

In attempting to shorten the time factor, a colorimetric method, based on the production of Runge's violet when aniline is treated with a solution of calcium hypochlorite, was investigated. As the work was carried out in a poorly equipped works laboratory, the apparatus used had to be constructed from materials found lying about; this appears as an advantage now, for it taught us that the apparatus costs almost nothing and is available everywhere.

The colorimeter was made by supporting in front of a tungsten lamp a thick cardboard in which two slits  $\frac{1}{4}$  in.  $\times$  2 in. had been cut 1 in. apart. Above each slit was a wire loop large enough to support a  $16 \times 120$  mm. test tube so that the latter hung directly in front of the slit. The test tubes used for the comparisons were  $16 \times 120$  mm. and all of the same internal diameter; this was determined by putting 20 cc. of water into a number of test tubes of this size, and selecting those in which the water stood at the same height.

As Runge's violet is not a permanent color a set of standard colors had to be prepared, each of which would correspond to the color produced by a certain concentration of aniline in water. In eight of the selected test tubes were put 5 cc. of aqueous solutions of aniline containing, respectively, 0.5, 0.4, 0.35, 0.3, 0.25, 0.2, 0.15 and 0.1 per cent of aniline. To each tube 1 drop of dilute sodium hydroxide, 3 drops of saturated aqueous phenol solution, and 4 cc. of fresh saturated filtered bleaching powder solution were added. After shaking, the tubes were allowed to stand for  $\frac{1}{2}$  hr., each sample was diluted with 50 cc. of water, and the tubes half filled with the diluted solutions. Permanent colors corresponding to the colors resulting from these solutions of known concentration were prepared as follows: A tube containing one of the above tests was hung in front of one slit and another of the selected test tubes containing 15 cc. of water was hung in front of the other. To the water, red and blue ink and powdered C. P. calcium carbonate were added until the depth and opacity of the Runge's violet were exactly matched. This was done for each of the above samples, and a set of permanent colors was secured corresponding to the above eight concentrations of aniline. The inks used were Stafford's Commercial Bright Blue and Carter's Carmine Red Non-copying Ink, the latter was diluted with an equal volume of water before use.

To determine the concentration of aniline in an unknown aqueous solution, take 5 cc. in one of the selected test tubes, add 1 drop of dilute sodium hydroxide solution, 3 drops saturated aqueous solution of phenol, and 4 cc. of fresh bleaching powder solution. After letting stand  $\frac{1}{2}$  hr. dilute with 50 cc. of water, and compare a sample of the diluted solution with the standard colors in front of the electric light. If the resulting color is deeper than the darkest standard solution, 5 cc. of the unknown solution is diluted with an equal volume of water, and this diluted sample is tested as above and the per cent obtained multiplied by two.

Anybody intending to use this method of analysis ought to make his own standard colors, following the method outlined above. Below is a table showing how much ink was used in making up the standards in my work.

Per cent of Aniline	15 cc. of Water plus		CaCO <sub>3</sub> <sup>3</sup>
	Blue Ink <sup>1</sup> Drops	Red Ink <sup>2</sup> Drops	
0.5	3 $\frac{1}{2}$	30	...
0.4	2	18	...
0.35	1 $\frac{1}{2}$	11	...
0.3	1	6 $\frac{1}{2}$	...
0.25	0	6 $\frac{1}{2}$	...
0.2	0	4 $\frac{1}{2}$	...
0.15	0	3 $\frac{1}{2}$	...
0.1	0	3	...

<sup>1</sup> One drop of the blue ink = 0.0545 g.

<sup>2</sup> One drop of the diluted red ink = 0.0541 g.

<sup>3</sup> I did not weigh the CaCO<sub>3</sub> added to secure the required opacity.

**PRECAUTIONS**—To secure the correct color the bleaching powder solution must be fresh and saturated. The tubes of standard colors must be shaken before using.

**ADVANTAGES**—This method is rapid (a dozen samples can be analyzed in an hour), is easy, and accurate enough for plant control work.

The following are check analyses run on samples of aniline water from an aniline rectifying house:

Colorimetric Method Per cent	Aniline Hydrochloride Method Per cent
0.30	0.32
0.35	0.39
0.35	0.38
0.76	0.84
0.07	0.08
0.08	0.09
0.70	0.69

419 MAGEE AVENUE  
ROCHESTER, NEW YORK

### AN IMPROVEMENT IN CASEIN MAKING<sup>1</sup>

By J. L. SAMMIS

Received April 9, 1919

Large amounts of casein are now used in the manufacture of water-proof glue for aeroplanes and other purposes. Lack of uniformity in casein as it comes from the creamery has been found to cause irregularities in the finished glue, or to necessitate variations in the glue-making process, which it is desirable to avoid if possible.

