

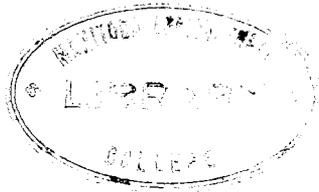
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# THE INFLUENCE OF CHEMICAL AND PHYSICAL FACTORS ON EGG-WHITE FOAMS

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# THE INFLUENCE OF CHEMICAL AND PHYSICAL FACTORS ON EGG-WHITE FOAMS

MARK A. BARMORE

The project under investigation, of which this study is a part, is "The Effect of Altitude on the Baking of Flour Mixtures."

Since egg white is one of the most important constituents of cake batters, particularly in the simpler types; and since the project is especially concerned with the effect of altitude on the cake-baking process, it was decided that a study of the influence of chemical and physical factors on egg-white foams should be the first point of attack.

It would, of course, be useless to attempt to interpret or explain the effect of atmospheric pressure on a complicated mixture, such as a cake batter, when the behavior of each ingredient by itself is but slightly understood.

Egg white is used in cake batters to leaven. It is able to do so by virtue of its ability to entrap air in a finely divided state and to permit its expansion by heat without allowing it to escape, at the same time becoming set. In other words, egg white has the property of forming a stable foam—a special type of an emulsion. Thus the initial problem, as applied to this field, narrows down to a study of the foaming properties of egg white.

## LITERATURE REVIEW

Considerable work on the structure of egg white has been reported, particularly as it is affected by storage. This work has been done largely under the direction of P. F. Sharp, at Cornell (1-5); J. L. St. John, at Washington State College (6-9); H. J. Almquist, at the University of California (10-17), and by others (18-31). These investigators have shown that the white in newly laid eggs has a pH approaching that of the blood of the hen, about 7.6, and that as soon as the egg has been laid it begins to lose carbon dioxide by diffusion. With the loss in carbon dioxide the pH, or alkalinity, increases to about 9.5 within a few days in a well-ventilated room (2). This change takes place more slowly at lower temperatures, and it may be entirely prevented by the presence of air containing the proper concentration of carbon dioxide (1).

Accompanying the above changes and dependent on them is a process known as liquefaction (12). This involves the transformation of the egg white from a firm, viscous state to a more

limpid state, due to a decrease in percentage of firm white and an increase in percentage of liquid white. Almquist and Lorenz (12) were able to show that firm white was composed of a fine, fiber net-work of pure ovomucin, which entrapped the ordinary liquid white. In the absence of sufficient carbon dioxide these fibers break up and so can no longer entrap the liquid white.

It has also been shown by Holst and Almquist (10) and by Almquist and Lorenz (13) that the total solids content in the liquid white of an egg is equal to that of the firm white, regardless of age.

There are two publications by St. John and Flor (7), and by Hunt and St. John (6) reporting work on the foaming properties of egg white. Their studies were undertaken to determine whether eggs containing a large percentage of liquid white (storage eggs) could be whipped as satisfactorily for the preparation of an angel food cake as could the eggs containing a larger percentage of firm white (fresh eggs). According to their findings the more-liquid whites give a foam of larger volume, and more desirable texture than the firmer whites. The liquid portion of the white, on the average, gives a cake of larger volume than the firmer portion. According to them a reasonable length of storage has little effect on the value of the egg white for angel cake.

Another article in which egg-white foam is discussed is that of Otto Rahn (32). In his explanation of why egg white forms a stable foam, he assumes that it is similar to whipped cream and then explains why cream forms a stable foam. Rahn states that it is necessary to have some substance present in the solution that concentrates in the surface, due to its lowering of the surface tension (Law of Gibbs), and then solidifies readily. His idea is that the foam of egg white is a typical emulsion that conforms to the present accepted theories of emulsion stability.

Bancroft (33) states that a foam is similar to an emulsion except that the dispersed phase is air instead of liquid or solid, and that the conditions for forming a froth are much the same as those for the forming of an emulsion, in that the droplets or bubbles must be surrounded by a sufficiently viscous or plastic film to prevent them from coalescing. This film is made up of an emulsifying or stabilizing substance. Wilson and Ries (35) believe that the film or skin is always plastic and not merely viscous. They quote Plateau (36) as having shown that the film viscosity was as much as 1,000 times that of the body of the liquid. The formation of a film is granted in every citation found on the subject except that of Holmes and Child (38), whose interpretation has been criticized (37).

According to Clayton (37) :

"The most stable arrangement accompanying interfaces in general is that the surface energy should be a minimum. Consequently, if a dissolved substance raises the potential energy at the interface, it will tend to leave the interface; if it diminishes the potential energy, then it will concentrate at the interface."

The concentration in the interface is governed by Gibbs law (50), to the effect that if the surface tension is decreased with increases in concentration of solution, the solute tends to increase in the surface in excess of that in the body of the solution; also if the surface tension is increased with increases in concentration, then the solute decreases in concentration in the surfaces, creating a deficit there in respect to the concentration in the body of the solution.

A film is never produced on a pure liquid, but all true solutions will foam if they give either a positive or negative adsorption. In order, however, to obtain a stable foam, the interfacial film or skin must be altered in some manner such that it becomes sufficiently viscous. Few crystalloids fill this specification but most colloids do, especially proteins and peptone (34). Due to the tight packing of the molecules in the film, they coagulate and in the case of protein and allied substances they are chemically altered, i. e., denatured. Coagulation may be produced in a way similar to that effected by Bridgman (41). He showed that egg albumin could be coagulated by excessive pressures.

Ramsden (56), as early as 1894, showed that mere agitation of various protein solutions produced coagulation and a few years later (57) that solid or highly viscous coatings were spontaneously and rapidly formed on the free surface of all protein solutions. Wu and Ling (58) have investigated some of the factors controlling the rate of coagulation of proteins, particularly egg albumin, by shaking solutions of them. They think that the process of shaking merely removes the coagulated protein, which was adsorbed and coagulated, thus exposing a new surface on which adsorption and coagulation may be repeated.

Freundlich (34) states that coagulation may lead to the formation of discontinuous flakes which then stabilize the foams in a manner similar to that of a powder. He goes on to say :

"When a bubble is formed the liquid medium has two surfaces separated by liquid. This liquid drains out slowly due to gravity. The friction is indeed very great for the velocity with which liquid moves in a capillary, according to Poisenille's law, is proportional to the fourth power of the radius. The actual viscosity of the liquid will also be unquestionably of importance; a large viscosity is favorable to the stability of the foam."

The viewpoint of Ware (39) is that emulsifying is a dispersion or thinning action, and that it may be assumed that the vis-

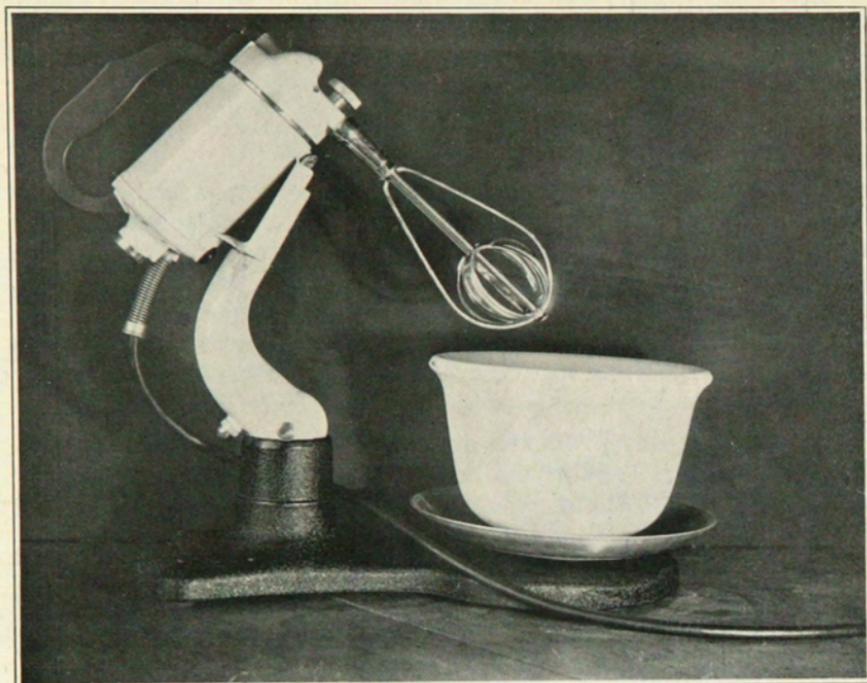


Fig. 1.—Food mixer used in egg-white studies.

cosity of the dispersed phase takes an active part in the process. The viscosity of the emulsifying agent and the dispersion medium are directly related to the stability of the system, and this is of greater importance than the susceptibility of the dispersed phase to a mechanical separation into droplets.

Roberts (40) gives an additional idea on the effect of viscosity, saying that it enters into the mechanism of emulsion formation, by decreasing the speed of adsorption.

Clayton (37), quoting Plateau (36), says that he recognized that in bubbles and foams the two chief factors necessary were a certain degree of viscosity of the liquid used and a low air-liquid surface tension. The former tends to resist thinning of the liquid films to the rupture point, while a low surface tension is necessary because it is the chief active force promoting thinning. Clayton sums up his discussion by the following:

“The conclusion that viscosity aids emulsification solely by virtue of the hindrance offered to coalescence of the dispersed globules, and is not the cause of emulsification, has been accepted by the majority of investigators in this field.”

## MATERIALS AND METHOD

The eggs used in the studies herein reported on were obtained from a local poultry flock of white leghorns. All eggs were obtained either the day when laid or the following morning and were stored at room temperature until used. Eggs used the day laid were considered fresh or of zero age.

The cream of tartar, potassium acid tartrate, was a standard "C. P." product.

The beater used to whip the egg whites was an electric food mixer (Figure 1), which was capable of operating the double whip free of any material at 400, 660 and 1,000 R.P.M. at first, second and third speed settings, respectively. The machine, when loaded, reduced in speed and at the third speed setting it was able to maintain a constant speed of 925 R.P.M. in the egg white and foam. A quart bowl of heavy glass, shown in Figure 1, was used.

The whites of from 12 to 15 eggs were stirred in the bowl of the mixer for 5 to 25 minutes at low speed. This insured a uniform mixture for that particular set of determinations. Fifty-three\* cubic centimeters were then measured out and placed in a similar quart bowl and the mixer started at third speed. The time of beating was taken by stop watch.

In making photomicrographs the small box (Figure 2) containing a removable ground glass, on which the image could be focused, was held in place above the microscope. After focusing, the glass was removed and a film in a film holder was put in its place. The exposure lasted about 10

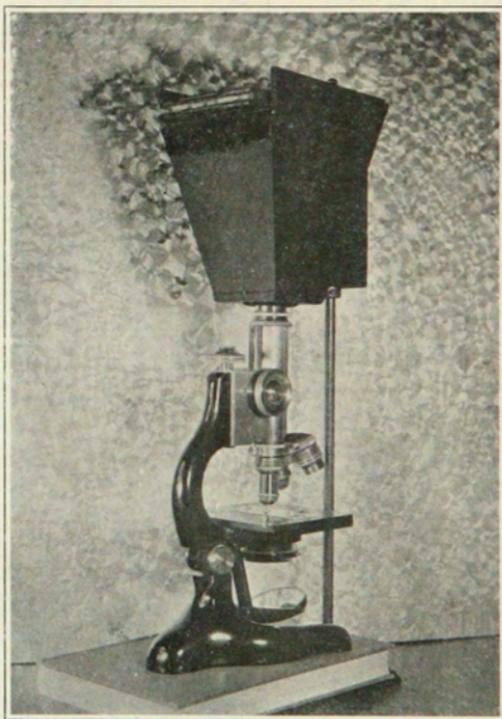


Fig. 2.—Photomicrographic equipment used in taking photomicrographs.

to 15 seconds, with reflected light from a 60-watt lamp at a dis-

\*Found to be the amount that beat the most satisfactorily. This amount was used thruout the entire investigation.

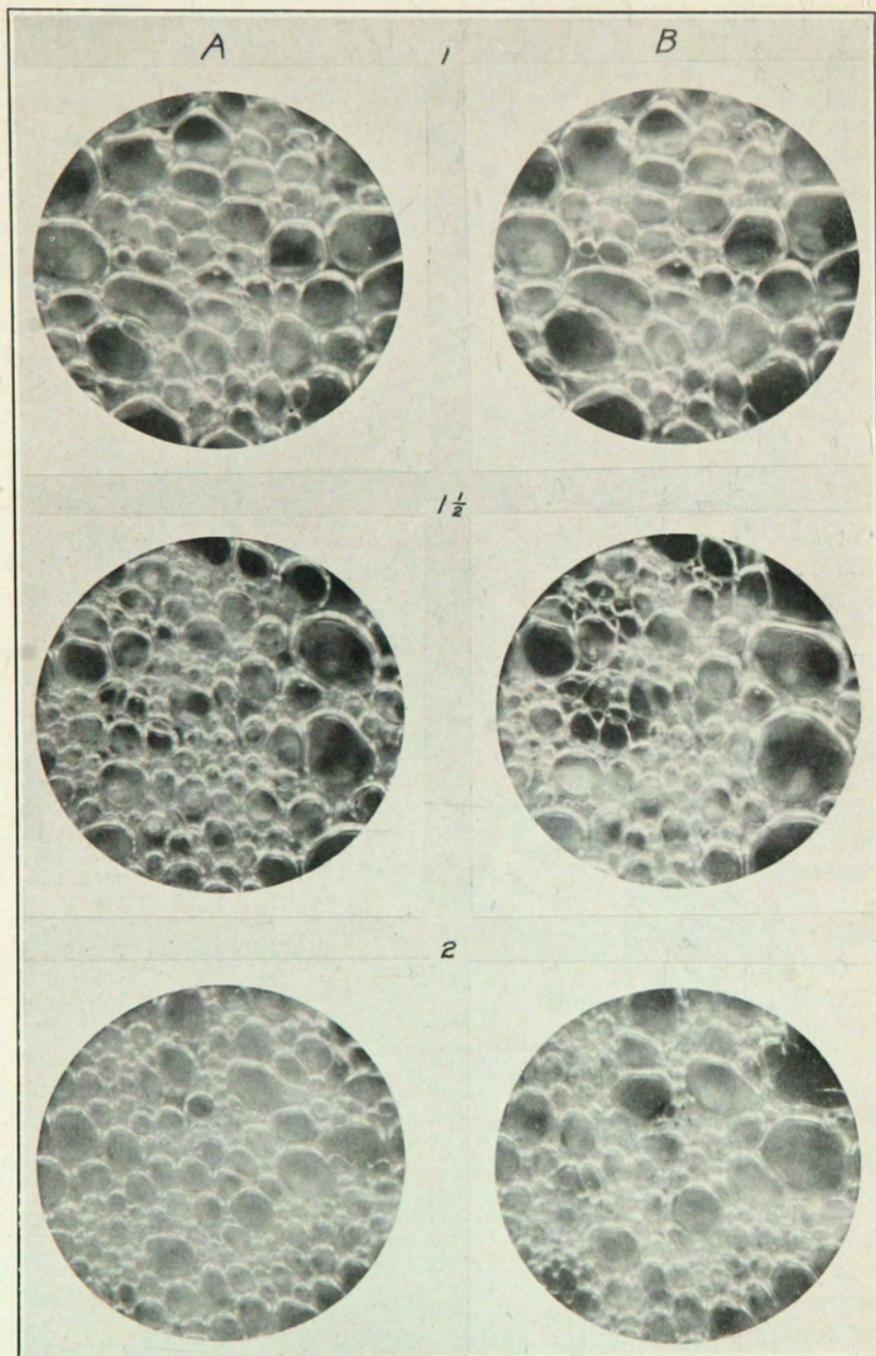


Fig. 3a  
Foam Photomicrographs (magnification 27 diameters). Column A pictures are of foams taken 2 minutes after beating stopped.

