Studies Relating to Foaming Tendencies in Edible Oils and Fats

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IT IS a well established fact that oils, fats and hydrogenated products made from these or various mixtures of these products will foam after a certain period of time when used as deep fat frying agents.

The length of time which any oil or fat may be used for deep fat frying is presumed to depend upon several factors, principally temperature of frying, the length of time used for frying, and the amount and type of product cooked in a single batch of oil. Usually, in continuous deep fat frying it is customary to replenish the supply of oil as it is absorbed by the material processed in it.

A search of the literature failed to reveal much fundamental information on the relationship of the various physical and chemical properties of shortenings, oils, and fats to their foaming tendency or resistance to foaming. There was no indication of a method which might be suitable for laboratory control studies of the foaming properties of oils and fats. It was necessary, therefore, that a suitable procedure be developed which would correlate to some degree with the practical use of these materials.

After some experimentation, the following test method was selected as most satisfactory:

Two hundred fifty grams of any deep fat frying material were placed in a 400 cc. beaker, the beaker partially immersed in an oil bath, electrically heated and thermostatically maintained at about 375°F. At intervals during the day, water-soaked pieces of bread were dropped into the beakers and the amount of foaming noted. It was readily possible to designate foam in the following manner, in watching the course of any experiments: Very slight, slight, appreciable, strong, very strong, and foaming over the top of the beaker. In all of our observations it was customary to maintain a standard control sample of an original source fat. In the course of developing this method, it was found that apart from the kind of food fried, time and temperature were the primary causative factors in the breakdown of an oil or shortening material to the point of foaming. No appreciable difference was found whether the fat was cooked in continuously or only every half to one hour when moistened bread was used.

FOAM STUDIES

Our first determinations, using the above-outlined method, were made on individual oils such as might be incorporated in shortening materials. Table I gives the results of these studies:

TABLE I.

Type of Oil	Hours Strong Foam	Hours Foamed Over
Bleached Cottonseed	14	16
Bleached Soybean	13	16
Bleached Cocoanut	10	12
Refined Palm	16	25
Unbleached Cottonseed	14	15
Very heavy bleached Cottonseed Oil	13	15
45-titer hydrogenated Cottonseed Oil	16	24
40-titer hydrogenated Soybean Oil	16	22

In Table II, are listed the results on foaming tendency, studying varying degrees of hydrogenation of cottonseed oil:

TABLE II.

Type of Product	Hours Strong Foam	Hours Foamed Over
Cottonseed Oil hydrogenated to 2° R.I. drop	15	19
Same—hydrogenated to 3° R.I.drop. (ZB)	15	22
Same—hydrogenated to 5° R.I.drop. (ZB)	21	24
Same—hydrogenated to 6° R.I.drop. (ZB)	21	29

The results shown in these two tables indicate that individual oils, with the exception of refined palm oil, have a tendency to foam at 15 to 16 hours. There was some indication that a relatively high degree of saturation of the oil in hydrogenation improved foam resistance.

A third series of tests was run on mixtures of oil to determine their foam quality:

TABLE III.

Oil Mixture	Hours Strong Foam	Hours Foamed Over
Cottonseed-Soybean Oil	13	15
Cottonseed-Soybean-Palm Oil	14	15

These results indicate that a mixture of oils foams somewhat worse than the individual oils themselves. These mixtures were made up in several varying proportions.

Viscosity determinations made on the various hydrogenated products particularly showed that original viscosities measured in arbitrary units by the pipette method at 50°C. ranged from 24.5 to 26.5 seconds. After these shortenings were heated in open beakers, placed in an oil bath maintained at 375°F. for 40 hours with occasional frying of wet bread in them, their viscosities ranged from 31 to 38 seconds, but no distinct correlation existed between the amount of increase in viscosity and the amount of foaming produced in various shortenings when the wet bread was introduced. This increase in viscosity indicated that a certain amount of polymerization occurred during heating. This was borne out by the observation that the iodine numbers decreased and the refractive index increased during heating, but again no distinct correlation could be found between the degree of change in these properties and the amount of foaming when various shortenings were compared. On a few samples of unhydrogenated and hydrogenated soybean and cottonseed oils, there seemed to be some relation between the increase in refractive index and the amount of foaming; the greater the amount of foaming the greater was the increase in refractive index during heating. The addition of 25% of highly polymerized blown cottonseed oil to a sample of shortening caused it to foam immediately, while the addition of 2.5% of the same blown oil caused foaming in 24 hours. The shortening alone foamed in 40 hours.

