trodes and stirrer and allow the electrodes to stand in distilled water. The glycerol content of the sample is calculated from the difference between blank and sample titrations.

The tungsten electrode should be cleaned about every 6 weeks by dipping for a few seconds into fused sodium nitrite held just slightly above its fusion temperature.

Care must be taken to use sufficient sulfuric acid to give an equivalent of, at least, 1.230 specific gravity (3). The excess of dichromate after heating must be such that a back-titration of at least 9 ml. of ferrous sulfate solution is obtained. For some samples of low glycerol content, a 100-ml. aliquot, 30 ml. of sulfuric acid, and 10 ml. of dichromate are used.

Summary

The method is very rapid and accurate with a sharp, positive end point, and can readily be operated under varying conditions of lighting by any analyst who can read a buret —even by one who is color-blind.

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STABILITY OF FATS USED FOR DEEP FAT FRYING

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Abstract

This paper presents the results of some commercial doughnut frying tests using types of shortening available to the baker. The broad conclusion is that, from the stability viewpoint, the difference in shortening when used for deep fat frying is exaggerated.

AN inspection of the convention programs of the A.O.C.S. for the past few years reveals the fact that very few papers have been presented to this society upon the uses of edible fats and oils and how they react when used. This is due, no doubt, to the fact that the majority of chemists in the fat and oil industry are concerned primarily with the prepartaion and manufacture and not with the consumption of the products. For this reason some information regarding the way the finished products perform should be of interest.

Up to the present time, chemists have been striving to prepare edible fats and oils having various supposedly desirable characteristics such as low free fatty acid, low color reading, a high smoke point, high stability as considered from the standpoint of resistance to rancidity, etc.

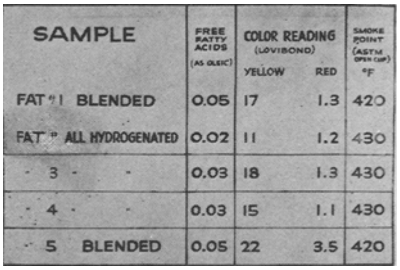
In considering these factors from the standpoint of the consumer, specifically the baker, it is questionable whether or not he derives as much benefit as is supposed by obtaining fats and oils having these characteristics, and also, whether or not he actually needs them.

The demand for shortenings which are practically neutral, of a chalky white appearance and high smoke point, appears to have been brought about by competition of the advertising departments in the various companies, many of whom make absurd claims for their products with respect to the appearance, purity, stability, and smoke point. Those familiar with the bakery trade journals have seen many shortening advertisements with such indefinite wording as: it's whiter; it's purer; higher smoke point; will not break down; withstands high heat, etc. As chemists, you know many such statements to be preposterous, but a baker, without technical training, does not know what to believe, and is thus led to demand shortenings which may or may not be to his best advantage. This reference to advertising is not to be construed as a criticism of the advertising, but to illustrate the fact that the consumer is led to believe that he is getting fats which will remain stable under working conditions.

One of the most severe uses which is made of edible fats and oils is deep fat frying in the preparation of doughnuts, nuts, potato chips, and in the new type of frying equipment used by restaurants for the deep fat frying of chicken, oysters, French fried potatoes, and clams. In all of these operations the fat is held at a temperature of 350°-400° F., sometimes for a long period of time.

To obtain accurate information regarding the behavior and breakdown of fats subjected to high temperatures, a doughnut frying test was planned and conducted on a commercial scale and of such scope that there could be no doubt concerning the accuracy of the results.

Arrangements were made to run the test in a commercial shop using approximately 600 pounds of shortening per day for frying alone. Two automatic doughnut machines, made by the same manufacturer, were used. Five different shortenings were tested. Three were all-hydrogenated shortenings, the other two were blended or compound shortenings containing about 80 per cent refined, bleached and deordized cottonseed oil. The analyses of samples representing the shortening were as given on Chart No. 1.