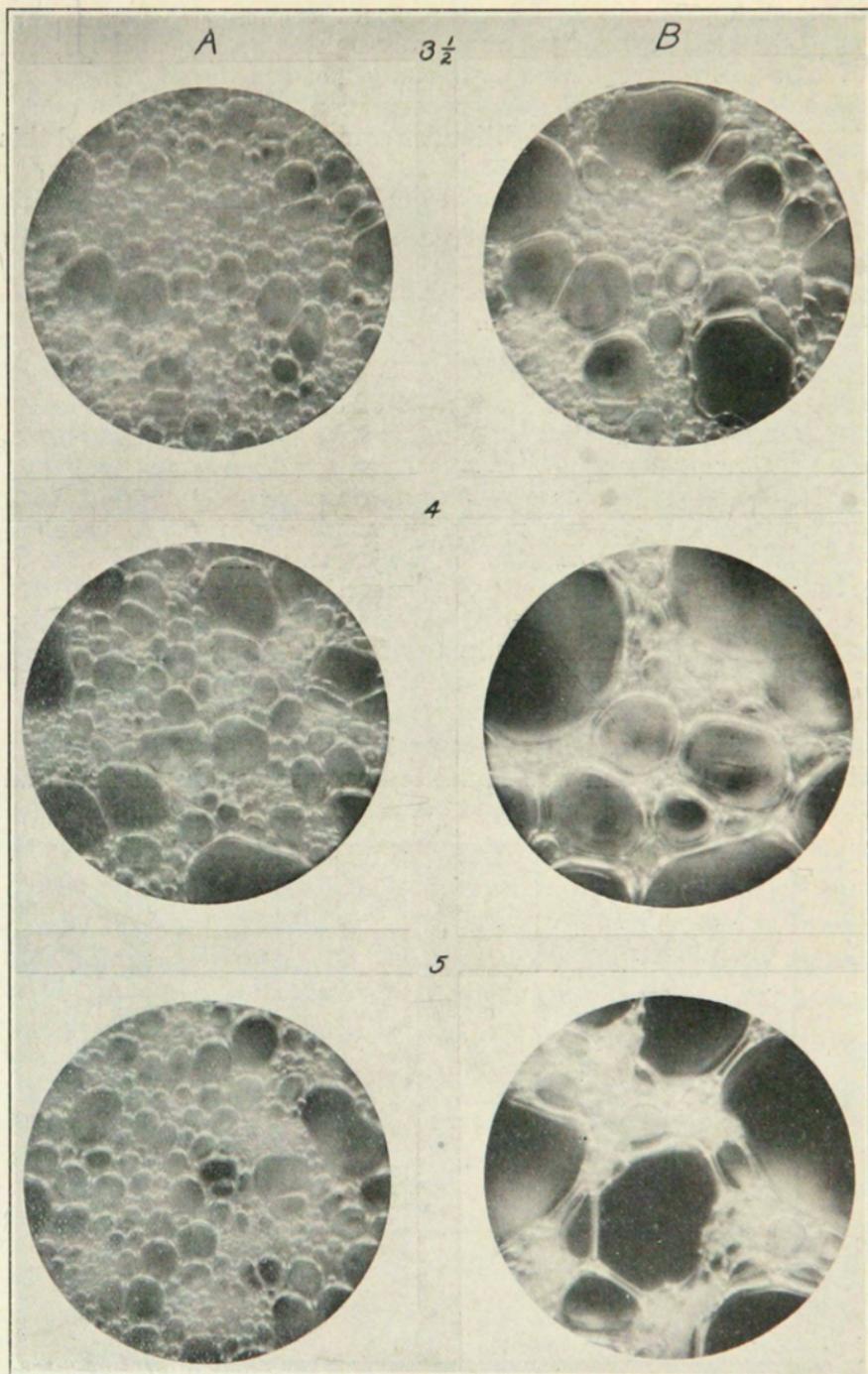


Fig. 3b

Column B pictures are of the corresponding fields taken 10 minutes after beating stopped. The period of beating is given in minutes at the top of each pair of pictures.

tance of approximately 12 inches from the object. The picture was taken either in a dark or a dimly lighted room and the length of exposure was regulated by the length of time the light was left on, since this homemade device contained no shutter.

Later a 9x12 cm. Voightlander camera was obtained and this was used for photomicrographic studies, it being placed above the microscope in the position of the box previously used. In this case, however, it was only necessary to set the camera for infinity distance, to focus the microscope for clear vision with the eye at the microscope eye-piece, then simply to slide it under the camera and take the picture.

### RESULTS

**THE INFLUENCE OF PHYSICAL FACTORS ON FOAM CHARACTERISTICS.**—The first variable studied was that of beating time. Egg whites (3 days old) were stirred for 15 minutes and then beaten at room temperature for periods varying from 1 to 5 minutes. Specific-gravity measurements were made immediately after the beating stopped, in crystallizing dishes 75 x 45 mm. and 180-190 cc. capacity. A small portion of the foam was placed on a microscope slide, covered with a cover glass and a photomicrograph made 2 minutes after beating stopped. The slide and microscope were allowed to stand and 8 minutes later another picture taken of the same field.

The foam specific gravity was plotted against the beating time (Figure 4) and was found to decrease rapidly at first and more slowly after beating had continued for 2.5 to 3.0 minutes.

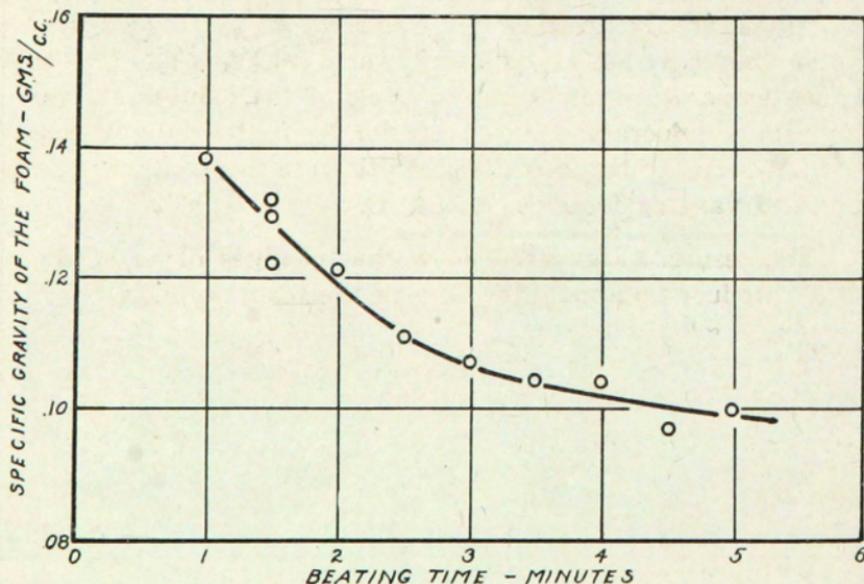


Fig. 4.—The effect of beating time on foam specific gravity.

Figure 3 shows that the longer the foams were beaten the smaller the bubbles and the more unstable they became.

The property of foam stability was investigated further by placing all of the foam produced from 53 cc. of egg white in a 135 mm. funnel and covering it with a watch glass, as in Figure 5.

The amount of draining was determined by weighing from time to time. A typical example of the results obtained is shown in Figure 6. A change of beating time shows a very marked effect, but merely shows quantitatively what was shown microscopically in Figure 3.

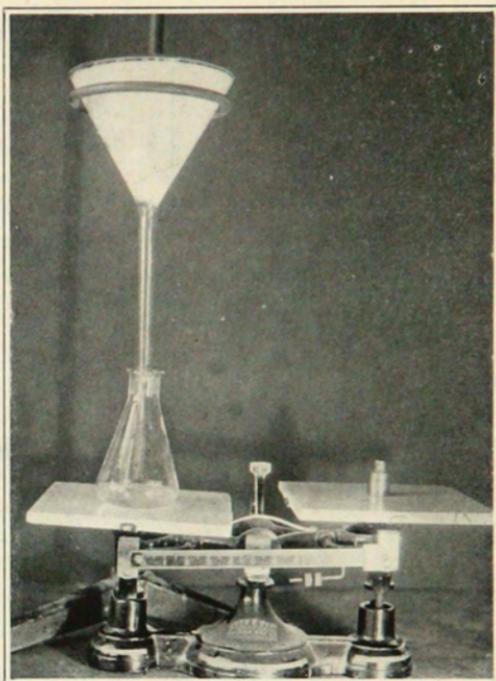


Fig. 5.—The method of determining the rate of draining of the foams.

It was thought that, due to the added time of beating, enough friction may have been produced to warm the foam and that this higher temperature might be the cause of the reduced stability. The rise in temperature on beating for 3 minutes did not exceed  $5^{\circ}$  C. A series of batches of egg white were then beaten at temperatures varying from  $20^{\circ}$  to  $34^{\circ}$  C.

The results (Figure 7) show that changes of as much as  $14^{\circ}$  C. produce no apparent effect on the foam stability.

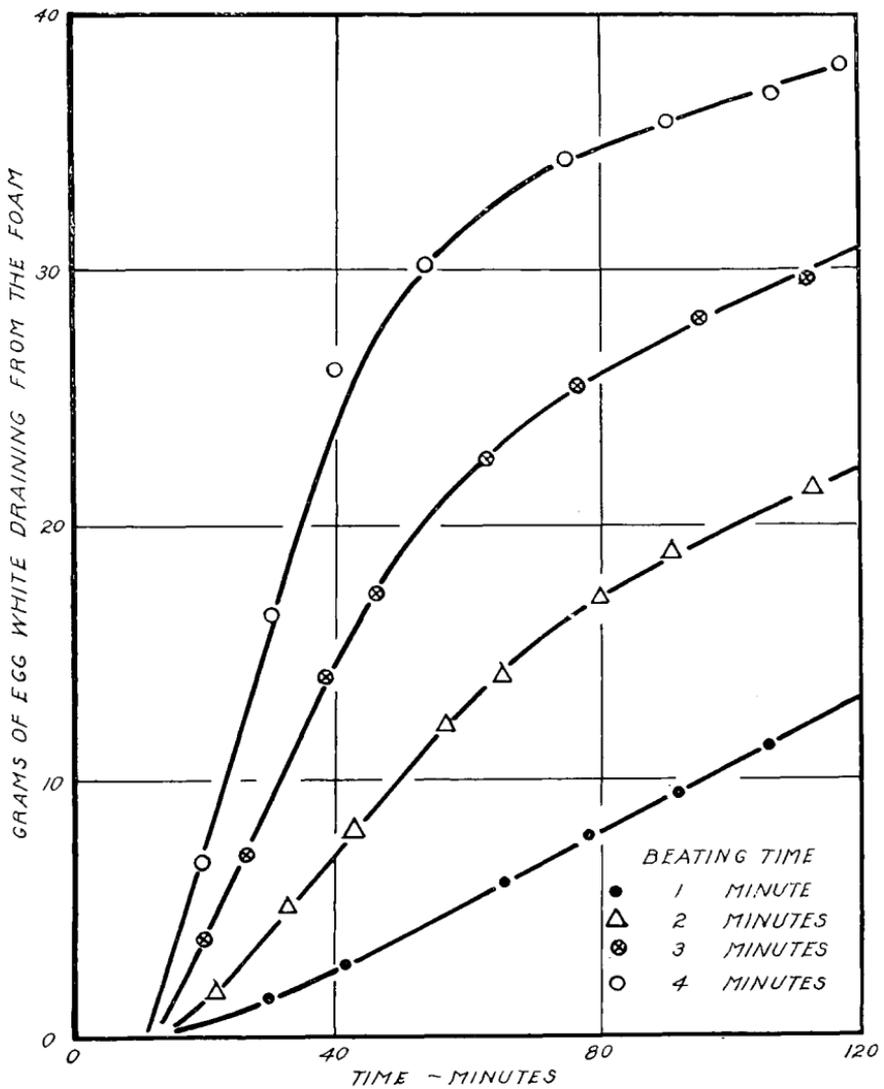


Fig. 6.—The rate of draining of foams produced by beating for various periods of time.

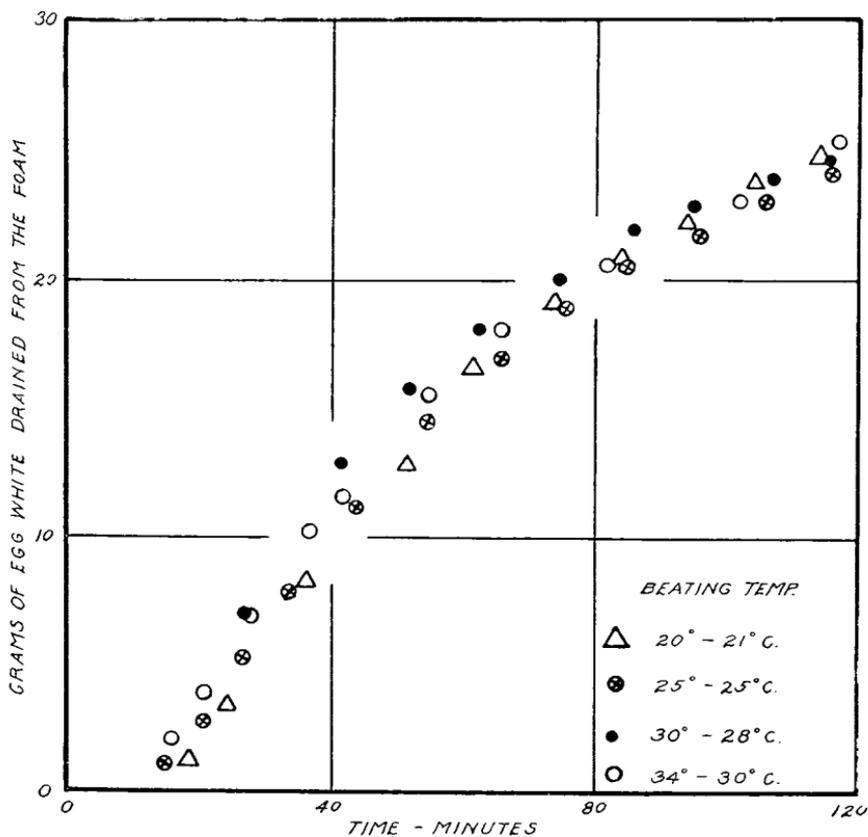


Fig. 7.—The rate of draining of foams beaten at various temperatures.

Several dozen eggs were purchased at one time and a number were beaten for various periods of time on the first, third, sixth and ninth days after obtaining. The data were then assembled and plotted in groups to show the effect of age on foam stability when beaten equivalent periods of time. (Figures 8, 9, 10, 11.)

The data show that when beaten equal lengths of time, increasingly less-stable foams were produced, the older the eggs, except in the case of the 4-minute beating period. However, in this exception the stability was found to be the same within the limits of experimental error.

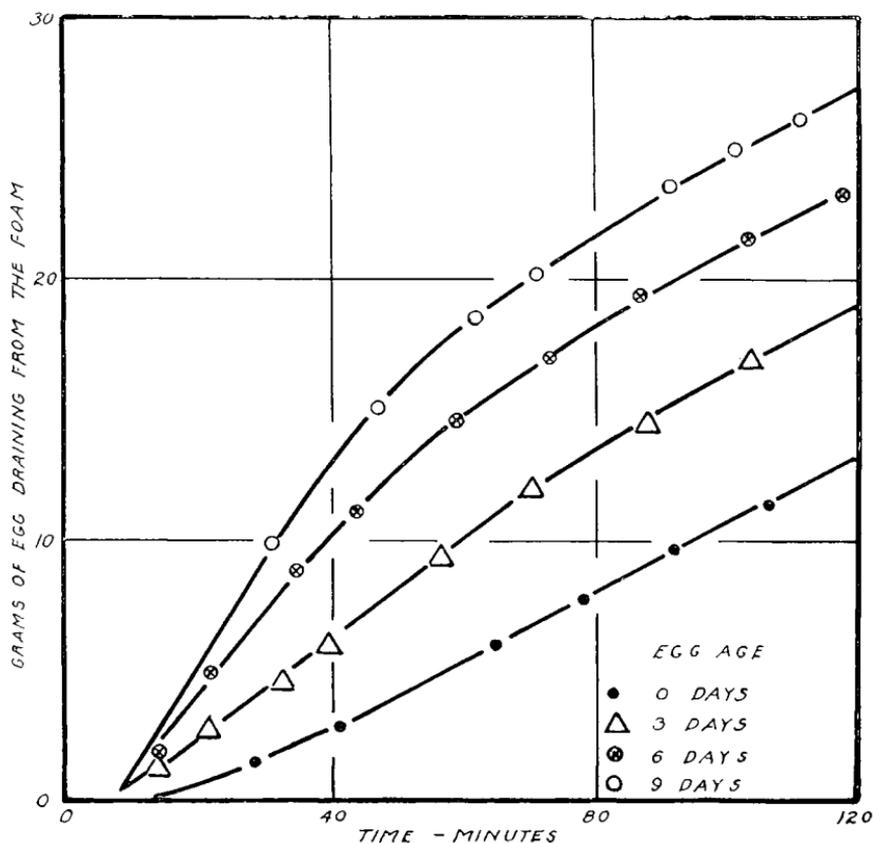


Fig. 8.—The rate of draining of the foams produced by beating eggs of various ages for 1 minute.