In July 1918 a request was received by this department from the Forest Products Laboratory, Madison, Wisconsin, that aid be given by the Dairy Department of the University so far as facilities would permit, in the study of these casein problems.

#### THE FAULTS TO BE OVERCOME AND THEIR CAUSE

Variations in ash and acid contents in the dried casein appear to be the main causes of trouble in casein for glue making. The high acid and ash contents of many commercial caseins appear to be due to use of excessive quantities of acid or to insufficient pressing or washing of the curd before drying. The older methods of precipitation were such as to make thorough washing difficult. The curdling temperature commonly used (120–130° F.) was so high that the precipitated curd quickly gathered into large masses

<sup>1</sup> Published by permission of the Director, Wisconsin Agricultural Experiment Station.

having the consistency of dough through which wash water could not be made to penetrate with any ordinary amount of manipulation.

Our first experiments were directed to find a method of treating the curd thus made, so that the wash water could readily penetrate it. For this purpose the precipitated curd was run through a grinder placed under water in the precipitating vat. This method of operation proved quite successful in reducing the impurities in the product, but the inconvenience and cost of putting the entire curd through an extra grinding led to a search for modified methods of precipitation which would permit thorough washing without the necessity of grinding the curd under water.

#### APPLICATION OF WELL-KNOWN PRINCIPLES TO PROBLEM

1—It was pointed out in 1907 in the 24th Annual Report of the Wisconsin Station, pp. 188-189, that milk can be curdled at different temperatures by slightly different proportions of acid.

2—Curd formed at low temperatures is fine grained, and has little or no tendency toward flocculation, but precipitated at a moderately high temperature, the curd collects in larger or smaller flocculent lumps, and at yet higher temperatures, at or above 125°, it forms large doughy masses, sometimes melting or softening to the consistency of a thick syrup due to the heat.

In view of these well-known facts about casein, it appears necessary only to select suitable temperature and other conditions of precipitation in order that the curd when formed may be slightly coherent so as not to be readily lost through the strainer in the form of a fine powder, but yet sufficiently loose and open so that wash water can readily penetrate it for the removal of acid and ash.

Some printed directions such as were formerly issued by casein buyers for the guidance of casein makers are reprinted here for reference by the reader.

#### DIRECTIONS FOR MAKING COOKED CURD CASEIN

All that is necessary for making cooked curd is a metal or wooden vat to hold the milk which is heated by turning live steam directly into it. This vat should have not less than 3/4 in. steam pipe to heat the milk and a water pipe so as to run cold water on the curd. You would also need an ordinary wooden hay rake to stir the milk while you are curdling it.

For each thousand pounds of milk contained in the vat, measure out one pint of sulfuric acid. Dilute the acid by adding it to double the amount of water. (Always add acid to water, never water to acid.)

Heat the skim milk to about 130° by turning steam directly into it.

When the milk is at the proper temperature, add the acid throughout the milk, stirring it as fast as possible with an ordinary rake.

When the curd has separated, drain off the whey, rinsing the curd by throwing several buckets of water over it.

Cover the curd in the vat with one or two inches of water.

Heat the water to 170° by turning steam directly into it.

When heated, stir the curd in the warm water several times, then draw off the water, after which turn the curd over several times with a shovel until it has matted together and is thoroughly drained.

Place in bags or barrels while warm and ship to the buyer.

Some other published directions call for the addition of an extra amount of acid after the coagulation is complete.

#### BUREAU OF AIRCRAFT PRODUCTION SPECIFICATIONS

Specifications No. 14018A of the Bureau of Aircraft Production, U. S. A., for casein intended for casein glue making, include the following:

**MATERIAL**—The casein shall be made of straight skim milk of low fat content, and shall be free from starch, dirt, and other foreign material or adulterants.

**MANUFACTURE**—The casein shall be precipitated by either the lactic acid, sulfuric acid, or hydrochloric acid methods. Casein precipitated by different methods shall not be blended.

The precipitating temperature should be about 120° F. and in no case shall exceed 130° F. Only sufficient acid to secure a clear separation shall be used.

