of a strong base anion exchange resin and vacuum co-distillation of the acid and xylene at maximum pressure of 4 mm. and pot temperatures of 60°C. There is an insignificant loss of epoxide content and a good recovery of resin from the anion exchange purification process. The particular anion exchange resin used is commercially available (Dowex 1) and is stated by the manufacturer to have a capacity of 3.3 milliequivalents per gram non-volatile. However a value of 2.75 has been found suitable for calculating the amount of dehydrated anion exchange resin to be used in the purification step. The resulting epoxide resin is a clear transparent product. Apparently the neutralization reaction of the anion exchange resin is accompanied by a hydration of the resin which can bind the water strongly enough so that it does not appreciably contaminate the product. The spent anion exchange resin may be regenerated with caustic soda for re-use after dehydration.
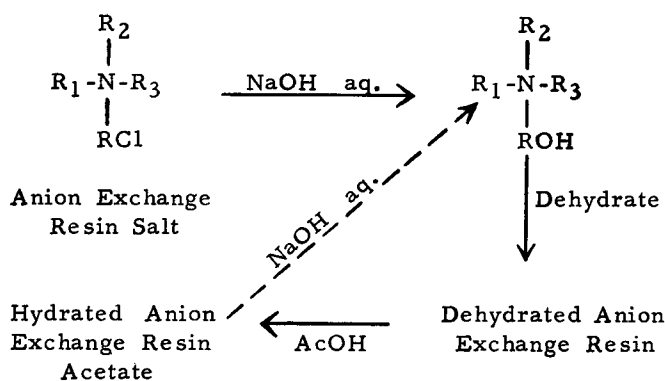

FIG. 1. Regeneration cycle of the strong base anion exchange resin.

Figure 1 represents the schematic regeneration cycle that has been used to prepare the anion exchange resin for re-use. This resin regeneration cycle has been performed many times on the same sample of anion exchange resin with the degree of success reported herein.

Co-distillation of the free acid with an aromatic solvent can alternatively be used for removing free acid from the epoxidized polyester. Sufficient distil-

lation can reduce the free acid to a level equivalent to the anion process. However there appears to be a slightly greater loss in epoxide content than in the case of the use of a dehydrated strong base anion exchange resin purification technique.

All of the trends observed in Tables II, III, and IV are summarized in Figure 2. The areas of most efficient conversion to epoxide have been used in de-
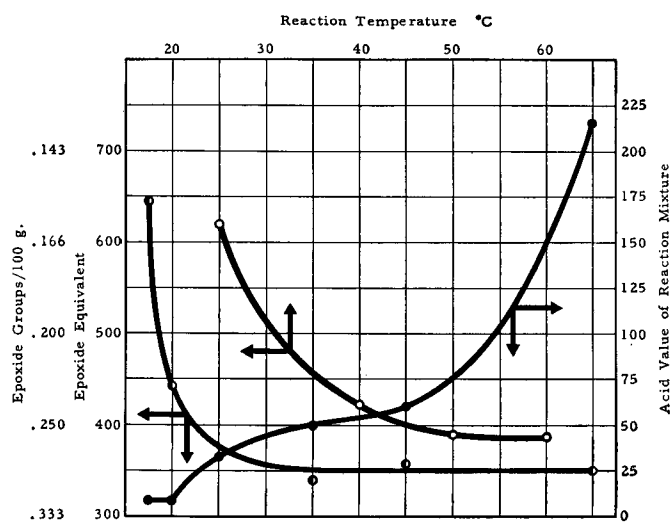

FIG. 2. The effect of temperature and amount of acetic acid on the conversion to the polyepoxide.

termining optimum reaction conditions for epoxidation of the subject unsaturated polyesters, using dehydrated styrene-divinyl benzene sulfonic acid ion exchange resins. The actual conditions chosen per olefin equivalent are,

0.50 mole acetic acid
100.0 g. of 50–100 mesh styrene-divinyl benzene exchange resin
1.1 mole H_2O_2
60°C. reaction temperature for reporting the results of Table VI

Table VI summarizes the results obtained for various unsaturated polyesters, using optimum reaction conditions reported above. These compositions have demonstrated customary coupling and converting reactions commonly attributed to active oxygen of an epoxide group, using BF_3, acid anhydrides, sodium phenoxide, etc.

