Effects of Sodium Hydroxide and Calcium Hydroxide on Polyester Fabrics

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ABSTRACT: The results of a comparison between the effects of sodium hydroxide and calcium hydroxide on poly(ethylene terephthalate) fabrics are presented. Calcium hydroxide can produce weight-loss effects similar to an aqueous solution of sodium hydroxide. The effects of some treatment variables on weight loss, fiber diameter, bending rigidity, and strength of yarns taken from fabrics are examined. The results are explained in terms of current views of polyester alkaline hydrolysis. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 631–637, 1999

Key words: polyester fabric; alkaline treatment; weight loss; calcium hydroxide; sodium hydroxide; hydrolysis

INTRODUCTION

Alkaline treatment of poly(ethylene terephthalate) (PET) is a well-known finishing process for fabrics.[1] Depending on the application procedure, it improves handle,[2,3] wettability,[3,4,5,6] resistance to abrasion damage,[7,8] soil-release properties,[2,8] and drape of fabrics.[9,10] The kinetics of polyester fiber alkaline hydrolysis,[3,11,12] the mechanism of hydrolysis of copolyesters,[13] effects of fiber structure,[14,15] time,[8,13,16] surfactants,[17,18] and delustrant[19] have been studied.

For this finishing process, only the use of sodium hydroxide is reported. Less information is available about the use of other, more active and cheaper alkalines.

Calcium hydroxide is classed as a strong base, and because of its activity and cheapness is used more extensively in commercial processes than any other base.[20] In general, the use of calcium hydroxide in textile wet processings is limited. This is likely due to the low solubility of calcium oxide in water and the diverse effects of temperature and dissolved carbon dioxide.[20,21] The solubility of calcium hydroxide can be improved by using such chemicals as sucrose, glycerol, and phenol.[21,22] The low solubility of calcium hydroxide may enhance reproducibility in the weight-reduction process for polyester fabric.

These peculiarities direct us to examine the effect of calcium hydroxide in weight reduction of polyester fabrics. For comparison, we also consider the effect of low-concentration sodium hydroxide.

EXPERIMENTAL

Materials and Chemicals

Plain woven fabric, 80 g/m^2, made from 100 den textured yarns (47 ends/cm and 22 picks/cm) were used. The sodium hydroxide, calcium oxide, sucrose, and acetic acid used were of analytical reagent grade. Tinegal PAC (a commercial product) used as a quaternary ammonium compound is a cationic surfactant. Surfactants and dyestuff were kindly supplied by local distributor, Ciba

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Geigy. Distilled water was used for the treatments and washings.

Treatments

Pieces of fabric were scoured, washed, dried at room temperature, and set at constant tension at 180°C. These samples were cut into pieces and conditioned at standard temperature and humidity for 24 h. They were then weighed and used for alkaline treatment. All weighing was done on a balance with an accuracy of 5 mg.

Calcium hydroxide solution was prepared by mixing calcium oxide in distilled water at room temperature, then filtering the mixture three times. A concentration of 1.228 g/L (.0338*N*) was obtained. For solutions with higher concentrations of calcium hydroxide, the proper amount of sucrose was added to the suspension solution. The concentration of alkali solutions was determined by titration with 0.1*N* sulfuric acid.

The alkali treatment of fabrics was done in a laboratory dying machine (Ahiba Texomat GVIIB, Brisfelden, Switzerland). Required amounts of alkali solutions were placed in the jars, fabric samples were immersed in the solutions, and the sealed jars were placed in an oil bath. The liquor-to-goods ratio (L : G) was 120 : 1. The bath temperature increased at a rate of 2.5°C/min.

Following the alkaline treatment, the samples were rinsed repeatedly with distilled water, neutralized with a solution of 1% hydrochloric acid, and rinsed. The samples were then dried at room temperature, conditioned at standard temperature and humidity, and weighed.

Untreated and alkali-treated samples were stained in a basic dye bath containing 0.5% malachite green, 0.5 g/L Irgasol NA (commercial dispersing agent), and 1 g/L acetic acid. The L : G ratio was 120 : 1, and the dying periods were 60 min. The stained samples were then thoroughly rinsed and dried.

Characterizations

The weight loss (WL) is expressed as relative WL according to the equation

$$\%\mathrm{WL} = ((W_1 - W_2)/W_1) \times 100$$

where W_1 and W_2 are the weights of the samples before and after alkaline treatments, respectively. The control fabric samples treated under identical conditions with distilled water instead of alkali solutions showed no significant weight reduction.

