

Laboratory Boiling of Soap in Glass

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CHEMICAL problems connected with the manufacture of boiled soaps impress laboratory workers with the desirability of boiling soap in glass, which would enable the operator to follow visually the progressive changes which take place when fats are saponified by aqueous alkalis and at the same time eliminate catalytic action proceeding from the metal or oxides of metal of which the soap kettle is constructed. In view of these considerations, we have been led to compile some notes from our experience which we hope may be useful to others who want to work along these lines.

Problem in Small-scale Boiling

When fats and aqueous alkali are brought together at the temperature of boiling water, chemical reaction begins at once at the surface of contact. If now the two liquids are mixed intimately by suitable agitation, saponification proceeds rapidly and will go to practical completion, provided a suitable excess of alkali hydroxide is present.

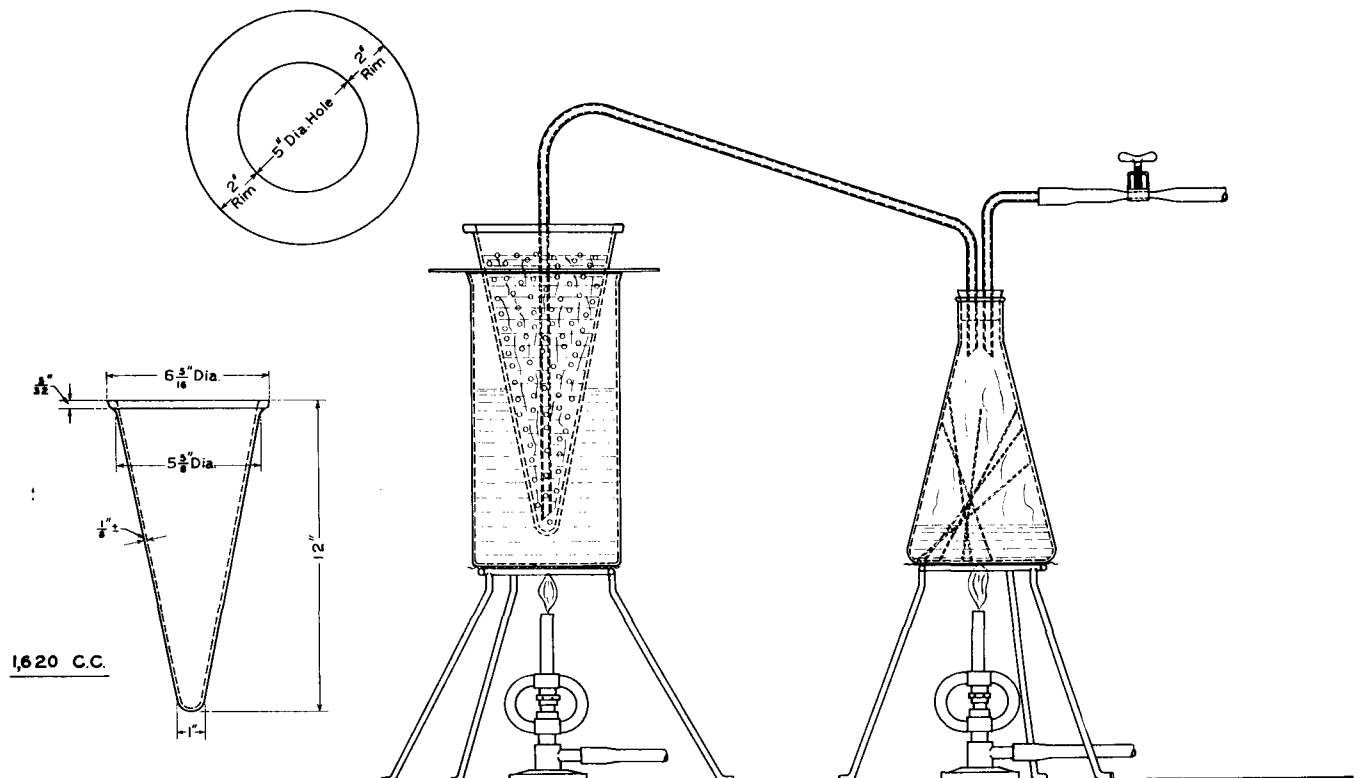
Attempts have long been made in the industry to boil soap on the small scale and derive data or products therefrom which may be applied to full kettle operations in the plant. The majority of workers have experimented in the range of 200-5000 gallon steel kettles and have been unsuccessful in duplicating full-scale operation for two main reasons:

