Lecithin Retards Hydrolysis of Fats*

Removal of Nitrogeneous Body Found to Accelerate Saponification Rate in Twitchell Treatments

By Ralf B. Trusler

MODERN technology of the treatment of fats and fatty oils for the production of fatty acids is chiefly the composite result of practical experiments, many of which were done upon a commercial scale. The treatment of fatty oils by the catalytic process of hydrolysis has therefore resulted in a rather universal method based upon accrued experience.

The commercial production of a fatty acid from a fat or a fatty oil is most frequently accomplished by splitting the fat by means of a catalyst, that most commonly used being known as Twitchell reagent. This is done by reacting one part by weight of the fat with from one to two parts by weight of water in the presence of 1 to 1½% (on the basis of the fat) of the catalyst, while the mixture is kept hot and thoroughly stirred.

Not all fats and fatty oils were found to react with the same ease, and if any uniformity of procedure and product was to be obtained it became necessary to wash the fat with about 5% to 7% of a moderately concentrated solution of sulfuric acid. This concentration may be in the neighborhood of 20% which is too dilute either to sulfate or to sulfonate the olefine acids. The sludge from the acid wash is drained off before the next step of splitting is begun, which is generally done in a separate chamber. Upon most occasions a small amount of sulfuric acid is added to the mixture of catalyst, fat and water as a further aid to splitting. The literature reveals an occasional idea why the sulfuric acid treatment is necessary, while about the plants the thought persists that this is some sort of necessary purification.

During a laboratory study of catalytic splitting of fats, it was observed that glycerides from various sources behaved in different manners. If the fats or fatty oils were given an energetic pre-treatment with the sulfuric acid solution, the difference in the hourly rate of hydrolysis and time required for a 90% to 95% split became less marked, but if the sulfuric acid in treatment was omitted no two fats responded alike to the process of splitting. When reactions were brought about between a fat and water aided only by 1½% to 3% of catalyst it was found that lard and tallow were subject to considerable amount of splitting and that from ten to eighteen hours treatment at 90° to 95° sufficed to produce approximately 90% free fatty acid. In contrast to this, a similar experiment conducted upon crude cottonseed oil and soy bean oil ended with little or no change for similar treatment.

This vast difference in behavior of these fatty compounds cannot be attributed merely to animal or plant origin, or to the difference in the compositions of the glycerides, because similar peculiarities were found in oils of both sources. The explanation for this difference seemed either to be the presence of a small amount of some compound in lard, in one instance, that aided hydrolysis, or the presence of a substance in cottonseed oil for example, that inhibited the decomposition of the fatty oil. Since lard is a relatively pure glyceride and crude cotton seed oil is known to carry small amounts of compounds other than glycerides of fatty acids, it was naturally suspected that the resistance of a fatty oil to hydrolysis must be dependent upon some sort of compound we may call an antihydrol.

The presence of an antihydrol was established in an indirect way. First of all, if such a body were present, in a fat or fatty oil, the fat should respond to splitting with the ease of lard if this compound were removed or destroyed. The removal of a compound that miyht be present only to the extent of about 0.1 to 0.25% did not appear as promising as some means for destroying it. Long heating had some effect in reducing the resistance to

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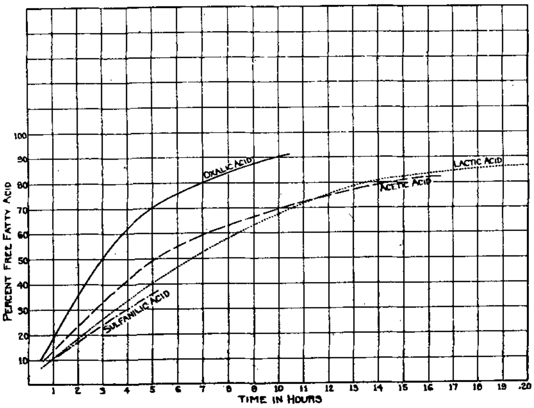

Fig. 1

hydrolysis. Chemical means were found the most efficient. If the oil was treated with from 1% to 3% of strong hydrochloric acid solution or with about 3% to 5% of a 20% sulfuric acid solution, preferably during heating, and thoroughly washed to remove all mineral acid afterward, hydrolysis could then be accomplished by the catalyst alone without difficulty.