From each fabric, yarns were removed and tested for load-elongation using an Instron Tensile Tester Model TM-SM 1026, with 15-cm gauge length. A minimum of 15 tests were made and averaged. To determine fabric stiffness, bending lengths were measured by a Shirley stiffness tester.[23,24] Fiber bulk density was determined using a density gradient column filled with the solution of calcium nitrate in water and thermostated at 25°C. The average diameter of fibers was measured using a Carl Zeiss (Jena, Switzerland) light microscope, equipped with a calibrated eye piece. One hundred measurements were made on each sample, and the average was calculated. A JEOL scanning electron microscope was used to obtain photomicrographs of fibers surfaces. Coating was done with gold in a vacuum evaporator. The color characteristics of dyed samples (L^*, a, b, and R) were measured with a Tex Flash Datacolor (Zurich, Switzerland) reflection photometer, and then the Kubelka–Munk coefficient (K/S) was calculated.[25]

RESULTS AND DISCUSSION

According to the present views of the hydrolysis of PET by alkali metal hydroxides, the hydroxide ions attack the electron-deficient carbonyl carbons, resulting in the production of hydroxyl and carboxyl end groups at the fiber surfaces. A low-molecular segment of the chains is removed, resulting in WL and decreased fiber diameter.[1] Calcium hydroxide attacks much faster than sodium hydroxide, possibly due to a greater ease of penetration to polyester.[26]

Increasing treatment temperature and sodium hydroxide concentration causes the WL to increase.[1,8,13] When the treatment temperature increases, partly due to the increases of segmental polymer chains motions above glass-transition temperature, a sudden change in the plot of WL versus temperature is reported.[8,13]

The increased reaction rate in the presence of quaternary ammonium compounds is due to the ability of long-chain molecules to transfer hydroxide ions into the polyester phase.[26] It is an induction effect that increases the tendency of polyester to hydrolysis,[1] or it is due to the coverage of the negative charges in hydrolyzed polyester, which eases the next attack of hydroxyl anions.[12]

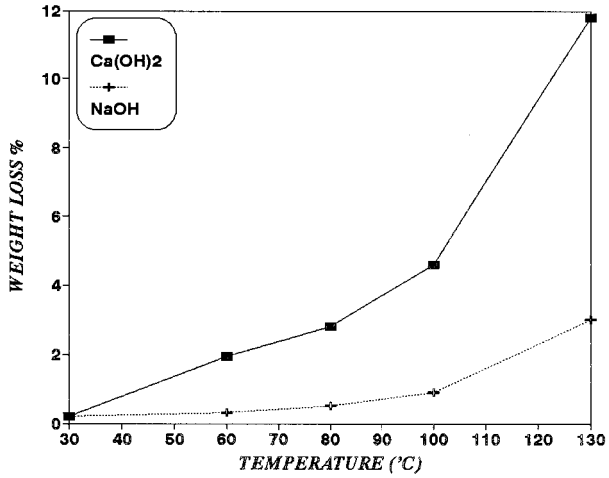

Figure 1 Percent weight loss (%WL) of fabrics with temperature of treatment with 1.288 g/L NaOH and $Ca(OH)_2$ after 60 min.

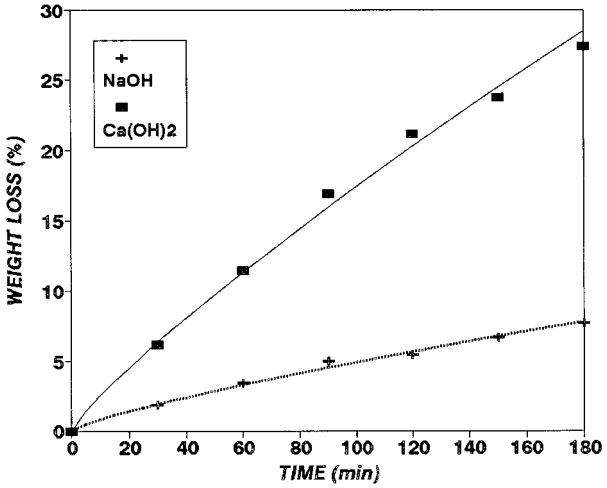

Figure 2 %WL of fabrics with time of treatment with 1.288 g/L NaOH and $Ca(OH)_2$ at 130°C.