In connection with other work it had been noted that some refined cottonseed and soybean oil purchasable on the market contained considerable amounts of gums and resins which could be removed by a re-refining with caustic. Since 1938 oils were generally quite low in free fatty acids, usually only small amounts of caustic were necessary for refining and, as a result, not all the gums were removed. Cottonseed and soybean oils, which had been refined on an acid basis and washed, were re-refined with 1% of 16° Be' caustic and the foots separated in the laboratory centrifuge. Part of the resulting oil was washed with water and part with dilute hydrochloric acid and then with water. Another part was filtered through kieselguhr. A portion of the original oil was bleached with 1% of Fullers' earth. Foam results on these oils follow:

TABLE IV.

	2 hrs.		9 hrs.		10 hrs.		12 hrs.		18 hrs.	
	Cotton-seed	Soy-bean	C.S.	S.B.	C.S.	S.B.	C.S.	S.B.	C.S.	S.B.
Orig. Refined Oil	OK	OK	OK	OK	OK	OK	SF	SF	BF	BF
Orig. Oil Bleached	OK	OK	OK	OK	OK	OK	VSF	VSF	F	F
Re-refined Oil	SF	SF	OK	VSF	OK	OK	OK		OK	OK
Re-refined Oil, water-washed	OK	OK	OK	OK	OK	OK	VSF	VSF	F	F
Re-refined Oil, acid then water-washed	OK	OK	OK	OK	OK	OK	VSF	VSF	F	F
Re-refined Oil, filtered	OK	OK	OK	OK	OK	OK	VSF	VSF	F	F

KEY:
SF—Slight foam
BF—Strong foam
VSF—Very slight foam
F—Foam

The re-refined oils darkened considerably and foamed at the start, but after 6 hours heating did not foam. When the same oil was water-washed, acid-washed, or filtered through kieselguhr, all of which procedures removed further traces of impurities, the oil foamed after 12 hours heating. From this it is evident that the presence of certain trace impurities in the oils may prevent foaming to a marked extent. Also, the oils that were re-refined and water-washed did not foam as badly as the commonly refined oils. Thus, the removal of gums left in the oils by light caustic refining increases the stability of the oils toward foam but excessive impurity removal will decrease foam stability.

Next, the effect on foam of the use of different amounts of caustic in the refining of soybean oil was tested. Seven pounds of extracted bean oil (F.F.A. 1.3) was refined with 3% of 16° Be' caustic and seven pounds with 6% of 16° Be' caustic. Half of each batch was run through the laboratory Sharples machine and half let settle in the conventional manner. Half of the conventionally refined oils was washed with 3% caustic solution. Finally all the oils were washed free of trace materials with water and the water separated in the laboratory Sharples machine. Foam data follows:

TABLE V.

	16 hrs.	20 hrs.	24 hrs.
3% Sharples refined	OK	Sl.Foam	Foam
3% Kettle refined	Sl.Foam	Foam	Foam
3% Kettle refined—Caustic washed	V.Sl.Foam	Foam	Foam
6% Sharples refined	OK	OK	Sl.Foam
6% Kettle refined	OK	Sl.Foam	Foam
6% Kettle refined—Caustic washed	V.Sl.Foam	Sl.Foam	Foam

From this, it is seen that the use of large amounts of caustic in refining somewhat increases the stability toward foam up to a certain limit.

The next test was to determine the effect on foam of the addition of alkaline earth soaps to a hydrogenated shortening. Alkaline earth soaps are considerably more soluble in oils than sodium soaps. The soaps used were prepared from commercial stearic acid and were practically neutral. The percentages of soap used are indicated in Table VI.

TABLE VI.

	2 Hrs.	6 Hrs.	20 Hrs.	26 Hrs.	30 Hrs.	44 Hrs.	50 Hrs.	55 Hrs.
0.01% Ca stearate	OK	OK	SF	F	F	BF	BF	VBF
0.05% Ca stearate	F	OK	OK	OK	VSF	F		
0.1% Ca stearate	BF	SF	OK	OK	OK	SF	F	F
0.05% Sr stearate	OK	OK	OK	VSF	F	F		
0.1% Sr Stearate	OK	OK	OK	OK	VSF	SF		
0.01% Ba stearate	OK	OK	SF	F	F	BF	BF	
0.05% Ba stearate	OK	OK	OK	SF	F	BF		
0.01% Ba stearate	OK	OK	OK	OK	OK	F		
0.01% Mg stearate	OK	OK	SF	F	F	BF	BF	
0.1% Mg stearate	BF	SF	OK	OK	OK	OK	SF	F
Control (no soap)	OK	OK	F	F	BF	VBF	VBF	VBF

KEY:
F—Foam
BF—Strong foam
VBF—Very strong foam
SF—Slight foam
VSF—Very slight foam

From this, it is evident that the addition of alkaline earth soaps increases the stability toward foam. Magnesium soaps were the most effective.