- 1—Rate of cooling much more rapid, not permitting sufficient settling.
- 2—Steam, both open and closed (if any) improperly disposed to give agitation and heat distribution as in plant kettles.

With unfavorable results the rule rather than the exception from small kettle operations, it has been generally assumed that experiments on a still smaller scale, as in laboratory glassware, could only be valueless, if not actually misleading. By maintaining the saponification vessel in a constant-temperature bath, by proper design of the vessel itself and the method of introducing open steam, it has been the experience in our own laboratory, and in some others, that the chemical results of best large plant operation may be duplicated consistently in glass vessels as small as 750 ml capacity (100 grams of fat), and in jacketed, thermostatically-controlled steel kettles of special design of 50 gallon capacity (100 lbs. fats).

Apparatus

If it is attempted to carry out a saponification by heating the vessel in which the mixture is contained directly with a flame or over an electric heater, as saponification proceeds, the soap will be almost sure to burn on the bottom of the vessel, or failing that, will boil over. If, however, the fat and alkali solution are heated by placing the container in a boiling water bath and passing at the same time a suitable current of open steam through the mixture to provide the necessary agitation, it is quite easy to carry the reaction to a satisfactory degree of completion in a relatively short time. In order that the agitation be adequate, we use a cone-shaped vessel of Pyrex glass in which to carry out the saponification, as shown in the accompanying figure. The cone is supported by a flat ring of galvanized iron in a large beaker of boiling water. Steam for agitating the charge of fats and



alkali is generated in a one liter Erlenmeyer flask. A glass tube conducts the steam to the bottom of the cone and the ascending bubbles of steam furnish the mixing required. The flask is also equipped with a short piece of rubber tubing and a screw clamp which serves as an air vent to safeguard against sucking the contents of the cone into the steam generator when heating is discontinued. As in any such development necessarily involving skill and personal judgment, variations of these details will occur to individual workers. We present this method only in the form of preliminary notes at this time.

Procedure

The cone has a capacity of about 1700 ml. It is suitable for handling 200 grams of fats at a time without danger of boiling over. Into the cone is charged the mixture of fats, and the water bath is heated to boiling, which is maintained throughout the time required. 200 ml of boiling water, containing 15 grams salt, are added to the fat charge. The desired quantity of caustic soda solution of 30 weight-per cent is placed in a separatory funnel with short stem supported directly over the cone. Steam is passed into the charge and when actively boiling, caustic soda solution is added dropwise from the separatory funnel at such a rate that about half an hour is required to run it all in. Thereafter steam flow is adjusted so that the contents of the cone are suitably agitated without overflowing. Saponification proceeds quite rapidly and is practically complete in an hour after all the caustic soda has been added.

The charge is now grained with dry salt. This should be added gradually while boiling the charge as vigorously as practicable, and boiling should be continued fifteen minutes or more after the charge is grained. While this lye change corresponds to the "Killing change" of large-scale soap boiling, if we do not have the glycerine recovery operations under consideration, it saves time to employ an excess of alkali in the killing change in laboratory operation, and then if the graining and subsequent boiling are properly done, a large amount of undesirable coloring matter passes into this first so-called "killing" lye. One may, however, readily operate one or more of these cones to conform to any desired schedule of manufacturing operations, involving counter-current flow of soap and lyes, etc.