The results obtained with calcium and sodium hydroxides in the present article are generally in agreement with the aforementioned views. The particular differences observed between the effect of calcium hydroxide and sodium hydroxide are discussed in the next section.

Weight Loss

Figure 1 shows the effect of temperature on the WL of samples in treatment with 1.228 g/L alkaline solution after 60 min. Increasing the temperature increases WL for both alkaline solutions. Despite the reduced solubility of calcium hydroxide in water with increasing temperature, a sudden increase in WL occurs. For both alkaline solutions, this steep rise of WL seems to occur above 80°C. Moreover, previous work[27] shows that when the temperature of treatment with calcium hydroxide exceeds 80°C, the WL becomes appreciable after 60 min.

Figure 2 shows the effects of treatment time on fabric WL, with 1.228 g/L alkali at 130°C. The rate of WL is faster with calcium hydroxide than with sodium hydroxide. For the treatment with calcium hydroxide, the estimated regression equation between %WL and time (t) is $\%WL = 0.366 \times t^{0.838}$, with correlation coefficient $R^2 = 0.994$, for the treatment with sodium hydroxide, the estimated regression equation is $\%WL = 0.131 \times t^{0.779}$, with correlation coefficient $R^2 = 0.991$. The nonlinearity of the relation between WL and time may be as owing to the reduced fiber surfaces or to the reduced —OH concentration.

Figure 3 shows the effect of alkaline concentration (measured at room temperature) on the WL of fabrics. With increasing temperature, the solubility of calcium hydroxide in water decreases and that of sodium hydroxide increases.[21] Apparently, the relation between WL and alkaline concentration (measured at room temperature) for both sodium hydroxide and calcium hydroxide is linear. The estimated linear regression equations have the correlation coefficient of $R^2 = 0.99$ for both treatments.

For prediction of WL, Latta[3] developed the following equation:

$$\%WL = 100 \times [(\exp - (aC^2t + bCt)) - 1]$$

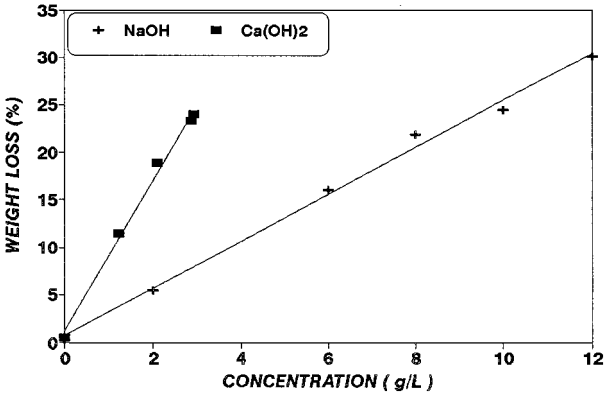

Figure 3 %WL of fabric with concentration of NaOH and $Ca(OH)_2$ at 130°C after 60 min.

Table I Comparison of Measured and Calculated Weight Loss for the Treatment of Fabric with 1.228 g/L Sodium and Calcium Hydroxide

	Weight Loss (%)			
	Calcium Hydroxide		Sodium Hydroxide	
Time (min)	Measured	Calculated	Measured	Calculated
0	0.0	0.0	0.0	0.0
30	6.1	5.7	1.9	1.6
60	11.5	11.1	3.4	3.2
90	16.9	16.2	4.9	4.7
120	21.1	21.0	5.4	6.3
150	23.7	25.5	6.7	7.8
180	27.4	29.7	7.7	9.2

where C is the (—OH^-) concentration in mol/L, t is the time of reaction in minutes, and a and b are rate constants and must be determined empirically. The values of these constants depend on temperature and fiber type.

We calculated the values of a and b from the data of WL versus alkaline concentration (see Fig. 2) by using multiple regression analysis. The values of the rate constants for sodium hydroxide are $a = -0.014$ and $b = 0.018$, and those for calcium hydroxide are $a = -0.957$ and $b = 0.134$.

Table I compares the measured (Fig. 3) and calculated values of WL for different reaction times with sodium hydroxide and calcium hydroxide, based on the foregoing equation. The agreement between calculated and measured results for reaction time <150 min is satisfactory. The differences at longer periods indicates that the sizes of the chain segments incorporated in the reaction possibly are not similar throughout the reaction periods.