SAMPLE	FREE FATTY ACIDS (AS OLEIC)	COLOR READING (LOVIBOND)		SMOKE POINT (ASTM OPEN CUP) °F
		YELLOW	RED	
FAT #1 BLENDED	0.05	17	1.3	420
FAT " ALL HYDROGENATED	0.02	11	1.2	430
- 3 - -	0.03	18	1.3	430
- 4 - -	0.03	15	1.1	430
- 5 BLENDED	0.05	22	3.5	420

CHART NO. I

Ten drums, about 3,800 or 4,000 pounds, of each shortening were used in the test. In order to eliminate any partiality on the part of the operators, all brands, marks, and names were removed from the drums, with the exception of the weights, before being delivered. The different shortenings were known to the operators only by a number stenciled on the drums. The doughnut machines each had a capacity of approximately 175 dozen per hour. The temperature of the frying fat was thermostatically controlled and was held between 380° and 395° F., the average temperature being 387.5° F. All of the ingredients used in the doughnut mixture were the same throughout the test and each batch of dough was given the same amount of mixing on the same mixing machine. In fact, every variable which could be controlled was kept constant with the exception of the frying fats. Fresh fat was added hourly to replenish that absorbed by the doughnuts. This amounted to about 300 pounds per day per machine for a 14 hour run. Samples of the frying fats were taken from the machines twice a day, the first sample being taken at the middle of the run and the other at the end of the day. These were analyzed for free fatty acid content, color, and smoke point. Almost 200,000 dozen or 2,400,000 doughnuts were fried.

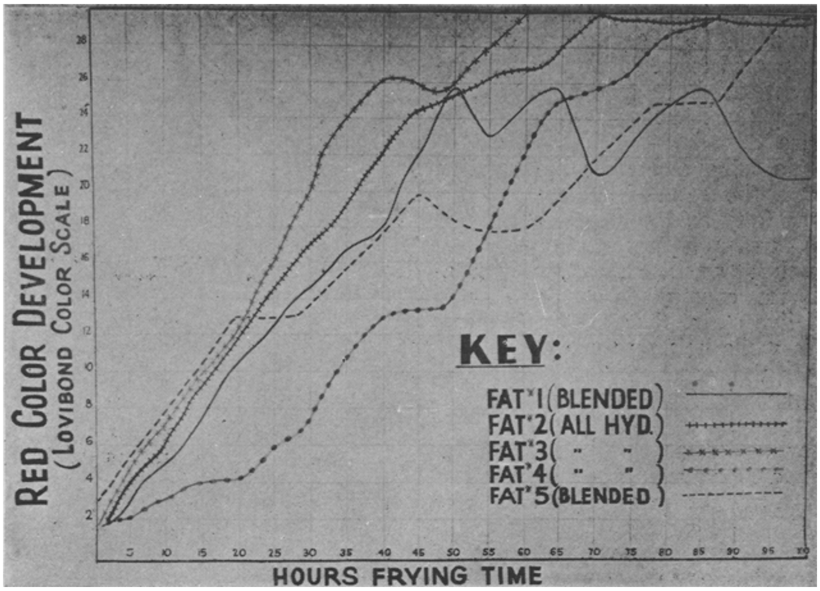
During the test, a close watch was kept upon the behavior of the fats in the doughnut machines; that is, they were observed for excessive smoking, gum formation, foaming, etc. No difference could be detected in the fats, either between the all-hydrogenated shortenings themselves or between the all-hydrogenated and blended shortenings, with the exception that the blended shortenings showed a little more tendency toward gum formation. This tendency, however, was not objectionable.

The results of the analytical tests, when shown graphically, reveal some interesting facts.

First, let us consider the red color development of the fats. (See graph No. 1.)

All of them show a steady increase in color, with one exception, for the first fifty hours of frying. By that time, the color had become so dark that satisfactory readings could not be made. This accounts for the erratic behavior of the upper parts of the curves.