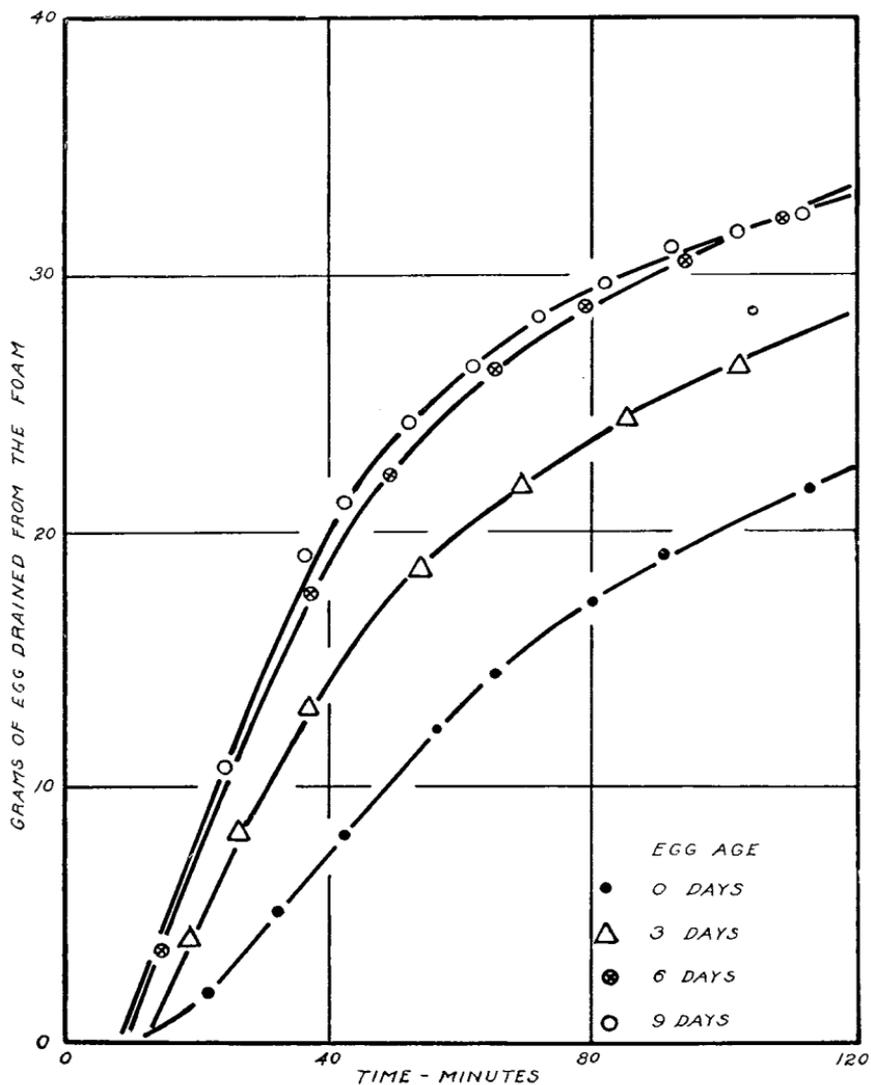


Fig. 9.—The rate of draining of the foams produced by beating eggs of various ages for 2 minutes.

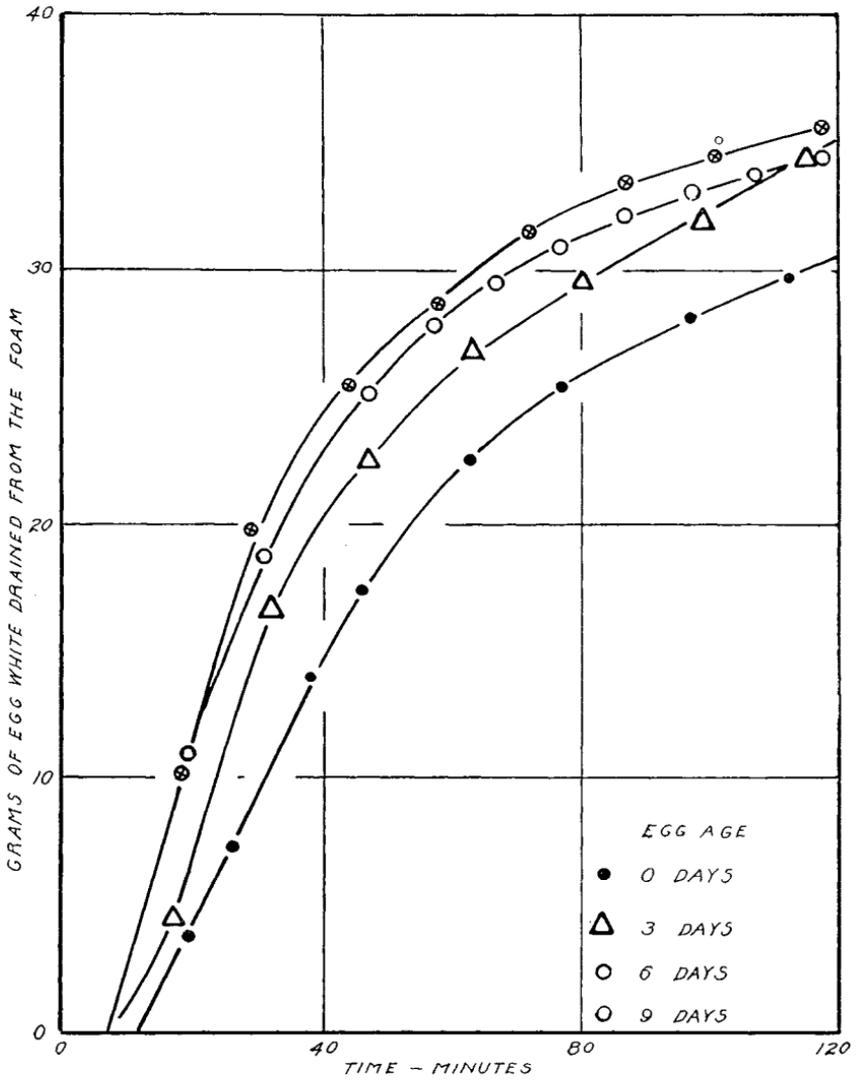


Fig. 10.—The rate of draining of the foams produced by beating eggs of various ages for 3 minutes.

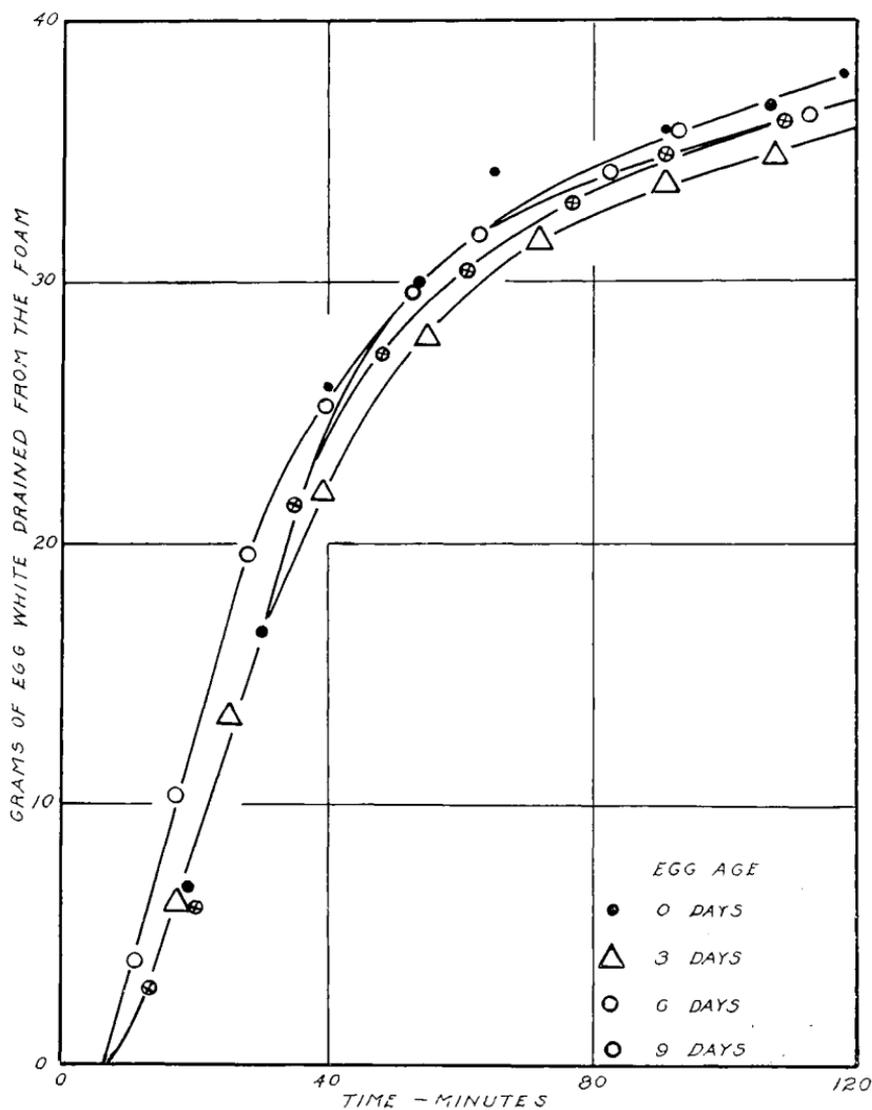


Fig. 11.—The rate of draining of the foams produced by beating eggs of various ages for 4 minutes.

On comparing the specific gravities of the foams produced (Table I), it will be noted that the specific gravity produced on beating for any given period, in almost every case, was progressively lighter, the older the eggs. The two exceptions are within the limits of experimental error.

Table I.—The Specific Gravity of Foams Produced From Eggs of Varying Ages.

Egg age	Specific gravity	Beating time	Egg age	Specific gravity	Beating time
0	.135	1	0	.109	3
3	.139	1	3	.110	3
6	.127	1	6	.101	3
9	.121	1	9	.095	3
0	.125	2	0	.104	4
3	.122	2	3	.092	4
6	.104	2	6	.091	4
9	.100	2	9	.091	4

A large number of batches of egg whites were beaten and various measurements made on the resulting foams. The viscosity measurements were made in Ostwald viscosity pipettes at 20° C. on the egg white drained out of the foam the first 2 hours, and are given in centipoises. These viscosity pipettes were calibrated with 20 and 40 percent sucrose, and 20 and 45 percent alcohol at 20° and 25° C., according to Bingham and Jackson (43). These concentrations of alcohol and sucrose covered the range of viscosities encountered in the collapsed egg white.

The value given as "grams of insoluble protein" was obtained by allowing the foam to drain for about 18 hours and then washing it vigorously with a total of 500 to 1000 cc. of distilled water on a weighed filter paper in a Büchner funnel. This was allowed to stand (in a room of a humidity of about 10 to 30 percent) until dry and then weighed.

The value termed "slope"\* was obtained by finding the maximum rate of draining from the foams and was taken from plots such as Figure 6.

Figure 12 shows the relation of foam specific gravity to stability, which was found to be linear, within the limits of experimental error.

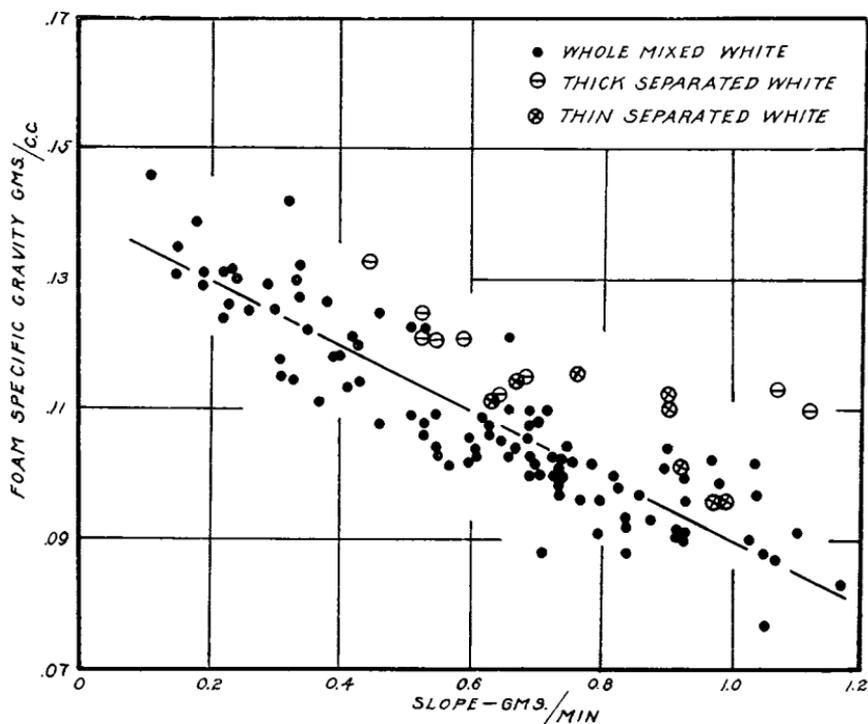


Fig. 12.—The effect of foam specific gravity on the slope or stability.

\*This value has been taken as the measure of foam stability. The three terms—rate of draining, slope and foam stability—have been used interchangeably thruout this report.

However, Figure 13 shows how the slope is dependent on a variable more fundamental than the specific gravity, i. e., the viscosity. It will be noted that the fresher eggs of equal viscosity tend to lie slightly below the others, especially those of high viscosity. This is probably due to the low pH of the fresh egg, because it will be shown later that egg white to which acid had been added produced a more stable foam than non-acid-treated egg white for equal viscosities of drained white.

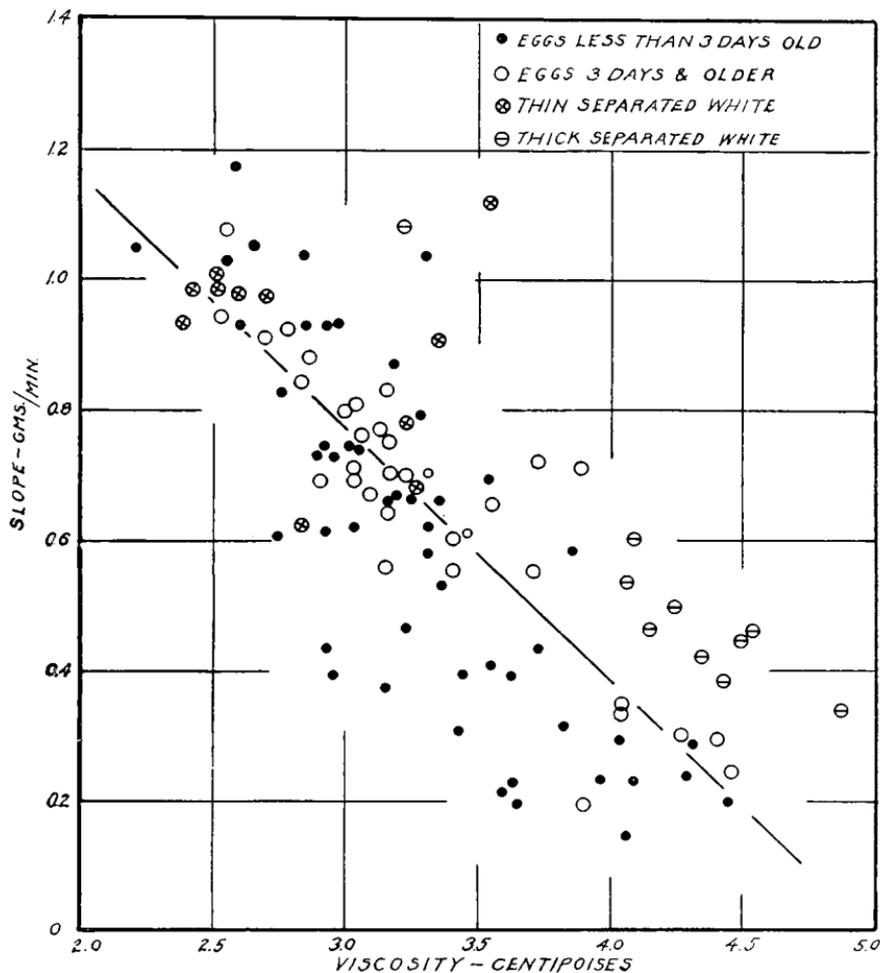


Fig. 13.—The effect of viscosity of the drained white on the foam stability.

