THESIS

A STUDY OF THE HARDNESS OF WATER

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A Study of the Hardness of Water.

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Dedication.

To Bruce L. Hartsuch, professor and friend, whose assistance has been so kindly given, I sincerely dedicate this report.

Contents.

Introduction.

In any textile processes such as scouring, bleaching, washing, or dyeing, the character of the water employed has a profound and lasting effect on the results obtained. If the water is at all hard, the soap left in the goods from the scouring bath will be precipitated in the fiber and remain as an insoluble metallic soap. Thus it is necessary to soften the water used in these processes first.

The hardness of water is due to salts of calcium and magnesium, occuring as bicarbonates, sulfates, and chlorides. When soap is used with water it must first precipate these metallic salts before any of it becomes available for cleansing purposes. Thus water containing many of these salts would waste much soap. The hardness due to bicarbonates is said to be "temporary" as it may be removed by merely boiling the water, but the other salts causing the "permanent" hardness have to be removed in some other way. The bicarbonates when heated decompose into carbon dioxide gas and an insoluble carbonate, which is precipitated.

Report.

a. Possible Methods of Softening Water.

There are, in general, two methods of softening water: (1) to add to it a certain calculated amount of pure washing soda, sodium carbonate, or of some commercial softener, or (2) by some industrial method such as sand filters, pressure filters, gravity filters or Zeolite process, which depends on the power certain silicates have to exchange the sodium they have in combination for the calcium and magnesium of the compounds in the hard water. In this discussion only the direct addition of a softener to the water is considered. A comparison of the efficiency of pure sodium carbonate solution with "Climaline" and "Rain Water Crystals" solutions is made, as well as a determination of the best method of softening as to manipulation.

b. Discussion of Methods Tried, but Found Unsatisfactory.

As long as the softener removes a good share of the hardness, it was necessary to find a method for determining hardness which would show up very small amounts. The first method tried was to first neutralize a sample with one tenth normal hydrochloric acid to methyl orange and then boil to expel the carbon dioxide which decolorizes phenolphthalein and hence must be removed before any titration using this indicator takes place. This was then cooled and filtered and titrated with one-tenth normal alcoholic soap solution until pink to phenolphthalein.

But it was found that the titration with phenolphthalein does not give a sharp enough end point because the pink is difficult to see above the yellow of the methyl orange. Moreover in some cases all of the hardness appears to be removed before any titration with soap occurs at all, so that a red color is obtained as soon as any phenolphthalein is added.

Tap water contains calcium bicarbonate, calcium chloride and carbonic acid. The calcium bicarbonate is titratable; it is acid both to methyl red and phenolphthalein. Phenolphthalein changes color when the hydrogen ion concentration is 1×10^{-8}. More acid must thus be present to change the color of the methyl orange. Therefore the hydrogen ion concentration must be greater than 1×10^{-9} and less than 1×10^{-5} and lie somewhere between these two figures, which might be the neutral point, 1×10^{-7}.

The carbon~~ate~~ic acid and calcium bicarbonate disappear on boiling and the bicarbonate is converted into carbonate. Therefore boiling removes titratable material and acidity due to carbonic acid. Calcium chloride and a saturated solution of calcium carbonate is present. This calcium carbonate (or magnesium carbonate) in solution is the only titratable material present. This will require 40% more acid for titration using methyl red. Boiled water is acid to methyl red, but alkaline to phenolphthalein showing that its hydrogen ion concentration must be less than 1×10^{-9}. It is really more alkaline than unboiled water, but its titratable alkalinity is less.

The next method tried was to use no indicator but methyl orange and add an excess of soap solution (giving yellow color); then the excess was back titrated with hydrochloric acid to a red color. Then the amount of soap solution actually used for titration indicated hardness. But the hardness figure which was obtained was very much too low. Phenolphthalein would be the better indicator as it changes color at a lower hydrogen ion concentration.