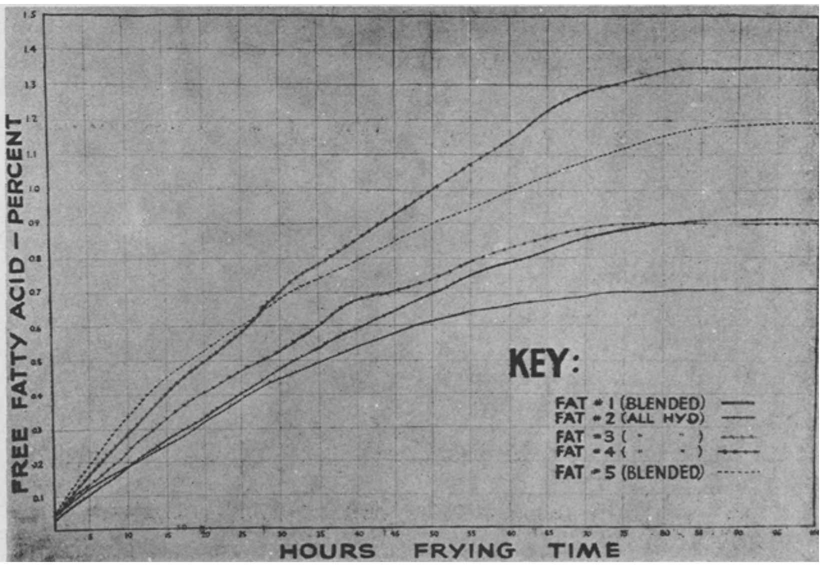
One of the blended fats (No. 5) was used in the test because of its initial high red color reading of 3.5, which was more than twice that of any of the other fats. The color of this fat increased in about the same ratio as the others for the first fifty-five hours and then dropped below all. This might indicate that fats which have not been highly bleached darken less rapidly than those which have.



GRAPH NO. I

In the case of the free fatty acid content increase (Graph No. 2), the curves were found to be very symmetrical. The increase was steady and rapid for the first fifty hours and then a point of equilibrium was reached where the addition of fresh neutral fat counterbalanced the rate of free acid formation. This point of equilibrium was widely divergent for the five fats which were tested, the curve for fat No. 1 straightened out at about 0.70 per cent while fat No. 3 reached 1.35 per cent. It is interesting to note that fat No. 1 was a blended shortening and not a hydrogenated shortening.

This means that most of the doughnuts in the United States are being fried in fat containing at least 0.75 per cent free fatty acid, and since very few doughnut friers produce as rapidly as the rate of this test, the point of equilibrium will average much higher. Many of them use it indefinitely by continuing to add fresh fat, but they do not fry a large enough number of doughnuts to necessitate a constant addition, and in such cases the free fatty acid content may become very high. It is not unknown for used fats containing even 4 to 5 per cent free fatty acids to be used with apparent satisfaction. It should not be



GRAPH NO. II

assumed, however, that fat containing a high percentage of free fatty acid is unfit for human consumption, since a number of investigations have shown this to be false.

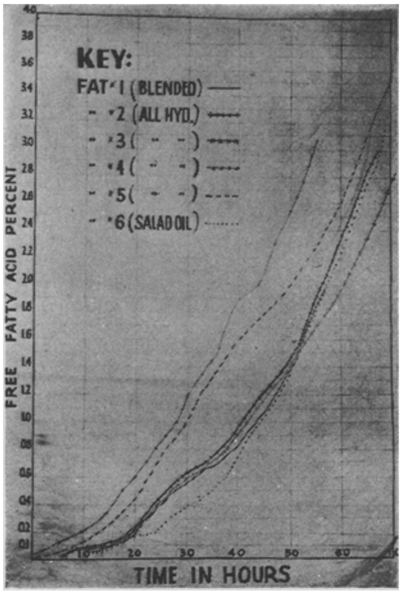
To obtain further information upon the rate of increase of the free fatty acid content in fats and oils under frying conditions when fresh fat was not added, an apparatus was constructed for the blowing of live steam through the fats and oils while holding them at 380° F. This was accomplished by filling a commercial frying machine with fat, heating it to 380° F., and then blowing steam through the fat at a constant rate. The fats were tested regularly for free fatty acid. The results which were obtained are shown graphically (Graph No. 3).

The rate of increase was found to vary as much as 100 per cent between some fats. One point, which is of interest, is that a sample of winter pressed cottonseed oil which was tested was found to have one of the lowest rates of increase in free acid. The cottonseed oil, however, showed much more of a tendency toward gum formation than any of the other fats. This indicates that the presence of unsaturated glycerides (as shown by the iodine number) may lower the rate of hydrolysis. These results also indicate that more attention should be given to the rate of increase of the free fatty acids and color, when used by the consumer, than has been the practice in the past. It is of little benefit to the consumer to buy a fat or oil which has a low acid and color if it is not stable and breaks down quickly. Many popular ideas concerning the stability of hydrogenated fats for deep frying seem to be founded on fancy rather than fact.

Very little can be said about the smoke point except that as the free fatty acid goes, so goes the smoke point, except that they go in different directions (Graph No. 4).

