Investigations into the Chemistry of Laundering

by W. F. Faragher

1910

Submitted to the Graduate School of the University of Kansas in partial fulfillment of the requirements for the Degree of Doctorate of Philosophy in Chemistry
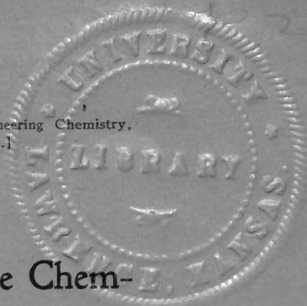
Doctor's Thesis

Faragher, W.F.   1910

Investigation into the

chemistry of laundering.

FARAGHER
1910
c.3

An Investigation into the Chem-
istry of Laundering

By W. F. Faragher

AN INVESTIGATION INTO THE CHEMISTRY OF LAUNDERING[1]

By W. F. FARAGHER

The laundry industry is one of a group which are not usually classified as strictly chemical industries, but which, nevertheless, depend in large measure upon the proper control of chemical reactions for their successful operation. The list includes, among others, bakeries, glass factories, brick plants, brass and iron foundries, confectioneries, tanneries and creameries. Although the laundry industry is one of the most important, both in point of the nature of the service it renders modern civilized communities and of the number of employees and the capital invested,[2] it is perhaps the last to avail itself of the benefits to be derived from an extensive adoption of the methods and teachings of chemical and engineering science.

A great deal of ingenuity has been displayed in bringing the processes and machinery employed to their present state, but investigation shows that before the industry may rightfully be classed as an efficient one, much improvement is necessary, especially in the case of the chemical processes which occur either as essential parts of the operation, or as harmful accompanying reactions.

As a result of the study given to the production of high-grade laundry work by the more progressive men engaged in the industry, empirical methods are now quite generally employed in the best plants which leave little to be desired as far as the appearance of the finished articles is concerned. But for the purpose of investigating the possibility of introducing more scientific methods, which would improve conditions by prolonging the period of usefulness of the articles laundered and also by reducing the cost of production

[2] The census of 1910 included power-laundries for the first time. The number of plants reported is 5184. This does not include the laundries in hospitals, public institutions and shirt and collar factories. A careful study of conditions in Chicago indicates an annual volume of business close to $3,000,000.

of the work, the experiments to be described were carried out.

The work of the laundry is necessarily complex, but may be conveniently divided into a number of parts. Exclusive of the collection and delivery of the bundles, and of the marking and listing of the articles in each bundle to make possible their return to the respective owners, the following operations may be enumerated: sorting, washing, extracting, that is, the removal of excess water by means of centrifugal machines, starching, drying, dampening, ironing, and finally finishing or folding into neat compact form, and sorting into lots to be tied up later into bundles.

Obviously, many of these operations have little to do with chemical processes, and it is only with the washing that these experiments are concerned. In fact, it is this part of the process alone which is distinctively chemical, and which seems most largely responsible for the complaints now made against the results obtained in well managed laundries.

On account of the great variety of articles brought to the washroom, it is evident that different treatment must be accorded to the different kinds of fabrics. The only classes which are of great importance are those consisting of articles made from cotton, linen, silk and wool. Greater diversity is caused, however, by the very large list of dyestuffs which are now employed on all of the above groups.

In the case of undyed fabrics of cotton or linen, the treatment employed is, perhaps, the most drastic, and it is largely on account of the too early disintegration of articles of this class that complaints are justly and so frequently made. Since all articles are submitted to the less harmful operations employed in the case of these undyed articles, the experiments were carried out in accordance with the modern practice of handling such articles as are made from cotton and linen only, and which have not been dyed. This seems justifiable, because these articles form the largest part of the work done, and also because the effects produced are necessarily similar in so far as the various operations are duplicated in the case of the other classes of articles. This does not apply to the effect on the dyestuffs, but rather to the weakening of the fabrics. The former problem was not taken into consideration here.

In the sorting room, all articles are separated into

lots, according to the kind of fabrics, the nature of the dyestuffs, and finally the extent to which the articles are soiled. Since these different lots are to be washed differently, this separation is preserved throughout the whole course of treatment.

The machines in which the washing is done consist of two concentric cylinders separated by a space of several inches. The outer cylinder is stationary and is carried on a metal stand for securing the whole machine in position. It is provided with the necessary boxing and gearing for causing the inner cylinder to revolve and to reverse automatically after several revolutions in one direction. It has also pipes for introducing hot and cold water and live steam, and a drain pipe for discharging the liquids after they have done their work. The inner cylinder into which the articles are placed, is perforated so that the liquids may have free access to the fabrics. Both cylinders are provided with suitably hinged doors, so that the articles may be readily introduced and removed. The sizes of the machines vary from small ones, washing fifty shirts, to very large ones, which can handle five hundred shirts at one time. After the articles are placed in the machine they are not removed until they have been cleansed and given the proper color by means of detergents, bleaches and bluing materials. The different solutions are introduced in order and run off after they have performed their respective functions.

The principle upon which the washing is effected is simple. By the revolution of the inner cylinder, the articles are carried part way up the sides, and then fall down into the solutions, causing the latter to be forced through the fabrics, and thus insuring intimate contact between the detergents and the substances to be removed.

LAUNDRY PROCESS IN GENERAL USE

In order to proceed with the problem in hand, the first step was the investigation of the process in general use, in order to determine what parts were defective, and the causes for, as well as the nature of the harmful results produced.