The alkalinity of the water was determined and the amount of acid required according to this figure, plus one cc. more was added. This was then boiled, cooled to room temperature, the phenolphthalein added and soap solution added to [illegible]. Then the [illegible] acid was used to back titrate. The amount of soap solution actually used in titration indicated the alkalinity of the water. But this method also proved to be very inaccurate, when checked up. A water of known hardness content when run through gave a result which indicated a hardness of only about one-half as much as it should be. Therefore this method as well as [illegible] the preceding ones is inaccurate in some respect.

c. The Permanent Lather Method.

Finally the lather method, which consists of determining how many cubic centimeters of standard soap solution are required to make a permanent lather with a certain amount of water, was used. A standard hard water (a solution of calcium chloride) was made up and used to standardize the soap solution so that it could be determined how many grams of calcium oxide are equivalent to one cc. of soap solution by titrating to a permanent lather a certain amount of this water with soap solution. It was found that one cc. of soap solution was equivalent to .00152 gms. of calcium oxide and that, using this figure, ordinary tap water had a hardness of .000228912 gms. of calcium oxide per cc. or 228.912 parts per million of hardness.

d. Comparison of the Efficiency of Softeners.

To compare the efficiency of the different softeners, standard solutions of pure sodium carbonate, "Climaline" and "Rain Water Crystals" were made up. The sodium carbonate solution was used as the standard and the results with the other two are expressed in terms of it.

The first method used was that wherein a given amount (ten cc.) of softener was added to 100 cc. of water, mixed with it thoroly, and the whole let stand for one hour at room temperature. This was then titrated with standard soap solution using just enough to obtain a permanent lather. With sodium carbonate (Na_2CO_3), 9.4 cc. soap were required, 12.4 cc. with "Climaline", and 12.[illegible] cc. with "Main Water Crystals". From previous determination it takes 1[illegible].[illegible] cc. soap for 100 cc. tap water, unsoftened. Therefore sodium carbonate removes [illegible]7.[illegible]% of the hardness, "Climaline", 17.[illegible]4% and "Main Water Crystals", 1[illegible].[illegible]%. This shows "Climaline" to be 75.44% as efficient as pure sodium carbonate and "Main Water Crystals", 71.[illegible]1%.

The next method used was to add [illegible]0 cc. of softener to 200 cc. of water, bring the mixture to a boil, cool to room temperature and then titrate 100 cc. of this mixture. Bringing results to a basis of 100 cc. of water, it was found that [illegible].61 cc. soap were required with sodium carbonate, 1[illegible].4 cc. with "Climaline", and 11.8 cc. with "Main Water Crystals" to titrate the remaining hardness. Or, Na_2CO_3 removes [illegible]2.[illegible]% of the hardness, "Climaline" 2[illegible].[illegible]%, and "Main Water Crystals" 21.7%, and "Climaline" is [illegible].[illegible]7% as efficient as pure Na_2CO_3 and "Main Water Crystals" [illegible]7.1[illegible]%.

The final method was to allow 10 cc. of the softener to stand in 100 cc. of water at room temperature for twenty four hours. [illegible].[illegible] cc. soap solution were required with Na_2CO_3 and 1[illegible].[illegible] cc. for both "Climaline" and "Main Water Crystals" to titrate the remaining hardness. Thus Na_2CO_3 solution removes [illegible]0.8% of the hardness and the other two only 1[illegible].[illegible]% by this method and the other two softeners are 51.75% as efficient.

Thus it may be seen that the efficiency of the various softeners vary depending on the methods used. Not so much difference is noticed in the first method, which, as a method, is less efficient than the other two. In the last two methods the commercial softeners are about 50% as efficient as the pure sodium carbonate.

e. Best Method for Softening.

The Na_2CO_3 solution was used under different conditions to show the best method to use for softening water. The methods will be given in the order of their efficiency; the least efficient first.

(1) 10 cc. of softener were thoroly mixed with 100 cc. water and allowed to stand at room temperature for one hour. [illegible] cc. soap were required to titrate, showing a hardness of 1[illegible].[illegible] parts per million (p. p. m.) remaining.