The curd shall be well pressed and dried quickly to prevent molding. With the hydrochloric or sulfuric acid methods of precipitation the cooked curd method is preferred, the temperature of cooking to be about 190-195° F.

**FINESS**—The casein must pass entirely through a 50-mesh screen.

**ACID**—The free<sup>1</sup> acidity shall not exceed the equivalent of 3.0 cc. of N/10 sodium hydroxide per gram of moisture-free casein.

**FAT**—The fat shall not exceed 1.5 per cent of the moisture-free casein.

**ASH**—The ash shall not exceed 3 per cent of the moisture-free casein for natural sour, and 4.5 per cent for sulfuric acid or hydrochloric acid caseins.

**MOISTURE**—The moisture content of the casein shall not exceed 8 per cent.

**NITROGEN**—The nitrogen content shall not be less than 14.25 per cent on a moisture-, fat-, and ash-free basis.

#### EXPERIMENTAL

**I. EFFECT OF USING A LARGE EXCESS OF ACID IN CURDLING MILK**—Two 10-lb. lots of skim milk in separate pails at 125° were curdled by adding, respectively, 25 cc. and 50 cc. of dilute (1 : 5) sulfuric acid. After the two lots of curd had been stirred 5 min., the whey was decanted, and the curd washed 10 min. with 4 lbs. of water in each pail at 125° F. The curds were then drained, cooled, and pressed in cloth bags. The 25 cc. curd was gummy in the whey, while the other was loose and flocculent in the whey. Addition of a larger proportion of acid to the milk than is actually necessary to cause coagulation tends to make the curd loosely flocculent, and prevent it from becoming doughy and gummy. This has been noted repeatedly.

However, the use of a larger proportion of acid simply to secure a loose curd, would seem to be an expensive way of accomplishing this result.

Two other effects of using larger proportions of acid are (1) the acid content of the finished casein is increased, and (2) the ash content of the finished casein is decreased as shown in Table I.

TABLE I—EXCESS ACID REDUCES ASH AND INCREASES ACIDITY OF CASEIN

EXPT. NO.	Amount of Acid Used Cc.	Ash in Dry Casein Per cent	Total Acidity of Dry Casein Cc.
6.1	25	4.87	9.2
6.2	50	2.85	15.2

<sup>1</sup> 3 cc. free acidity + 8.9 cc. casein acidity = 11.9 cc. total acidity.

In so far as an excess of acid reduces the ash content, and tends to make the curd loose, instead of compact and gummy, it is an advantage, but in so far as it increases the cost and the acidity of the finished casein, it is a disadvantage. As the percentage of ash is within the standard limit in both cases, a minimum amount of acid appears satisfactory for casein making.

**II. EFFECT OF VARIOUS TEMPERATURES OF PRECIPITATION**—Four 10-lb. lots of skim milk in pails at 80°, 90°, 100°, and 110° F. were curdled by adding dilute sulfuric acid slowly from a graduate. The physical properties of the curd thus formed without excess of acid were observed with reference to ease of washing and draining at these temperatures. Formed at 80° F., the curd was fine grained, settled slowly, and did not tend to collect in lumps. At 90° F. the curd grains showed a slight tendency to flocculate into small lumps. Neither of these two curds settled rapidly so as to be readily drained and washed. The curd formed at 100° F. was slightly gummy and coherent, flocculating to a sufficient degree so that it settled readily, and drained easily without loss, and could be washed without difficulty. The curd formed at 110° was quite gummy and collected rapidly into large lumps of such coherence that it was impossible to wash the curd inside the lumps.

The results of the 90° experiment and the 100° experiment indicated that the most suitable temperature lay between these figures. After a number of trials, 95° was selected as the proper temperature for precipitation, giving curd of suitable texture for most convenient draining and washing. A number of experiments were made which confirmed this choice.

**III. EFFECT OF ADDING ACID SLOWLY OR RAPIDLY**—Using 10 lbs. of skim milk in a pail, and adding acid slowly from a graduate, while stirring vigorously, the smallest amount of dilute acid which would cause clear coagulation was determined. With 10 lbs. of the same milk in other pails, but adding the same quantity of acid at one instant, it was often found that the milk was not fully coagulated, but that the curd was surrounded by milky whey. This experiment, repeated several times, indicated the desirability of adding acid slowly in making casein, while mixing the milk by vigorous stirring. When all the acid is added at once, mechanical inclusion of part of the acid in the curd first formed may deprive the last portion of the whey of the quantity of acid necessary to make it clear, unless an excess of acid is used.

