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Bleaching with Sodium Hypochlorite: Interactions of Temperature, Time, pH and Concentration with Stain Removal and Fabric Strength

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ABSTRACT

In response to recent concern for energy conservation while laundering at lowered temperatures, this study investigated stain removal and fabric degradation effects of sodium hypochlorite bleach on stained cotton fabrics. Blue and green reflectance readings were used to calculate both whiteness values and percentage of stain removal values, while tensile strength measurements were used to determine fabric degradation. An "acceptable bleach treatment" category was established, having a minimum of 75% whiteness and 90% of original breaking strength. Temperature, bleach concentration, time and pH were investigated, with each factor except pH being significant. Low bleach concentration was more satisfactory than high concentration, while cold and warm temperatures were more acceptable than very cold and hot temperatures. An overnight bleach soak treatment of up to 16 hr was not damaging if a cold temperature of 25 C was chosen. Selecting cold (room) temperatures for chlorine bleaching could provide energy savings for the consumer, textile mill or commercial laundry, while providing acceptable whiteness and fabric strength retention.

INTRODUCTION

In the 1980s, sodium hypochlorite or liquid chlorine bleach continues to be the major oxidizing bleach used by American consumers (1). With the current emphasis on energy conservation, cooler temperatures are being used more frequently than before for laundering (2). In addition, detergent formulations have changed over the past 15 years. Formerly, detergents were high in phosphates with a resulting high pH value. Today's detergents have phosphate substitutes and combinations of builders (3) which may result in lower alkalinity or lower pH values.

Review of related literature (4-7) showed that conditions surrounding hypochlorite bleaching activity at cold temperatures had not been established, nor had the effectiveness of stain removal been thoroughly evaluated. Such information is needed to provide consumers, commercial laundry operators and textile manufacturers a basis for making wise decisions regarding sodium hypochlorite bleach usage.

Objectives of this research were twofold. The first was to ascertain the bleaching action of a sodium hypochlorite bleach soak treatment upon stained cotton fabrics, when cold and very cold temperatures of 25 C and 5 C were compared to warm and hot temperatures of 45 C and 65 C, and were evaluated at selected times, concentrations and pH levels. Conditions for safe bleaching action were of major importance in this study. The second major objective, therefore, was to determine bleach soak treatments where optimum performance for both stain removal and fabric strength retention occurred.

EXPERIMENTAL PROCEDURES

Two types of experimental fabrics and two stains were used in this study. Fabric I was a 100% cotton purchased from Testfabrics in both red-wine stained and unstained white yardages (EMPA 114 and 302). Fabric II, also 100% cotton, was purchased unstained from US Testing Corporation. Half of fabric II was stained with a boiling tea solution in the laboratory, as prescribed by McLain (6). Four specimens, one from each of the 4 categories (wine stained, no wine stained, tea stained, no tea stained) were soaked in the designated bleach solution in a glass beaker for the specified time. One bleach soak cycle and one replication were used at all levels of the four independent variables: concentration, time, pH and temperature.

Bleaching Variables

Two concentrations were selected: a low concentration of 200 ppm available chlorine, based upon the amount of bleach recommended on the bleach label for general laundering conditions; and a high concentration of 1600 ppm available chlorine, as recommended for stubborn stain removal.

The five bleaching times designated were 5 min, 15 min, 1 hr, 4 hr and 16 hr. The first 2 times were representative of home laundry bleach treatment times used during a short and a long wash cycle. The latter 3 times were typical of those used in an extended-soak situation for stubborn stains, with the 16-hr treatment representing an overnight bleach soak.

Three levels of buffered pH used were 8.5, 9.5 and 10.5 pH. Four temperatures were chosen for evaluation: 5 C, 25 C, 45 C and 65 C. The first 2 temperatures selected were representative of cold water and its lower and upper range. A warm temperature of 45 C and a hot temperature of 65 C were also selected, for comparison purposes.