Finally, when it is judged that this operation is satisfactorily concluded, the air vent on the steam generator is opened and heating of cone and steam generator discontinued. The spent lye separates quickly, but it is desirable to allow the contents of the cone to stand at rest at least two hours. Cooling will take place to an extent permitting very little soap to be retained by the highly-colored lower layer of spent lye. If it is attempted to remove this lye before sufficient cooling has taken place, there is danger of withdrawing considerable soap, particularly if the charge contains a maximum of coconut oil, or if the graining of the soap has not been thorough.

Some workers have used an extractor type of cone known as a percolation cone, having a bottom draw-off valve. In our experience, any bottom opening under the conditions involved, may permit accidental loss of material, and if rubber stoppers or rubber tubing are used, contact with hot alkaline solutions introduces impurities.

The spent lye is withdrawn by substituting an empty

flask for the steam generator and sucking on the air vent. The lye is easily drawn over into the flask, with an insignificant amount remaining in the cone with the soap. Having removed the spent lye, our apparatus is connected up as at first, and the soap is heated initially by means of the boiling water bath alone. 200 ml water with 10 grams of salt and 12 grams of 50% caustic soda (or its equivalent) are heated to boiling and added to the soap. When all is suitably hot, open steam is passed again at such a rate that the soap and alkali are kept in mild agitation. This is maintained for from one to one and one-half hours. The soap is now ready to be finished by graining out and settling. It may be grained with dry salt as before, but we prefer to use dry salt only to incipient graining and finish with saturated brine. There is a tendency for cold brine solution to produce coarse granules which do not break up readily on subsequent boiling. We find that a more satisfactory result is obtained if the brine solution is heated to near boiling temperature before running into the boiling soap. It is inevitable that some practice is required to accomplish a satisfactory graining, and many little artifices suggest themselves to a worker who is engaged in this kind of work continuously. It is possible to transfer the entire charge to a suitable beaker after graining, if desirable to release the cone for another boiling operation. To settle the finished soap, we select a clock glass of the right size to drop into the body of either beaker or cone and float on the soap itself without leaving a wide space between the outer rim of the clock glass and the sides of the vessel. We then place another clock glass of the same diameter with the convex side uppermost resting on the first one. Finally, the vessel is covered with a third which rests on the rim or flange. In this way drops of condensed water will be deflected to the sides instead of falling into the soap. The vessel containing the soap with the under layer of lye is placed in a constant temperature oven or air bath at 85°C. Settling will take place and may be observed with the aid of a flashlight or similar source. The settling process will require about 24 hours or more, depending upon the composition of the fat charge and its titre, as well as the temperature employed. Recent experience has shown that better settling takes place if most of the spent lye is removed prior to placing in the constant temperature oven.

Experience will best guide each operator and nothing may take the place of it.

Some workers have used a thermostatically controlled water bath surrounding the cone during settling, but we have found the oven simpler and more satisfactory. In this way the entire vessel and contents may be maintained at a constant temperature equal to the average temperature of a large kettle during settling, and as a result excellent settling takes place, perhaps even superior to ordinary plant practice.

Separation of Neat Soap

After a satisfactory separation of spent lye, nigre, neat soap, and fob has taken place, as shown by inspection, the vessel containing the soap is removed from the air bath and allowed to cool spontaneously, which will require several hours. The soap is then loosened from the vessel with a knife, the spent lye poured off, the cake of soap dried with absorbent paper, and the nigre and fob are cut away with a knife. The neat soap is dense and hard and easily distinguishable from the nigre and fob, which are mushy and spongy re-

spectively. It is to be expected that the operator must learn to boil soap by this method in exactly the same sense that a man learns to boil soap in a kettle on the large scale, with this important exception in favor of the laboratory operation: it is possible to see what is taking place through the glass apparatus, while on the large scale the operator depends upon observation of the soap on a trowel.

On the other hand it must be remembered that the large-scale operation is capable of finer manipulation through the use of closed steam coils for which our boiling water bath is in no way a substitute.