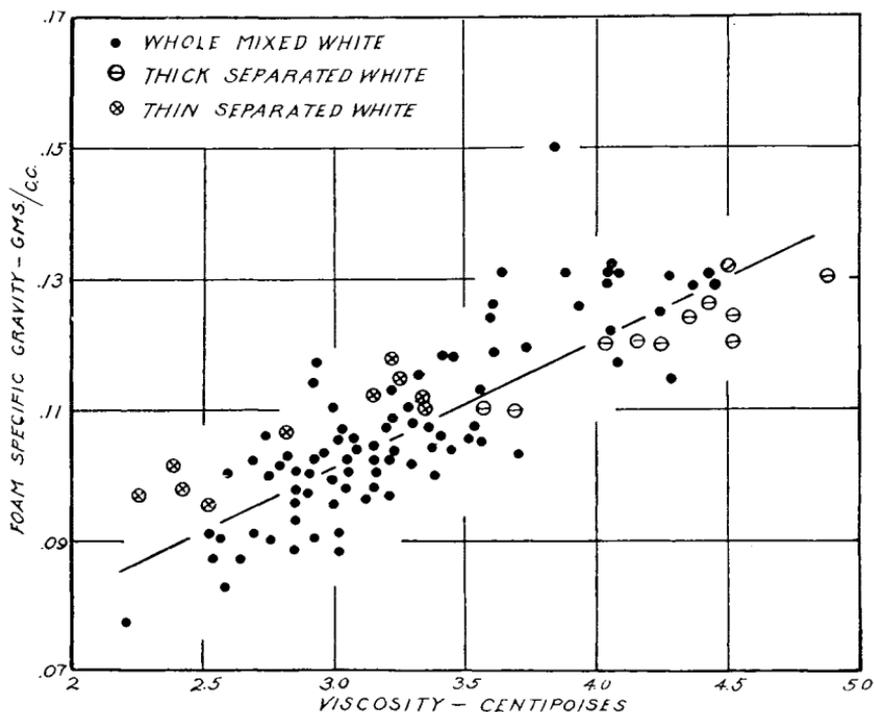


Fig. 14.—The relation of foam specific gravity to the viscosity of the drained white.

Since it was shown in Figure 12 that the slope depends on foam specific gravity and in Figure 13 that the slope is dependent also on the viscosity, it follows that the specific gravity will be dependent on the viscosity. This was found to be the case and is shown in Figure 14.

The equation of the line drawn as the approximate average of the data in Figure 12 is Sp. Gr. =  $-.050 \text{ Slope} + .140$ , and in Figure 14 is Sp. Gr. =  $+.0195 \eta + .043$ . Equating these two equations results in the equation  $\text{Slope} = -0.39 \eta + 1.94$ , which was then drawn into Figure 13.



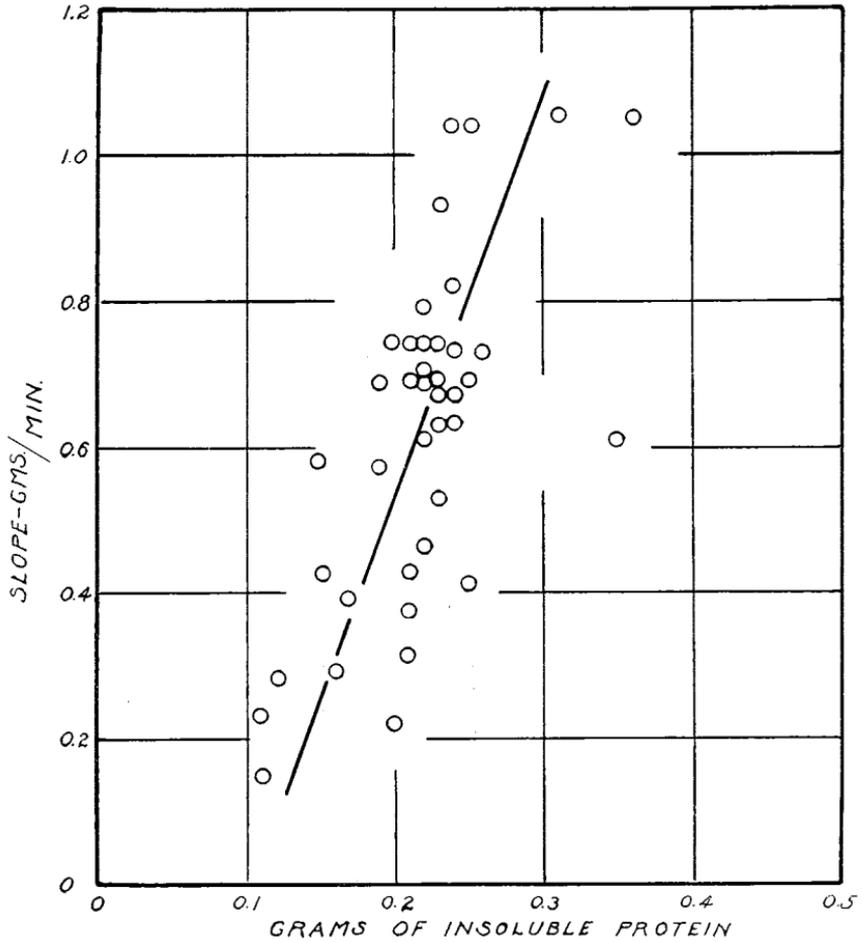


Fig. 16.—The effect of foam stability on the grams of insoluble protein.

In foams produced from milk and whey proteins, a marked increase in stability of the foams was produced by heating previous to beating (44, 45). This improvement in foaming was thought to be due to changes in viscosity, peptization and, in particular, to an accelerated denaturation of the protein, resulting in a gelatinized or semi-solid film.

It was thought that possibly heat treatment might likewise improve the foaming properties of egg whites. Therefore, batches of egg white were heated at various temperatures from 45° to 60° C. for 30 minutes and at 65° C. for 15 minutes. They were allowed to cool to room temperature and then beaten 2 minutes. In those heated to 60° and 65° C. some coagulation of the egg white was produced, much more, of course, in the one heated to 65° than in the one heated to 60°. Controls of non-heat-treated egg white were also run.

Examination of the experimental slopes and of the slopes calculated from the equation derived from Figure 12 indicates that heat treatment of egg white to temperatures up to 50° C. for 30 minutes had no effect on the foams produced from this material, but treatment at higher temperatures decidedly decreased the stability.

Table II.—Effect of Heat Treatment on Foam Stability.

Temperature of treatment	Sp. Gr. of foams	Exp. slope	Cal. slope	Remarks
.....	.102	.60	.76	Untreated
.....	.106	.60	.68	"
.....	.122	.66	.36	"
.....	.121	.53	.38	"
45°	.103	.60	.74	Treated
50°	.111	.53	.58	"
55°	.146	.70	0	"
56°	.140	.86	0	"
60°	.177	1.60	0	"
65°	.159	1.60	0	"

A test was made to see what effect would be produced by the difference in sharpness of the whip used in producing the foam. It was thought that possibly a sharpened beater edge would produce more change in viscosity for an equivalent period of beating. Three batches were beaten with the edges of normal sharpness (radius of curvature about .2 mm.); two batches were beaten with the beating edges covered with two thicknesses of adhesive tape (radius of curvature about 1 mm.); and one batch was beaten with the beater sharpened to knife-edge sharpness.

The results are given in Table III and they show that, within the limits of experimental error, neither the viscosity nor the stability were affected by the radius of curvature of the beating edges.

Table III.—Effect of Beater Sharpness.

Sp. gr.	Slope	Viscosity	Remarks
.105	.71	3.14	normal beater
.106	.71	3.00	normal beater
.111	.51	3.38	taped beater
.104	.64	3.08	taped beater
.110	.66	3.19	sharpened beater
.112	.76	2.93	normal beater

Cook books in general state that one must not get any yolk into the white, on separating the eggs, when the white is to be used in cakes of the type of angel food. St. John and Flor (7) state that their foams containing a small amount of yolk were very unstable to heat.

Experiments were carried out to test the effect of egg yolk on egg-white foam. Batches were beaten containing from 0 to 3 drops of yolk per 53 cc. of egg white. The results failed to show any apparent difference in the stability of the foams produced from egg white containing the small amounts of egg yolk indicated above.

A series of batches of egg whites were beaten 3 minutes at various altitudes in our altitude laboratory\* to determine if changes in air pressure would produce any change in the foam behavior.

A sufficient amount of egg white was stirred to produce a uniform mixture. Two batches were beaten at Fort Collins altitude, i. e., 5,000 feet, as controls and then two more batches were beaten at another altitude from each day's supply of egg white. This method was used to be sure that the different lots of egg white would produce similar foams under similar conditions.

Photomicrographs were taken 1½ minutes and 10 minutes after beating had stopped, and are shown in Figure 17a, b and c. Specific gravity measurements were also made, but both failed to show any effects of the variation in altitude. Stability, bubble size and specific gravity seem to be about equal regardless of altitude.

\*See Ref. 46 for a description of the altitude laboratory. However, since this bulletin was published, changes have been made to the extent of installing humidity and temperature controls. A detailed description will be published at a later date.

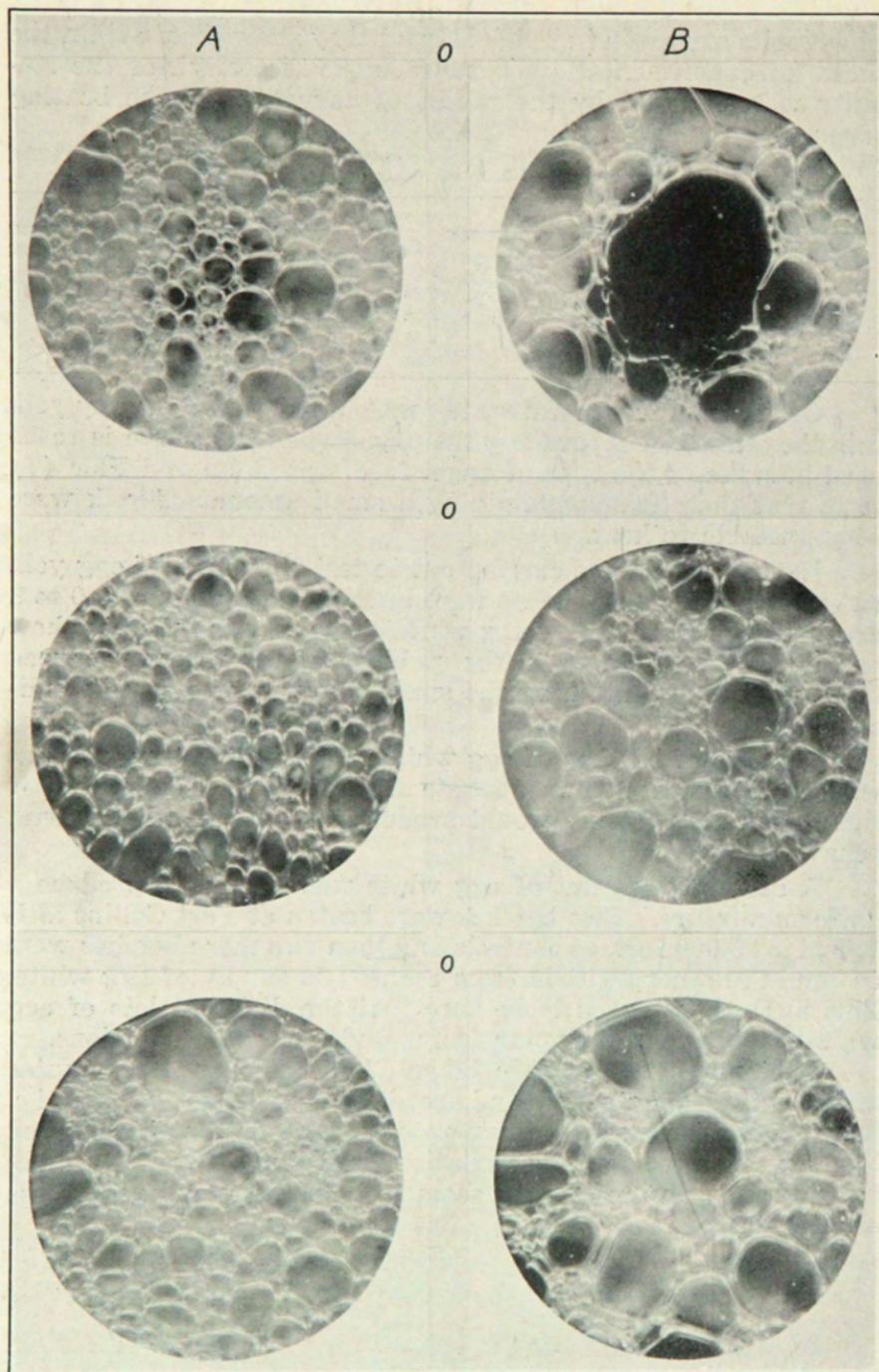


Fig. 17a

Photomicrographs of foams produced at various altitudes. (Magnification 27 diameters.)