Bleach Treatment Procedures

Bleach soak treatments were performed in 1500-mL glass beakers. One liter of the buffered bleach solution (see Table I) was used. Temperatures were maintained at ± 2 C by suspending the glass beaker in a Terg-O-Tometer bath throughout the designated bleach time. One each of the four fabric specimens, 6 in. by 8 in., was wet in distilled water, and squeezed in a pressure wringer to approximately uniform wet pick-up. The four specimens were then placed in one liter of the bleach solution, stirred for 1 min, and allowed to soak beneath the surface of the bleach solution for the specified time. No further agitation during bleach soak was used; neither were any detergents added. This experimental procedure gave a weight ratio of 40:1, bleach solution to fabric. After the bleach treatment, the specimens were plunged into an antichlor bath of 10 g sodium bisulfite to 2 L distilled water, designed to stop the oxidation action of the chlorine bleach. Specimens were rinsed for 3 min in running tap water and wrung dry. An automatic clothes dryer set on "cotton" for 35 min was used to tumble dry the test specimens. Dried specimens were smoothed and stacked but not ironed.

TABLE I

Content of Bleaching Solutions

Concentration of solution[a]	pH	Bleach (mL)	Buffer: borax (mL)	Buffer: other	Distilled water (mL)
Low: 0.02% or 200 ppm	8.5	3.6	50	22 mL of 0.1N H_2SO_4	924
	9.5	3.6	50	4 mL of 0.1N NaOH	924
	10.5	3.6	50	24 mL of 0.1N NaOH	922
High: 0.16% or 1600 ppm	8.5	28.6	50	52 mL of 0.1N H_2SO_4	869
	9.5	28.6	50	16 mL of 0.1N H_2SO_4	905
	10.5	28.6	50	9 mL of 0.1N NaOH	912

[a]Initial available chlorine content titrated at 5.6%

Calculations

Physical degradation of the cotton fabric was evaluated using average tensile strength measurements of 5 one-in. ravel strips per specimen as outlined in ASTM D-1686 (8) and recorded on an Instron Model 1122 in kilograms of force. Percentage of original breaking strength values were calculated from these data, using the formula A/B × 100, where A equals the average tensile strength of specimens after bleach treatment and B equals the average tensile strength of specimens before bleach treatment (i.e., controls). High values for percentage of original breaking strength indicated that the bleached fabrics were nearly as strong as the original.

The degree of stain removal was determined by taking blue and green reflectance readings on the bleached specimens, using a Photovolt Reflectometer Model 67. Four blue (B) and four green (G) readings were recorded and averaged for each specimen, two on the face and two on the back. Reflectance readings were converted into whiteness percentage values by the Hunter-Judd-Selling formula (9) which allowed for yellowness of stains: whiteness percentage = $((200\ (G\text{-}B)/G + 0.242B) + (100\text{-}G/2)^2)^{0.5} \times 100$. The whiteness percentage value was then used to calculate a percentage of stain removal value for each specimen using the formula (A-B)/(C-B) × 100, where A equals the average whiteness value of a stained specimen after bleaching, B equals the average whiteness value of a stained specimen before bleaching, and C equals the average whiteness value of the original unstained specimens (controls). This calculation allowed for comparison of the tea and wine stains even though they had differing amounts of stain applied. High values for percentage of stain removal indicated nearly all the stain was removed.

Statistical Treatment

The statistical treatment of data involved a factorial analysis of variance to determine the effects of individual factors (temperature, concentration, time and pH) and their simultaneous interaction upon breaking strength and upon stain removal. Data on the categories of replicate and stain were each initially analyzed by Student t-tests to determine if significant differences at the 0.05 level existed between means within each variable group for breaking strength and for stain removal. Analysis revealed that wine stains were more difficult to remove by bleaching than tea stains. Therefore, analysis of variance tests for stain removal were performed separately on each stain. Because no significant differences in breaking strength values were found between the two stains, analysis of variance tests for breaking strength were performed on combined data from wine and tea stains. Replicates were also examined by t-tests and, as there were no significant differences in first and second replicates, the two were treated as one when the analysis of variance tests were performed. As a post hoc examination, a Newman-Kuels' multiple range test was used to determine rank orders and like sets. Canonical correlation, a complex multiple regression statistical procedure, was used to analyze relationships between the dependent variables (stain removal and breaking strength) and the independent variables (temperature, concentration, pH and time).

