Light Colored Saponified Fatty Acids

By R. B. TRUSLER[*]

DISCOLORATION of fatty acids produced by catalytic hydrolysis (or splitting) of fats and fatty oils is a serious technical problem. Much study of this reaction has been made in an effort to find why a pale, or nearly water-white fatty oil produces a deep red to dark brown fatty acid during the splitting process, whether in the laboratory or in the plant.

A brief review of recent investigative researches upon this subject reveals interesting observations. Hydrolysis[1] of fats by three well known catalysts of the Twitchell type in the presence of acetic, formic, oxalic, sulphuric and hydrochloric acids were made. Acetic and formic acids retarded hydrolysis while the others accelerated it. The color change progressed with the degree of splitting, and oxalic acid was found to give less discoloration than mineral acids. Both sulphuric and hydrochloric acids caused equal discoloration. It was concluded that the presence of the acids did not explain the darkened product.

In studying the comparative values of commercial catalysts, it was found that these have some bearing upon the color of the resulting fatty acids.[2] All the fatty acids obtained were dark, however, and were not altered by selecting different mineral acids as aids for the reaction.

An olive oil[3] was first refined with 60° Bé. sulphuric acid, and then subjected to hydrolysis with seven different catalysts. It was found that the addition of sulphuric acid was not the reason for the darkening of the fatty acids obtained by the Twitchell process. All reactions increased in depth of color with the time of heating. The presence of air was reported as contributory to the darkening.

Another investigator[4] has reported that the dark color produced during the splitting of fats is caused by a change in naturally occurring dyes and in the formation of new dyestuffs in the presence of unsaturated fatty acids. In example, he mentions that light colored stearic acid is not changed by boiling with dilute sulphuric acid and a saponification catalyst while oleic acid turns brown under the same conditions.

Hydrolysis of fats in the presence of antioxidants has been tried[5] without any reduction in color, indicating that discoloration is not entirely due to oxidation. The writer also has investigated this possibility, but likewise obtained negative results.

Commercial Hydrolysis

In the commercial production of fatty acids, the fat or fatty oil raw material must be given a preliminary acid treatment.

It has been occasionally stated that the dark color of the catalyst is largely responsible for the dark fatty acids. In reality, a mahogany colored catalyst used in proper amount contributes only a moderate shade of yellow, which can be determined by dissolving some of the catalyst in the correct amount of water-white mineral oil.

Hydrolysis of fats and fatty oils is technically accomplished by reacting fat and water in the presence of a catalyst and sulphuric acid while heated and agitated. The proportions by weight employed are fat 100 parts; water from 150 to 300 parts; Twitchell reagent as the

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[*] Presented before Fall Meeting, American Oil Chemists' Society, Chicago, 1931.

[1] Nishizawa and Matsuki, *J. Soc. Chem. Ind. Japan,* 33 Suppl. binding 179-82 (1930).

[2] Nishizawa and Sakuma, *J. Soc. Chem. Ind. Japan,* 33 Suppl. binding 412-4 (1930).

[3] Nishizawa and Fuzimoto, *J. Soc. Chem. Ind. Japan,* 33 Suppl. binding 500-4 (1930).

[4] Eramus *Allgem, Ol. u Fetztg.* 27, 201-2, 222-3 (1930).

[5] Private communication with Wm. Shields, Emery Industries Inc., Cincinnati.

catalyst from 0.75 to 1.50 parts and sulphuric acid from 0.5 to 1 part. Experience has shown that sulphuric acid must be employed in commercial practice, if the reaction is to be completed in less than 24 hours.

In the experiments herein described, a uniformity of procedure was maintained by employing 500 grams of fat or fatty oil as the case may be and 750 grams of distilled water. The amount of Twitchell reagent was varied according to the experiment, likewise the amount of acid added. The reactants were contained in a two liter beaker immersed in an oil bath. The oil bath of about four liters, was heated to 95°C-100° C. before the experiment was begun and hot water was always added to the oil to shorten the time required for bringing the liquids to the reacting temperature of about 95°. Practically no splitting occurs until the catalyst is added to a mixture of fat, water and acidulant, hence by adding the catalyst at 95° C. all tests had uniform starting conditions. The beaker was provided with a cover to retard evaporation. A motor driven glass stirrer and a thermometer were inserted through the cover.