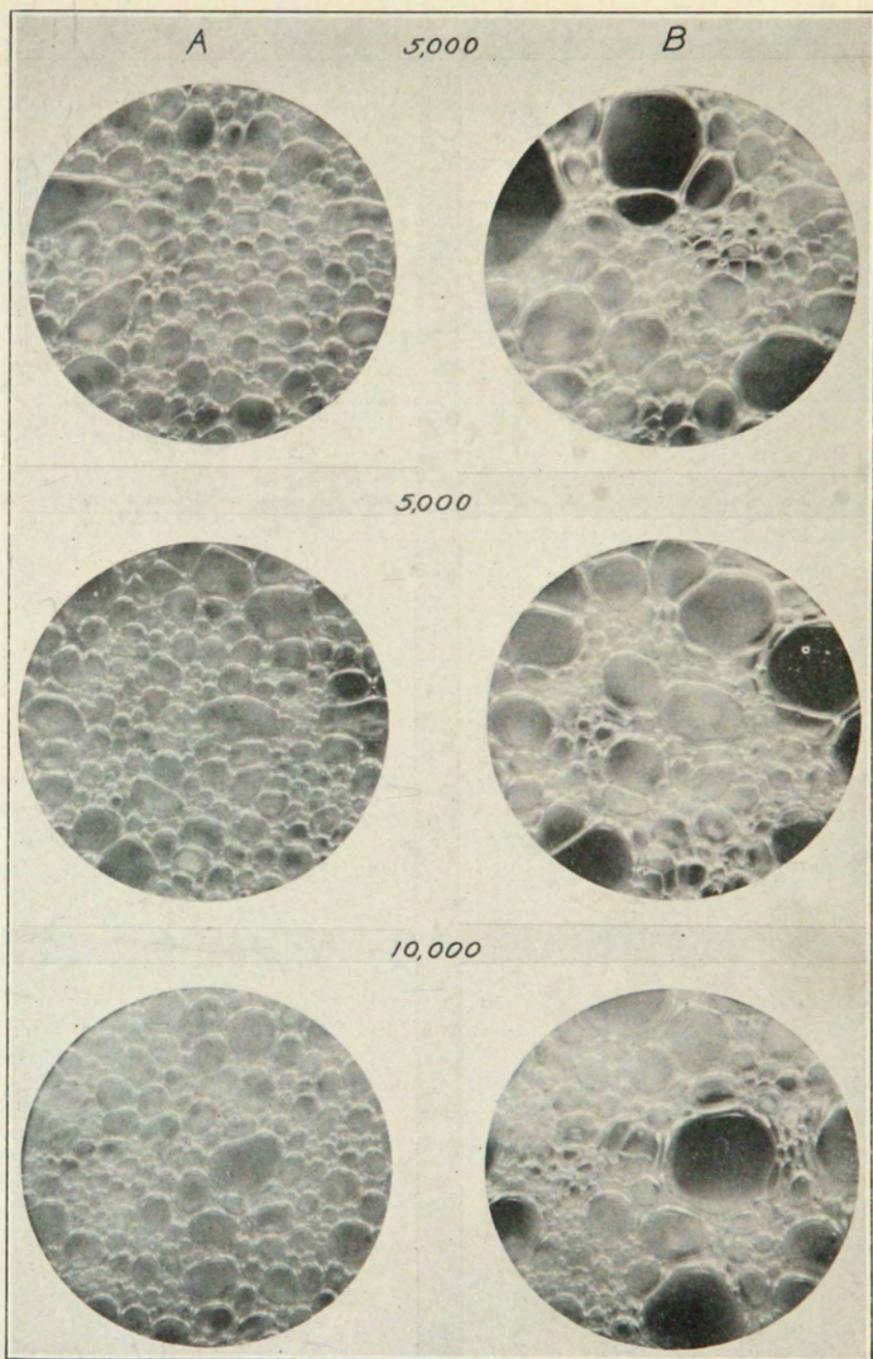


Fig. 17b

Column A pictures are of foams taken  $1\frac{1}{2}$  minutes after beating stopped and Column B pictures are of the corresponding fields taken 10 minutes after beating stopped.

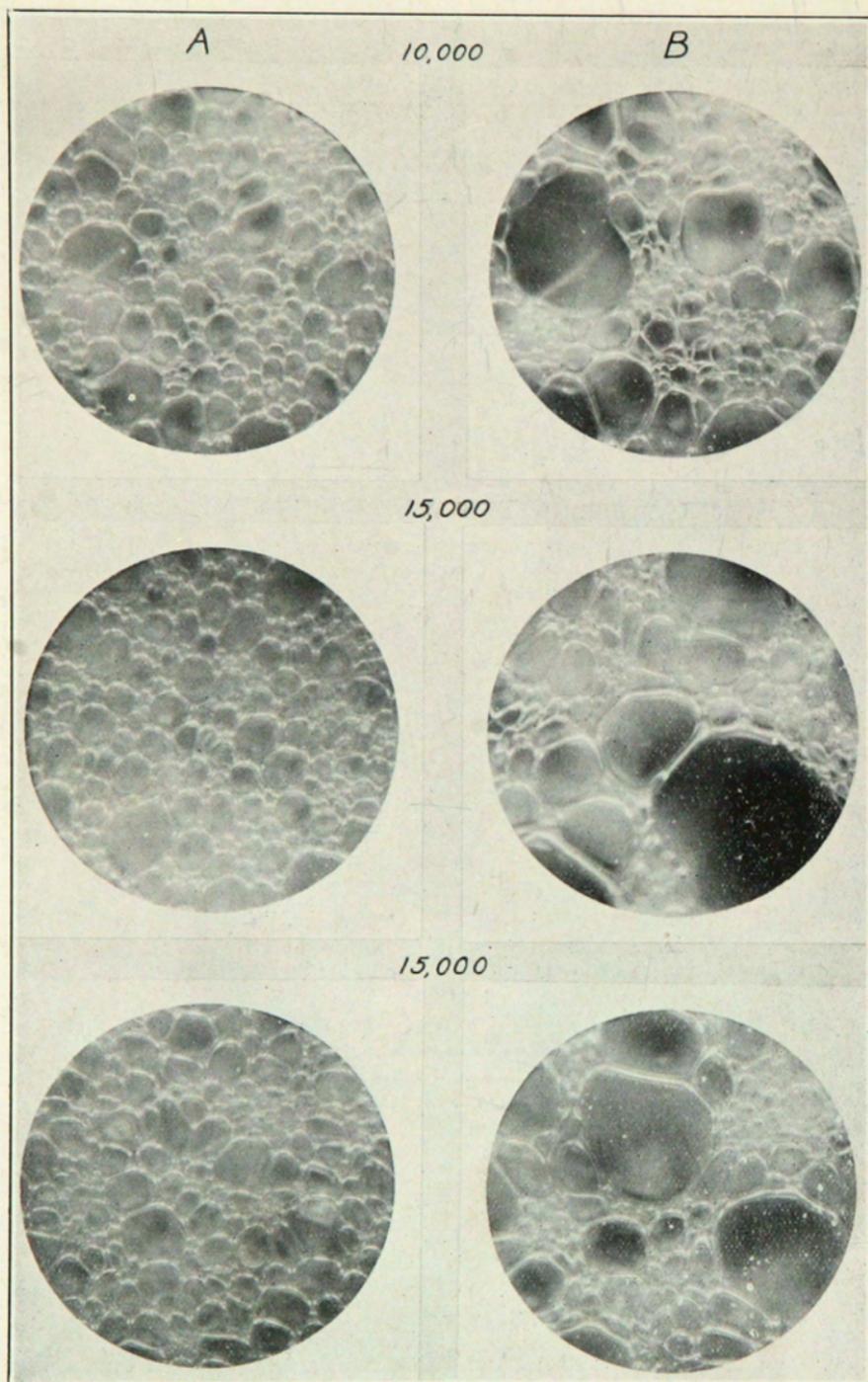


Fig. 17c

The altitude at which the foam was produced and studied is given in feet at the top of each pair of pictures.

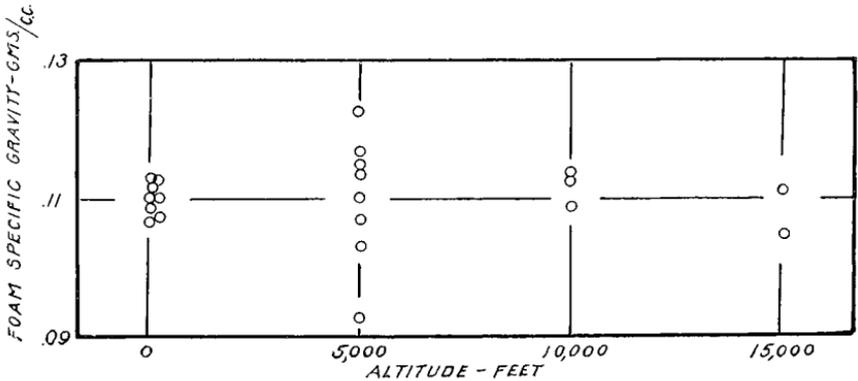


Fig. 18.—The specific gravity of foam beaten at various altitudes.

THE INFLUENCE OF CHEMICAL FACTORS ON FOAM CHARACTERISTICS.—Invariably, in food products produced from egg white, some acid or acid salt is introduced, and it is beyond a doubt essential in the white sponge type, commonly called angel cake. It has been shown (42) that the effect produced is dependent on the pH of the cake and that one acid is as good as another for the purpose. Because of the necessary use of acid in angel cake baking, it was considered worth while to study the changes, if any, produced in the foams by treatment with acid.

Various amounts of potassium acid tartrate were added to batches of egg white which were then beaten for 2 minutes. The results are shown in Figure 19 and it is evident that this acid salt produces a marked effect on the stability of the foam.

On treating egg white with other acids this same effect of increased stability of the foams was produced. The results obtained are shown in Table IV.

Table IV.—The Effect of Various Acids on the Foam.

Sp. gr. gms./cc.	Slope gms./ /min.	Viscosity centipoises	Amount	Substance
.109	.62	3.30	None	.....
.....	1.02*	2.94	0.75 gm.	$\text{KNaC}_2\text{H}_3\text{O}_6$
.109	.29	3.43	0.35 gm.	$\text{NaHC}_2\text{O}_4 \cdot \text{H}_2\text{O}$
.119	.34	2.42	0.31 gm.	Succinic
.108	.27	4.28	0.32 gm	$\text{C}_6\text{H}_7\text{COOH}$
.119	.33	3.31	0.15 gm.	Citric
.114	.35	2.15	5 cc. 0.32 N	$\text{HC}_2\text{H}_3\text{O}_2$
.096	.35	3.31	2.2 cc. 1.09 N	$\text{H}_2\text{SO}_4$
.111	.50	2.49	5 cc. .47 N	HCl

\*Note the possible negative effect of sodium potassium tartrate on the stability of the foam.

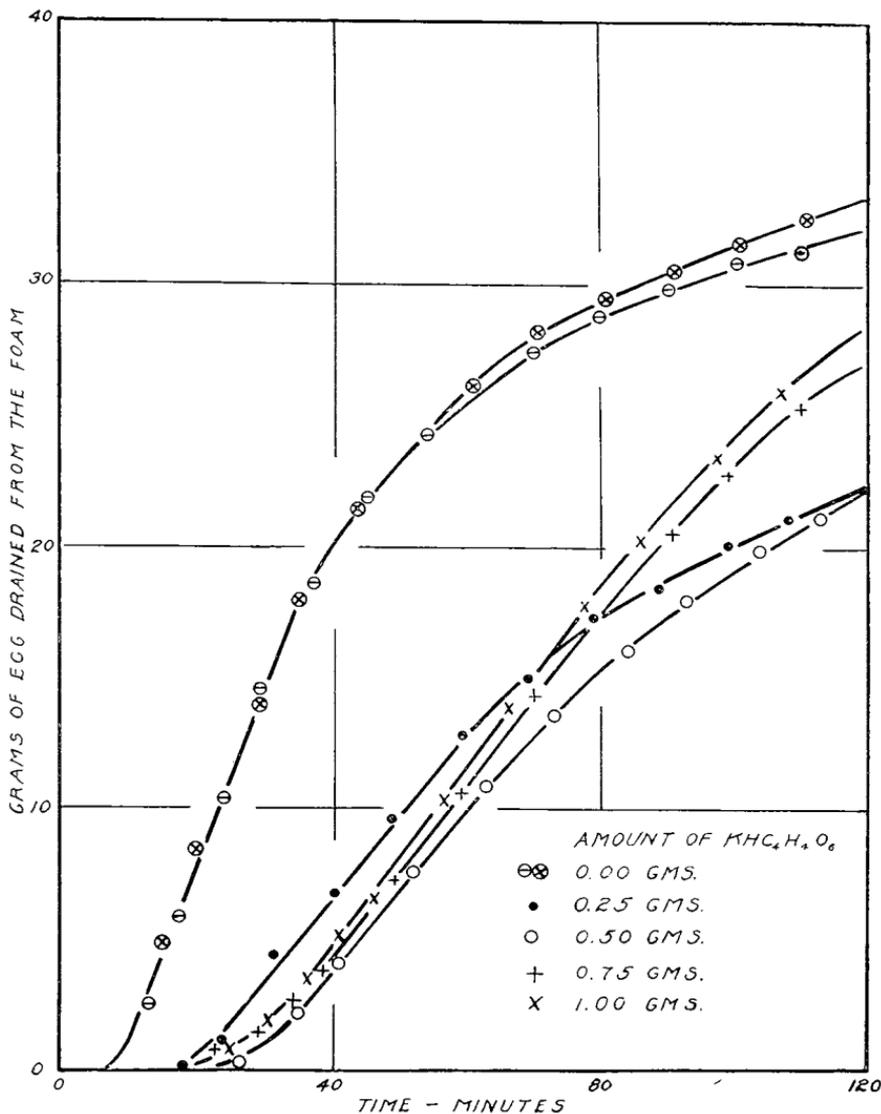


Fig. 19.—The effect of potassium acid tartrate on the rate of draining of the foams.

The behavior of the foams treated with three different acids was examined to see if it could be determined why the acids produce this stabilizing effect. The specific gravity, the slope, or rate of draining, the viscosity, the pH and in some cases the surface tension were determined for the foams treated with potassium acid tartrate, acetic acid and citric acid.

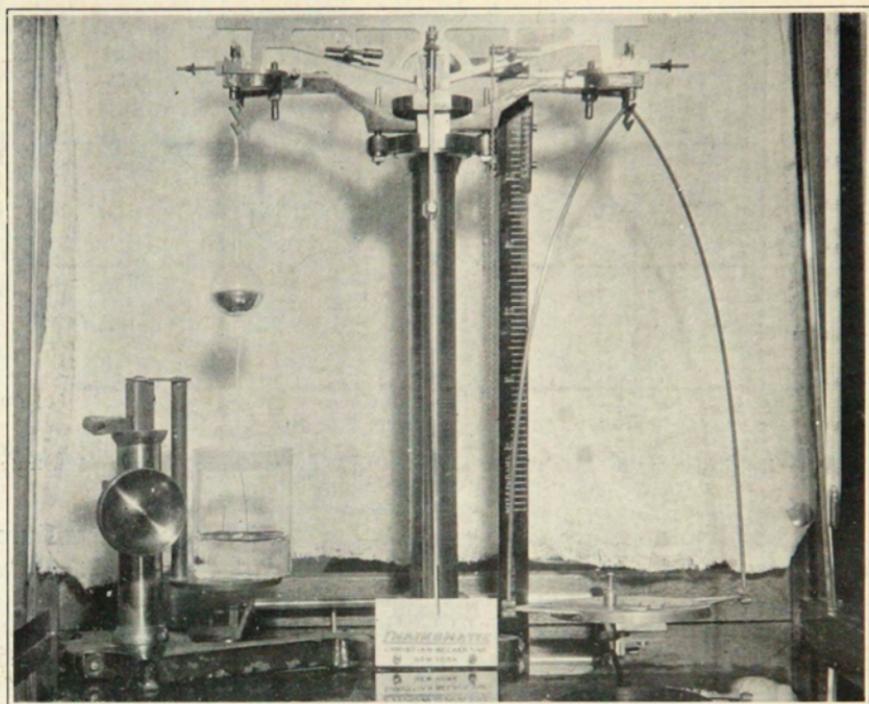


Fig. 20.—The method of determining surface tension. (The purpose of the white cloth, which was kept damp, was to increase the humidity and so reduce evaporation from the surface of the egg white as much as possible.)

The surface-tension measurements were made with a ring of platinum-iridium, the circumference of which was 3.94 cm., by means of a chainomatic balance, Figure 20, first described by Durrell, Person and Rogers (52). The pH measurements were made by means of a quinhydrone and saturated KCl—calomel electrodes.

It has been pointed out by DuNoüy (49), Bancroft (33), Freundlich (34) and others that surface tension changes with time, due to the building up of the film at the liquid-air interface. The values for surface tension were obtained 10 minutes after the surface had been renewed by stirring. This period seemed to be long enough for the rate of change of the surface tension to be fairly low. It was also shown to be a sufficiently long enough time, according to measurements cited by DuNoüy (49), p. 48, for serum which was considered to be similar to egg white.

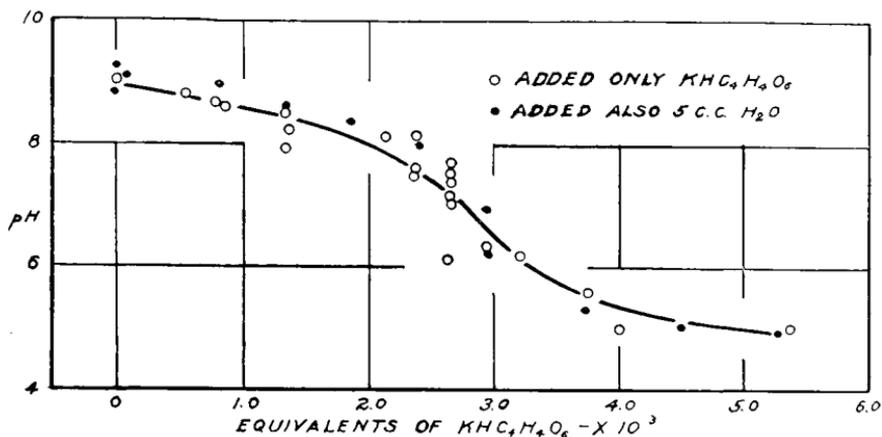


Fig. 21.—The change in pH of the drained egg white on treating with potassium acid tartrate.

