Mayonnaise Oils, Mayonnaise and the Kreis Test

Phloroglucinol Reaction Said to be of Value As Indication of Acceptability of Oils for Salad Dressings

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IN point of percentage composition vegetable oil is the most important component of mayonnaise. According to the Federal Standard** the latter must contain not less than 50% oil and in some commercial formulæ it makes up over 80% of the product. The vegetable oils used are relatively unstable, oxidative changes readily occur and once started rapidly reach the stage where the flavor and odor are such as are described by the term "rancid", that is the oils are no longer edible.

To the mayonnaise manufacturer the *chief* concern is not to guard against the use of such inedible oil, but to guard against the buying of oil which might reach that stage, either while in stock or in the form of mayonnaise before being consumed. That is, it is not the question of whether a given oil is sweet and edible but rather, how long will it remain in that condition? How to test this has been the cause of much research and even more controversy. Undoubtedly the best method is to actually observe the length of time it takes a sample of the oil in question, subjected to definite standard conditions, to develop a rancid odor. Unfortunately this involves not only too much time, but a well-trained nose. Another test is that used by Holm and Greenbank.[1] These authors measured the socalled induction period by determining the rate of oxygen absorption by the fat and used this as an indication of the keeping quality of the fat. Unfortunately their method requires apparatus too involved for routine purposes. Several new chemical tests have been suggested recently[2] but so far none have been studied sufficiently to prove them preferable to the so-called Kreis test. The latter is simple enough to be performed by an unskilled workman. Its major requirement is rigorous cleanliness to exclude contamination by oily films on either the laboratory glassware, or the sampling devices. The major criticisms of this test have been that it is not actually a test for the substances causing the rancid test or odor, but rather a test for substances that occur incidentally in the rancid fats, and that under certain conditions sweet fats will give a positive test.[3] However, under normal conditions the Kreis test, as shown by Kerr,[4] and by Kerr and Sorber,[5] enables one to describe the intensity of rancidity in terms of the degree to which the oil may be diluted with an inert or inactive diluent and yet give a definite pink reaction.† Thus an oil may be reported negative, +1 or more depending upon whether the undiluted oil is negative or positive and how far it may be diluted and yet produce a definite pink color reaction. Now if the oil were to be tested by odor or taste certainly the oil giving +1 or even +5 would be judged sweet, and would be perfectly wholesome for food purposes. In other words, on the basis of actual rancidity as discerned by the nose and the taste organs, the test is supersensitive, and this may well lead the average lay observer to question its applicability to a fair evaluation of the oil. The writers believe it might have been less confusing to others than chemists, to describe the test as one for the detection of the keeping quality of the oil. Holm and Greenbank[1] show this relationship and state "The sensitiveness of the Kreis test and its strict quantitative relationship to oxygen make it an exceedingly good measure of oxygen absorbed, other changes being excluded."

** "Mayonnaise, Mayonnaise Dressing, Mayonnaise Salad Dressing, is the clean, sound, semisolid emulsion of edible vegetable oil, egg yolk or whole egg, a vinegar or lemon juice, seasoned with one or more of the following: salt, sugar, spice, commonly used in its preparation. The finished product contains not less than 50 per cent of edible vegetable oil, and the sum of the percentages of oil and egg yolk is not less than 78."

* Before Fall Meeting, American Oil Chemists' Society, Chicago, October, 1931.

† Details of Kreis Test. To 5 cc. sample of oil in clean test tube are added 5 cc. concentrated hydrochloric acid, and the mixture shaken 30 seconds. Five cc. of 0.1% ethereal solution of phloroglucinol are then added, and again shaken for 30 seconds, and allowed to stand until clear. Development of pink color constitutes positive tests. Blank test on reagents is required to be negative. By "Kreis Number" is meant the proportion to which a sample of oil may be diluted with petroleum ether before a negative test results.

Table 1

KREIS TEST OF OIL BEFORE AND AFTER INCORPORATION IN MAYONNAISE

Oil after Separation from Mayonnaise stored for Indicated periods at 70° F.