The machine of average size will permit the washing of about one hundred shirts, weighing about seventy-five pounds. The volume of the different solutions

used in such a machine is approximately twenty-five gallons. The method of washing is as follows: Cold or luke warm water is admitted and the machine is allowed to run for from five to ten minutes. Very frequently sufficient sodium carbonate, or so-called neutral washing soda,[1] is added to make from $1/4$ to 1 per cent solution. The water, or weak alkaline solution, removes some of the starch from starched goods, carries off surface dirt and dissolves stains of an albuminous character, which otherwise might be set by coagulation of the albuminous substances, if hot water were used at once.

Warm water is next admitted and soap added together with some alkaline substance, such as sodium carbonate, neutral washing soda, caustic soda or borax. The first two are the ones most frequently used. The soap is used in from $1/4$ to $1 1/4$ per cent solution, and the alkaline substance in about the same strength. Steam is then admitted and the temperature brought to the boiling point in from ten to twenty minutes. The time of running in this solution is usually from twenty to thirty minutes.

This solution is discharged and another of from $1/2$ to $2/3$ the strength of the first is added. In some instances a hot rinse is given between the two solutions in order to carry off the remaining dirty suds. The bleach is also added in this second suds, and the whole run for about the same length of time as the previous one. The bleach used is prepared by adding sufficient

[1] These sodas are mixtures of sodium bicarbonate and sodium carbonate. Analyses which are perhaps typical for articles of this kind are:

Na_2CO_3............................	46.3	36.1
$NaHCO_3$.........................	37.7	50.0
H_2O and impurities..............	16.0	13.9
	100.0	100.0

These articles find large sale because they do not yield as strongly alkaline solutions as when sodium carbonate alone is used. The hydrolysis of the sodium carbonate is less extensive in the presence of the bicarbonate than when alone. Theoretically, it is possible to prepare a solution from sodium carbonate which will have the same concentration of hydroxyl ions as is present when a given concentration of these neutral sodas (so-called) is employed. The weight of sodium carbonate is in every case less than that of the neutral soda, and as the price of the two products is nearly the same, a material saving can thus be effected. The difficulty met with in the laundries seems to be attributable to the fact that in replacing a neutral soda by sodium carbonate, the same weight is used, owing to ignorance of the above conditions, and this naturally yields a solution which is too strongly alkaline. Several plants have been induced to decrease the quantity of sodium carbonate to half (or even less) of that used in the case of the neutral sodas, and results have been obtained which are satisfactory in every respect. Summer soda crystals have also been used as a neutral soda ($Na_2CO_3.NaHCO_3.2H_2O$).

sodium carbonate to bleaching powder to convert the calcium salts into the more soluble sodium salts. This has the advantage that none of the soap is decomposed with the formation of lime soap, as would be the case if bleaching powder itself were used. The quantity of bleach used varies from the equivalent of $^1/_4$ to $^3/_4$ of a pound of commercial bleaching powder. The bleach liquor is generally added at the beginning of the run, the steam being admitted so as to bring the temperature to the boiling point in from fifteen to twenty minutes. The boiling is continued, and the whole time of run made from twenty to thirty minutes. From two to four hot rinses follow this suds-bleach treatment.

The next solution is an acid bath. The acids most frequently used are acetic and oxalic. Sufficient acid is added to make the solution about $N/50$ (equivalent). This acid is used for the purpose of neutralizing any alkaline substances which have not been rinsed out, and to cause the aniline blue, which is used subsequently, to produce an even color. If the blue is not added in the acid bath, it is used in the next water. From one to four rinses, sometimes hot, sometimes cold, are given after the bluing.

After the above course of treatment the articles are removed from the machine and placed in the basket of a centrifugal machine, in order to remove the excess of water. Articles which need no starching are usually ironed at once after removing from the centrifugal machine, while the others are sent to the starch room. After starching, all articles are dried by being placed in a drying-room heated to 100° C. by steam coils, and provided with a ventilating fan for removing the moist air. After dampening to the proper degree, the ironing and shaping are next done.

PRELIMINARY EXPERIMENTS ON DIFFERENT PARTS OF ABOVE PROCESS

The first plan adopted for comparing the harmful effects of the different parts of the process outlined above, was to take four series of turnover collars, five to a series, and submit each series to one of the above parts of the washing process, that is, one series to the soap-alkali, one to the bleach, one to the acid and one to water only, in order to have a check on the mechanical effects produced in the washer and in the ironing machines. After each treatment in the laboratory wash machine, under conditions as nearly as

possible like those obtaining as an average in general practice, the collars were rinsed (except in the case of the acid series), then taken to a custom laundry to be starched and ironed. The plan was to repeat this treatment in each case until the edges of the collars broke, thus showing the relative harmfulness of the different treatments.

The quantities of soap and soda ash used were 190 grams soap and 95 grams of soda ash per gallon of solution. These quantities are larger than those generally employed, but were chosen rather than quantities below the average. The soap used was a neutral soap made from good red oil or commercial oleic acid, and analyzed as follows:

Water..............................	20.7
Na_2O as soap........................	9.3
Fatty acid anhydrides................	69.5
Soda ash...........................	0.1
NaCl..............................	0.2
Unsaponified........................	0.1

The soda ash was analyzed and found to be a good commercial product, containing only a small percentage of soluble and insoluble impurities.

The bleach solution was made by taking 12.5 grams of bleaching powder and 8.2 grams of soda ash per gallon of water. It was necessary to add sufficient cloth so that the ratio of the weight of cellulose to the weight of the solution might be comparable to that in practice. The bleaching powder was analyzed and found to contain 26.8 per cent available chlorine. It was a sample obtained from a custom laundry and was of poor grade. The acid used was oxalic and a sufficient amount of it was added to make the solution approximately $N/50$. As has been stated above, no rinse was given after the acid was used, although most laundries now rinse at least once. However, at that time many plants were found which did not rinse subsequently, and this more severe test was made in order to compare its effects with the bleaching which was expected to prove quite harmful. The results obtained were as follows:

Bleach Series: Two broke on 7th time; one on 8th; all on 9th time.
Acid Series: One broke on 5th time; one on 6th; two on 7th; all on 9th time.
Soap and Alkali: All intact 15th time.
Water: All intact 15th time.