(2) 10 cc. of softener were thoroly mixed with 100 cc. of water and allowed to stand at room temperature for twenty-four hours 6.75 cc. soap were required to produce a permanent lather, showing a hardness of 102.6 p.p.m. remaining.

(3) 20 cc. of softener were thoroly mixed with 200 cc. of water, the mixture brought to a boil and allowed to cool down to room temperature. 100 cc. of the mixture were

titrated, which is equal to [illegible]0.9 cc. of water alone. 5.6 cc. of soap were required which is equivalent to 6.16 cc. for 100 cc. of water. This shows [illegible] p.p.m. hardness remaining.

(4) 20 cc. of softener were mixed with 200 cc. of water, boiled for fifteen minutes and allowed to cool down to room temperature. 5.94 cc. soap were required for 100 cc. of water or [illegible] p.p.m. hardness remaining.

(5) Let 20 cc. of softener stand in 100 cc. of water, after mixing thoroly, for twenty-four hours at room temperature. Then filter before titrating. [illegible].9 cc. of soap were required; 63.68 p.p.m. of hardness remaining.

(6) 20 cc. of softener were boiled with 200 cc. of water for fifteen minutes, cooled to room temperature and filtered. [illegible] cc. soap were required for 100 cc. of water or [illegible] p.p.m. hardness remaining.

(7) 20 cc. of softener were heated to boiling in 200 cc. of water and 100 cc. of this mixture titrated at once. [illegible].61 cc. of soap solution were required for 100 cc. of water or [illegible] p.p.m. hardness remaining.

(8) 20 cc. of softener in 200 cc. of water were boiled for fifteen minutes and 100 cc. of the mixture titrated at once. 5.[illegible] cc of soap solution were required for 100 cc. of water or 79.34[illegible] p.p.m. hardness remaining.

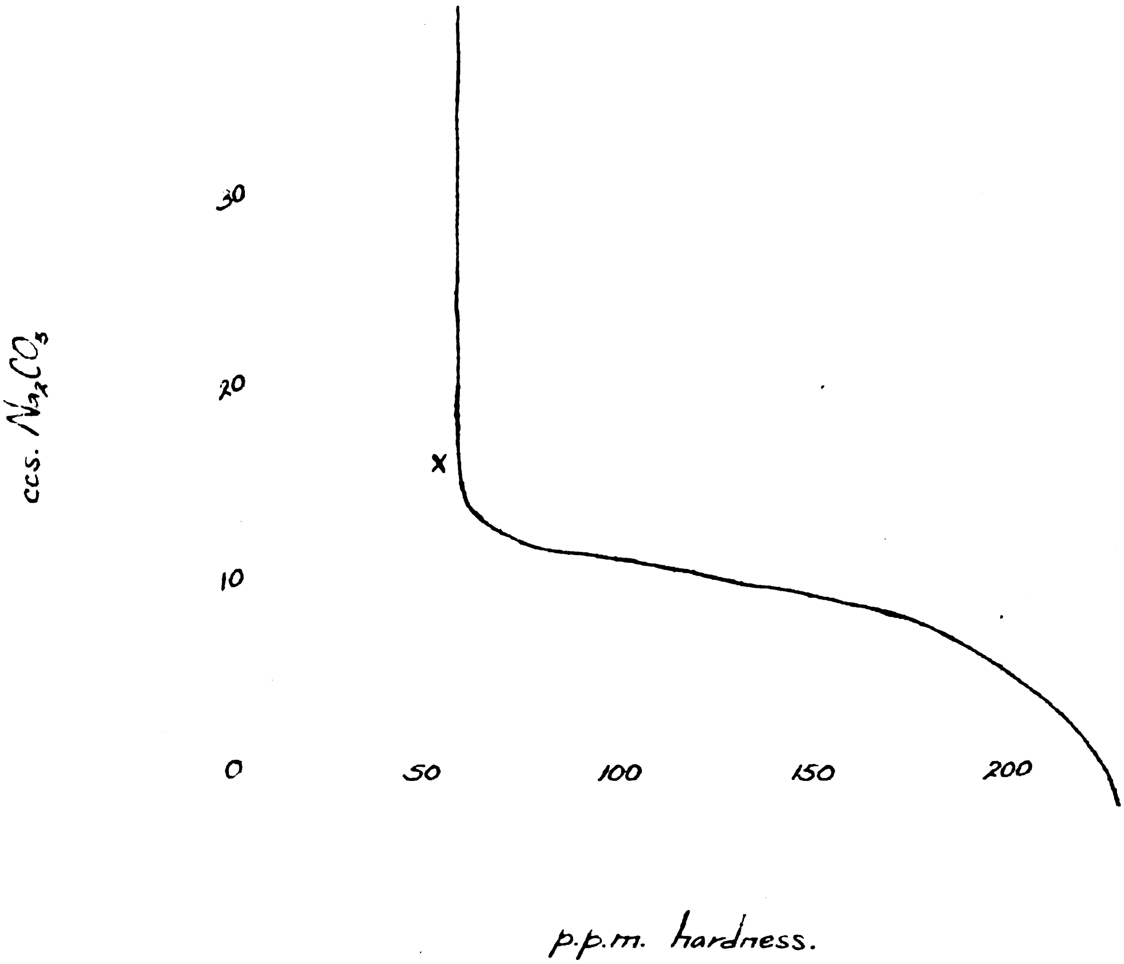
Thus we see that heating the softener and the water together is more efficient than letting it stand, even for a long period of time at room temperature. Heating for fifteen minutes is a little more efficient than merely bringing the mixture to a boil. Methods (5) and (6) showing the use of filtering prove that some substances are removed by filtering which the soap would have to react with if they remained; these methods are therefore more efficient. The last two methods showing that a lather is more easily obtained in hot water. They are not reliable for giving accurate hardness figures.