RESULTS AND DISCUSSION

Stain Removal Effectiveness

Results of a four-factor analysis of variance test revealed that temperature, concentration and time were very highly significant (0.001) in affecting the degree of stain removal, whereas pH was not (see Table II). Increased stain removal

TABLE II

Means and Frequencies for Significant Main Effects on Percentage of Stain Removal after Bleach Treatments

Significant factors	Wine stain (%) Mean values	Wine stain (%) No. of cases	Tea stain (%) Mean values	Tea stain (%) No. of cases
Main effects:				
Temperature				
5 C, very cold	19.1	60	43.1	60
25 C, cold	49.3	60	68.0	60
45 C, warm	73.4	60	87.4	60
65 C, hot	89.7	48	97.3	48
Concentration				
Low, 200 ppm	49.4	114	65.9	114
High, 1600 ppm	62.9	114	79.6	114
Time				
5 min	29.8	48	48.1	48
15 min	41.8	48	59.1	48
1 hr	61.9	48	79.8	48
4 hr	74.8	48	89.4	48
16 hr	77.9	36	92.2	36

occurred with the following treatments (Fig. 1): higher temperatures rather than low temperatures; high concentrations rather than low concentrations; and longer time periods rather than shorter times.

Three two-factor interactions were found to be significant in the removal of both wine and tea stains: temperature and concentration, time and temperature, and time and concentration. In Figure 2, note that high concentrations were only slightly better in stain removal than were low concentrations, yet 8 times more bleach product was being used. The interactive effects of time and temperature on stain removal are shown in Figure 3. As time increased, stain removal effectiveness increased. Note the unusual phenomenon shown at the lower left of Figure 3, where the wine stain actually darkened after 5 min at the very cold temperature. Tea stains also visually darkened during the first 2 min of very cold treatment, but by the end of 5 min had risen to a 20% stain removal value. This initial darkening of stains at very cold temperatures was not mentioned in any of the literature reviewed. No explanation can be offered for this although comments from other laboratory operators doing stain evaluations have verbally expressed similar results. In Figure 4, interactive effects of time and concentration are shown graphically. A high concentration was more effective in stain removal than was low; but at 4 hr and 16 hr the differences in stain removal effectiveness become less apparent. Figures 1-4 only evaluated stain removal, without considering fabric degradation.

Retention of Fabric Tensile Strength

The next phase of evaluation dealt with percentage of original breaking strength values of the bleached specimens, in which both tea and wine stain data were combined, as explained previously. Results of a four-factor analysis of variance revealed that all four main effects (temperature, time, concentration and pH) were highly significant at the 0.001 level (Table III). Bleach soak main effects which led to higher retention of original breaking strength were (Fig. 5) cold or very cold temperatures rather than warm or hot; low bleach concentration rather than high; higher alkaline pH values; and shorter times of 5 min to 1 hr rather than 4 or 16 hr.

Results of the analysis of variance tests revealed that three significant three-factor interactions existed for fabric strength values. Figures 6-8 show these relationships affecting fabric degradation. In Figure 6, the interactions of temperature, concentration and pH are shown. The temperature factor was very influential at high concentrations, with warm and hot temperatures causing a drop in strength values to 66% of original breaking strength. A higher pH

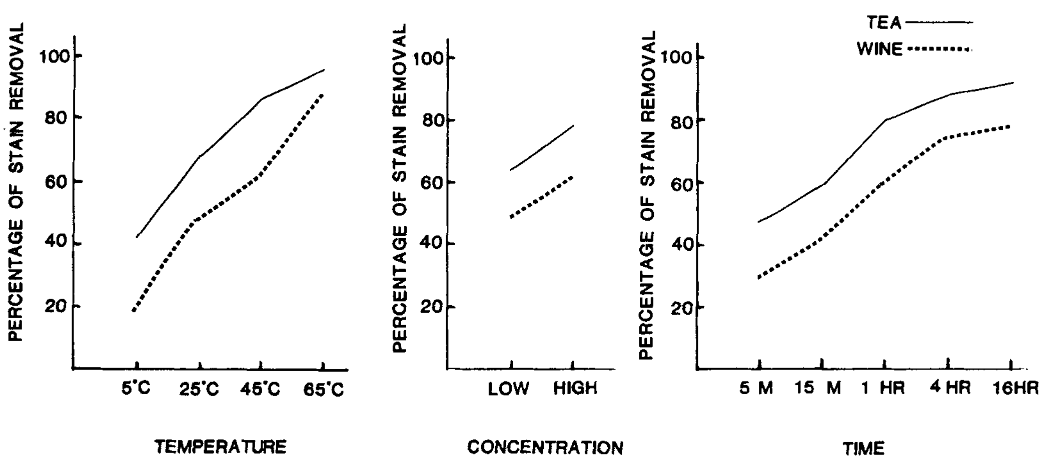

FIG. 1. Mean values for main effects of temperature, concentration and time on stain removal for bleached wine and tea specimens.