The last two series were lost on account of an accident in the laboratory, but they had run sufficiently long to establish the fact that under the conditions of the tests the acid and the bleach are the most destructive chemicals employed. Other series which were com-

parable to the soap-alkali series were later run as high as twenty-five times before a break occurred, showing that the conclusions drawn above were justified.

THREAD ADOPTED FOR TEST PIECES

The above method was not considered satisfactory for further comparisons, because of the length of time necessary to carry it out and also because of the uncertainty of being able to give all of the collars the same treatment during the starching, ironing and finishing. For this reason the method of determining the breaking strengths of test pieces before and after the various treatments was adopted. On account of the difficulty encountered in attempting to use test pieces in the form of strips of cloth or skeins of yarn, for the reason that it is almost impossible to distribute the strain equally throughout the pieces, the use of single threads as test pieces was decided upon. It was thought that the warp or weft threads of a good grade of muslin or linen cloth might be used, but these were found to be too irregular to make their use advisable. The most suitable material that could be found was a good grade of white thread.

TESTING MACHINE USED

The testing machine used was designed and made in the University Instrument Shop. It is similar in principle to the machines which are in general use for determining the tensile strength of paper. The test piece, about five inches in length, is fastened between two clamps, and the force is applied by causing a weighted arm, to which one end is clamped, to move through an arc by turning a geared wheel which moves a slow-motion screw to which the other clamp is fastened. A scale graduated by means of known weights is placed in front of the weighted arm, and the position of the arm at the time of breaking is marked by a light rider which is caused to move along the scale.

METHOD OF TESTING

Because of the fact that thread is not uniform in cross-section and in the twist, that is, the number of turns per inch due to the spinning, the breaking strengths of pieces from the same spool show large variations. Numerous tests showed that the strength for a No. 20 thread ranged from 1300 to 1900 grams. On account of this great variation it is necessary to employ a large number of test pieces in each series, in order that the mean value may be significant.

The thread was sampled by taking every twentieth length of five inches for twenty series of one hundred test pieces each.

Experiments made with a number of these series, after the sizing materials had been removed by boiling the threads for an hour in 1 per cent sodium carbonate solution, showed that the different mean values agreed satisfactorily, usually well within one per cent. With this agreement, the method seems well adapted for making comparisons of the effects of different chemicals, used under various conditions, upon the tensile strengths of cotton thread. It is evident that the breaking strength is closely related to the wearing qualities of threads, and hence of pieces of fabric, under the conditions to which they are subjected in use.

It was found that different spools of thread differed from one another more than the series of threads from one spool differed from each other. For this reason it is necessary to determine the breaking strength for each lot of threads prepared.

COMPARISON OF METHOD WITH PRELIMINARY EXPERIMENTS

Tests were run upon threads, employing solutions of the same kinds and of the same strengths as were used in the experiments on the collars. After each of the processes had been repeated ten times the breaking strengths were determined. The conditions were made as nearly the same as possible, both as regards the times of treatment and ratios of the weights of solutions to the weights of cellulose. The results were as follows:

Original breaking strength, ave.............	1724 g. (1722, 1723, 1724, 1726)
Soap-alkali series........................	1861 g.
Bleach series............................	181 g.
Oxalic acid series........................	265 g.

The probable error in the original figured by method of least squares is ± 7 grams. These figures confirm the results of the practical tests with collars, and the agreement speaks in favor of the use of the new method which is more rapidly carried out and is more easily controlled.

As has been stated above these results do not permit the drawing of conclusions concerning the actual amount of damage done in the different processes in the best plants. The figures do, however, indicate the parts wherein most care must be exercised and in which improvements are most needed.

The soap-alkali treatment is, perhaps, the least harmful of all the different operations. Experiments showed, however, that if the quantities of alkaline substances were not kept low, the threads were attacked and, although the breaking strength was not affected as greatly as in the bleach and acid series, the appearance suffered, owing to the formation of a woolly coating of loose ends of fibers. The damage done in the acid bath is easily made less than in the case of the tests, for thorough rinsing will remove the acid and prevent its doing damage in the dry room or in the ironing machines.

<div align="center">REACTIONS OF CELLULOSE</div>

Cellulose, which is chemically one of the most inactive of the carbohydrates, is nevertheless extensively attacked by acids, alkalies and bleaches under conditions which often exist in laundries. In the presence of hydrogen ions, cellulose is converted into another substance, hydrocellulose, which differs from the former in many ways. The most important difference for the purpose in hand is that hydrocellulose is a friable substance and, therefore, is valueless under the conditions to which fabrics are subjected in use.

The acid solutions employed in laundry work are relatively dilute, and the extent to which the cellulose is acted upon while in these solutions is small. It is essential, however, that the acid be thoroughly removed because when the articles are placed in the drying room, or are caused to pass over the heated surfaces in the ironing machines, the dilute acid is concentrated and this, together with the high temperature, produces rapid conversion of the cellulose. This practice of rinsing after the acid is discharged is now quite general and is a decided advance in the right direction.

The velocity of this reaction is proportional to the concentration of hydrogen as ion present, and is also greatly accelerated by rise in temperature, in accordance with the general rule for the effect of temperature on chemical reactions.