The results show that on treating with either potassium acid tartrate, acetic acid or citric acid, the pH of the egg white draining from the foams decreased as is shown in Figures 21, 25 and 29, the foam stability reaching a maximum at a pH of 8.0. On adding more of any one of the three acids the pH is reduced further—i. e., below 8.0—but only in the case of treatment with acetic or citric acids is the stability reduced.

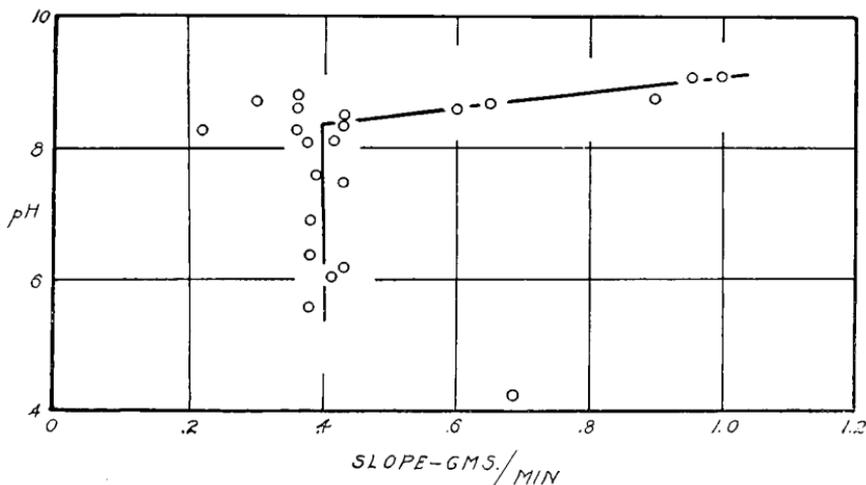


Fig. 22.—The change in slope or rate of draining of the foams with pH on treating with potassium acid tartrate.

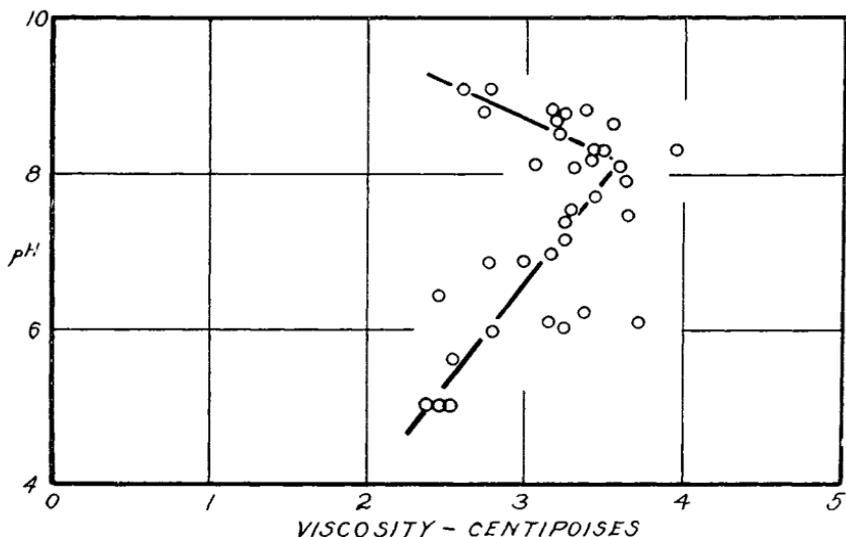


Fig. 23.—The change in viscosity of the drained egg white with changes of pH on treating with potassium acid tartrate.

The viscosity on treating with potassium acid tartrate alone (Figure 23), or potassium acid tartrate and 5 cc. of water. (Figure 24), or citric acid (Figure 31) increases at first to a maxi-

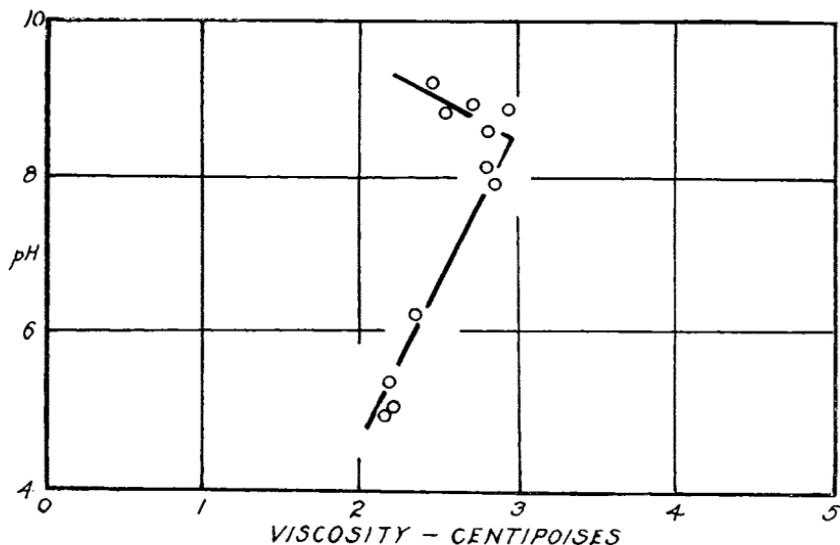


Fig. 24.—The change in viscosity of the drained egg white with pH on treating with potassium acid tartrate and 5 cc. of water.

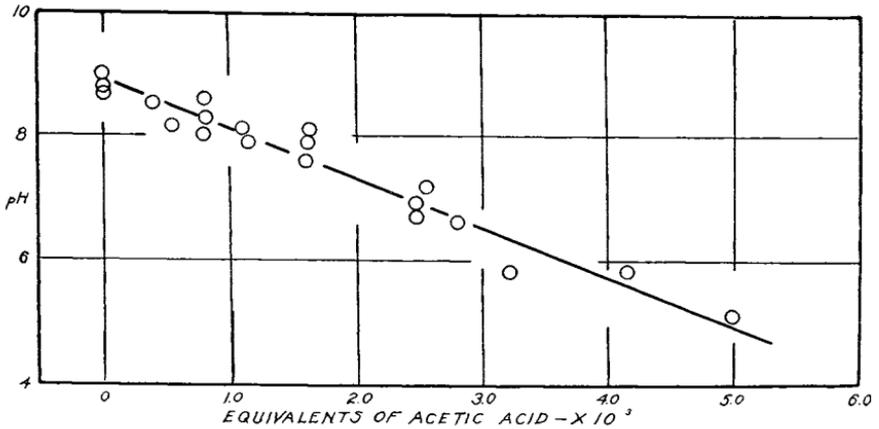


Fig. 25.—The change in pH of the drained egg white on treating with acetic acid.

mum, the pH being at this point 8.5 to 8.0, and then on further additions of any one of the above it decreases. In the case of treatment with acetic acid the viscosity (Figure 27) increases only slightly, if at all, but at a pH lower than 8.0 it decreases as it does in the other three cases, the decrease being much more rapid, however, with acetic acid than with any one of the others. It will be noted that at a pH of 5.0, produced by treatment with either acetic acid or citric acid, the viscosity is lower than for those foams treated with potassium acid tartrate alone or with water.

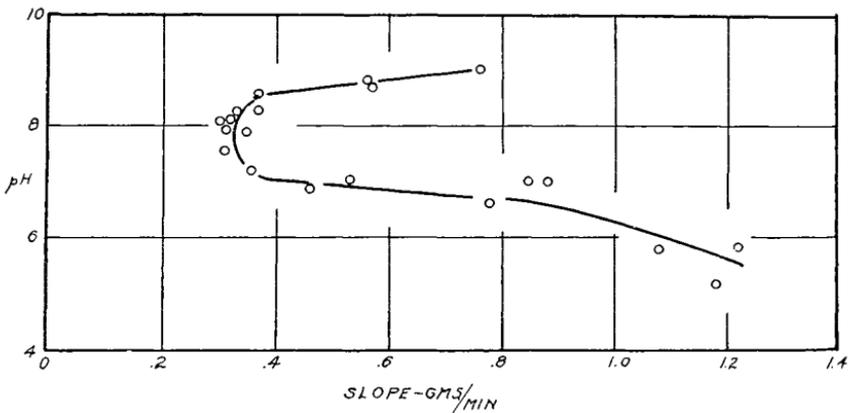


Fig. 26.—The change in the slope, or rate of draining, with changes in pH on treating with acetic acid.

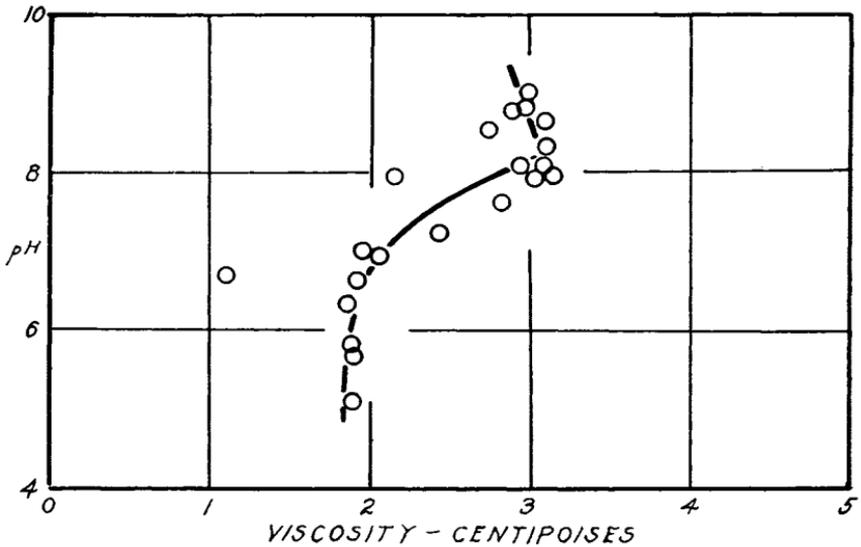


Fig. 27.—The change in viscosity with changes in pH on treating with acetic acid.

Figure 28 shows that there is no significant difference in the amount of soluble protein obtained with changes in pH.

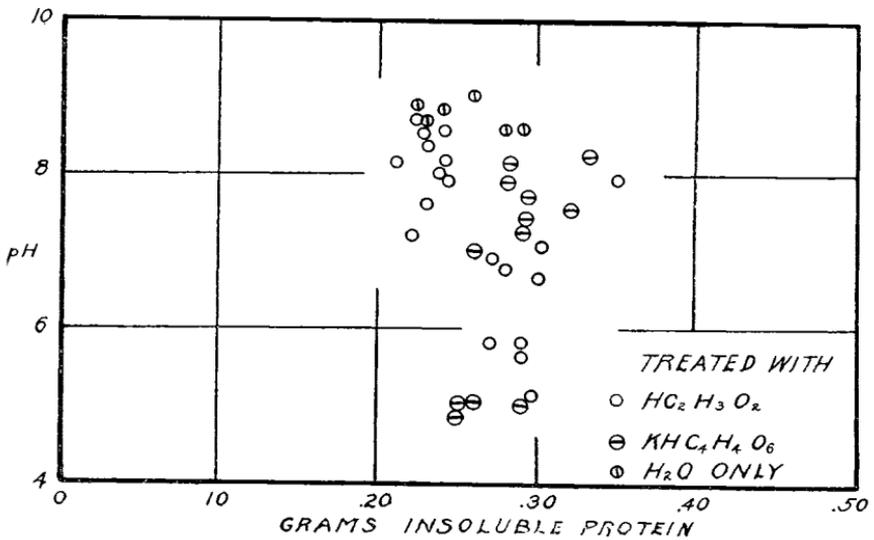


Fig. 28.—The variation in grams of insoluble protein with pH on treating with acetic acid or potassium acid tartrate.

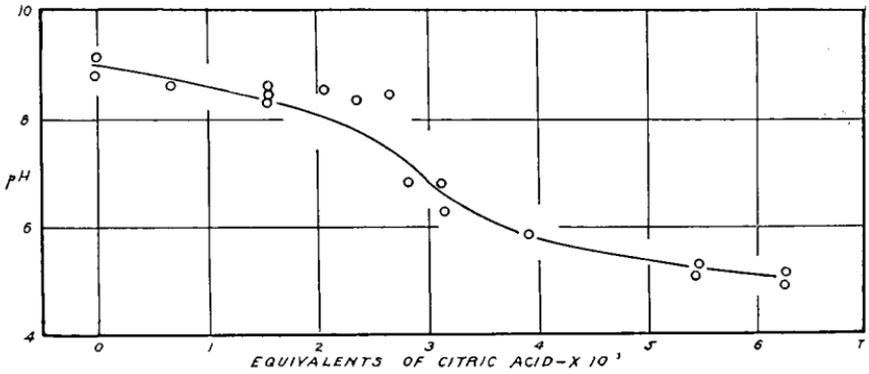


Fig. 29.—The change of pH of the drained egg white on treating with citric acid.

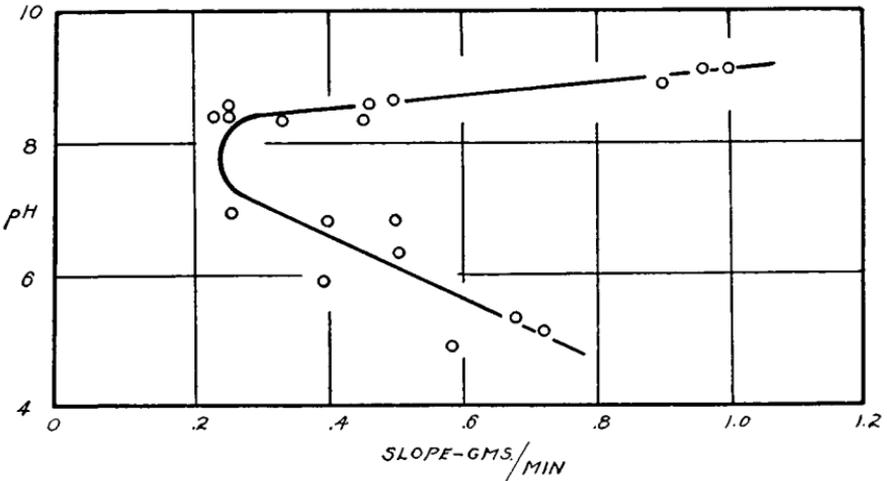


Fig. 30.—The change in the slope with pH on treating with citric acid.





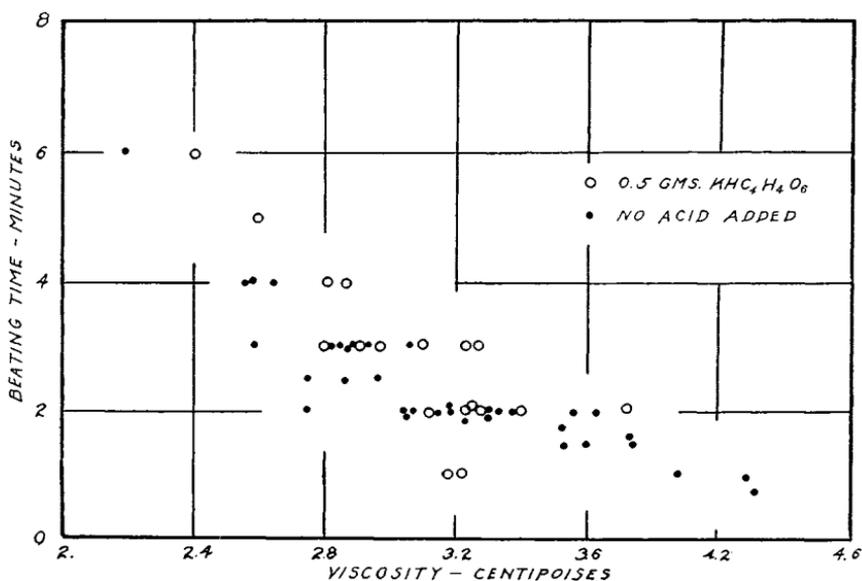


Fig. 33.—The change in viscosity of the drained egg white produced by beating acid treated and non-acid treated egg white for various periods of time.

