This article outlines the relationship of Baudouin fall to bleaching action of various bleaching agents to determine their suitability.

In general, the suitable earths and carbons are manufactured in dollar areas which are inaccessible to Indian importers and manufacturers of Banaspati, and those earths and carbons manufactured in sterling areas, which are open to Indian importers, are unsuitable. This works a hardship on Indian manufacturers of Banaspati as this product is required by law to pass the Baudouin test.

A comprehensive investigation of the effect of different bleaching agents upon the change in color of the oil and of the sesamol and color bodies adsorbed by different earths is now being conducted by the authors.

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Catalysis of Fat Hydrolysis by an Acid Regenerated Cation Exchange Resin

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ION-EXCHANGE resins have been used in recent years as catalysts in a number of chemical reactions. An acid regenerated cation exchange resin (Zeo-Karb H.) was used by Sussman (4) in 1946 as a catalyst for certain esterification and ester hydrolysis reactions. A cation exchange resin (Amberlite I.R. 100) was investigated by Thomas and Davies (5) in 1947 and found to be an effective catalyst for ester hydrolysis. Levesque and Craig (2) have studied the kinetics of esterification by a cation exchange resin, and in a recent paper Schlenk and Holman (3) used an anion exchange resin to catalyze the methanolysis of triglycerides. Hydrolysis of triglycerides, employing an ion exchange resin catalyst, has not yet been reported.

In the Twitchell process of fat splitting a mineral acid is used as catalyst. The use of a cation exchange resin catalyst, instead of a mineral acid, would have many features to recommend it. Corrosion of equipment could be reduced, the resin catalyst could be recovered and used again, and the acid-neutralization stage in the treatment of the crude glycerol-water would not be necessary. Fatty acids produced by fat splitting with mineral acid catalysts are often dark in color, but an ion exchange resin catalyst may yield a lighter product.

It was therefore considered of interest to investigate certain cation exchange resins as fat splitting agents. This paper describes the use of an acid regenerated cation exchange resin (Dowex-50) as a catalyst in the hydrolysis of tallow. The properties and operating characteristics of Dowex-50 have been described by Bauman *et al.* (1).

Materials

The tallow samples used in this investigation were: a) a "special" grade tallow, refined and bleached in the laboratory, b) a "special" grade tallow, used without any further treatment, and c) a No. 1 grade tallow. The catalyst employed was an acid regenerated cation exchange resin (Dowex-50, 200-400 mesh, 12% cross links). The resin was weighed out in the moist condition and used in the hydrogen form. The fat splitting reagent employed was Petronate L (low molecular weight), described by the manufacturer as "a highly refined petroleum sulfonate." This reagent produces a good emulsion of the fat in distilled water and ensures intimate contact of these two components. Reagent grade hydrochloric acid was used for catalyst regeneration.

Experimental Method

In each experiment the reaction mixture consisted of 150 g. of tallow, 60 g. of distilled water, and 2.50 g. of Petronate L. The amount of water used throughout this investigation was maintained at 40% of the weight of tallow. The resin was weighed out in the moist condition. Generally 4.50 grams of Dowex-50 (200-400 mesh) were used as catalyst. This amount was 3% of the weight of tallow.

The weighed amount of resin catalyst was placed in a liter round-bottomed flask. The Petronate L was dissolved in 60 g. warm distilled water, and this solution was poured into the flask. The tallow sample was heated on a steam bath until liquid, and the liquid tallow poured into the flask. The contents of the flask were thoroughly mixed by careful swirling of the flask to produce a fat-water emulsion. This mixture of emulsion and resin catalyst was now refluxed at 100°C. with continuous stirring for 6 hours. Stirring was discontinued after 6 hours, and the emulsion readily separated into two layers. The resin remained at the bottom of the flask in the lower layer of glycerol-water. Fatty acid and glycerol-water layers were separately decanted off from the resin catalyst. The resin particles were washed in the flask with about 500 ml. of distilled water. After the resin particles had settled, the water was decanted off.

The yield of free fatty acids (stated as % oleic acid) at the end of this first stage of the two-stage fat splitting operation was approximately 88%. The resin catalyst was used in the second stage of the fat splitting operation without any further treatment.

In this second stage the glycerol-water was removed and replaced by 60 g. distilled water. The reaction mixture was again refluxed for 6 hours at 100°C. At the end of the reaction fatty acids, glycerol-water, and catalyst were separated. The final yields of free fatty acids (stated as % oleic acid) ranged from 96% to 100% in a number of experimental runs. No additional fat splitting reagent was required for the second stage of the reaction.