Finally, the effect of several "surface active" agents was tried. Table VII shows the percentage of each product used. The materials used are sold as detergents and wetting agents and some of them contain as high as 60-70% of inorganic salts. The products listed in Table VII were the only ones which, at the time of these experiments, showed promise as anti-foam agents.

TABLE VII.

	2 Hrs.	6 Hrs.	20 Hrs.	26 Hrs.	30 Hrs.	44 Hrs.	50 Hrs.	55 Hrs.
Control (Hydrogenated C.S.Oil)	OK	OK	SF	F	F	BF	VBF	VBF
0.01% MP 89	OK	OK	VSF	VSF	SF	F		
0.1% MP 89	OK	OK	VSF	VSF	SF	SF		
0.01% Aerosol	OK	OK	VSF	SF	SF	F		
0.1% Aerosol	OK	OK	SF	SF	SF	F		

KEY:
F—Foam
BF—Strong foam
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SF—Slight foam
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The following table shows the effect of some of these foam reducing materials on the color, free fatty acids, refractive index, viscosity, initial peroxide value and active oxygen, in comparison to similar constants on the untreated oil after all had been heated at 375°F. with occasional frying of wet bread in them. Also, data is given on the original unheated shortening.

TABLE VIII.

	Time before foam starts (Hrs.)	FFA as oleic	Lovibond Color Read.		R.I. Z.B. Nad 60° C	I.P.V. Mg/kilo	Active Oxygen (Hrs.)	Viscosity at 50° C
			Yel.	Red				
Hydrogenated cottonseed oil—unheated	....	0.04	13	1.0	38.0	2.2	over 150 hrs.	26.1 sec.
Same—heated 55 hrs.	26	0.83	100	15.4	42.4	7.8	5	52.9
Same—heated 55 hrs. with 0.1% Ca Stearate	44	1.51	75	8.4	40.7	10.8	7	40.9
Same—heated 55 hrs. with 0.1% Mg Stearate	55	0.58	100	16.3	39.5	9.8	3	32.4
Same—heated 44 hrs.	26	0.73	50	3.9	41.6	9.0	5	49.0
Same—heated 44 hrs. with 0:05% Ca Stearate	40	0.48	40	3.3	40.3	10.5	5	38.8
Same—heated 44 hrs. with 0.1% MP 89	50	0.33	60	5.8	39.6	7.4	7	33.0

Observation of the foregoing table reveals that the shorter the time before foaming starts the greater is the increase in refractive index and viscosity. Also, with one exception, the shorter the time before foaming sets in the greater is the increase in free fatty acids. Thus, it seems that foaming is tied up with increase in viscosity, as well as increase in free fatty acids in the oils.

In addition to the tests enumerated above, on the effect of adding various materials to shortening in relation to foam resistance, the following compounds were tried out in percentages varying from 0.01% to 0.1%:

Tergitol
Alkanol
Nacconol NR
Cholesterol
Ursolic Acid
Sucrose Octaacetate
Surfasol
Impervium
Opalwax
Monolaurin
Monostearin
Ferric Stearate
Aluminum Stearate
Ferrous Stearate
Sodium Acetate
Sodium Sulfate
Calcium Propionate
Lanolin
Morpholine Stearate
Boric Acid
B-OH Ehtyl Palmitate

None of the materials used was outstanding in preventing foaming of oils or hydrogenated fats and oils. In the case of ferric soaps and monoglycerides there was a decrease in the time before foaming started. Ferric soaps were found to be worse for causing foam than ferrous soaps. It is possible that if any appreciable amount of iron soaps found their way into shortening materials, the tendency to foam would be increased.