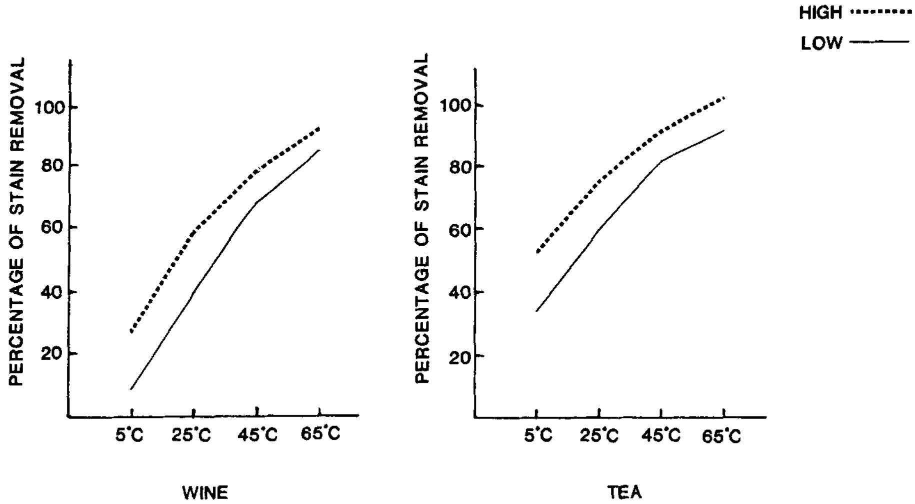

FIG. 2. Interactive effects of temperature and concentration on stain removal for bleached wine and tea specimens.

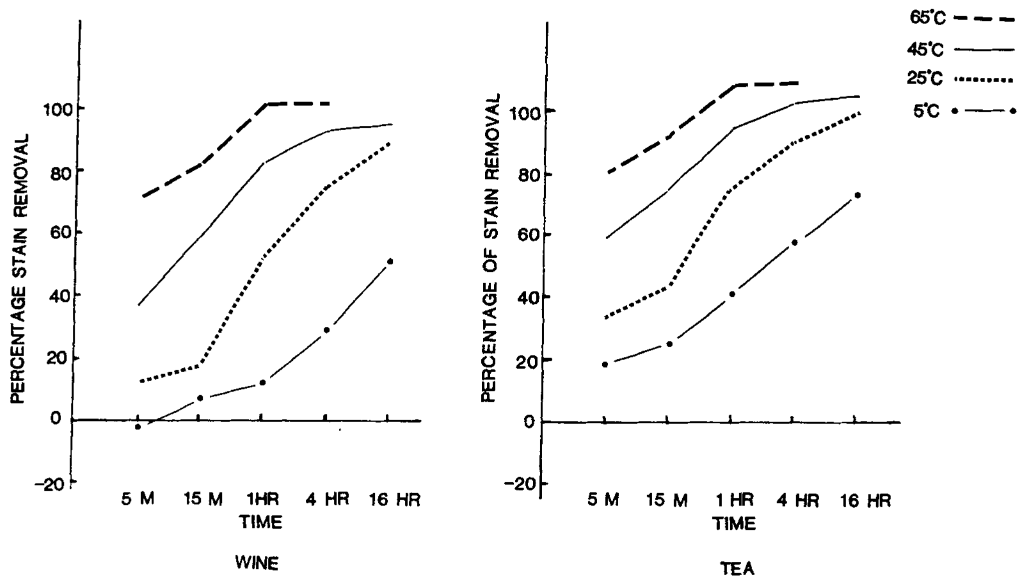

FIG. 3. Interactive effects of time and temperature on stain removal for bleached wine and tea specimens.

level of 10.5 produced better retention of fabric strength than did lower pH values, but these small differences were noted only at the high concentration. In Figure 7, a second significant interaction of temperature, concentration and time is graphed. Low concentrations again provided higher retention of fabric strength than did high concentrations, with percentages remaining above 85% for all time periods, except the 16-hr, 65 C cell. In Figure 8, temperature, pH and time factors were the third significant interaction affecting breaking strength. Severe fabric strength losses occurred at 45 C and 65 C for extended times of 4 hr and 16 hr and at all three pH levels.