A 5 g. sample of fat was removed for analysis for free fatty acids. This fat was dried with Fuller's

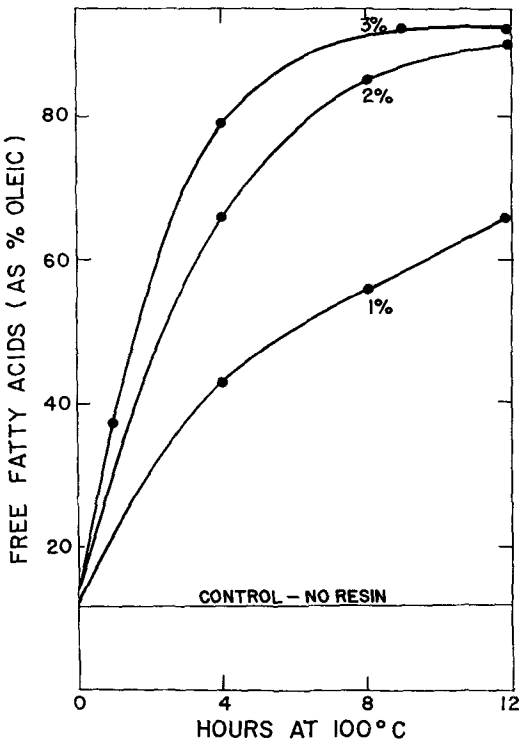

FIG. 1. Effect of catalyst concentration on the rate of hydrolysis of tallow by a cation exchange resin.[a]

[a] Dowex-50, 200-400 mesh, 12% cross links, hydrogen form.

earth and filtered. One gram of the filtered sample was dissolved in about 50 ml. neutral isopropanol. Free fatty acids were titrated against 0.25 N. sodium hydroxide, using phenolphthalein as indicator, and calculated as % oleic acid.

After a complete two-stage splitting operation the resin catalyst was regenerated with dilute hydrochloric acid and used in the next operation. The resin was washed out of the flask with distilled water onto a filter paper in a small filter funnel. It was regenerated by washing with two 50-ml. portions of 4N. hydrochloric acid. The first portion of acid was used to wash the resin three times, followed by three washings with the second portion of acid. The resin was now washed with distilled water until free of excess hydrochloric acid. The regenerated catalyst was used in the moist condition in the next operation. A fresh 100-ml. portion of 4N. hydrochloric acid was used for each regeneration of resin catalyst. This regeneration procedure completely reactivated the catalyst as judged by a consistently high yield of fatty acids in five complete operations.

Results and Discussion

Experimental data presented in Figure 1 indicates that the cation exchange resin, when used in the hydrogen form, acts as a catalyst in the hydrolysis of tallow. In the absence of the resin there is a negligible amount of fatty acid production in 12 hours at 100°C. During the first six hours of the reaction the rate of production of fatty acids increases as the percentage of catalyst is increased up to 3%. The rate of production of fatty acids rapidly decreases after this initial 6-hr. period, and finally the system attains a state of equilibrium.

The fat-splitting operation can be carried out in two stages. The glycerol-water is removed after the first 6-hour stage and replaced with distilled water. Results of two-stage tallow splitting operations are shown in Table I. The rate of production of fatty acids is approximately the same whether 3% or 4% resin is used. Under these experimental conditions there seems to be no advantage in the use of more than 3% Dowex-50 as resin catalyst.

TABLE I

Fatty Acid Production from Tallow,[a] Using a Cation Exchange Resin as Catalyst in a Two-Stage Operation [b]

Time Hours at 100°C.	Free Fatty Acids (as % oleic acid)	
	3% Dowex-50	4% Dowex-50
Stage 1		
4	81	81
6	89	88
Stage 2		
2	94	94
4	97	96
6	97	96

[a] No. 1 grade (initial F. F. A. 12%).
[b] The glycerol-water was removed after stage 1 and replaced by distilled water.

The results in Table I indicate that a fat splitting operation carried out in two 6-hour stages is capable of giving a final yield of at least 96% fatty acids.

Further investigations were made to determine whether partial inactivation of the catalyst occurs during a 12-hour two-stage splitting operation. The results presented in Table II show that, in the case of a No. 1 grade tallow, re-use of catalyst in a second complete operation gives a much lower yield of fatty acids. In the case of a "special" grade tallow, laboratory refined and bleached (A.O.C.S. standard methods), the resin may be used in two complete operations with little loss in activity but shows partial inactivation when used in a third operation. This loss of activity of the resin catalyst may be due to a slow conversion of the Petronate L (sodium salt of Petroleum Sulfonic Acid) to Sulfonic Acids, with formation of a "sodium resin." This exchange of sodium may account for the optimum resin content being at the 3% level. In the case of tallow hydrolysis, using the above experimental conditions, it is necessary to regenerate the resin after each complete operation.