Summary

New polyepoxides are reported which are epoxidation products of unsaturated polyesters. These poly-

TABLE VI

Species	Polyester			Polyepoxide				
	Iodine value	Olefin equivalent weight	Acid value	% Resin isolated	% Oxirane oxygen	Epoxide equivalent	% Conversion to epoxide	Acid value
THPA[a]-1,5-pentanediol	98.1	258.8	3.4	89.6	4.82	333.8	80.4	2.3
THPA-1,4-butanediol	93.0	273.0	8.6	89.5	5.27	303.3	95.3	10.7
THPA-ethylene glycol	101.5	250.1	3.9	90.0	5.96	268.6	99.1	6.2
THPA-diethylene glycol	104.6	242.3	10.1	93.2	4.82	331.6	77.9	13.2
Unsaturated alkyd	78.9	321.2	10.5	96.1	3.36	474.8	71.0	11.5

[a] THPA—Tetrahydrophthalic acid.

epoxides are unique in that they may be formulated to have a large number of epoxide groups per molecule; 10 or more may be practically obtained.

An *in situ* process for the formation of peracetic acid, using dehydrated cation exchange resin of the styrene-divinyl benzene sulfonic acid type, has been described for the efficient epoxation of the unsaturated polyesters reported.

A dehydrated strong base anion exchange resin will remove free acid, the major impurity resulting from the peracid epoxidation reaction, without contaminating the polyepoxide polyester with appreciable water and without appreciable loss in epoxide content during the purification. Alternatively co-distillation of the free acid with aromatic solvent *in vacuo* may be used as a method of purification but with some loss in epoxide content. These techniques are desirable in preparations of compositions of the type described wherein the usual washing techniques cannot be employed.

REFERENCES

1. Findley, T. W., and Swern, Daniel, U. S. Patent 2,567,930.
2. Terry, D. E., and Wheeler, D. H., U. S. Patent 2,458,484.
3. DuPont Technical Bulletin P 61–454.
4. Gall, R. J., and Greenspan, F. P., Ind. Eng. Chem., 47, 147 (1955).
5. Schmitz, W. R., and Wallace, J. G., J. Am. Oil Chemists' Soc., 31, 363 (1954).
6. Jungnickel, J. L., Peters, E. D., Polgar, A., and Weiss, F. T., "Organic Analysis," vol. I, p. 131, New York, Interscience Publishers Inc., 1954.
7. Findley, T. W., Swern, Daniel, and Scanlan, J. T., J. Am. Chem. Soc., 67, 412 (1945).

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Pilot Plant Development of the Alkali Cooking Process for Cottonseed Meats. II. Effect of Additional Comminution

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COTTONSEED MEALS of low free-gossypol content, high nitrogen solubility, and high nutritive value can be produced by processing the flaked meats at high moisture levels in the presence of alkali (3, 4). Under these conditions the pigment glands are ruptured and the gossypol inactivated without adversely affecting the nitrogen solubility. At the same time, semi-refined crude oils, depending upon the amount of alkali used, are produced. The preparation procedure consists of conventional hulling and rolling, followed by the addition of sufficient sodium hydroxide, in the moisture adjustment phase of the operation, to bring the pH to 8.2, mixing or prestirring at moisture levels of 25 to 40%, and then cooking at low temperatures under conditions which effect evaporative dehydration. The usual range of free-gossypol content of meals produced by the above method is from 0.02 to 0.04% and is considered low enough for unlimited use of the meal in growing chick and broiler rations but not low enough to prevent discoloration of eggs when fed to laying hens (2).

Earlier work disclosed the tendency of increased cooking temperatures and time in the presence of high moisture content to reduce the free-gossypol content of the meal. Concurrently, however, such conditions resulted in decreased nitrogen solubility of the meals produced. The only variable studied which showed a tendency to reduce the free-gossypol content of the meal without adversely affecting the nitrogen solubility was the fineness of comminution (flake thickness) of the raw cottonseed meats. This indicated that finer comminution than had previously been used might result in a further reduction of the free-gossypol content of the meal without a corresponding reduction in the soluble nitrogen content. Experiments were designed to determine the effects of additional comminution by grinding after rolling (or flaking), of temperature and moisture during rolling, and of the addition of alkali upon the characteristics of the meals produced.

The close relationship between the extent of comminution and the mixing operation, which is usually performed after the moisture and alkali are added to the comminuted raw meats, indicated that some additional reduction in the free-gossypol content of cottonseed meals could be expected during mixing. The present study therefore includes experiments designed to determine the optimum conditions for mixing, which would accomplish reduction in free-gossypol content of the meal without effecting a reduction in nitrogen solubility.

Tables I, II, and III outline the experimental plan for the evaluation of the effects of the variables under consideration.

Equipment, Material, and Methods of Analysis

Pilot-plant scale Carver cleaning, hulling, and purification equipment [2] was used to prepare the essentially hull-free meats used for these experiments. Flaking was performed on a pilot-plant stand of five-high rolls (7). A Bauer peanut butter mill and a

[2] The use of trade names does not constitute an endorsement by the Department of Agriculture of those products over similar products of other manufacturers.