	Oil used Cottonseed	Initial Kreis test	Age days	Kreis Taste		Age days	Kreis Taste		Age days	Kreis Taste		Age days	Kreis Taste		Age days	Kreis Taste	
1.	Non-winter ...	neg.	0	neg.	O.K.	6	neg.	O.K.	16	neg.	O.K.	28	neg.	"off"	38	neg.	"off"
2.	Winterized ...	neg.	0	neg.	O.K.	6	neg.	?	16	?	"off"	28	neg.	"off"	38	neg.	"off"
3.	Winterized ...	6	0	4	O.K.	9	neg.	?	21	neg.	O.K.	31	4	"off"			
4.	Non-winter ...	3	0		O.K.	10	neg.	"off"									
5.	Winterized ...	22	0		"off"	10	15	Rancid									

On this basis therefore, we considered the Kreis test to be useful, although there remained to be determined whether for practical purposes a negative Kreis test was absolutely necessary. To test this question we obtained several samples of refined cottonseed oil ranging in Kreis test from strictly negative to a positive 22. Mayonnaise was prepared with each of these. Two series of observations were made, first, a comparison of the taste of the mayonnaise with the Kreis test of the oil separated therefrom, and second, a correlation of the rate of development of stale flavor in the mayonnaise with the original Kreis test on the oil as used. In each case the oils were tested just before being used and periodic observations were subsequently made until a definite stale or "off" oil flavor had developed in the mayonnaise.

Experimental

AS STATED above two types of observations were made (a) to correlate the Kreis test on oil separated from a mayonnaise with the actual condition of the mayonnaise at that time, as determined by taste and odor; and (b) to correlate the Kreis test of the oil as used with the taste and keeping quality of the mayonnaise made with it.

When oil is incorporated into mayonnaise it is no longer just cottonseed oil, or corn oil, as the case may be, but a mixture of such an oil with the oils and other fatty substances from the egg yolk and from the spices. The emulsifying process causes it to come into intimate contact with an acidified aqueous surface well saturated with atmospheric oxygen. Whether under these circumstances the changes produced in the oil are at all related, and in what manner, to the changes which such an oil normally undergoes, is not known.

We tested this point by comparing Kreis test of the original oil with the same test on oil after having been incorporated into mayonnaise, and we also compared the onset of stale or "off" oil flavor with the Kreis test. We used two lots of negative cottonseed oil kindly furnished by Procter & Gamble Co., as well as several samples of oil of varying degrees of rancidity, as determined by the Kreis test. In each case the Kreis number was determined just prior to preparing the mayonnaise. Subsequently the mayonnaise was stored in clean 3½ oz. glass jars and at intervals samples were removed to be tasted and then frozen to obtain a clear separation of oil for use in determining the Kreis number. The results are given in Table 1.

There is but one conclusion to draw from Table 1, namely, that the Kreis test on oil separated from mayonnaise bears no relationship to the staleness of the mayonnaise. Unless the oil is very bad no positive test is obtained. Additional observations were made to determine the rate of staling of mayonnaise made with these different oils. The results are shown in Table 2.

Table 2

RELATION OF KREIS TEST OF OIL TO DEVELOPMENT OF "OFF" FLAVOR IN MAYONNAISE

Batch Number	Kreis Number of oil used	Type of oil (Cottonseed)	Latent Period or Approx. time to develop "off" oil taste in Mayonnaise Storage at 70° F. in light. Days
1	negative	non-winterized	28
2	negative	winterized	16
3	3	non-winterized	10
4	6	winterized	31
5	8	winterized	8
6	20	winterized	0
7	22	winterized	0

The length of time in days, from the preparation of the mayonnaise until the latter develops a definite "off" or stale oil flavor, we have termed the *latent period.* It seems proper to conclude from Table 2, that as the Kreis test color of the original oils increased in intensity the shorter was the latent period, that is, the more rapid was the subsequent development of undesirable flavor in the mayonnaise. Thus there is a definite advantage in purchasing oils giving a negative Kreis test. While this condition represents the ideal, it is still possible to use oils having low Kreis numbers with satisfactory results. For our own purposes we believe that +4 should be regarded as the upper limit of acceptability, and such oils should be used only on relatively rare occasions. For safety the major shipments of oil should be below this Kreis number and preferably, Kreis-negative.