<div align="center">REAGENTS USED IN TESTS</div>

As has been stated, the soap and soda ash used were of good quality. Very different results have been obtained by others when the soaps and sodas used were adulterated. Dr. Kind[1] has carried out a large

[1] "Die Wirkung der Waschmittel auf Baumwolle und Leinen," A. Ziemsen Verlag, Wittenberg, 1909.

number of experiments and has proved conclusively that detergents which contain large percentages of silicate of sodium cause a rapid deterioration in cotton and linen fabrics. Kind attributes this effect to the action of the hydroxyl ions formed by the hydrolysis of the silicate and to the deposition in the fibers of silicic acid, and also of insoluble silicates which are formed when hard water is used. These deposits are shown to be very extensive under some conditions, amounting, in one case where a series of test threads were washed thirty times in a 2 per cent solution of 38° Bé. sodium water glass, to 14.2 per cent. The water glass analyzed 27 per cent silicic acid and 0.12 per cent free caustic soda. These threads were brittle owing to the presence of the encrusting substances which did not allow the fibers to yield when subjected to a bending strain, and the threads were also weak on account of the disintegration caused by the loosening up and separation of the fibers composing the thread. Kind's work shows that the action is more severe in the case of linen than of cotton.

In the case of soaps and sodas which contain peroxides and perborates, Leimdoerfer[1] has shown that the harmful effect is also great.

The presence of rosin in soaps has been shown to be objectionable because of the fact that the rosin acids which are formed by hydrolysis of the soap settle in the fibers and produce a decided yellow cast in the finished products. Professor Herbert Jackson[2] has shown that soaps which contain as little as 5 per cent rosin are objectionable for this reason.

Many sodas have been found to contain adulterants: some harmful, as sodium silicate and caustic soda, and some inactive, such as common salt and sodium sulfate. It seems certain from the above tests, however, that if pure soap and pure alkalies are used in quantities no larger than are necessary, the weakening of the fibers treated is not very great.

ACTION OF ALKALI

The following experiments were performed, using solutions of sodium carbonate which are much stronger than those used in practice. The threads were suspended from cords in the boiling solutions and were provided with glass weights to keep them immersed. The boiling was done in open beakers and the water

[1] "Wasch-, Bleich-, Blau-, Staerke- und Glanz-mittel," L. Andes, 1909, Hartleben, Wien, p. 14.
[2] Cantor Lectures for 1907, p. 12.

removed by evaporation was replaced at regular short intervals. The times of boiling, strength of solutions and position of the test threads were as indicated.

The reason for exposing some of the series to the action of both the alkaline solutions and the air, was to determine whether or not the weakening produced was greater under these conditions than when oxygen was excluded by complete immersion. Text books describing the manufacture of textile fabrics generally state that cellulose must not be exposed to the air when it is being boiled in alkaline solutions because the oxidation of cellulose which occurs under these conditions will render the fabrics tender.

Original breaking strength, ave...............	1696 (1693, 1709, 1696, 1684)
Boiled in 1 per cent Na_2CO_3 5 hrs., one-half exposed to air and one-half immersed in the solution....................................	1711–1666
Same as above, but completely immersed.....	1634, 1634
Boiled in 2.5 Na_2CO_3, for 3.5 hrs. half immersed....................................	1648
Same as one above but completely immersed...	1636
Boiled in 5 per cent Na_2CO_3 for 3.5 hrs., immersed completely..........................	1625, 1622
Same as above, except half immersed.........	1627, 1610

These results show that even if much stronger solutions than those ordinarily used are employed, the damage done is not excessive. The color, however, is not so clear, and the same roughening of the threads mentioned above is noticed. The formation of lint is also greatly increased when large quantities of alkali are used.

Since the boiling of threads, even in quite strongly alkaline solutions, does not produce great deterioration, it was thought well to determine the effect of alkalies which are not completely rinsed out. The tests were made by dipping the test pieces into a 1 per cent sodium carbonate solution, squeezing dry by hand to about the same extent as would be the case in a centrifugal machine, and then placing in a drying oven heated to 100°. This process was repeated ten times, rinsing with distilled water between each treatment, and the breaking strength determined. Repeated weighing of the dry threads and also of those which had been wrung after dipping into the solutions showed that a weight of the solution about equal to that of the threads was retained. It was possible to get the amount of solution retained to agree to within about two per cent. The result was as follows:

Original strength......................	1696
After ten treatments..................	1420

It is, therefore, very necessary that the alkali be removed by rinsing and by the acid bath which is given later, as otherwise both the color of fabrics and their wearing qualities suffer markedly.

HOT WATER—The advantage of using hot water for rinsing is obvious, for if cold water is used and soap is present in the hot fabrics in quantities larger than are soluble in the cold water, this soap will be precipitated and will redissolve slowly. All of the substances which are to be removed are more soluble in hot water than in cold, and in addition diffuse more rapidly with rising temperature. Consequently hot water is the more desirable.

HARD WATER—Since hard water forms difficultly soluble calcium and magnesium soaps with the soluble sodium soap remaining after the washing process and as these do not form a suds, rinsing appears to be more quickly and efficiently done with hard water than with soft. In order to test this assumption which is general among launderers, the following experiments were made:

Pieces of cloth of about the same size were weighed under the same atmospheric conditions, when air-dry. These pieces were then dipped into and washed about in the soap solution such as has been used throughout this work. Some of the pieces were then rinsed three times in tap water and some in distilled water, care being taken to give the test pieces the same mechanical treatment. The tap water analyzed 14.5 degrees of hardness. After standing until air-dry the pieces were reweighed under the same atmospheric conditions. The results were as follows:

Weight in grams	No. 1	No. 2
Of cloth after rinsing in soft water	22.074	21.510
Of cloth air-dry at start	21.877	21.396
Of substances retained	0.197	0.114
Of cloth after rinsing in hard water	22.230	21.643
Of cloth air-dry at start	21.895	21.394
Of substances retained	0.335	0.249

DISTILLED WATER—The last rinse water in the case of the pieces rinsed in distilled water was soapy and considerable suds was formed. However, the weighings show that the rinsing was much more efficient in the case of the distilled water series. This is due to the fact that the insoluble soaps which are formed in the fibers when hard water is used are very difficult to remove.