Table VI contains data on some nitrogen determinations in the foam and in the drained white, in the presence and in the absence of potassium acid tartrate. The foams were allowed to drain for a period of time and then samples of each were taken.

The results show that in both instances there is a decided increase in nitrogen or protein content in the foam. The values, however, do not give any evidence to explain why the foams containing potassium acid tartrate are more stable than those containing none of the acid salt.

Table VI.—Analysis of Foams.

Foam Sp. gr. gms./ cc.	Slope gms./ /min.	Contained gms. $KHC_4H_4O_6$	Percentage nitrogen	
			Foam	Liquid
.091	.68	0.00	2.00	1.59
.103	1.15	0.00	2.28	1.50
.104	.49	0.50	1.94	1.53
.106	.36	0.75	1.76	1.43

A test was made of the beating characteristics of soaked dried egg white. A sample of commercial dried egg white was obtained and found to contain 12.7 percent nitrogen. A quantity of this material was soaked in enough water over night to give the resulting solution a nitrogen content of about 1.70 percent, which is about an average nitrogen content of fresh eggs. This regenerated egg white was beaten with various amounts of acetic acid and a small amount of sodium hydroxide, and also beaten for various lengths of time. The data, Table VII, show that neither acid, small amounts of base, nor a variation in beating time have any apparent effect on the foam stability nor on the viscosity of the material draining from the foam. The length of beating time does apparently produce a lighter foam, however, as would be expected.

Table VII.—Characteristics of a Foam Produced From Regenerated Egg White.

Beating time	Sp. gr.	Slope	Viscosity	pH	Treated with 5 cc.of
2	.104	.57	2.20	6.4	H <sub>2</sub> O
2	.101	.57	2.33	6.4	H <sub>2</sub> O
2	.098	.51	2.18	7.2	.108 N NaOH
2	.100	.60	2.11	5.8	.16 N HC <sub>2</sub> H <sub>3</sub> O <sub>2</sub>
2	.103	.69	2.02	5.4	.32 N HC <sub>2</sub> H <sub>3</sub> O <sub>2</sub>
2	.105	.60	2.02	5.1	.48 N HC <sub>2</sub> H <sub>3</sub> O <sub>2</sub>
4	.092	.57	2.18	.....	H <sub>2</sub> O
2*	.095	.60	1.64	.....	.....
4*	.089	.54	1.62	.....	.....

\*Used a solution containing about 1.30 percent nitrogen instead of 1.70 percent, as in the others.

Previously it was stated that the presence of very small amounts of yolk in the egg white failed to exhibit any apparent effect on the stability of its foam; however, the effect of small amounts of yolk in the presence of potassium acid tartrate was not considered. The data given in Table VIII show that a small amount of yolk does have an effect, in the presence of acid, which is particularly evident in the specific gravity obtainable for a given amount of beating. The reduction in viscosity takes place without the usual decrease in specific gravity. The presence of yolk and acid in egg white results in a foam that is much more unstable than one in the absence of yolk, when compared on the basis of viscosities and even more unstable on the basis of their specific gravities.

Table VIII.—The Characteristics of Foams Produced in the Presence of Small Amounts of Yolk and Potassium Acid Tartrate.

Beating time	Foam Sp. gr.	Slope	Viscosity	Amount of $\text{KHC}_4\text{H}_4\text{O}_6$ contained	Drops yolk
3	.114	.70	2.80	0.00	0
2	.108	.33	2.50	0.75	0
2	.105	.35	2.54	0.75	0
2	.109	.45	2.33	0.75	0
3	.150	.44	3.14	0.25	3
3	.146	.60	2.80	0.50	3
3	.147	.70	2.32	0.75	3
2	.124	1.02	2.18	0.75	3
3	.119	.78	2.26	0.75	3
3	.121	.85	2.26	0.75	3

Peter and Bell (44) found that whey proteins treated with  $\text{Ca}(\text{OH})_2$ ,  $\text{NaOH}$ ,  $\text{Na}_2\text{SO}_3$ , and alternate additions of acid and base gave improved foams as compared to untreated proteins. This same treatment was tried on egg white. The data show that neither  $\text{Na}_2\text{SO}_3$ ,  $\text{Ca}(\text{OH})_2$  nor  $\text{NaOH}$  have any marked effect on the foam stability or other measured characteristics of egg foam. However, it is interesting to note that  $\text{Ca}(\text{OH})_2$ , in a quantity sufficient to at least neutralize the acid tartrate, does not decrease the stability of the acid-treated foam.

Table IX.—Chemical Treatment of Foam.

Sp. gr.	Slope	Viscosity	Beating time	Contained
.103	.88	2.80	3	1.5 gm. $\text{Na}_2\text{SO}_3$
.104	1.04	2.75	3	0.2 gm. $\text{Ca}(\text{OH})_2$
.100	.48	2.46	3	1.0 gm. $\text{KHC}_4\text{H}_4\text{O}_6$ and later 0.2 gm. $\text{Ca}(\text{OH})_2$
.106	.48	2.41	3	1.0 gm. $\text{KHC}_4\text{H}_4\text{O}_6$
.099	.99	2.61	3	untreated
.111	.80	2.94	2	5 cc. $\text{H}_2\text{O}$
.106	.85	2.93	2	5 cc. 0.366 N $\text{NaOH}$
.109	.97	2.92	2	5 cc. 0.277 N $\text{NaOH}$
.108	.97	2.92	2	5 cc. 0.188 N $\text{NaOH}$
121	.48	3.09	2	5 cc. 0.302 N $\text{HCl}$

The effect of alternate addition of acid and base was investigated further. The eggs were beaten  $\frac{1}{2}$  minute, the potassium acid tartrate added and beaten  $1\frac{1}{2}$  minutes, then the  $\text{Ca}(\text{OH})_2$  added, and the beating continued for  $\frac{1}{2}$  minute. In later experiments the  $\text{Ca}(\text{OH})_2$  was replaced by  $\text{NaOH}$ .

The results obtained are given in Table X and they show, within the limits of experimental error, that the stability, or rate of draining, produced by potassium acid tartrate added at the beginning is not affected by the later addition of enough base to completely neutralize the acid.

Table X.—Acid-Base Treated Foam Data.

Sp. gr.	Slope	Viscosity	pH	Equiv. of $\text{KHC}_4\text{H}_4\text{O}_6$	Equiv. of base $\text{Ca}(\text{OH})_2$
.115	.47	3.64	8.4	$2.66 \times 10^{-3}$	$2.70 \times 10^{-3}$
.113	.53	3.43	8.4	2.66 "	2.70 "
.111	.47	3.10	7.7	2.66 "	0.00 "
.111	.49	3.07	7.7	2.66 "	0.00 "
					NaOH
.117	.61	2.95	7.8	2.66 "	$0.00 \times 10^{-3}$
.113	.59	2.72	7.4	2.66 "	0.00 "
.117	.55	2.77	7.4	2.66 "	0.00 "
.115	.68	3.10	9.5	2.66 "	2.66 "
.115	.62	3.08	9.7	2.66 "	2.66 "
.111	.62	2.96	9.6	2.66 "	2.66 "

From the following data it is apparent that the first portion of the beating period is far superior to the later for the adding of the acid to the egg-white foam when stability is a desired property. This follows from the results given in the previous section. In every case the rate of draining was decidedly slower when the potassium acid tartrate was added in the first part of the beating period. Just why the pH was less in one case than in another is difficult to explain, unless it is possible that due to less stirring the potassium acid tartrate did not completely dissolve. The higher pH can hardly explain the difference in stability, since it has been shown in Figure 22 that a pH of 8.3 was low enough to produce a low rate of draining.

Table XI.—Foam Characteristics vs. Time of Adding Potassium Acid Tartrate.

Sp. gr.	Slope	Viscosity	Gms. $\text{KHC}_4\text{H}_4\text{O}_6$ added	pH	Remarks
.120	.33	3.75	.50	7.5	Dissolved first
.115	.50	3.17	.50	7.6	Dissolved first
.119	.38	3.65	.25	7.3	Dissolved first
.118	.32	3.26	.50	7.5	Dissolved first
.121	.38	3.24	.50	7.4	Added at start of beating
.109	.49	3.43	.50	7.8	Added after $\frac{1}{2}$ min. of beating
.115	.52	3.32	.50	7.7	Added after $\frac{1}{2}$ min. of beating
.106	.77	3.19	.50	7.9	Added after $1\frac{1}{2}$ min. of beating
.107	.71	3.34	.50	8.3	Added after $1\frac{1}{2}$ min. of beating
.124	.63	3.32	.25	8.1	Added after $1\frac{1}{2}$ min. of beating
.119	.60	3.40	.50	7.7	Added after $1\frac{1}{2}$ min. of beating

A number of batches of egg white were beaten with hand beaters, in order to determine if the data on foams from them would correspond with foams produced by the electric beater. The three beater types used are shown in Figure 34.

The properties of these foams (Table XII) were in some respects different from those produced by the electric beater. The rate of draining calculated from the viscosity is in fair agreement with the experimental values, but those calculated from the specific gravity were in every case different from the experimental values by considerably more than experimental error. This means that the beating with the hand beaters was less effective—that there was more reduction in viscosity for the corresponding reduction in specific gravity—than with the electric beater.

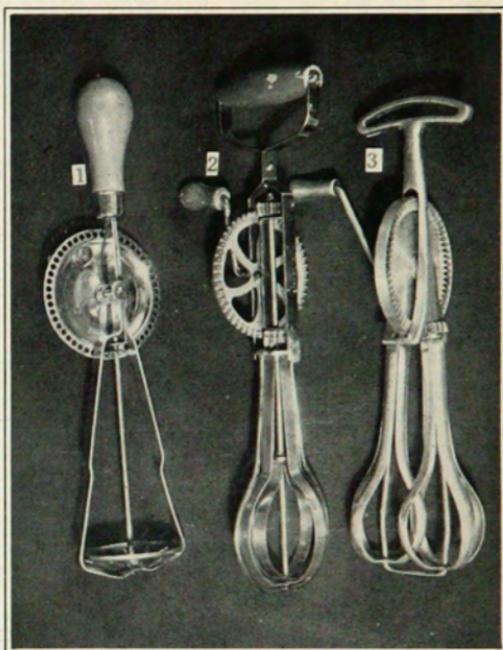


Fig. 34.—Hand beaters used.

Table XII.—Foam Characteristics Produced by Hand Beaters.

Sp. gr.	Slope	Viscosity	Beater number	Cal. slope from sp. gr.	Cal. slope from viscosity
.130	.41	3.91	1	.20	.41
.153	.58	5.51	1	.00	.00
.166	.27	5.73	1	.00	.00
.132	.38	4.39	1	.16	.23
.130	.87	4.06	1	.20	.37
.120	.75	3.75	1	.40	.48
.220	.92	3.53	2	.00	.56
.135	.89	2.75	2	.10	.86
.129	.65	3.30	3	.22	.65
.129	.65	3.05	3	.22	.75
.131	.62	3.26	3	.20	.69
.137	.41	3.62	3	.06	.53

## DISCUSSION

In no instance have we obtained data for which we can claim any appreciable degree of accuracy. It is very difficult to estimate the experimental error. The material dealt with is, at the outset, variable from day to day. Altho the eggs all come from the same flock under uniform feeding, 12 to 15 eggs were certainly not a large enough sample to assure uniform protein content.

The various measurements were the best at hand, the measurement of viscosity probably being the most accurate. Even in this case the first run thru the capillary gave a higher viscosity than the second, showing that the pulling of the liquid up into the measured bulb of the pipette, in preparation for a run, doubtless reduced the viscosity slightly. It is believed, however, that the results are significant to the first decimal.

For specific gravity measurements it was necessary to use a large open dish and to put the foam in place with a spatula. It was quite possible to have air pockets in this foam, altho every precaution was taken to prevent them. Some of the foam was doubtless destroyed by the handling.

The foam was weighed to  $\pm .2$  gm., on the balance shown in Figure 6. Allowing for possible air pockets of 2 cc., and an error in weighing of 0.2 gram of a foam, whose specific gravity was 0.100, an error of about 1 percent would be incurred. This, however, does not take into account the amount of foam destroyed by handling, but that would probably not make the total error greater than 5 percent.

The amount of drained white was weighed to  $\pm 0.2$  gram. The greatest probable error was doubtless due to the holding up of liquid egg white in pockets, that had actually drained from bursted bubbles. By taking the maximum rate of draining as the slope, the accuracy was increased to the maximum. There was, of course, some error in taking the slope from the plots of time vs. weight.

In the case of the determination of "grams of insoluble protein" it seems that the largest likely error would be in not being able to wash away all of the uncoagulated protein from the coagulated. Therefore these values were probably too high.

The pH was determined by means of the quinhydrone electrode—a hydrogen electrode not being available—which is at its best inaccurate above a pH of 8.0. A steady potential was never obtained, but the variation was not great. The pH values below 8.0 are probably accurate to  $\pm 0.1$  pH and above 8.0 to  $\pm 0.3$  pH.

In testing the accuracy of the method of measuring surface tension on water at 25°, the value 72.8 dynes per cm. was ob-

tained (an average of five measurements), an error of about 1 percent. However, it has been pointed out by Wilson and Ries (35) that in surface-tension measurements by ring or drop weight methods in solutions of sodium oleate and sodium stearate, considerable error was introduced due to the frictional force corresponding to the yield value of the plastic solid surface film which it is necessary for the ring to overcome. This causes the surface tension apparently to increase with time in dilute solutions, because the film is increasing in strength. This is doubtless also the case in our albumin solutions, because it was actually found that the apparent surface tension increased with time. Thus a very uncertain error was introduced, that could not be estimated.

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During the beating, the egg whites were agitated tremendously in the presence of air, and it might be expected that the viscosity would have little, if anything, to do with the formation of the foam. However, according to the results herein given, it was found that, within the limits of experimental error\*, *the specific gravity of the foam was directly proportional to the viscosity of the egg white draining from that foam* (Figure 14). We assume the viscosity measured to be equal to that of the liquid within the foam. This would lead one to believe that as the viscosity is reduced the beater is able to tear the liquid into thinner and thinner liquid layers that then entrap the air. Peter and Bell (44) and Clayton (37) state that a low viscosity increases the ease with which a foam or an emulsion may be formed, but the above relation has never before been pointed out.

Schnurmann (54) found, on passing air thru porcelain filters into aqueous solutions, that the bubble size was independent of the filter and dependent on the viscosity. This may or may not be related to our investigation.

The data plotted in Figure 12 were originally plotted with the age of the eggs designated by different symbols. The remarkable thing, at once apparent, was that the age made no difference. (The eggs were aged at room temperature from 0 to 11 days.

It has been definitely shown by others (see literature review) that the egg white liquefies on aging and so becomes, as a whole, less viscous. This means that with an increase in age the difference becomes less between a given viscosity, corresponding to a given specific gravity, and the viscosity† of the unbeaten egg

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\*It was regretted that nitrogen analyses were not run, because it is possible that the apparent experimental error might have been reduced by making a correction for protein content.

†Perhaps plasticity or limpidness might be a better word than viscosity in this case. It is realized that natural egg white can have no true viscosity. However, altho it has not been tested, it is believed that the egg white draining from the foam was very nearly a true liquid.

white. Since it has been maintained above that it is necessary to have a definite viscosity in order to obtain a given specific gravity of foam, then the older eggs should, on beating, arrive at the given specific gravity quicker than fresh eggs. This is exactly the case as is shown in Table I.