Lecithin Retards Hydrolysis

Many oils and fats contain traces of some nitrogeneous compound similar to lecithin, which must be first destroyed, in order to successfully hydrolyze the fat.

When white grease was subjected to catalytic splitting, hydrolysis was caused to take place in water under the following conditions: (1) With a catalyst; (2) with a catalyst and an organic acid; (3) with a catalyst and an inorganic acid. The rate of splitting varied with any one of these conditions. Three experiments were made according to these methods. In the first case 2.5 per cent of catalyst was used on basis of the grease, in second instance 1 per cent catalyst and 1 per cent oxalic acid and in the third reaction 1 per cent catalyst and 1.5 per cent sulphuric acid. After nine hours' treatment the fatty acid contents were 92, 90 and 88 per cent,† respectively. This allowed comparison of the products under approximately equal states of splitting.

The results of these three experiments may be condensed as follows:

Catalyst Used.	*Organic Acid Used.*	*Mineral Acid Used.*	*Remarks.*
(1) 12.5 g (2.5 per cent of wt. of oil used).			Orange colored fatty acids.
(2) 5.0 g (1 per cent of wt. of oil)	5.0 g oxalic.		Pale orange fatty acids.
(3) 5.0 g (1 per cent of wt. of oil).		5.0 g sulphuric.	Deep brown fatty acids.

A set of similar experiments was made upon bleached light yellow cottonseed oil. A splitting was first attempted in the presence of 1.25 per cent of catalyst, and after 12 hours there was only a detectable change. When 5 g. of catalyst and 5 g. oxalic acid were used, again practically no splitting occurred but when 5 g. of sulphuric acid was used with 5 g. of the catalyst in a new portion of oil an 88 per cent split was obtained in 12 hours. The resulting product was nearly black. Numerous experiments involving other oils gave dark fatty acids when normal procedure was followed. Without exception in every instance where sulphuric, phosphoric or hydrochloric acid was used, the product of the reaction was some shade of deep red or brown approaching black. So few glycerides can be split without the aid of sulphuric acid, and with the scarcity of examples showing successful hydrolysis by Twitchell reagents without an auxiliary treatment with sulphuric acid, the darkening of the reaction product can not be attributed to the sulphuric acid without more information. It is a well known fact that in the commercial production of fatty acids the fats or fatty oils must be given a preliminary acid treatment, and during hydrolysis the catalyst should be associated with some sulphuric acid to insure a faster splitting.

Mineral Acid Accelerates Darkening

Hydrolysis of fatty oils and greases in the absence of mineral acids is conducive to the production of light colored fatty acids.

In a previous paper[6] it was shown that many oils and fats contain traces of some compound

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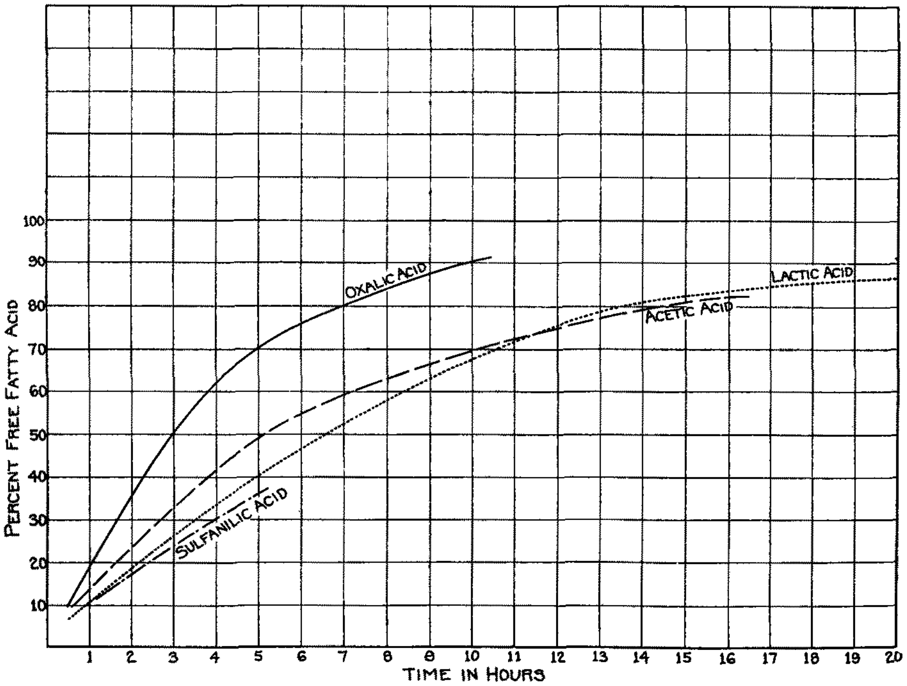
†Total acidity of fatty content determined as oleic acid.