Nevertheless, the laboratory method is a useful device capable of providing a reliable answer to many chemical problems connected with the making of soap. Where larger quantities of soap are required for further processing, we use a battery of three steel kettles of 50 gallon capacity each, which we hope to describe in a later paper.

Acknowledgment

We wish to acknowledge our indebtedness to members of the technical staff of the Procter and Gamble Company for helpful suggestions which led us to the particular adaptation and procedure described herein.

Deterasive Efficiency of Tetrasodium Pyrophosphate - Part I

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THE data in this paper are the result of an intensive laboratory program to determine the value of tetrasodium pyrophosphate as a soap builder, with particular reference to its use in household built soaps. It was felt that the first step in the program was to determine the effect of single builders with soap in order to obtain data on the specific action of each alkali. For this reason a series of tests were run in which soap was combined with only one builder. The list of alkalies include tetrasodium pyrophosphate, 1:3.3 silicate, 1:2 silicate, metasilicate, trisodium phosphate, disodium phosphate, soda ash and borax.

Since most built soaps contain a mixture of two or more builders, the program was extended to include both binary and ternary combinations of alkalies. To date, however, only the single and binary combinations have been completed. It is expected that the ternary combinations will be completed within the next few months and results of these tests could be the subject of a second paper.

During the first series of runs the ratios of soap to builder were 95:5, 90:10, 80:20, 70:30, and 60:40. The 95:5 ratio was dropped soon after the program was under way since the early results showed that this combination seldom showed an appreciable effect on the shapes of the curves. The reason for not increasing the amount of builder above 40% will be apparent from the data since they show that in most cases maximum detergency was almost always reached at higher ratios than 60:40 of soap to builder.

Three concentrations were used for each series of tests, namely, 0.10%, 0.15% and 0.20% in "soft" water (50 ppm hardness) and 0.27%, 0.32% and 0.37% in "hard" water (300 ppm hardness). These points were chosen to represent, first, a decided deficiency in detergent strength, second, a slight deficiency and third, maximum soil removal. Previous tests had shown that the concentrations of detergent in the hard water tests would have to be increased appreciably over the concentrations used in the soft water tests. Hence, concentrations were increased in these tests so as to obtain approximately the same degree of soil removal as in the soft water series.

All builders and soaps are used on the anhydrous basis.

pH values and height of suds were determined for each wash test. These data are recorded on the charts.

Description of Wash Tests

The washing tests will be described but briefly in this paper since Committee D-12 of the A.S.T.M. is now conducting a cooperative program in an effort to set up a standard method for this procedure. Mr. Harris is a member of this committee. A laundrometer is used for all tests. The cloth used is Indian-head, a cotton fabric, which has been desized and then soiled with a mixture of Oil-dag and vegetable oil. The test swatches are 6" by 5". The initial swatch is first given a ten minute wash in the detergent solution. After the first wash, a strip representing a quarter of the total is cut off, rinsed, dried, and the soil removal measured. The remainder of the swatch is then washed 10 minutes longer in a fresh detergent bath and another 1½" strip removed. This procedure is repeated until the last strip, representing one-fourth of the original swatch, has been washed for 4 ten minute periods each time in a fresh detergent solution. Each determination was made in duplicate and the results for each series were then repeated. Each point in the curves therefore represents the average value of four determinations.

The soil removal is measured by a photoelectric photometer. The results shown in this paper are the average percent soil removal for the four washes.

The temperature used in all cases was 140° F. ($\pm 2^\circ$)

The soap used throughout the program was a well known medium titre soap. The alkalies used were all industrial grade products.

Curves for tetra sodium pyrophosphate, 1:3.3 silicate, 1:2 silicate and metasilicate in soft water are presented in the first group of graphs. They show that there is little advantage to be obtained from the use of builders in soft water, particularly at the higher concentrations. 1:3.3 silicate is actually detrimental rather than advantageous at the two lowest concentrations. 1:2 silicate and metasilicate give slightly better results at 0.15% than at 0.20%. This is believed to be due to the fact that the high concentration of hydroxyl