#### SUGGESTIONS FOR AN IMPROVED METHOD OF MAKING CASEIN

The plan adopted as a result of our experiments is to heat skim milk to about 95°, stir vigorously while adding dilute acid slowly until a clear whey is obtained, avoiding excess of acid. The curd obtained at this temperature is just coarse and coherent enough to settle rapidly and permit draining the whey, but sufficiently loose and open to permit ready washing with water, with a minimum expenditure of labor and time.

After settling in the whey for a minute or two, the curd is pushed away from the gate with a rake, and the whey is drawn out through a strainer. Water at 95° equal to one-quarter the volume of the milk used is added to the curd, and after a few minutes' stirring the water is drained out and the curd put to press in the usual manner. Thorough pressing to remove as much water as possible is recommended.

It has not seemed necessary or desirable to use a test for the acidity of the skim milk employed for casein making, or to prepare a table showing the amounts of acid required, as this will vary with the acidity of the skim milk to start with, and other conditions, such as the temperature of precipitation.

Trials of the method described above have been made as follows, with entirely satisfactory results.

**CASEIN 14**—1900 lbs. of skim milk of 0.16 per cent acidity were heated to 95° in the vat. Dilute sulfuric acid (1 : 5) was poured in a small stream while stirring the milk vigorously with a wooden rake. No more acid was added than was necessary to produce clear whey. The 4.6 lbs. of concentrated sulfuric acid diluted in 20 lbs. of water required 3½ min. for its addition to the milk in the manner described.

The acidity of the clear whey was 0.37 per cent by the acidimeter. This is stated here as a matter of record, but the use of the acidimeter is not required in practice. The curd was pushed away from the gate and the whey was drawn out without clogging the strainer in the least. Sample 14.1 was then taken from the curd, and pressed in a cloth bag without any washing.

The curd in the vat was washed by adding water at 95° F. equal to one-quarter of the volume of the milk used. After vigorously stirring up the entire mass of curd in the wash water with the teeth of the rake turned downward, the wash water was drawn out through the strainer. A sample of the curd was taken and marked 14.2. Another sample of the curd was taken and given a third washing in a pail with water at 95° F., and this was then drained and pressed, and marked 14.3. The main bulk of the twice-washed curd was pressed as dry as possible, milled, and dried in a commercial sized casein dryer recently installed in the Dairy Building. Caseins 16 and 17 were made by the same method as described above.

The analyses of the products are given below, showing that they come well within the standard limits of ash and acidity.

TABLE II—ANALYSIS OF CASEINS MADE BY NEW METHOD

No.	Moisture-free substance		Moisture Per cent
	Ash Per cent	Acid Cc.	
14.1	2.80	9.6	5.65
14.2	2.28	9.5	5.48
14.3	1.98	9.4	6.17
16.2	2.36	8.6	5.12
17.2	2.80	8.33	5.74

Casein 14.2 gave excellent results when used for making water-resistant glue according to three formulas at the Forest Products Laboratory.

The chemical analysis of about thirty-five samples of experimental casein for ash, acid, moisture, and in some cases nitrogen, as well as the glue-making tests were made by the Forest Products Laboratory, U. S.

Department of Agriculture, at Madison, Wisconsin, for which acknowledgments are due.

The card of directions for making casein reprinted above may be revised as follows:

#### REVISED DIRECTIONS FOR MAKING CASEIN

A metal or wooden vat is needed to hold the skim milk which is heated by turning steam directly into it. This vat should have not less than  $\frac{3}{4}$  in. steam pipe. Some arrangement for heating the water to be used in washing the casein should be provided. An ordinary wooden hay rake is used to stir the milk while curdling it.

For each 1000 lbs. of milk in the vat, measure out one pint of sulfuric acid. (Muriatic acid may be used with equal success.) Sulfuric acid when used must first be diluted by adding it to double the amount of water. (Always acid to water, never water to acid.)

Heat the skim milk to 95° F.

Add the acid in a small stream or streams to the milk while stirring the latter as vigorously as possible with one or more rakes. Use no more acid than necessary to obtain clear whey.

When fully curdled, let the curd settle for a few minutes, then push it slowly with the rake away from the gate toward the upper end of the vat. Put in the strainer and draw out the whey. Have ready in cans, water at 95° F. equal in weight to one-fourth of the milk used. Add this at once to the curd in the vat and stir up thoroughly with the rake, teeth down, so as to break up all lumps and wash every particle of curd.