The rate constant a for calcium hydroxide is 68.3× and that for b is 7.4× the corresponding values for sodium hydroxide. The value of a for sodium hydroxide obtained in this work is 10× the corresponding value determined by Latta.[3] The difference is likely due to differences in fiber type and treatment temperature.

Figure 4 shows the effects of concentration of surfactant (Tinegal PAC) on the WL of fabrics after 60 min, with 1.228 g/L alkali at 130°C. This result suggests that the effects of this surfactant on the WL rate are different for the two alkalis, but its effectiveness decreases for both alkalis when the surfactant concentrations exceed about 0.3 g/L.

Diameters

Figure 5 shows change in fiber diameters with WL. It seems that the WL is proportional to the square of fiber diameter. The correlation coefficients between WL and square of diameters are $R^2 = 0.98$ for the treatment with sodium hydroxide and $R^2 = 0.96$ for the treatment with calcium hydroxide. The differences in the slopes of the two linear equations are not statistically significant. In agreement with previous works,[7] this result indicates that the reactions are topochemical degradation; that is, the reactions are confined to the surface.

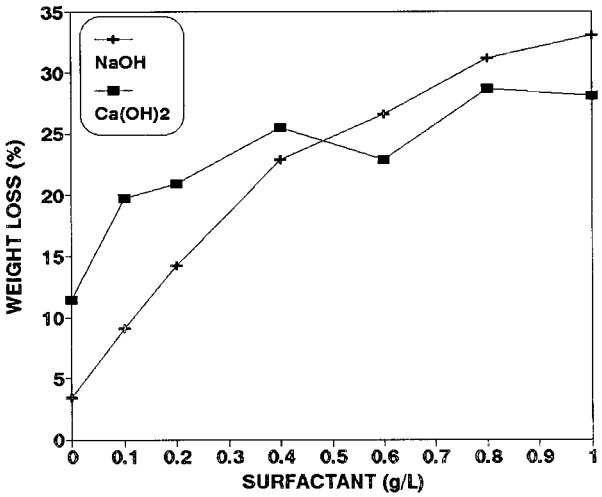

Figure 4 Effect of surfactant (Tinegal PAC) on the WL in the treatment with NaOH and $Ca(OH)_2$ at 130°C after 60 min.

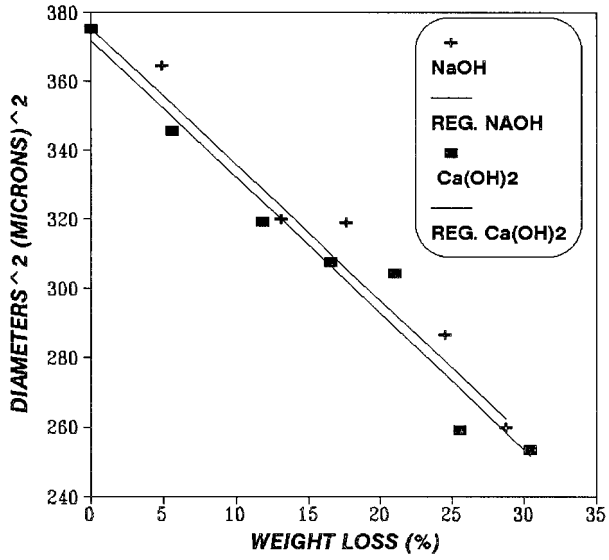

Figure 5 Change of square of diameter of fibers with WL of fabrics for the treatment with NaOH and $Ca(OH)_2$.

Density

Table II shows the WL of the fabrics and the density of fibers taken from the fabrics. Fiber density is a measure of its crystallinity. Hydrolysis of polyester affects only the surfaces of fibers, leaving the internal structure intact.[1,14,15] The results of Table II indicate that the density of fibers after treatment with both alkalis at relatively high temperature remained unchanged. Although the surfactants eased the penetration of alkaline into the fibers, the internal structure, measured in terms of density, remained unchanged.

Table II Density of Fibers

Treatment	Weight Loss (%)	Density[a]
None	0	1.3938 ± 0.0006
NaOH	2	1.3958 ± 0.0017
NaOH	19	1.3962 ± 0.0023
NaOH + Tinegal PAC	4.8	1.3939 ± 0.0001
NaOH + Tinegal PAC	35	1.3924 ± 0.0014
Calcium hydroxide	6	1.3942 ± 0.0026
Calcium hydroxide	31	1.3948 ± 0.0031

[a] 95% confidence limit.