[6] The writer, *Oil & Fat Industries*, VIII, 141-3, 157 (1931).



apparently nitrogenous and similar to lecithin closely related to it, that retards hydrolysis. In some instances the retarding action is so effective that hydrolysis scarcely occurs in its presence. In order to successfully hydrolyze a fat, this protective body has first to be destroyed. This is accomplished by sulphuric acid. The acid treatment may be effected by phosphoric acid which does not prove as satisfactory or by hydrochloric acid. The latter has a decided discoloring action upon olefinic fatty oils even before they have contact with the Twitchell reagent.

It was also mentioned[7] that when a fatty oil was treated with from 3 per cent to 5 per cent of a 20 per cent sulphuric acid solution during heating, the recovered oil after being washed free of the mineral acid was more easily split by the catalyst. Further experiments upon the acid pretreatment for the purpose of rendering fatty oils more easily hydrolyzed have shown that more concentrated sulphuric acid is desirable. The quantity is not as important as the concentration, for in general more satisfactory results can be obtained with 3 to 4 per cent of a 45-55 per cent sulphuric acid than with from 10 to 15 per cent of a 20 to 25 per cent sulphuric acid. In fact, a still faster and more thorough decomposition of the protective bodies can be accomplished with still more concentrated acid, but this is prevented from commercial application since more concentrated sulphuric acid has a tendency to react and combine with the fatty oils, thus preventing the removal of the remaining free sulphuric acid through causing emulsions frequently difficult to handle. All oils do not respond with the same ease to this treatment. Lard, tallow, yellow grease, coconut oil are among those that are quickly rendered reactive by the acid treatment while soy bean and cottonseed oils are more resistant.

The accelerating action of some organic acids upon the Twitchell type of catalyst has been studied[7] and a comparison of the curves, indicating relative amounts of fatty acids produced in similar intervals shows that oxalic acid is a very active agent. It is also a very desirable acid to use in that it easily permits of its removal from the glycerine sweet water, as will be described later.

The results of many experiments discussed up to this point may be briefly summarized as:

(1) Mineral acids present in the reaction mixture probably are accountable for much of the discoloration of the fatty acids.
(2) An acid treatment of a fat is necessary for a satisfactory splitting.
(3) Oils, or fats, in which the protective substance is absent or has been destroyed, can be split by means of the Twitchell reagent in the presence of an organic acid activator with a minimum discoloration.

A means for employing the information gathered and the principles above in the fat splitting process is the next consideration. The sulphuric acid pretreatment of a fat or fatty oil is an accepted necessity, but some modifications can be made by the following procedure:

Inedible white grease was chosen for the first

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[7] Ibid.

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example because it represents a commercial source of a high grade of raw materials. This grease was of such quality that when melted in a test tube it gave a pale yellow color in cross section view; 500 grams of this grease were melted and to it were added 15 grams of 45 per cent sulphuric acid heated with stirring at 90° to 95° C. for 20 minutes. It was allowed to settle for about three hours in a separatory funnel, then as much of the acid layer as possible was drawn off. This was followed by two thorough hot water washes of 100 c.c. each. The washed grease was then transferred to the two liter reaction beaker and to it were added 750 cc. of boiling water and 0.5 grams of calcium hydroxide (slaked lime). The mixture of oil and water was then heated to 95° C. during stirring for thirty minutes. This allowed any sulphuric acid remaining in the hot oil to be neutralized and it also took up any sulphuric acid that might be removed from combination with the oil, such as any sulphate esters or other loose grouping. This lime treatment is quite necessary as it was found that very small traces of free sulphuric acid (or other mineral acid) in the splitting reaction that follows, cause discoloration.