According to the method which we have developed and used for studying the foaming tendencies of oil, it would seem that time and temperature are the main factors in the breakdown of an oil which causes it to foam. Hydrogenated oils have a greater resistance to foam than the original oils from which they were produced. Some mineral soaps have a tendency to retard foaming, and use of excess caustic in refining of oils is of some assistance in building up foam resistance. In general, it may be said that there is a fair correlation between the increase in the refractive index and viscosity of a shortening material and the tendency to foam. It was also noted that the shorter the time before foaming sets in, the greater the increase in free fatty acids. There was no tremendous difference found between any type of oil, as to resistance to foaming properties. Some animal fats which are not reported in this study were found to have a higher resistance to foaming than the vegetable oil materials. It would seem possible that in seasons when the fatty acid content of original oils is rather low, there may be a tendency for shortening materials produced therefrom to show a greater foaming tendency than in years when the use of larger amounts of caustic in refining is practiced.

Abstracts

Oils and Fats

Edited by
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Synthetic fatty acids. F. Wittka. *Soap 16,* No. 8, 28-32, 73 (1940).

Mono- and di-glycerides—their use in the food manufacture. *Food Manufacture, 15,* 187-8 (1940). Mono-and di-glycerides of stearic and lauric acid are being used in ever-increasing amounts by many manufacturers of diverse food products. While triglycerides are plentiful in nature, the mono- and di-glycerides have never been found in natural products. These products, having a hydroxyl-containing group at one end and a fatty group at the other end, are thus compatible with polar and many non-polar materials. They are used in food products because they act as emulsifying agents, thickeners, stabilizers, surface tension reducing agents, texture improvers, homogenizers, binders and protective film-forming media. Some of the food products in which they are used are breads, cake, nut butters, margarine, shortenings, ice cream, frozen eggs, salad dressings and dairy feeds.

Determination of acetyl values (of oils). P. M. Bogatyrev, et al. *Org. Chim. Ind. (USSR) 6,* 558-9 (1939). One hundred g. of oil is heated at 75° with 3-5 g. of p-$C_6H_4Me.SO_3H$, 70 ml. of white spirit is added, and the soln. is heated in a Dean-Stark app. for 80 min. at 150-180°; the Ac value is given by 28 n, where n is the vol. of H_2O collected *(Chem. Abs.).*

Chemistry of the spoilage of fats. X. participation of catalase. K. Täufel and R. Müller. *Biochem. Z, 304,* 275-84 (1940). Catalase by decompg. H_2O_2, which aids the oxidation of unsatd. fats, acts as an antioxidant. The presence of catalase in all fat-contg. biol. materials suggests that it may possibly function to prevent undesirable oxidation. Addn. of a liver catalase prepn. to olive oil definitely inhibits the autoxidation, but the inhibitory effect is not parallel to the catalase activity, and may partly depend on some other factor present in the ext. This is actually corroborated by the observation that the antioxidant action of the ext. persists even after the removal of the catalase *(Chem. Abs.).*

Sterols from crude soybean oil. H. R. Kraybill et al. *Ind. & Eng. Chem. 32,* 1138-9 (1940). A combined adsorption and extraction method for the production of a phosphatide-free sterol concentrate from soybean oil, having 15 to 20 times the sterol content of crude oil, is described. From this concentrate without saponification a large portion of the mixed sterols crystallized readily and may be recovered by filtration. The remaining sterols, some of which are combined as esters, are readily recovered by the saponification of a relatively small volume of oil. This method results in the production of "nonbreak" soybean oil and also permits the recovery of the greater part of the sterol glucosides present in the crude oil. In one experiment 234 g. of sterol glucosides and 1,778 g. of mixed sterols were obtained. From 20 to 25% of stigmasterol was separated from different portions of these mixed sterols.

Sterol glucosides from expressed soybean oil. M. H. Thornton, et al. *J. Am. Chem. Soc. 62,* 2006-8 (1940). Sterol glucosides occur to an appreciable extent in com. expeller soybean oil. These glucosides were removed from the oil by adsorption methods and were obtained by acetone extraction of the adsorbed material. The sugar was obtained from the glucosides in almost theoretical yield by first forming the ethyl glucoside and subsequently hydrolyzing the easily soluble ethyl glucoside. The sugar was identified as d-glucose. The sterols obtained by hydrolysis of the glucosides are very similar to the uncombined sterols of the oil and consist of a mixt. of sterols in which stigmasterol occurs to the extent of approx. 24%.

Bodying of dehydrated castor oil. J. D. von Mikusch. *Ind. & Eng. Chem. 32,* 1061-9 (1940). The bodying of dehydrated castor oil proceeded 3 to 4 times as fast as that of linseed oil; for instance, 3.4 hrs. were required to obtain a 40-poise viscosity at 560°F. with raw dehydrated castor oil.