f. Proper Amount of Softener to Add.

By figuring from previous determinations, wherein we saw that 10 cc. of softener in 100 cc. of water removed [illegible]7.8% of the hardness, 20.[illegible] cc. would theoretically remove all of the hardness. Various amounts of softener were added and hardness determinations made. Then by plotting cc's. of softener (Na_2CO_3) against p.p.m. hardness remaining, it is seen (see graph) that 15 cc's. Na_2CO_3 for 100 cc. of water is the most efficient. Beyond that point practically no more softening reaction takes place.

g. Alkalinity Content.

But another important consideration is: after the water has been completely softened, what is its alkalinity


ccs. Na_2CO_3
30
20
10
0
x
50
100
150
200
p.p.m. hardness.

content? It may be a perfectly soft water and yet have an alkalinity which would be very harmful, not only to textile fibres, but to the skin of the hands if it is to come into contact with them. [illegible] determination of this phase must be made.

Ordinary tap water, unsoftened, as well as tap water which has been boiled and filtered, has an hydrogen ion concentration of 1 x $10^{-8.6}$ as was found by comparing them with a series of standard buffer solutions. This is beyond the neutral point (1 x 10^{-7}) on the alkaline side by $10^{-1.6}$. Therefore the alkalinity of softened waters should be observed and care should be taken not to have the hydrogen ion concentration too much less than the above figure. For example 1. cc. [illegible] solution in 100 cc. of water gave a hydrogen ion concentration of 1 x $10^{-8.7}$ which would not be too little, making the alkalinity too high.

Conclusion.

The figutes obtained may be easily applied to any problem, by using proportional amounts. A standard solution of Na_2CO_3 containing 3.92 grams per liter is the most efficient when used about 16 cc. in 100 cc. of water. This is .06272 grams.

The method which for a certain purpose will be the most efficient may also be easily adapted. If for some process it does not appear practical to filter the water, some combination of the other methods, giving the same efficiency may be used. Boiling the water and softener together, is probably the easiest method as well as the most practical in the long run.