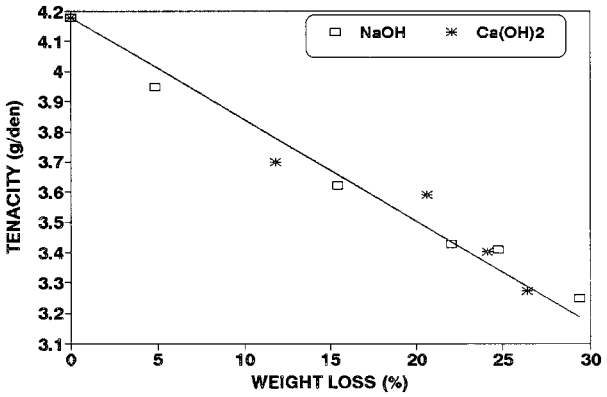

Figure 6 Effect of WL loss on the tenacity of yarns taken from fabrics.

Strength

Similar to the results reported earlier,[7,8] the strength of yarn taken from the fabrics decreases with WL. Figure 6 illustrates the relation between WL and tenacity for treatments with sodium hydroxide and calcium hydroxide. For both alkaline solutions, the regression equations between tenacity (TEN) and WL is of the form TEN = 4.178 − 0.334 WL. The correlation coefficients of the regression lines are $R^2 = 0.86$ for treatment with calcium hydroxide and $R^2 = 0.88$ with sodium hydroxide. The alkaline solutions probably caused more damage at 130°C than at lower temperatures.[8,27]

Stiffness

Stiffness, or limpness, of fabric can be determined by measuring bending length. Flextural rigidity of fabric is proportional to the product of fabric arial density and bending length to the third power.[24] Figure 7 shows the results of bending length measurements on fabrics with different WLs for the weft and warp directions. The decreased bending length could be a result of the reduced diameter of fibers (see Fig. 5) from the process of alkaline treatment.[10] The differences in bending lengths in the warp and weft directions are due to differences in yarn packing. No differences in the reduction of bending length for the different fabric treatments can be detected. Both treatments—reduction with solution of sodium hydroxide and reduction with calcium hydroxide at the same temperature and concentration—reduce bending lengths to comparatively low and constant values.

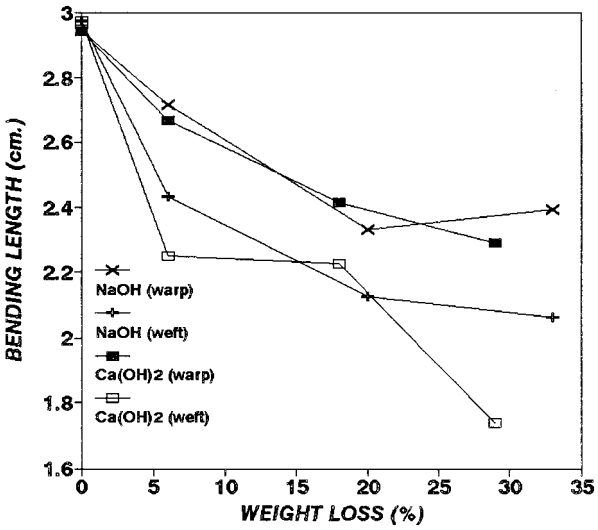

Figure 7 Effect of WL on bending length of fabrics.

Scanning Electron Microscopy

Figure 8 presents a typical scanning electron microscopy (SEM) micrograph for untreated fibers; Figure 9 shows the same and for fibers treated with calcium hydroxide and sodium hydroxide. In agreement with previous findings for sodium hydroxide,[1,8,19] the fibers became progressively thinner, and the fiber surfaces become pitted with ditches and holes. In general, similar results were obtained for calcium hydroxide–treated fibers. But the surface ditches and pits differ for the two treatments. The pits on the surface of fibers treated with calcium hydroxide seems to be hazier, flatter and less deep, causing the fabric to scatter the light differently.