Upon drying the different pieces in an oven at 100° for thirty minutes, the pieces rinsed in soft water were of much better color than the others. Pieces which were allowed to dry at room temperature showed after several weeks a much yellower color in those rinsed with hard water than in those rinsed with soft water.

That rinsing with soft water is advantageous is shown by the observation that the color of articles laundered in plants where this is the custom is uniformly better than that obtained in other plants.

DEPOSITION OF SALTS IN FIBERS OF FABRICS

A reason for the breaking of threads in fabrics which is thought by launderers to be, perhaps, the most frequent is the deposition in the fibers of calcium carbonate and lime soaps or the crystallization of soluble salts such as sodium chloride or sodium sulfate.

A saturated solution of slaked lime was neutralized with acetic acid. Threads were dipped into this solution, then into a 0.6 per cent solution of sodium carbonate. They were then well rinsed in distilled water and dried for thirty minutes at 100°. This operation was repeated ten times. In one case the calcium carbonate was allowed to accumulate, while in another it was removed after each treatment by means of cold dilute acetic acid followed by rinsing in distilled water.

```
Original strength.............................  1696
Calcium carbonate accumulated.................  1656
Calcium carbonate removed each time...........  1633
```

Two other series were treated with solutions of sodium sulfate, allowing the salt to crystallize out after removing the excess of solution as was done in the experiments with sodium carbonate. The threads were dried for thirty minutes at 100°, and rinsed well between treatments. Ten treatments were given each series.

```
Original......................................  1696
5 per cent sodium sulfate.....................  1584
10 per cent sodium sulfate....................  1614
```

These tests seem to indicate that this cannot be considered a large factor in the disintegration of laundered articles.

ACTION OF ACIDS

MINERAL ACIDS—Owing to the high price of oxalic and acetic acids it was thought advisable to determine whether or not cheaper acids could be substituted.

Sulfuric and hydrochloric acids were chosen as the most desirable ones, and a series of tests was run to compare the harmful effects produced.

The test threads were dipped into $N/50$ (equivalent) solutions, wrung dry, as has been described above, then dried in an oven at 100° for thirty minutes. This was repeated ten times in each case, rinsing with distilled water after each operation to remove the acid left in the threads.

Original strength................	1717	Mean of (1706, 1680, 1718, 1716, 1767)
Acetic acid.....................	1611, 1610	
Oxalic acid.....................	682, 676	
Sulfuric acid...................	Less than 10	
Hydrochloric acid..............	Less than 10	

The results show clearly that the use of the cheaper acids should not be recommended for general adoption because the wash-room help cannot be depended upon to rinse sufficiently to remove the excess of acid employed. If the rinsing were sufficient, however, these strong acids might be used with entirely satisfactory results, as will be explained below.

USE OF ACID NECESSARY

It would seem that the use of acids might be dispensed with, or at least be made much less objectionable than at present. There are two facts, however, which seem to make the use of some acid indispensable. The small quantity of alkaline substances which is not removed by rinsing would have but little effect in weakening the fabric even if the articles were placed in the dry room or were passed over the heated rolls of an ironing machine. This alkali is objectionable, however, because it forms a bright yellow product with the oxycellulose which is produced by the action of the bleaching solution on the cellulose. Very small quantities of alkali are able to produce an undesirable color in a piece of bleached cloth, as will be shown later. Some acid is necessary, too, for the purpose of removing colored compounds of iron which are present as individual stains or as a general discoloration which results from the use of water or of supplies containing even small quantities of iron salts.

These tests indicate that by the use of acetic acid the damage done may be made almost negligible.

Acetic acid being a weak acid, that is one only slightly dissociated, yields relatively small concentrations of hydrogen as ion, and consequently the conversion of cellulose into hydrocellulose is effected by it less

rapidly under corresponding conditions than when the stronger acids are used. The volatility of acetic acid also makes it less harmful than any of the other acids experimented with. It is interesting to note that the order in which the acids attack cellulose and decrease the breaking strength of the threads is the same as that in which they are found to be dissociated into their ions. In many localities, however, oxalic acid is the only substance which will remove the iron compounds sufficiently, and for this reason must be used. The troublesome iron compounds are either oxides or basic salts of iron, which are soluble in the presence of sufficiently large concentrations of hydrogen as ion. Oxalic acid possesses the additional property of forming a complex ion with iron as ion, and consequently is a more efficient solvent for these colored products than is acetic acid. Under these circumstances it has been found possible to effect an improvement by using acetic and oxalic acids together, using only as much oxalic as is required to correct the discoloration, and the acetic for making up the bulk of the acid. Careful rinsing is, of course, necessary in any case.

A series of threads was boiled in $N/10$ sulfuric acid for two and a half hours, and the final breaking strength was found to be 216. It is evident, then, that with the weaker solutions of the weaker acids used, and at the lower temperatures, the damage done while the articles are in the machine is not great.

POSSIBLE SUBSTITUTES FOR ACIDS

Acid sodium sulfate is a cheap substance which might be used for the acid bath. Theoretically, however, it offers little advantage over the use of sulfuric acid itself, because the concentration of hydrogen as ion from acid sodium sulfate is relatively large. This is so because sulfuric acid is a strong dibasic acid, and the bisulfate ion is, therefore, largely dissociated in weak solutions.