Usually much of the calcium sulphate precipitate settles out, thus allowing easy separation. It was found that the splitting reaction could be started even if some of it remained in the oil. One per cent of Twitchell reagent and one per cent of oxalic acid crystals were then added to the mixture and stirring was continued. When the level of the liquid fell, more water was added to the beaker to maintain a uniform oil and water ratio. Samples of the mixture were taken at intervals for the purpose of determining the progress of the reaction. At the end of the twelfth hour, reaction was discontinued and contents were allowed to cool to about 65° until the oil and glycerine water layer separated. The glycerine water layer was siphoned off and saved for glycerine recovery. The oily portion was allowed to cool and crystallize and after two days standing at 10° to 12° C. it was pressed in a small pressure filter and the liquid portion collected. This fatty acid, corresponding to what would ordinarily be saponified red oil, was light orange in color. In place of the slightly acrid odor frequently possessed by saponified red oil, the new product had a wholesome fatty odor. The fatty acid derived in this way had a marked resistance to rancidity and a sample kept in a hot room in sunlight throughout summer did not become rancid.

Coconut oil or yellow grease can be treated in the same manner as white grease. After a preliminary acid wash they become readily reactive. Cottonseed oil, like some other oils, requires an energetic acid pretreatment. Stronger sulphuric acid is needed to break down the protective substance naturally occurring in the oil. To render it active, 500 g. of light colored cottonseed oil was gradually heated to 110° C. with 10 g. of 52.5 per cent H_2SO_4, with stirring for 25 minutes. The sulphuric acid was so well dispersed that settling was very slow, and to hasten the removal of the acid 20 g. $NaHSO_4$ dissolved in 50 cc. of water were added with brief stirring. A quick separation was effected, but the oil at this point was somewhat discolored. This was followed by two water washes, the second one containing 0.5 g. lime, after which the oil was ready for saponification as described for white grease. Hydrolysis proceeded readily, yielding light brown fatty acids.

Glycerine recovery from the sweet water presented a simple problem. The resulting solution, consisting of about 46 to 50 parts by weight of glycerine, 5 grams of oxalic acid and 750 grams of water, was treated with a milk of lime solution containing about five grams of slaked lime. Just enough lime was added to give a permanent pink when the solution was tested with phenolphthalein. The reaction of the lime with the oxalic acid was always rapid in a hot solution. The resulting product, calcium oxalate, settled out as a crystalline precipitate during cooling. The liquid layer was a clear, frequently water-white, solution of glycerine and water, which was filtered off. In place of lime, magnesium oxide in water may be used to precipitate the oxalic acid from the glycerine water. In this case, the insoluble precipitate is magnesium oxalate. For every five unit weights of oxalic acid in solution, slightly less than two unit weights of magnesium oxide are required. The small quantity of this material and its low price make this commercially feasible.

The recovery of the oxalic acid from the precipitates is not equally easy. Owing to the extreme insolubility of calcium oxalate, less than 0.0006 parts per hundred in water at 18° it is not completely converted into oxalic acid and calcium sulphate, since the latter has a higher solubility (about 0.170 at 18°). However, the magnesium oxalate can be heated with sodium or ammonium carbonate to give soluble oxalates and a residue of magnesium carbonate, both useful.[8]

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[8] The magnesium carbonate thus regenerated can be used to precipitate oxalic acid, and thus pass through many cycles of regeneration.

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This study of hydrolysis may be extended to other organic acids whose salts of oxalic acid will be sufficiently insoluble to separate from the glycerine water, later to be converted into free acid by means of sulphuric acid.

Summary.

HYDROLYSIS of fatty oils and greases in the absence of mineral acids is conducive to light colored fatty acids. This method with its necessary commercial adaptation, together with process improvements suggested by other investigators, should make possible still greater gains in the quality of the finished products.

On February 17th, the Procurement Division of the U. S. Veterans' Administration opened sealed bids covering the supply of 8,760 gallons of salad oil and 95,960 pounds of vegetable shortening for use in the veterans' hospitals at 61 locations throughout the country during the period from April 1st to June 30, 1932.