Draw off the wash water, and press the curd as thoroughly as possible, if pressed curd is to be made for immediate drying.

If cooked curd is to be made, cover the washed and drained curd with hot water and run in steam to heat it to 180–190° F., until the curd unites into a single large mass which can be shoveled into barrels or boxes for shipment.

#### SUMMARY

In this paper, it is shown that by modification of the former factory process as to temperature, washing, etc., casein can be uniformly obtained which is suitable for making water-resistant glue.

MADISON, WISCONSIN

#### SOME NOTES ON PAINT ANALYSIS

By GEORGE J. HOUGH

Received May 9, 1919

The methods described in this paper were devised by the writer to meet particular cases occurring in the course of regular work on the testing of paint supplies; and it is hoped that they may prove useful to those engaged in paint analysis who may have to deal with similar problems. Of course it is understood that with mixed paints, the paint vehicle must be extracted, and the pigment dried, before they can be analyzed.

#### DETERMINATION OF CUPROUS COPPER IN COPPER PAINTS

This method was devised for ship-bottom paints specified to contain a certain amount of copper in the form of cuprous oxide. The method is as follows:

To 0.5 g. of sample add 10 cc. of concentrated hydrochloric acid, stir well, heat gently for several minutes to dissolve all copper, dilute with cold water to about 200 cc., add 5 cc. of phosphoric acid, and titrate at once by potassium permanganate. The results are good except when the sample contains much unextracted matter, which causes a slight error in the titration.

**EXAMPLES**—(1) 0.5 g. of sample required 12.8 cc. of permanganate, equal to 28.8 per cent copper. (The same sample titrated one year later gave the same result.) Taking 0.5 g. of the same sample, separating the copper as copper sulfocyanate ( $\text{CuCNS}$ ), and determining it by titration of the sulfocyanic acid gave 28.9 per cent copper.

(2) In another sample the cuprous copper titrated by permanganate was found to be 24.5 per cent. In the same sample, the copper separated by aluminum and determined by the iodide method was found to be 24.8 per cent.

To prove the accuracy of this method for commercial purposes, a sample of dry commercial cuprous oxide was taken, and 0.5 g. samples were dissolved and titrated as above; 0.5 g. of pigment used 27.3 cc. of permanganate with a value of 10 mg. iron per cc. equal to 11.66 mg. copper, showing the copper content to be 63.6 per cent; 2 more duplicate tests gave the same result. It will be noted that the factor 1.166 is used, instead of the theoretical factor 1.125, to change the iron value of the permanganate to the copper value; this factor was found by standardizing the permanganate against a carefully prepared sample of cuprous oxide.

Then samples of 0.2 g. were each treated with a solution of silver sulfate made by dissolving 1.3 g. of silver nitrate in 100 cc. of water and adding 10 cc. of concentrated sulfuric acid; the tests were made with cold solutions, and were allowed to stand for 1 hr. with occasional stirring; they were then filtered and washed, and the metallic silver that had been reduced by reaction with the cuprous copper was dissolved in nitric acid, and the silver titrated by Volhard's method, using a standard solution of ammonium sulfocyanide. In the reaction between cuprous copper and silver sulfate, one part of silver is reduced by one part of cuprous copper. The results of 4 determinations were, 63.85 per cent, 63.55 per cent, 63.85 per cent, 63.55 per cent of copper; this proves that the method is within allowable limits for commercial work. This test with a solution of silver sulfate cannot be made on an extracted pigment, as it is almost impossible to free the sample from oil and organic matter, which interferes seriously with the reaction between the copper and silver.

#### A RAPID METHOD FOR LIME IN WHITE LEAD

It is sometimes desirable to test white lead for lime, especially in putties, to ascertain how much lime has been added in the form of whiting. The following method depends on the solution of the white lead in a hot dilute solution of caustic soda, and it is removed by filtration from the insoluble whiting:

To 0.5–1.0 g. of sample add 50 cc. of 5 per cent caustic soda and heat to boiling for several minutes, decant on filter, add a little more caustic soda and then hot water, and decant; wash well by decantation with hot water and wash filter about four times; dissolve the residue in hot hydrochloric acid (1:2), dilute, neutralize with ammonia (filter off any lead precipitate), boil, and precipitate lime with a saturated