In both commercial and in domestic baking fresh eggs are not considered to be as good for the production of angel cake as eggs a few days (2 to 4) old. The preceding data indicate that the only reason why the fresh eggs should not produce as good a cake is that they were more difficult to beat. Provided the eggs were whipped to equivalent specific gravities the fresh eggs should, and do, produce angel cake identical with those from eggs a few days older. The beating of fresh egg whites to a sufficient volume by hand is practically impossible, while older eggs beat much more easily.

However, the data also indicate that eggs still older should produce just as successful a cake as the fresher eggs, but this prediction does not hold good. Evidently some change other than simple liquefaction takes place during the aging of eggs that has an effect on the production of angel cakes.\*

It is probable that with other types of beaters the specific gravity for a given viscosity will be different (see Table XII), but the same relationship between viscosity and specific gravity should still hold true. A highly desirable type of beater would be one in which the same foam lightness could be produced at a higher viscosity, thus increasing the stability of the foam, which appears to be so important, especially in angel cakes. Small changes in viscosity produce considerable change in foam stability in the presence of acid. (Compare Figure 32 with Figure 13.)

The decrease in viscosity, as the period of beating increases, adds further evidence to the findings of Almquist and Lorenz (12), who were able to show that thick egg white is composed of a fine fiber network of protein entrapping the ordinary liquid white. They also showed that as the egg ages this fiber network disintegrates or becomes so weak that it can then hold only a small amount of liquid white. Beating evidently tears up the fibers and destroys the structure. As the age of the egg increases the ease with which the viscosity may be reduced increases.

The structure of firm egg white is similar to, and has many properties in common with jellies. The effect of mechanical agitation, or stirring, has a liquefying effect on jellies (55) (33) similar to the effect produced in egg white on beating.

The behavior of the foams produced from dried egg white show the lack of the above jelly structure.

The liquid draining from the foams is probably made up of liquid draining from between the two liquid-air interfaces with-

\*See Balls and Swenson, 1934, Ind. and Eng. Chem. 26, 570.

out any actual breaking of the bubbles, and also from accumulations of the liquid resulting from the bursting of the bubbles. The major part probably comes from the collapse of the bubbles, because it was found that the finer the bubbles the more rapid the draining. Since the rate of draining is a linear function of specific gravity, it is not likely that it is made up, in the main, of more than one factor. If it were, any change in the rate of bubble collapse would have to offset exactly the decrease in the flow of liquid between the two interfaces as the bubbles decrease in size.

Further evidence for the above conclusion is that as the bubble size decreases the surface area increases and so the thickness of the liquid layers between bubbles must decrease with decreases in bubble size. The rate of draining, according to Poiseuille's law, is proportional to the fourth power of the radius of the cross section of flow (34), which means that the rate of draining of liquid from between the interfaces should decrease with the specific gravity. The observed effect, however, is exactly the opposite.

Other workers on foams and emulsions have used the period of time for a layer of liquid, or for a distinct separation of the two phases to become evident, as a measure of stability. In this laboratory a much superior means of stability measurement has been used. We have admittedly measured the rate of draining of the liquid from the foam, but this is merely a measured speed of separation into two layers. In our case, especially, it has proved to be a good measure of stability because we have shown, by applying Poiseuille's law, that our "rate of draining" must be made up largely of liquid draining from bursted bubbles with only a small fraction of it composed of liquid actually draining from between interfaces.

The nearest approach to this method has been described, since the work in this report was finished, by Epstein (47). He used the amount drained after 15 to 20 minutes as a measure of the stability instead of the maximum rate of draining.

It has been generally accepted, as stated in the review of literature, that viscosity aids emulsification solely by the hindrance offered to the coalescence of the dispersed globules. The same can be stated in terms of foams, which are merely special cases of the general class—emulsions. In foams, the process which takes place after formation (34) is apparently a draining of the liquid from between the interfaces until at some point the structure becomes so weak that it will no longer support the weight or forces about it. The bubbles then collapse, releasing a much larger amount of liquid which drains away.

Clayton (37, 50), and Freundlich (34), quoting others, state that increases in viscosity increase the stability of emulsions and foams, other things being equal. The conclusion was drawn from comparisons of similar systems of different stability and viscosity, or systems in which the viscosity was changed by chemical means; not in a single instance were they able to use identical systems in which viscosity changes were produced by purely physical means, as we have been able to do. The experiments were far from ideal, but we believe them to be accurate enough to show some interesting relations.

In Figures 13 and 32 it is evident\* that for a given pH the *stability of the foams produced from egg white is a linear function of the viscosity.*

This gives us an explanation as to why the slope or stability is a function of the specific gravity. Since the slope is related to the viscosity and the specific gravity related to the viscosity, it simply follows that the specific gravity should be related to the slope, or stability.

It has been shown that by beating egg white to a low specific gravity an extremely unstable foam was produced, which explains why large holes are produced in angel cakes made from eggs beaten to extreme lightness.

Since this work was finished an article appeared on "The Beating Properties of Egg White," by Henry and Barbour (51) giving results that agree in every case with the corresponding findings of this more extensive investigation.

They found that beating egg white at temperatures varying from 15° to 25° C. had no effect on the stability of the foam produced, and that even at 10° C. the stability was only slightly less. They also go on to say that their methods of measuring foam stability† indicate that the longer the egg white was beaten the more unstable the foam became.

On adding sulphuric acid it was stated that the stability increased, but on adding sufficient acid to reduce the pH to 5.47 an exceedingly unstable foam resulted (see Figure 26 in which a pH of 5.5, produced by acetic acid, resulted in a very unstable foam). No change in stability was produced by the addition of small amounts of sodium hydroxide.

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\*Here it is necessary for us to disregard the data on thick separated egg white. Our excuse for doing so is that we think it likely that the kinds of protein are different in the case of thick white from that of the thin or whole white, altho the nitrogen content has been shown to be the same (13, 15). The data on thick egg white by themselves show a linear relationship between stability and viscosity.

†They used the size of a given volume of foam that had dried at room temperature and the penetrometer method of Peter and Bell (44) as measures of stability.

We have attempted in the following calculations to arrive at some idea of the amount of liquid-air surface existing in these foams. Freundlich states that the cross section of the bubbles making up a foam would be irregular hexagons with equal angles of  $120^\circ$  (34). This requires that the cells or bubbles have the shape of an irregular dodecahedron, a figure bounded by 12 pentagons. It is a figure resulting from the compression of a mass of plastic spheres, all the same size, packed as closely together as possible.

The average bubble size for a foam whose specific gravity was .137 was estimated to be .02 cm. On assuming the cells to be all spheres of this size\*, the minimum specific gravity obtainable was calculated to be .265. Bogue (48) says that they are polyhedra and not spheres. Assuming the above average cell size and that they are regular dodecahedra, it is possible to have as low as .076 for the specific gravity if the thickness of the separating layer between the units is allowed to approach zero.

In the regular dodecahedron the angle between faces is  $116^\circ 34'$ . Assuming that a space is filled with regular dodecahedrons of equal size, the first problem will be to find the number filling a cubic centimeter. The radius of an inscribed sphere in a dodecahedron was found to be  $1.114a$ , where  $a$  is the side of the pentagon making up the surface of the dodecahedron. The diameter of the inscribed circle is equal to the distance per cell along the  $x$  axis. Then along the  $y$  axis the effective diameter equals  $(2 \times 1.114a) \cos 26^\circ 34'$  and along the  $z$  axis  $(2 \times 1.114a) \cos 26^\circ 34' \times \cos 18^\circ$  times the diameter of the inscribed circle. The surface of a dodecahedron is given as  $20.646 a^2$  and the volume as  $7.663 a^3$  (59).

Average bubble size†	Sp. gr.† of foam	Total vol. of foam	Space occupied by air
.020 cm.	.137	402 cc.	86.9%
.015 cm.	.120	459 cc.	88.0%
.010 cm.	.100	552 cc.	90.0%

†These were taken from actual data obtained.

DuNoüy (49) gives what he thinks the most probable dimensions of the albumin molecule, i. e.,  $41.7 \times 30.8 \times 30.8 \text{ \AA}^\circ$ , and mass of  $51.3 \times 10^{-21}$  gms. per molecule. Assuming that in this concentrated solution the molecules would crowd so as to stand on end, we calculate the following:

\*This calculation does not, of course, represent exact conditions because small bubbles which lie in between the larger bubbles would occupy considerable volume and so reduce the foam specific gravity.

Sp. gr.	Total surface of cells	Total no. molecules on the total surface	Weight of molecules	Wt. of insol. protein from Fig. 15
.137	106,300 sq. cm.	$1.12 \times 10^{18}$	.058 gms.	.15
.120	168,500 sq. cm.	$1.77 \times 10^{18}$	.091 gms.	.20
.100	304,000 sq. cm.	$3.20 \times 10^{18}$	.164 gms.	.28

The agreement between the calculated value and the value of insoluble protein obtained is remarkable considering the approximations and assumptions. In the first place we have used the dimensions of the albumin molecule when it is uncertain whether or not the surface active protein is albumin. The method of determining insoluble protein is far from accurate. The assumption that the unit cells are irregular dodecahedrons is open to question. The calculations were based on the regular dodecahedron which is admittedly in error because they cannot possibly be regular when thrown in together as they are in foam. The average bubble size is very plainly a guess since the size varies over a wide range, as may be plainly seen in Figure 3.

It is, however, entirely possible to explain the apparent dimolecular layer of coagulated protein by assuming that, due to the agitation, the first coagulated-protein-surface-layer was immersed and a fresh liquid surface exposed on which a second layer of albumin molecules coagulated.

There is apparently a very good reason why a small amount of acid is added to egg whites when beaten. We have found that in general the proper amount of acid will reduce the rate of collapse from 2 to 3 times what it would have been in the absence of the acid.

For the first additions of acid there was (with the exception of acetic acid) a definite increase in viscosity. This does not account for the increased stability, however, which can be shown by comparing experimental values of the rate of draining with those calculated from their viscosity by means of the equation  $\text{Slope} = -0.39\eta + 1.94$ . Also, the treatment of the egg white with acetic acid did not produce an increase in viscosity, but did produce an increase in stability. Therefore the stabilizing effect must be due to something other than the increase in viscosity. The only other possible part that could be affected by the acid, and at the same time increase the stability, would be the surface, or liquid-air interface.

There are several possible explanations: 1.—The adsorption at the surface might be greater, thereby producing a thicker protein film. 2.—The film might be made up of a protein-acid

addition product or protein salt, the increased stability being due merely to the better structural properties of this film-building material. 3.—The change in acidity may simply improve the structural properties of the film, or it may increase the “superficial viscosity,” or it might do both.

If the first were true we would expect a marked change in the surface tension, thus indicating a change in the adsorption at the surface. In addition, it would be expected that the increase in thickness of the protein film could be detected in the “grams of insoluble protein.” From the data in Table V and Figure 28, it will be seen that there is no significant change in the surface tension nor in the “grams of insoluble protein.”

Wu and Ling (58) were able to show that the rate of coagulation of purified egg albumin on shaking was a maximum at the isoelectric point ( $\text{pH} = 4.8$ ), and that it decreased rapidly for any change in  $\text{pH}$  from this point. It is difficult to see how this would explain the improvement in the stability of the foam unless the more rapid coagulation would increase the amount of coagulated protein. This was not found to be the case. In addition, the maximum stability was obtained at a  $\text{pH}$  considerably different from 4.8.

To test the second possibility we attempted to show by analysis an increase in chloride and sulphate content in the foam over that in the drained white. The foam had been treated with hydrochloric or sulphuric acid. We did not succeed.

The fact that the addition of sodium hydroxide, in sufficient amounts to neutralize the previously added potassium acid tartrate, has no effect on the stabilizing ability of the acid salt is rather surprising, since we have shown that sodium potassium tartrate has no stabilizing effect. It shows that changes are produced by potassium acid tartrate that are irreversible, and they probably are denaturation, or coagulation changes or both. It also shows that it is likely that the stabilizing effects of acid treatment are not due to a protein-acid addition product or protein salt, but are due to changes which improve the structural properties of the protein film, which in turn are due to the acidity.

The evidence points to the third possibility as being the answer to the puzzle. It has been shown and pointed out by Freundlich (34), Bancroft (33), Clayton (37, 50), Wilson and Ries (35), and others that a large superficial viscosity is necessary for foam stability. Lee and Wu (53) state that the compressibility of an albumin film was the greatest at the isoelectric point and that the force necessary to push a DuNoüy ring thru the film surface was a maximum at the isoelectric point. The mean-

ing of compressibility and surface strength may possibly be distorted to mean elasticity or toughness which would lend support to the idea that the film had a higher superficial viscosity at this decreased pH. It was not possible for us to investigate this phase of the problem. It would, however, be very interesting to investigate the properties of these films as affected by changes in pH by means of a torsion pendulum similar to the type used by Wilson and Ries (35).

Thus it has been shown that acid improves the stability of foams and it is believed that this is one of the reasons why the presence of acid makes possible a successful angel cake. The increased stability, due to the presence of the acid, permits the batter to expand with heat and the setting to take place before the foam has broken down sufficiently to form large holes in the center or heavy layers on the bottom.

However, acid undoubtedly has some other essential effect, because base neutralizes the effect of acid in angel food cakes, altho an equivalent amount does not neutralize the effect of acid in producing increased foam stability. In other words, the neutralization of the acid by base in the production of angel cake causes the cake to shrink abnormally during the last few minutes of baking which the unneutralized condition prevents. An equal number of equivalents of all acids do not produce equivalent effects in the production of angel cake— $12 \times 10^{-3}$  equivalents of acetic acid per 100 grams of egg white gave a very coarse-grained cake, while  $12 \times 10^{-3}$  equivalents of citric acid gave a finer-grained product and the same amount of potassium acid tartrate produced a still finer-grained cake, exactly as predicted from the data on the effects of these acids on the foam stability.

We believe that acetic acid and citric acid in larger amounts were not so effective in stabilizing the foam as potassium acid tartrate, because of the changes in viscosity which they produced. It appears as tho there is a critical viscosity in the neighborhood of 2.0 centipoises, below which the surface changes produced by the acid in the foam were no longer able to neutralize the forces causing collapse of the bubbles. It will be noted that in the case of treatment with citric acid, or acetic acid the viscosity reached 2.0, but in those foams treated with either potassium acid tartrate alone or with potassium acid tartrate and water the viscosity did not reach 2.0 centipoises. However, there is not much margin in the last case, and this weakens the argument.

## SUMMARY

A new method of measuring foam stability has been developed and used which is believed to be superior to any other method.

In spite of some deviation in results, it has been shown for the first time that egg-white foams conform to the modern ideas of foam structure, i. e., that there is an adsorption of stabilizing agent at the liquid-air interface and that this adsorbed film coagulates, forming a non-soluble solid film, thereby stiffening and stabilizing the foam.

In addition, it has been independently shown that the following are characteristics of egg-white foams:

1.—The foam stability is directly proportional to the viscosity of the liquid medium, and the specific gravity of the foam is inversely proportional to the viscosity. It follows from these two statements that the stability is inversely proportional to the specific gravity of the foam.

2.—Beating tears up the fiber structure of the egg white, thus reducing its viscosity, at the same time that the foam is formed. Natural egg white behaves similar to a typical jelly, but regenerated egg white does not have these jell-like properties.

3.—There is a concentration of protein at the liquid-air interface which is rendered insoluble during the formation of the foam and the amount of this protein is roughly proportional to the specific gravity, or surface area of the foam.

4.—Neither  $\text{Ca}(\text{OH})_2$ ,  $\text{NaOH}$ ,  $\text{Na}_2\text{SO}_4$ , nor heat treatment have any apparent effect on the foams, but acids and acid salts increase the foam stability considerably. This effect is thought to be due to a change in the protein concentrated at the liquid-air interface.

5.—Not all acids produce equivalent effects in stabilizing foam, potassium acid tartrate having the most desirable effect of the three acids used—acetic, citric and potassium acid tartrate.

6.—If potassium acid tartrate is added in the first part of the beating period and then during the latter part of the period sufficient sodium hydroxide is added to completely neutralize the potassium acid tartrate, the stabilizing effect of the acid is changed only slightly, if at all.

7.—In the presence of potassium acid tartrate, egg yolk reduces the stability of the foam.

8.—Changes in altitude have no effect on foam characteristics.

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