Inasmuch as the relative sensitivities of treated and untreated oils could best be determined by splitting the fats under identical conditions and then by comparing curves for time of treatment plotted against degree of split, it became necessary to select a method capable of giving uniform results. A few runs in which lard was used as the fat to be hydrolyzed, revealed that considerable variation occurred when the catalyst was used without an additional acidulant. If about 1% of sulfuric acid was added to the reactants (based upon the weight of lard) a uniform set of reactions would be obtained, but this was not applicable to cottonseed oil and other kinds of resistant oils because mineral acids decomposed the protecting bodies. However, an experiment in which lard was hydrolyzed by the Twitchell catalyst in the presence of an organic acid showed that definite aid was obtain from this acidulant, and a similar experiment upon cottonseed oil gave the same result as if the acidulant had not been present. In other words, the stabilizing body present in cottonseed oil was not decomposed by the organic acid acidulant. Only mineral acids or compounds capable of liberating mineral acids appeared to have the ability to render the antihydrol inactive.

Experimental Results

A SERIES of fat splitting experiments was conducted upon lard to note the relative value of various organic acids as an aid to the Twitchell catalyst so that the most active compound might be selected for pursuing this investigation. The reaction mixtures consisted of 450 grams of pure lard, 675 g. distilled water, 4.5 g. Twitchell reagent and such a quantity of an organic acid that the available carboxyl groups would be comparable to those in 4.5 grams of oxalic acid, which was taken as the standard for comparison. Each reaction mixture was constantly stirred and kept heated in an oil bath at 95° while the water content was kept fairly constant. In this manner a comparison was obtained between acetic, lactic, oxalic and sulfanilic acids. Curves for these runs are shown in Figure 1. It is apparent that oxalic acid is very good aid to the catalyst. Acidity, or degree of ionization can hardly be the cause for the difference between these acids because of their large dilution.

A number of fats and fatty oils including lard, yellow grease, chicken fat (body), menhaden oil, cod liver oil, palm oil, palm kernel oil, coconut oil, soy bean oil and cottonseed oil, were subjected to a similar treatment in which 450 g. of the fat, 675 g. of water, 4.5 g. Twitchell reagent and 4.5 g. oxalic acid were used. The reactions were all carried out at 95° and the rate of splitting was determined by taking small samples for fatty acid determinations at frequent intervals. These experiments showed that fats used for storage purposes such as lard, tallow, palm oil, etc. hydrolized with varying degrees of ease, while fats pressed from glands, such as cod liver oil, and from seeds containing the seed germ, most generally resisted hydrolysis under the same conditions. There were some moderate exceptions. A few curves showing this difference in rate of hydrolysis appear in Fig. 2.

An examination of the fatty oils that resisted hydrolysis revealed that they contained pre-