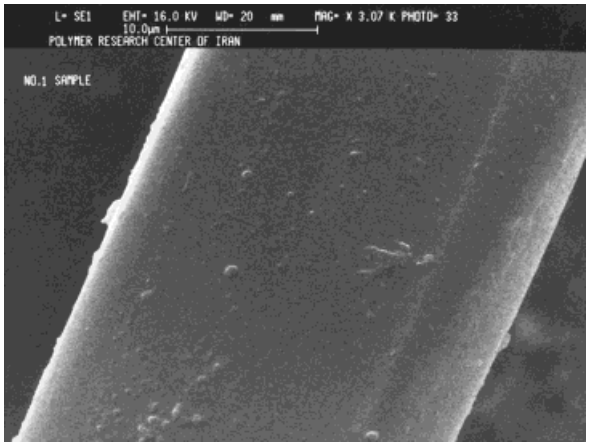

Figure 8 SEM photomicrograph of fibers taken from untreated fabrics.

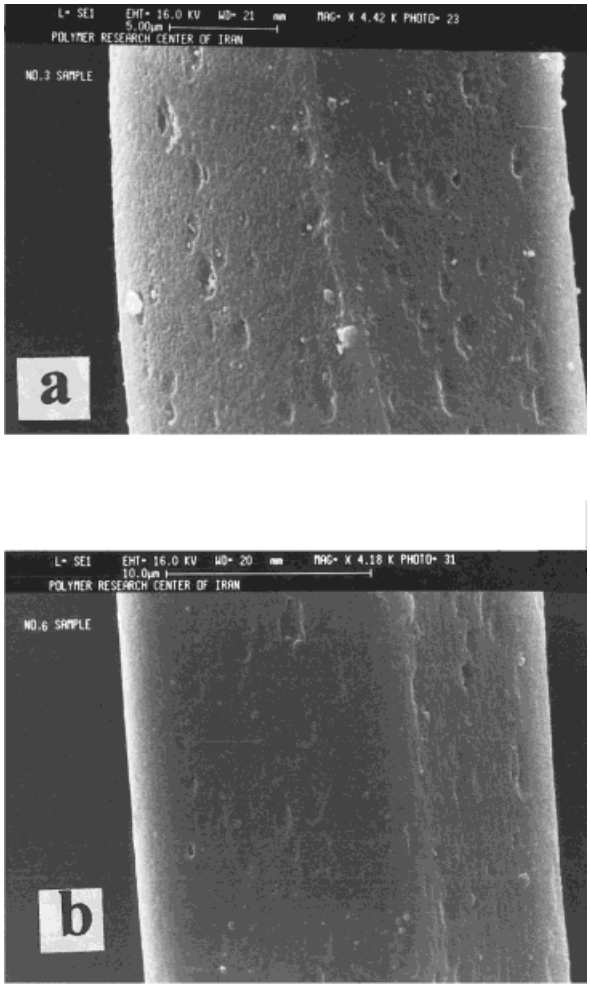

Figure 9 SEM photomicrograph of fibers taken from treated fabrics with sodium hydroxide (a) and with calcium hydroxide (b).

Staining

Table III presents dying characteristics (K/S) of samples of fabrics with similar WLs and untreated fabric dyed with malachite green. Cationic dye is absorbed more fully in treated fabrics than in untreated fabrics, as indicated by K/S values. According to the literature,[1,3,8] the enhanced dye absorption of treated fabrics is due to

Table III Color Specification of Dyed Samples

Fabrics	Weight Loss (%)	K/S
Untreated	0	0.52
Treated Ca(OH)2	20	0.75
Treated NaOH	18	0.85

an increase in negative carboxyl ions on the fiber surface. The difference in K/S values for treatment with calcium hydroxide and sodium hydroxide may be due to the difference in COOH concentration on the surface of fabrics.

CONCLUSIONS

Treatment with calcium hydroxide reduces the weight of polyester fabric similar to treatment with sodium hydroxide. In the absence of solubilizing agents, a significant weight reduction with calcium hydroxide requires a treatment temperature above 110°C. Fabric WL depends on alkali concentration, temperature, time of treatment, and the presence of surfactants.

Treatment with both alkalis has no effect on the density of fibers, but it does decrease the strength of fibers. This treatment also causes the fibers to become thinner. Hence, increased WL reduces fabric stiffness. Pits and ditches were observed on the fiber surfaces after treatment with both alkalis. Fabrics treated with both alkalis can be stained by cationic dyestuff.

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