At present our observations are not extensive enough to be definitely conclusive, yet they provide, we believe, enough data for drawing a rough curve of the life expectancy of mayonnaise from the standpoint of fresh sweet flavor. This curve is shown in Figure 1. Actual length of time that a given sample will remain fresh of course, will differ with conditions of storage but we feel warranted in making the following general conclusions:

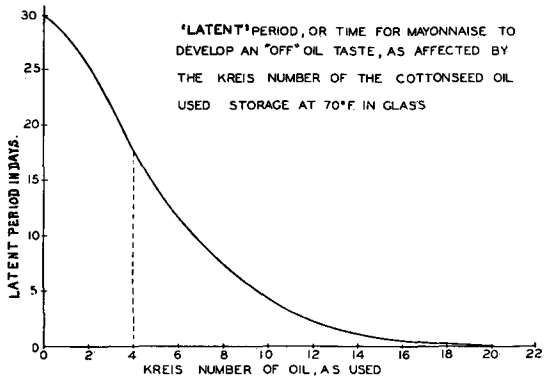

Fig. 1

1. The Kreis test is of no value in following rancidity changes in oil *after* its incorporation into mayonnaise.

2. Despite its empirical nature and its practical shortcomings the Kreis test should be retained as a rapid test which gives some indication of the acceptability of oils for mayonnaise. Oils with Kreis numbers up to about +4 may be regarded as acceptable. This, however, should be regarded as the upper limit of acceptability, or even bordering upon the danger zone. For safety the major shipments of oil should be Kreis-negative.

3. *Latent* period is defined as the time in days for mayonnaise to develop an "off" or stale oil flavor. The greater the Kreis number of the oil, the shorter the *latent* period of the mayonnaise.

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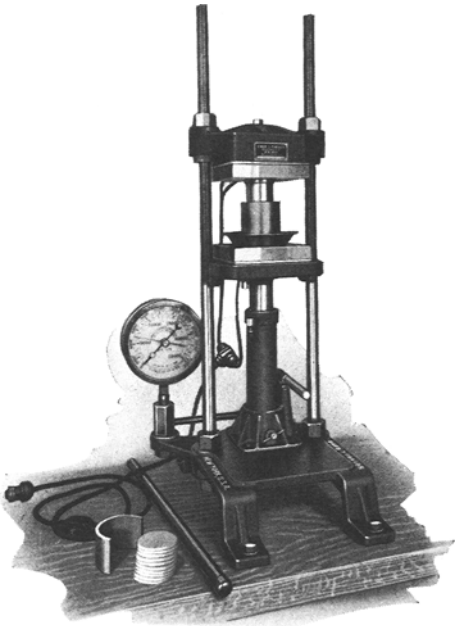
[1] Holm, G. E. and Greenbank, G. R.; J. Ind. Eng. Chem. 15 (1923) 1052.

[2] See for examples: Schibsted, H.; 81 Meeting Amer. Chem. Soc. Spring 1931 (Roseaniline).
Kilgore, L. B.; Mayonnaise Manufacturers Association Bull. No. 98, June 25, 1931 (Phenylhydrazone).
Davies, W. L.; J. Soc. Chem. Ind., 47 (1928) 185-7T.

[3] See for instance, Kerr, R. H.; J. Ind. Eng. Chem. 10 (1918) 471 and Smith, W. B.; J. Ind. Eng. Chem. 12 (1920) 764; also Powick, W. C., J. Ind. Eng. Chem. 15 (1923) 66 and J. Agr. Res. 26 (1923) 323-62.

[4] Kerr, R. H.; J. Ind. Eng. Chem. 10 (1918) 471.

[5] Kerr, R. H. and Sorber, D. G.; J. Ind. Eng. Chem. 15 (1923) 385.

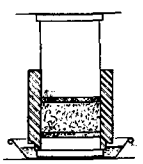


Laboratory Hydraulic Press

Fred S. Carver, 345A Hudson Street, New York City, has recently perfected a laboratory type of hydraulic press, especially designed to obtain hydraulic oil from samples of oil-bearing seeds and nuts, for determination of free fatty acid percentage in such oil or for other analyses.

The Carver Laboratory Press is equipped with electrically heated platens and with special container for the accommodation of samples of cottonsed or other oil-bearing seed. When the seed is properly ground and pressed in the Carver hydraulic press, only a few minutes are required to obtain a sample of hydraulic oil for the determination of free fatty acid. Obtaining the oil in this way in the laboratory assures the chemist of a free fatty acid test on oil obtained in a manner entirely analogous to that of mill practice.

The special container is furnished complete with filter pads and oil-receiving pan and the entire assembly is neat and compact. The press and all accessories are well-machined and finished and the complete outfit will undoubtedly find a variety of applications in the oil-chemists' laboratories.