An acid sold under a trade name was analyzed and found to be commercial acid sodium sulfate. It was said to be absolutely harmless for laundry use. From the above considerations, this statement seemed very improbable. To test this assertion a series of threads was treated with an $N/50$ solution of the bisulfate in the same way that the experiments were made with the other acid solutions. The results show that the claims for this article were not founded upon fact.

Original breaking strength............................. 1717
After ten treatments with $N/50$ bisulfate................. 170

The bisulfate is somewhat less harmful than sulfuric acid, owing perhaps to the fact that the salt crystallizes out during the drying process. It is more conveniently handled than sulfuric acid, which is a liquid, but certainly the launderer should know that he is dealing with a very strongly acid substance, and not with some harmless acid, as is often claimed in advertisements.

BLEACHING

Since the bleaching is unquestionably the most harmful of all the parts of the washing process, and it seems impossible to produce a sufficiently white color to satisfy the trade when no bleaching agent is used, a great deal of experimenting was done with a view to improving this operation. The objection to the method now employed is that the hypochlorite solution acts not only on the objectionable colored substances, but also upon the cellulose of the fabric, changing it into the brittle compound, oxycellulose. This formation of oxycellulose not only weakens the fibers to the extent to which they are thus attacked, but the oxycellulose is objectionable for a number of reasons. It is well known that oxycellulose is more readily dyed by basic dyestuffs than is cellulose itself, and for this reason any oxycellulose which is not removed is more deeply colored than the other parts. The behavior of oxycellulose in the presence of alkalies, which has been spoken of, is also a frequent source of trouble.

In order to determine whether or not this behavior is the cause for the yellowing of certain lots of clothes in the laundry and also of those which are stored after having been laundered, the following experiments were performed:

Some pieces of bleached muslin and of cambric were procured on the market and used as the test pieces. Parts of each of these were bleached to the extent of five treatments in the laundry, and parts to the extent of ten such treatments. Test pieces about three inches square were cut and treated as described below. The pieces were dipped into standard solutions of reagents and then the excess of the solution squeezed from them by hand. After standing at room temperature the pieces were examined at intervals to compare their color with that of the original untreated samples. The sizing was removed from all of the cloth by boiling in distilled water.

EFFECT OF ALKALI ON COLOR

No.	KIND OF CLOTH	Strength of sod. carb. solution used	Time after removing from solution	Condition after treatment
1	Original muslin	N/10	3 hrs.	Slightly yellow
2	Muslin, bleached medium (Muslin A)	N/10	3 hrs.	Very yellow
3	Muslin, bleached strongly (Muslin B)	N/10	3 hrs.	Yellower than 2
4	Muslin B	N/10 rinsed 3 times with distilled water	3 hrs.	Yellower than 1
5	Original muslin	N/10	3 hrs.	Less yellow than 1
6	Muslin A	N/10	3 hrs.	About like 2
7	Muslin B	N/10	3 hrs.	About like 3
8	Cambric, medium bleached (Cambric A)	N/10	3 hrs.	Yellower than 6
9	Cambric, strongly bleached (Cambric B)	N/10	3 hrs.	Yellower than 7
10	Original muslin	N/50	16 hrs.	Slightly yellow
11	Muslin A	N/50	16 hrs.	Much less yellow than 2
12	Muslin B	N/50	16 hrs.	Less than 3
13	Original muslin	N/100	72 hrs.	Slightly yellow
14	Muslin A	N/100	72 hrs.	Yellower than 1
15	Muslin B?	N/100	72 hrs.	Yellower than 4
16	Original cambric	N/100	72 hrs.	
17	Cambric A	N/100	72 hrs. after 52 days	Yellower than 4 Much yellower than blank
18	Cambric 13	N/100	after 72 hrs. after 52 days	Much yellower than blank Much yellower
19	Muslin A	N/250	after 52 days	Much yellower than blank
20	Muslin B	N/250	after 52 days	Much yellower than blank
21	Original muslin	N/500	after 52 days	Same as blank
22	Muslin A	N/500	after 52 days	Same as blank
23	Muslin B	N/500	after 52 days	Yellower than blank
24	Muslin B	N/1000	after 52 days	Very little yellower than blank

From these tests it is evident that the yellow color is greatest for a given concentration of the carbonate in the case of the pieces which have been most strongly bleached, that is, which contain most oxycellulose. The presence of even minute quantities of sodium carbonate is able in time to cause a very noticeable yellowing in articles which have been strongly bleached.

Test pieces which were treated with oxalic acid under varying conditions, some of which were boiled in $N/10$ oxalic acid for an hour, did not develop a yellow color even after the expiration of five months. This shows that no colorless compounds were formed by reduction, which subsequently yielded the original colored substances by the oxidizing action of the air. The yellowing of articles on standing has often been attributed to this latter cause.

BLEACHING IN SEPARATE SOLUTION—For the purpose of determining whether or not it would be better to bleach in the second soap solution or in a separate solution after the washing was finished, the following experiments were performed.

A soap-alkali solution of about the strength used in the collar tests was heated to boiling. No cellulose was used in this test. Sufficient bleach solution was added to make the concentration of the hypochlorite the same as that used in the above tests. The boiling was continued after the addition, and the hypochlorite was found to have disappeared after 18 minutes. Another quantity of the bleach solution was diluted so that it had the same concentration as in the soap solution. The proper quantity of cellulose was weighed out and added, so that the ratio of the weights of the cellulose and the solution might be the same as in the previous tests on collars and threads. The boiling was continued and the hypochlorite found to have disappeared in about the same length of time as above—18 to 19 minutes.