There is a terrific drop in the smoke point during the first few hours of heating and then a gradual straightening out of the curve as the free fatty acid content reaches a point of equilibrium.

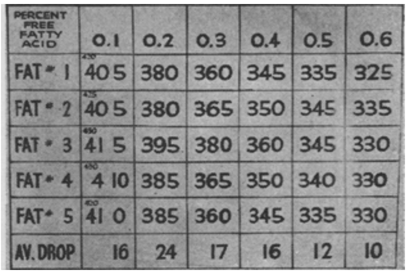
The smoke point of all five fats dropped down to the frying temperature of 385° F. in ten hours' frying time or less.



GRAPH NO. III

The operators and manufacturers of deep fat frying machines know that the smoke point of the frying fats soon drop below the frying temperature and for that reason most of them have made some provisions for carrying off the smoke. Many of the larger machines are completely enclosed and have outlets equipped with fans to draw off the smoke and fumes. If this were not done, it would be almost impossible for the operators to work in the acrid atmosphere.

The relationship between the free fatty acid content and the smoke point is very marked. (See Chart No. 2.) For any definite concentration of acid, the smoke point of all five fats is almost the same up to and including 0.7 per cent. Thus the slower the rate of increase of the free fatty acids, the slower the drop in the smoke point and the higher the point at which it will reach an equilibrium.



PERCENT FREE FATTY ACID	0.1	0.2	0.3	0.4	0.5	0.6
FAT # 1	430 405	380	360	345	335	325
FAT # 2	425 405	380	365	350	345	335
FAT # 3	430 415	395	380	360	345	330
FAT # 4	430 410	385	365	350	340	330
FAT # 5	400 410	385	360	345	335	330
AV. DROP	16	24	17	16	12	10

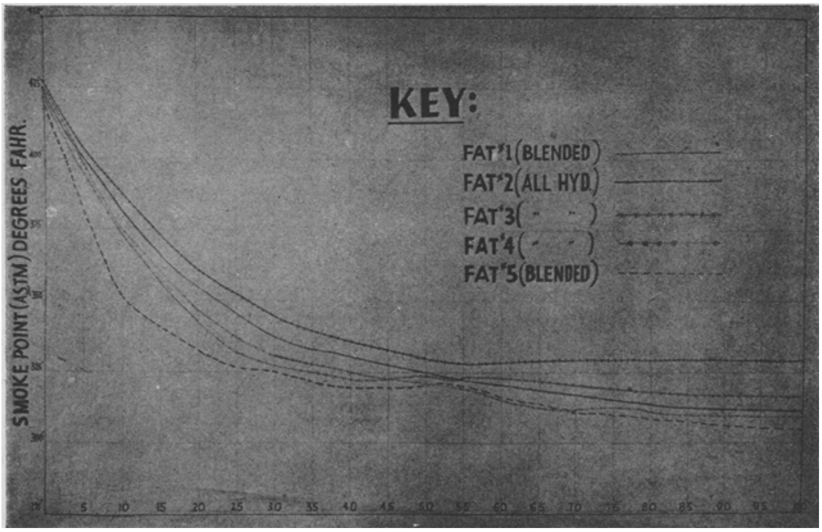
CHART NO. 2

Most of the results which have been presented here were obtained in a test which was run primarily to determine if there was much difference in the absorption rate of different fats when used for frying doughnuts. The results, from the standpoint of absorption, may be of some interest.

All of the fats showed wide variations in their rate of absorption during the first four days they were in use. After they reached a point of equilibrium between the used and fresh fat, the rate became fairly constant. This shows the fallacy of basing any conclusions on tests of short duration.

The absorption rate, in ounces of fat per dozen doughnuts, weighing twelve ounces, was found to be as follows:

Fat No. 3 (all hydrogenated).......	1.646
Fat No. 2 (all hydrogenated).......	1.682



HOURS FRYING TIME

GRAPH NO. IV

Fat No. 5 (blended)	1.762
Fat No. 4 (all hydrogenated)	1.777
Fat No. 1 (blended)	1.792

The spread between the highest and lowest being 0.146.

When the question of cost is considered, the blended shortenings were the cheapest to use due to their lower initial cost.

Since the free fatty acid content, color, and smoke point of fats and oils, have been shown to change rapidly when used for deep fat frying, perhaps this paper should have been entitled "Unstability of Fats Used for Deep Fat Frying."