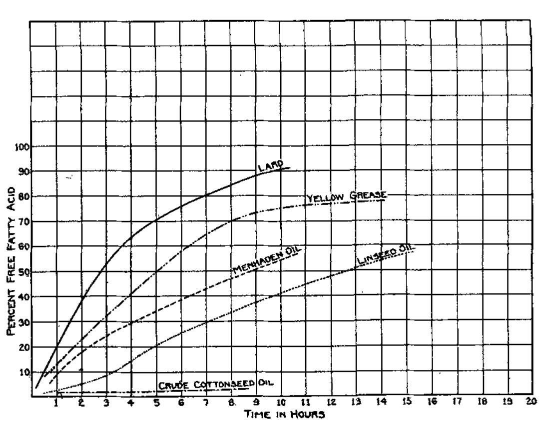

Fig. 2

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Lecithin

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servatives or antihydrol which appeared to be lipoid in character and was probably lecithin or a closely related substance.[1] The ingredient, which could be partially covered by the cadmium chloride method, was easily rendered inactive by treatment with hydrochloric acid or the 20% sulfuric acid solution, thus explaining why the pretreatment with sulfuric acid is necessary in the plant prior to "splitting" a fat with the Twitchell catalyst. The protective action of lecithin upon a fat against hydrolysis was nicely shown by the following experiment. Eight grams of commercial lecithin of about 50% concentration from soy bean was incorporated in lard, which was then subjected to hydrolysis with water and catalyst in the presence of oxalic acid in the customary manner. Even after six hours of energetic treatment only 20% of fatty acids had been produced. The curves in Fig. 3 show the comparison in the rate of hydrolysis between lard with and without lecithin.

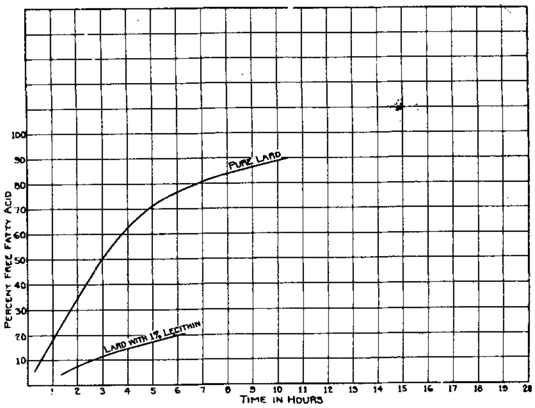

Fig. 3

Hence the resistance of certain fatty oils to hydrolysis is indirectly attributed to lecithin, or a related body, which is known to be present in these oils.

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[1] The following valuable information was contributed by Dr. A. S. Richardson.

"Work by Mr. C. V. Conley in the Chemical Division of the Procter & Gamble Company some years ago indicated that 'poisoning' of Twitchell saponifier is a property of oil soluble nitrogen bases generally. Diethyl aniline affords a good illustration of this action."

Margarine Legislation

(*From Page* 145)

of the crude gum (oleoresin) from which derived: Gum spirits of turpentine and gum rosin, as defined in the Naval Stores Act, approved March 3, 1923."

Sec. 4. This Act shall take effect upon the expiration of ninety days after the date of its enactment except section 3, which shall take effect upon the approval of this Act.

Nicholas Longworth,
Speaker of the House of Representatives.
Charles Curtis,
Vice President of the United States
and President of the Senate.
Approved, March 4, 1931,
Herbert Hoover.

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Higher fatty acid peroxides and peroxy compounds, such as valeryl, caproyl, capryl, lauryl, palmityl, oleyl, stearyl and ricinolyl peroxides and peracids, suitable for bleaching, for use in pharmaceutical preparations, for synthesis, as bactericides and in dentifrices, are prepared by treating higher fatty acid chlorides with a solution of an alkali metal peroxide preferably of a concentration not over 10 percent. Br. Pat. No. 334,531.

The clouding point of a soap solution has been defined as that temperature at which a soap solution containing three per cent of fatty acids combined with alkali becomes turbid. In washing textiles, if the clouding point lies above the temperature of the washing water, soap is precipitated on the fibres and interferes with subsequent dyeing or printing. Apparatus for determining the clouding point comprises a jacketed beaker fitted with a thermometer and stirrer, and placed in a vessel filled with hot water. The jacket has a narrow vertical slit in one side and a slit three times as wide with a narrow strip down the middle on the opposite side. Soap solution heated above its clouding point is poured into the beaker and viewed through the narrow slit, illumination being provided behind the wider slit. The temperature at which cloudiness first begins to appear is taken as the clouding point. *Chem.-Ztg.* 49, 1012 (1930).

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Sulfonated oils are said to possess practical advantages over soap as emulsifying agents because of the greater stability and uniformity of the former, their greater stability in acids, alkalies and hard water and their greater powers of dispersion and penetration. *Am. Silk. J.* 49, No. 64-6 (1930).