A solution of the hypochlorite with no soap or cellulose was evaporated to dryness. Water was then added to redissolve the salts, the volume being made equal to that of the original solution. This process was again carried out and after the third evaporation a strong test for available chlorine was obtained. Lunge[1] has shown that a neutral solution of hypochlorite, or one which is slightly alkaline, can be

[1] *J. Soc. Chem. Ind.*, **4**, 722; also, "Manufacture of Sulfuric Acid and Alkalies," second edition, Gurney and Johnson, London, 1896, pp. 417 and 419.

boiled for two hours with a disappearance of only 24.6 per cent of the available chlorine. It is evident, therefore, that the hypochlorite reacted with the soap and the cellulose in the above tests, and was not decomposed by the high temperature to which it was subjected.

From these tests it was concluded that the soap was attacked by the hypochlorites about as readily as the cellulose, and if this were the case a smaller quantity of bleaching agent than that used with the soap should be able to do the same work if used separately. This was tried both in the laboratory and in several laundries, and besides a saving of from one-half to two-thirds of the bleaching material, better looking work was obtained in every case.

REDUCING AGENTS—On account of the objectionable properties of oxycellulose, it was thought advisable to try the use of reducing agents instead of the oxidizing agents which are generally used. Sodium hydrosulfite was chosen as being the one most likely to give satisfactory results at a reasonable cost. Laboratory experiments showed that this substance when used in quantities chemically equivalent to the ordinary bleach solutions gave results that promised to be satisfactory. The best results were obtained when the hydrosulfite was used after the second suds, although a good color was obtained when the bleach was used along with the soap. Although the cost of the hydrosulfite was high, it was considered possible to produce it at a sufficiently low price to justify its use if it proved satisfactory in other respects.

A test on a series of threads showed that very little decrease in their breaking strength was caused when they were boiled in relatively strong hydrosulfite solutions. The solution was made up 10 grams per gallon, and the boiling continued for two hours, to correspond to ten treatments.

Original strength.........................	1696
Final strength...........................	1685

This process was tried out on a large scale in two custom laundries. After a large number of runs it was found that although a considerable bleaching was effected, the color was not as good as when the old method was used. The quantities of hydrosulfite used for a hundred shirts (75 lbs. of cellulose) in twenty-five gallons of the solution were varied from $1/4$ to $1^1/_2$ lbs. The bleaching effected by the smaller quantity

was good, but owing to the fact that whiter work could be gotten by the use of hypochlorites the method was abandoned, as it was not thought likely to be generally accepted.

On account of the failure of the reducing agents to produce work that would compare in whiteness with that obtained in practice, attention was again turned to other oxidizing agents. It was hoped that an oxidizing agent might be found which would not attack cellulose as much as do the bleaches now in use, and which would effect the desired whitening of the article to be treated.

MAGNESIUM AND SODIUM HYPOCHLORITES

Magnesium hypochlorite was tried, as was also neutral sodium hypochlorite. Since the oxidation is caused by the hypochlorite ion, and the concentration of this was made the same with each of the hypochlorites, the only chance for a difference in their actions was the possibility that the concentration of hydroxyl ion might influence the reaction between cellulose and the hypochlorite ion. Since magnesium hydroxide is difficultly soluble, it is impossible for the magnesium hypochlorite solution to contain a large concentration of hydroxyl ion.

Many text books contain the statement that magnesium hypochlorite has a much less harmful effect on cotton and linen fabrics than calcium or sodium hypochlorites. A thorough search through the literature showed that this statement is copied from the patent specification submitted by Hermite,[1] concerning his process for preparing magnesium hypochlorite by electrolysis from a solution of magnesium chloride. No data are given in support of this statement in this patent specification, and none have been found in any other place.

Equal weights of threads were used with equal volumes of the different hypochlorites, which were made of equivalent strengths. The conditions of boiling the threads in all cases were the same.

Original strength	1696
Sodium hypochlorite	468, 488
Magnesium hypochlorite	474, 492

OZONE FOR BLEACHING

Ozone is another oxidizing agent which was experimented with, and .it was chosen because the only decomposition product which could be formed is oxygen

[1] English Patent 13,929, *J. Soc. Chem. Ind.*, **4**, 673.

and this, of course, is not objectionable. Preliminary tests indicated that the bleaching could be done satisfactorily, and if precautions were taken to prevent the simultaneous formation of oxides of nitrogen or to remove them if formed, the strength of threads was not greatly decreased after several successive treatments.

Original strength......................................	1696
Exposed to current of ozone, oxides of nitrogen not removed......................................	less than 5
Oxides of nitrogen removed by tower filled with slaked lime......................................	575
Oxides removed by bubbling ozonized air through water......................................	937

The percentage of ozone by volume was 1.2, and the temperature of the room 22.5° C. The time of passing the current of ozonized air was three and a half hours. The threads were introduced moist, about as they would have come from a laundry centrifugal machine. It could not be decided, however, by the use of the small laboratory apparatus whether the process was sufficiently economical and the bleaching action sufficiently rapid to be practical.

The laboratory ozonizer used was the regular Siemens-Halske apparatus, composed of five cells. By varying the rate of flow of the air it was possible to get a mixture which analyzed from 0.5 to 1.5 per cent by volume of ozone. The quantity of air thus furnished varied from 0.5 to 2 cu. ft. per hour. The concentration of the ozone was determined by titrating the iodine liberated by a known volume of ozonized air from a neutral potassium iodide solution. It was necessary to add acid to decompose any iodates which might have been formed before the titration was made with standard thiosulfate. A gas meter was connected ahead of the ozonizer to show the rate at which the air passed through the apparatus. The air was carefully dried with calcium chloride and concentrated sulfuric acid, in order to reduce the quantity of oxides of nitrogen formed.