Acceptable Bleach Treatment

Both the degree of stain removal and the amount of fabric damage usually must be considered when bleaching conditions are selected. Thus, a major objective of this research was to determine the factors which could provide both adequate stain removal and adequate retention of fabric strength. A category designated "acceptable bleach treatment" was established, having a minimum of 75% whiteness and 90% of original breaking strength. Criteria used to determine these levels were based upon examination of the L22 Performance Standards (10) for breaking strength, and upon panel evaluation of treatment stains with visual ratings of the AATCC Gray Scale for Staining (3). The AATCC-established classes and nomenclature; along with the assigned whiteness values, as determined by a panel of three textile researchers, are given in Table IV. A rating of Class 4—slightly stained, comparable to a whiteness value of 75%—was selected as the lowest value which would be rated as being visually acceptable. Note that, interestingly enough, a whiteness value of 90% was as high as was necessary to be rated as white as the two original white fabrics.

Of the total 456 stained specimens receiving bleach soak treatments, 176 occurred within the acceptable bleach treatments category. Thus, 39% of the specimens met acceptable performance limits as defined herein.

Specimens in the high concentration bleach category are shown in Figure 9, and those bleached with a low concentration are shown in Figure 10. In both cases, it was possible for each pH cell (across the top line) to have a maximum of four stained specimens: one tea, one wine, and one replicate of each stain. A total of 12 possible specimens

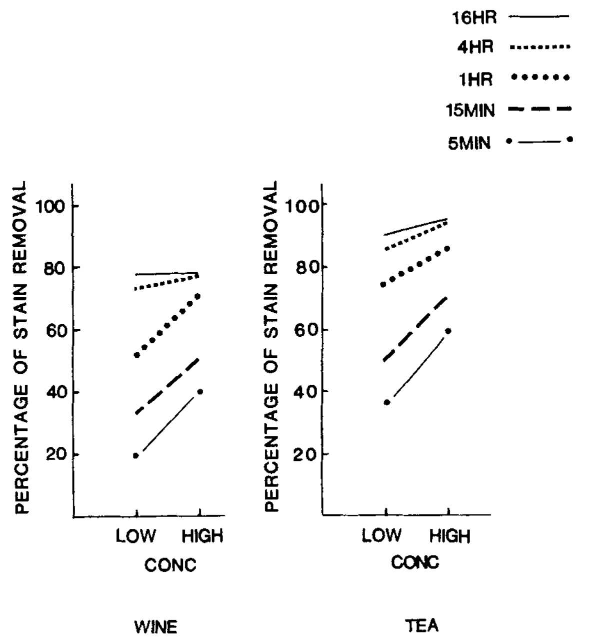

FIG. 4. Interactive effects of time and concentration on stain removal for bleached wine and tea specimens.

TABLE III

Means and Frequencies for Significant Main Effects upon Precentage of Original Breaking Strength of Stained Fabrics after Bleach Treatment

Significant factors	Mean values	No. of cases
Main effects:		
Temperature		
5 C, very cold	94.1	120
25 C, cold	90.7	120
45 C, warm	82.4	120
65 C, hot	79.4	96
Concentration		
Low, 200 ppm	92.3	228
High, 1600 ppm	81.7	228
pH		
8.5	85.9	152
9.5	87.1	152
10.5	88.1	152
Time		
5 min	91.4	96
15 min	89.8	96
1 hr	91.2	96
4 hr	81.8	96
16 hr	78.8	72