TABLE II

Effect of Continued Use on the Catalytic Activity of a Cation Exchange Resin (Dowex-50) When Used in Two-Stage Tallow [a] Splitting Operations

Experiment No.	Type of Tallow	Catalyst [b]	Free Fatty Acids—as % oleic acid after 12 hr. at 100°C.
1	No. 1 grade	A. Fresh resin, 3%	98
2	No. 1 grade	A. Used again	87
3	No. 1 grade	B. Fresh resin, 4%	96
4	No. 1 grade	B. Used again	86
5	"Special" grade	C. Fresh resin, 3%	98
6	"Special" grade	C. Used again	98
7	"Special" grade	C. Used again	89

[a] No. 1 Tallow: initial F.F.A. 12%. "Special" tallow was refined and bleached in the laboratory: initial F.F.A. 0.05%.
[b] Percentage based on weight of tallow.

The data of Table III shows that, using 100 ml. of 4N. hydrochloric acid as catalyst regenerant after each operation, the original resin may be used in at least five complete operations with little decrease in fatty acid yield.

TABLE III

Continued Use of a Cation Exchange Resin Catalyst (Dowex-50) in Two-Stage Tallow [a] Splitting Operations—Employing Acid Regeneration After Each Operation

Experiment No.	Resin Treatment	Free Fatty Acids (as % oleic acid) after 12 hr. at 100°C.
1	Used 3% Fresh resin	100
2	With 100 ml. 4N. HCl	100
3	With 100 ml. 4N. HCl	100
4	With 100 ml. 4N. HCl	98
5	With 100 ml. 4N. HCl	96

[a] An untreated "Special" grade tallow: initial F.F.A. 3%.

In each operation considerable mechanical breakdown of resin particles occurs because of abrasion due to refluxing and stirring. Some of the resulting fine particles are carried away during separation, regeneration, and washing of the resin. It was found that after four complete operations only one-third (*i.e.*, 1%) of the original resin remained. Despite this loss the residual resin, when regenerated for a fifth operation, maintains a high yield of fatty acids. These results indicate that there is a considerable increase in catalytic activity when the average particle size is decreased. The continued use of the resin in such "batch" operations results in a loss of catalyst, but this loss is partly compensated for by increased catalytic activity due to increased resin surface.

The continued efficient "batch" operation of such a tallow splitting process would require: a) regeneration of the residual resin at the end of each complete operation, b) addition of fresh resin to replace mechanical loss. Column operation of this tallow splitting process would minimize mechanical loss of catalyst, but there may be some difficulty in maintaining an adequate flow rate with 200-400 mesh particles.

The investigation of cation exchange resin catalysts in fat hydrolysis is being continued with comparative studies of mineral acid and resin catalysts, using "Sulfonate" and "Sulfonic Acid" types of fat splitting agents.

Summary

An acid regenerated cation exchange resin (Dowex-50, 200-400 mesh) is an effective catalyst for tallow splitting. The optimum level of catalyst was approximately 3% of the weight of fat. A two-stage operation for 12 hr. at 100°C. gave fatty acid yields which ranged from 96% to 100% (calculated as % oleic acid).

The Dowex-50 catalyst was easily recovered after each operation, regenerated with 100 ml. of 4N. hydrochloric acid, and used again in the next operation with no appreciable decrease in catalytic activity.

The original resin can be used in continued efficient tallow splitting operations if the residual resin is regenerated after each complete operation and additional fresh resin is added to make up mechanical loss.

Acknowledgment

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Report of the Refining Committee, 1952-53

DURING the year 1952-53 the activities of the Refining Committee were confined to the work of a subcommittee consisting of V. C. Mehlenbacher, Wales Newby, E. H. Tenent, and W. T. Coleman, chairman. The subcommittee undertook to study the refining characteristics of cottonseed oil solvent extracted from pre-pressed seed with a view toward recommending a tentative laboratory procedure.

Mr. Coleman reported to the Refining Committee at the 1953 meeting in New Orleans to the effect that the behavior of this oil was so erratic that the subcommittee had not been able to determine any method of refining it in the laboratory which would give concordant results. He stated that in his opinion the behavior of the oil was due to wide processing variations which were extremely difficult and costly to control. Therefore he doubted whether a uniform oil of this type would be produced in the near future.

After considerable discussion it was decided to discharge the subcommittee with the thanks of the Refining Committee for their work since it was the consensus that no useful purpose would be served at this time by any further study of the oil in question.

This action of the Refining Committee means that it will be the responsibility of the seller to specify the method to be used by the buyer in refining the official sample; *i.e.*, expeller, hydraulic, regular, or slow breaking.

E. M. JAMES, chairman.