The first plan tried was to pass the current of ozonized air into the drying room either before the drying was commenced or while it was in progress. To test this method some starched collars which had not been bleached previously were placed in a large glass desiccator through which the ozonized air was led. After half an hour, the color of the collars was very satisfactory, being better than that obtained in the usual way. When these collars were ironed, however, a

very yellow color developed which was due, perhaps, to the fact that part of the starch had been converted into dextrine and this developed a yellow color at the high temperature because of the alkaline substance which had not been removed by rinsing. It was evident that this method could not be used unless the bleaching were done before the articles were starched. As this would necessitate an extra handling of the pieces, and would lengthen the time of treatment, the method was abandoned. The ozone was then used in a different way, which also gave satisfactory results in regard to color. The current of ozonized air was led into the washer while the washing was being done. Tests were run on a series of threads which were boiled for five hours, with the same strength soap-alkali solution as was used in the tests described above, and a strong current of ozonized air passed through continuously. This corresponded to the effect of ten successive treatments such as were to be used in practice.

Original breaking strength	1696
After treatment	1389

In order to test the commercial efficiency of the latter method, a large ozonizer furnished by the Gerard Ozone Process Co. was installed in a custom laundry. The current of ozonized air was led into the washer by means of a perforated brass pipe, and allowed to bubble through the fabrics while they were being run in the machine. This large ozonizer was rated to furnish a current of air containing from 0.5 to 0.7 per cent ozone by volume at a rate of 25 cu. ft. per hour. Tests were run in which the ozone was admitted at all possible times during the regular washing process.

The results obtained when the ozone was passed into the soap-alkali solution were not satisfactory. Fruit and coffee stains were not removed sufficiently well to make the method serviceable. This was thought to be due in part to the fact that the ozone was largely decomposed by the hot water before it came into contact with the stains.

In order to overcome this difficulty, the ozone was used with the clothes in luke-warm water either before or just after the washing with soap was done. The color of the articles was not satisfactory in either case, although the passage of ozone was continued in some cases for forty minutes. Because of the expense of

operating the apparatus, and also because of the length of time necessary to do the bleaching, the method was abandoned as not practical.

ACTION OF HYDROGEN PEROXIDE

Some preliminary experiments were performed with hydrogen peroxide, but it was found that even with solutions of considerable strength the action was very slow. Very satisfactory results were obtained with hydrogen peroxide in bleaching woolens, and this method is being extensively used for treating fine woolen articles. The solution is made slightly alkaline with ammonia in the latter case.

DISCUSSION OF USE OF BLEACH

The fact that colored articles last much longer than undyed ones made from the same kind of material, is proof that the use of excessive quantities of alkalies and bleach is responsible for the greater part of the damage done in the wash room. It is general experience that a colored shirt will outlast a white one by considerable, and the reason would seem to be that in the case of the colored shirt alkalies and bleaches must be used very sparingly or not at all.

A great advance would be made if all laundries used much less bleach than they do at present. If bleach is used once on a piece of fabric, it is necessary to use it every time the article is laundered. This is because the oxycellulose formed the first time bleach is used yields the objectionable yellow substance already spoken of when alkalies are used subsequently, and the use of more bleach becomes necessary.

These experiments with bleaching agents seem to show that if excessive damage is to be avoided, some sacrifice in the color of the finished articles will need to be made. This might be accomplished either by using hydrosulfites, or other reducing agents, or by using much smaller quantities than are now considered necessary, of some of the oxidizing agents in use at the present time.

CONCLUSIONS

1—The bleaching and treatment of fabrics with acids are the most harmful parts of the process now in general use in steam laundries. The bleaching not only weakens the fabrics, but also produces oxycellulose, which yields an objectionable yellow substance when treated with even dilute solutions of alkalies. The hydrolysis of cellulose produced by the hydrogen

as ion in acid solutions weakens the fibers. Thorough rinsing is essential to remove as much of the acid used as possible. The quantities of bleaching solution and acid used should be kept as small as possible.

2—The use of alkalies in excess affects prejudicially the color and strength of fabrics, and leads to the formation of much lint.

3—Contrary to the common belief of launderers, soft water is superior to hard water for all purposes, rinsing included.

4—The deposition in the fibers of insoluble salts or the crystallization of soluble salts does not greatly affect the wearing qualities of fabrics.

5—The use of mineral acids in the laundry cannot be generally recommended, because of the extent to which they attack cellulose if they are not thoroughly removed by rinsing.

6—One cause for the yellowing of fabrics composed of cellulose on standing is the formation of yellow products by the action of hydroxyl ions on the oxycellulose which is formed during the bleaching process.

7—A saving in the quantity of bleaching solution required and an improvement in the color produced are possible when the bleaching is done as a separate process. The usual practice is to combine washing and bleaching.

8—Hydrosulfites may be used for effecting the bleaching, but the color obtained is not as good as that produced by hypochlorites.

9—Magnesium hypochlorite solutions present no advantages over the slightly alkaline solutions of sodium hypochlorite now employed, as far as their destructive actions are concerned.

10—Ozone produces a satisfactory color when allowed to act on fabrics before or during the drying which is effected in the drying rooms. The fabrics are less attacked than in the present method, but the ozone process is not well received by the trade because it necessitates extra handling of the articles, and increases unduly the length of time necessary to complete the laundering operation.

DEPARTMENT OF INDUSTRIAL CHEMISTRY
UNIVERSITY OF KANSAS, LAWRENCE