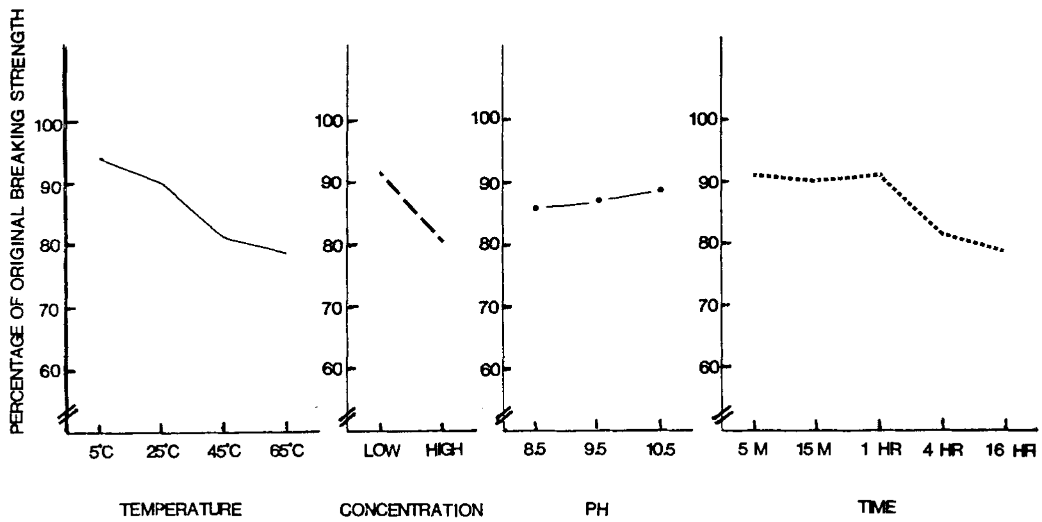

FIG. 5. Mean values for main effects of temperature, concentration, pH and time on breaking strength of bleached stained specimens.

could occur within a cell, when the three pH levels were combined. Combining pH cells was done for two reasons: because pH was shown not to be a significant main effect for stain removal; and because breaking strength was significant with only an average of 1% difference in breaking strength between each of the 3 pH values.

When analyzing bleach concentrations for the acceptable bleach treatments group, less than 40% of those specimens occurred within the high bleach concentration level, while slightly more than 60% were treated with low concentrations. Analysis of all stained data (456 specimens) by the canonical correlation procedure also confirmed the fact that the low concentration, rather than the high, was more appropriate when both stain removal and retention of fabric strength are desired. With high concentrations, acceptable bleaching positions were maintained for a shorter period of time and fabric degradation occurred sooner. However, at cold and very cold temperatures, the optimum cell was at the same location whether low or high bleach concentration was used.

The distribution of acceptable bleach treatment specimens treated with a low bleach concentration is shown in Figure 10. Note the greater frequency of specimens and the wider range at which they appear. The empty cells indicate the bleaching conditions to be avoided, if maximum stain removal and maximum retention of fabric strength are desired. Absence occurred either if the fabric was not bleached white enough, as in the lower left cells; or if fabric strength loss was greater than 10%, as in the upper right cells.

For very cold and cold temperatures (5 C and 25 C) at low bleach concentrations, Figure 10 shows that once the

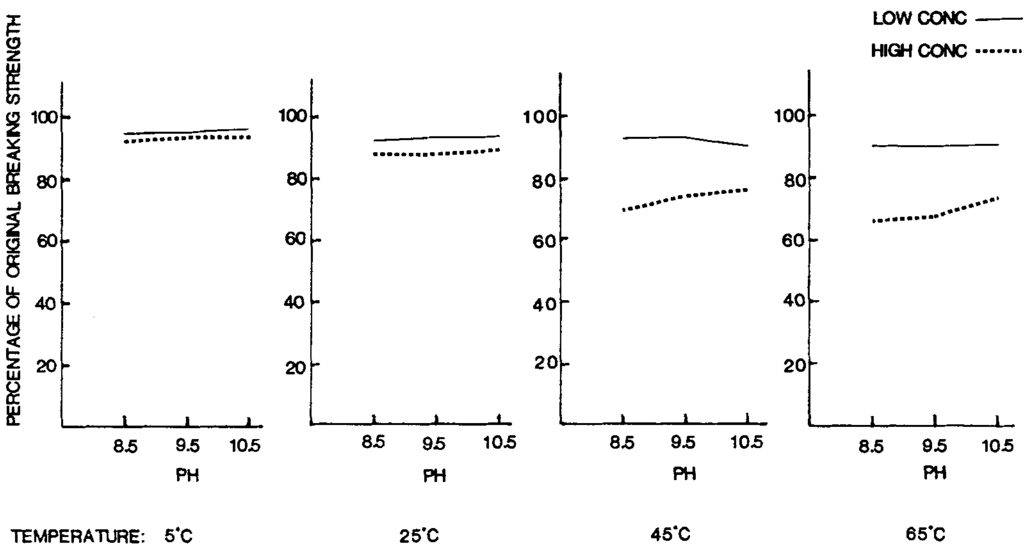

FIG. 6. Interactive effects of temperature, pH and concentration on percentage of original breaking strength of bleached stained specimens.