Special Seed Container for Carver Laboratory Hydraulic Press

Cottonseed meal used as fertilizer during the 12 months ending July 31, 1931, is reported by the Agricultural Economic Bureau of the Department of Agriculture to have been 215,329 tons, or about 9 per cent of the total production of cottonseed meal from the 1930 cotton crop. Manufacturers of commercial fertilizers used 76,023 tons and farmers applied 139,306 tons directly to the soil. This is an increase of about 30,000 tons used by farmers over the amount they used the previous year, the amount used in commercial fertilizers having been approximately the same both years.

The fact that cottonseed meal is too valuable as feed to be put to fertilizer purposes, is becoming generally recognized. It is not so many years ago that from 20 to 25 per cent of the production was thus used. Farmers are learning that they may feed cottonseed meal to cattle and retain over 80 per cent of its ammonia value in manure.

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Sulfation of castor oil is said to take place, in part, at the double bond; a stable gamma-hydroxy-stearic acid is not obtainable from stearolactone without first separating the stearolactone from the accompanying fatty bodies. Although determination of the actual composition of a fatty modification obtained by the action of sulfuric acid is not always possible and even though the identification of the parent oil is often difficult, one can always ascertain that modification has taken place. *Ind. and Eng. Chem. Anal. Ed.* 3,243, (1931).

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The weak point in the determination of unsaponifiable matter in fats by the wet method is said to be the contamination by soap of whatever solvent is used for extracting the unsaponifiable matter from the aqueous soap solution. It is proposed to treat the petroleum ether solution of the unsaponifiable matter with anhydrous sodium sulfate instead of washing it with 50 per cent alcohol before evaporating. *Chem. Ztg.* 55,363 (1931).

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Procter & Gamble Manufacturing Co. has filed an appeal against a recent decision of the U. S. Customs Court which held that whale oil rendering on board a Norwegian vessel in the Antarctic and brought into the United States was a foreign import and so dutiable under the 1930 Tariff Act. Procter & Gamble denied that the Antarctic was Norwegian territory and also attacked the validity of the Court's claim that ships at sea and the property in them are a part of the country to which they belong. The appellants claim that the whale oil should be admitted duty free.

In the determination of acid number and saponification number of fats, to overcome the errors due to the presence of lime soap or other metallic soaps, the following method of determining acid and saponification number is recommended: Dissolve 4-5 grams of the fat in a neutralized mixture of 90 per cent by volume of 70° petroleum ether and 10 per cent by volume of absolute alcohol; add 30 cc. of 50 per cent alcohol, then titrate the warm lower aqueous solution to permanent rose color to phenolphthalein. Determine the saponification number as usual after decomposing the fat with acid. The percentage of soaps is calculated from the acid numbers before and after decomposing the soaps in the fat. *Seifensieder-Ztg.* 58, 254-5 (1931).

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In making "non-freezing" lubricants, oils or fats are mixed with a glycol or with a hydroxyl containing ether of a glycol and a dispersing agent such as soap, a high-molecular-weight sulfonate or an alkylolamine; for example, a mixture of spindle oil and tallow, colophony or paraffin oxidation products is mixed with ethylene glycol, borax, benzyl alcohol and an aqueous potash solution to form homogeneous product suitable for lubricating locomotive axles, electric contacts, rail switches, etc., or for use in hydraulic presses or brakes or as a rust preventing coating. Brit. Pat. No. 240,294.

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The oxidation of fats is accelerated sensibly by weak artificial light, while exposure to direct sunlight for a few minutes suffices to produce rancidity. The reaction is autocatalytic, and even brief exposure to light accelerates the subsequent oxidation. Bleaching of the lipochrome of beef fat occurs at a comparatively early stage of the oxidation process. A distinct parallelism exists between the active oxygen content of a fat and the intensity of its response in the Kreis reaction, but at low temperatures the content of active oxygen increases more rapidly than the ability to respond to the test. In bright sunlight, the reverse is true. *Proc. Roy. Soc.* (London) B108, 175-89 (1931) *Chem. Abstr.* 25, 4424 (1931).

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The composition of the fat of sow milk is approximately: oleic acid 64.5, palmitic 26.6, myristic 2.6, volatile acids, (caprylic and caproic) 1.4, glycerol 4.9%. *Ann. fals.* 24,87-8 (1931).