THE OCCURRENCE OF PHOSPHORUS IN SOYBEANS

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Abstract

The phosphorous compounds present in soybeans have been tentatively divided into four groups. Methods for determining these groups have been studied and applied to the analysis of a sample of soybeans.

WHENEVER phosphorus is mentioned in reference to soybeans it is usually associated solely with the phosphatides known to be present in this legume. The phosphatides, however, contain only a small part of the phosphorus present in soybeans. It is the purpose of this paper to point out the other compounds of phosphorus occurring in soybeans and to indicate their relative abundance. Compounds of phosphorus found in seeds may be classified in four groups, namely, phytins, phosphatides, nucleic compounds, and inorganic phosphorus compounds (5).

The phytins are salts of inositol phosphoric acid and on the basis of the work of Anderson (1) are recognized as hexaphosphates. In the isolation or separation of these substances from natural sources one or more phosphate groups may be removed. Consequently phytins have often been reported as containing only four or five phosphate groups. Phytins usually occur as calcium, magnesium, or potassium salts.

Any lipid ester of phosphoric acid may be defined as a phosphatide. Soybean phosphatides have been discussed in several recent papers appearing in this journal (12) (7) and no further discussion is needed here.

The nucleic-phosphorus compounds include phosphoproteins and nucleic acid derivatives. They occur in various amounts in living material, but only in relatively small amounts in soybeans. Comparatively little is known about them. The inorganic phosphorus compounds may occur either as potassium acid phosphates, as suggested by Osborne (9), or as other similar substances.

In connection with certain experimental work of the U. S. Regional Soybean Industrial Products Laboratory, it was considered essential to be able to determine the relative amounts of the different types of phosphorus compounds present in soybeans. When considering the analysis of the soybeans in connection with the agronomic data available for each sample, the change in total phosphorus is of value, but it is more important to know in which of the several possible compounds the variation occurs. Information of this type is essential in attempting to reach an understanding of the metabolism of the bean.

Some of these phosphorus compounds are relatively unstable when removed from the soybean. For example, the phosphatides are easily oxidized and the soybean proteins in general are altered by almost any kind of treatment. Separation by solvents at temperatures not much above that of the room, while perhaps not the ideal way, is the best method available. It is exceedingly difficult to ensure complete removal of any one type of phosphorus compound from the bean by the use of solvents.

Nottbohm and Mayer (8) analyzed several samples of commercial lecithin from soybeans as well as from other sources. They determined phosphorus, nitrogen, and choline and showed that the value for lecithin varied greatly according to whether it was calculated from the phosphorus, nitrogen, or choline content. Other phosphorus compounds such as the salts of phosphatidic acid (6) can lead to erroneous values for lecithin if calculated solely on the basis of phosphorus content. The recently proposed color reaction for choline (2) is not specific since similar colors are developed with many other amino compounds. In this laboratory the precipitation of choline with iodine and subsequent titration of the choline-iodine complex (10) has proved most satisfactory. The precipitation is not affected by ethanolamine and can therefore be carried out in the presence of cephalin.

Experimental work carried out so far in this laboratory on the distribution of phosphorus in soybeans has been of a preliminary nature. Typical values for the amounts of phosphorus extracted from soybeans by various solvents are shown in Table 1.

These values were obtained with a four-hour extraction in a Butt type extractor. The samples contained 6 to 7 per cent water, and the phosphorus removed by petroleum ether was low. This has been confirmed by other experiments showing that within limits higher moisture content increases manifold the phosphorus removed by petroleum ether. The phosphorus extracted by these solvents is probably derived chiefly from phosphatides and perhaps also from some inorganic compounds. Phytin probably is unaffected by the treatment. Although repeated extraction with some of the more efficient solvents failed to remove additional phosphorus, it is questionable whether all the phosphatides were removed.

Phytin, which contains most of the phosphorus present in soybeans, is difficult to determine. The

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[1] A cooperative organization participated in by the Bureaus of Chemistry and Soils and Plant Industry of the U. S. Department of Agriculture, and the Experiment Stations of the North Central States of Illinois, Indiana, Iowa, Kansas, Michigan, Minnesota, Missouri, Nebraska, North Dakota, Ohio, South Dakota, and Wisconsin.