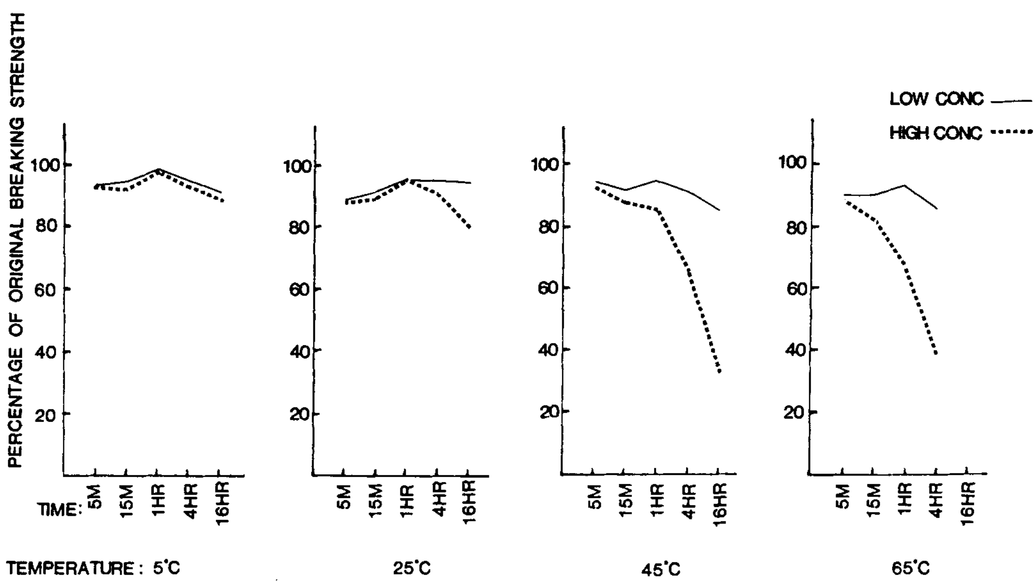

FIG. 7. Interactive effects of temperature, concentration and time on percentage of original breaking strength of bleached stained specimens.

optimum bleaching activity was reached, the extension of bleaching time did little harm to the fabric. The results of this study supported the possibility of using an overnight or extended bleach soak treatment. Times of 1 hr, 4 hr, and 16 hr all proved quite acceptable, when cold temperatures of 25 C and low concentration were used. In certain commercial laundry operations, a procedure for heavily stained items could be implemented, whereby low bleach concentrations could be used on an overnight soak basis at room (cold) temperatures.

If bleaching must occur in a shorter 15-min time period such as a home laundry cycle, warm temperatures of 45 C should be selected with low concentration. Low concentration and hot temperatures of 65 C could be used, but choosing warm over hot temperatures would mean an energy saving. A time of only 5 min would be acceptable either if high concentration and 45 C were selected, or low concentration and 65 C were selected.

High bleach concentration of 1600 ppm used 8 times more bleaching product than did the low concentration of 200 ppm. A considerable savings in cost of bleach product would thus be realized if low concentrations were selected with appropriate times and temperatures.

The use of cold temperatures (25 C) was supported by findings of this study. Concern for energy conservation has led many people to use cold temperatures in laundry-bleach cycles. Effective bleaching is possible at 25 C and at low bleach concentrations when the time period is lengthened to 1 hr or longer, up to 16 hr. The optimum bleaching position appeared to be that of low concentration at 1 hr and 25 C. Specimens were still acceptable in whiteness and strength, when either the time was extended from 1 hr to 4 hr or 16 hr; or the temperature was raised from 25 C to 45 C or 65 C, as shown in Figure 10. Bleaching with sodium hypochlorite is, therefore, an effective way to remove stains in cotton fabric, while realizing energy savings and/or incorporating extended bleach times at colder temperatures.

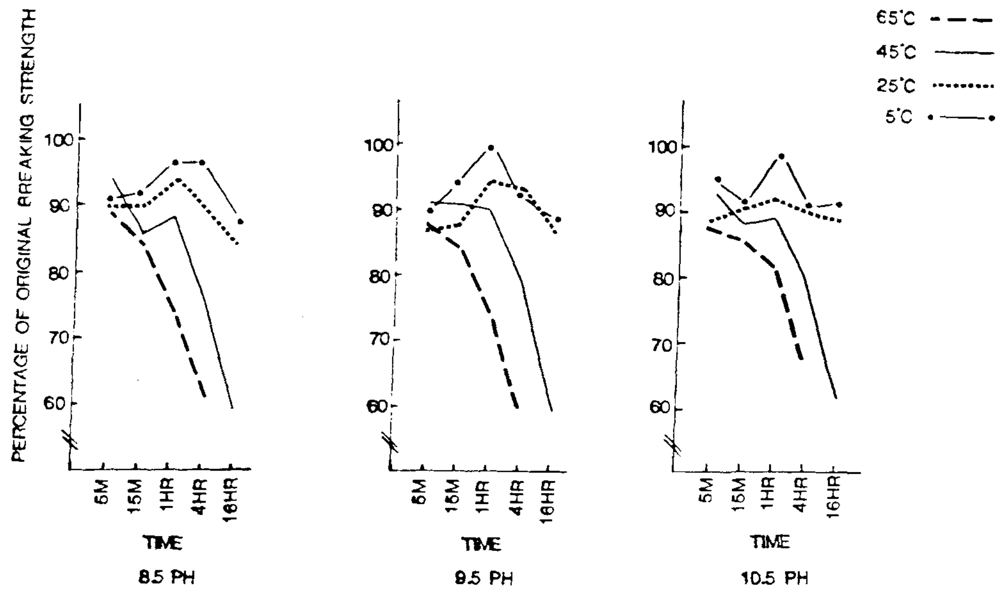

FIG. 8. Interactive effects of temperature, pH and time on percentage of original breaking strength for bleached stained specimens.

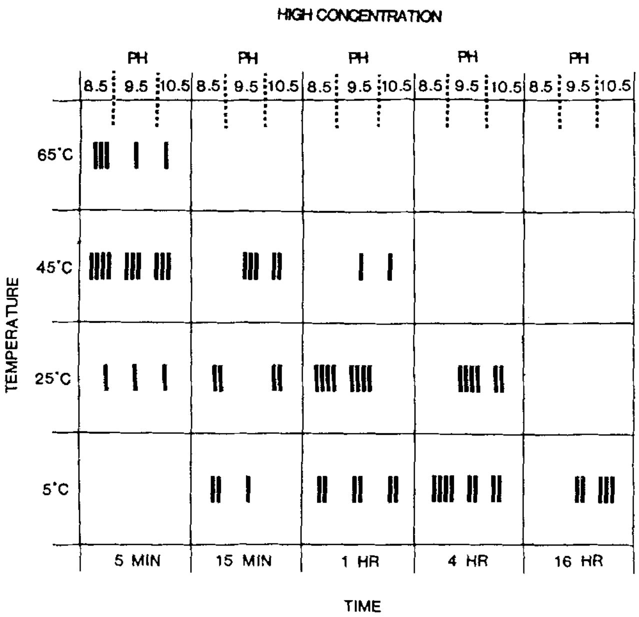

FIG. 9. Distribution of specimens in "acceptable bleach treatment" group at high concentration.

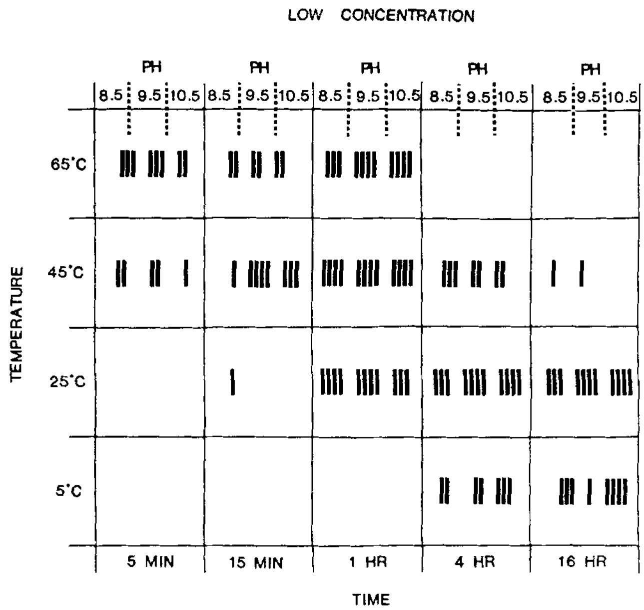

FIG. 10. Distribution of specimens in "acceptable bleach treatment" group at low concentration.

TABLE IV

Gray Scale Stain Ratings and Whiteness Values Determined by Panel

AATCC Class	Whiteness value (%)	AATCC Nomenclature
5	90	Negligible or no staining
4-5	85	———
4	75	Slightly stained
3-4	70	———
3	65	Noticeably stained
2-3	55	———
2	45	Considerably stained
1-2	—	———
1	—	Heavily stained

ACKNOWLEDGMENTS

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