

Effect of Oxidizing and Reducing Agents on Indian Wools: Part I—Treatment and Evaluation of Damage

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Four varieties of wool, viz. Chokla, Rambouillet, Ramb. $\times$ Chokla (50%) white, and Ramb. $\times$ Chokla (50%) canary coloured, were subjected to chemical treatment under different conditions with two oxidizing agents (hydrogen peroxide and peracetic acid) and two reducing agents (thioglycollic acid and sodium metabisulphite). The deterioration in strength and the chemical damage of wools are maximum in the case of samples treated with thioglycollic acid and peracetic acid. Chokla wool could withstand chemical attack of greater severity as compared to Rambouillet and other crossbred wools without serious impairment in strength.

Several protein groups (thiol, disulphide, thioether, imidazole, phenolic and indole) are susceptible to oxidation attack and a number of reagents cause their oxidation under various conditions. For example, hydrogen peroxide is used as a bleaching agent¹⁻⁷, chlorine, bromine and potassium permanganate are used to confer shrink resistance on wool⁸, and performic and peracetic acids are used for preparing soluble derivatives. Studies on the action of reducing agents on keratin fibres have been confined mostly to the behaviour of the disulphide bond, not only because of its use for the preparation of soluble derivatives but also because it is the basis of some setting methods.

During chemical processing, the wool fibres and yarns are treated with a wide range of chemicals at moderate to high temperatures. The conditions of treatments being very severe, the fibres are damaged resulting in loss of strength and increase in alkali solubility and harshness. The processing of wool with different chemicals under industrial conditions is carried out for different durations and at different temperatures and concentrations. It is desirable to study the combined effect of these variables by conducting a series of experiments in such a way that each variable covers the values used in industry.

In the present study the effect of two reducing agents (thioglycollic acid and sodium metabisulphite) and two oxidizing agents (hydrogen peroxide and peracetic acid) on the strength and the chemical damage to Indian and crossbred wools has been studied.

Experimental Procedure

Rambouillet, Chokla and Ramb. $\times$ Chokla (50%)

wools of autumn clip and Ramb. $\times$ Chokla (50%) wool of spring clip were scoured and spun on woollen system to make a yarn of uniform twist (127.2) and constant count (5.3). The following chemical treatments were given to yarns as well as loose wool of all the varieties:

Treatment with thioglycollic acid—Wools were treated with thioglycollic acid by the method described elsewhere^{9,10}. The temperature in the reaction mixture was maintained at 35°C for 20 hr at pH 4.5 at four different concentrations (0.2 M, 0.4 M, 0.8 M and 1.0 M). The treated wools were first washed thoroughly with water and finally with six changes of distilled water. The samples were dried at room temperature and stored for testing.

Treatment with sodium metabisulphite—The reduction of wool fibres and yarns was carried out by soaking the wool samples in sodium metabisulphite solutions of different concentrations (1, 3, 5 and 7%) for 30 min at room temperature^{11,12}. The material to liquor ratio was 1:25. The pH was maintained at 5.0 by using sodium acetate-acetic acid buffer. The wool samples were then treated with an identical solution of sodium metabisulphite which was preheated in a boiling water bath to 90-95°C. The samples were kept at this temperature for another 30 min. The bisulphite reduced wool was washed thoroughly with distilled water and then dried in air.

Treatment with hydrogen peroxide—The procedure of Smith and Harris¹ was employed for carrying out the oxidation of wool. The wool samples were treated with hydrogen peroxide (2 vol) at 50°C for different durations (2 hr, 4 hr, 6 hr, 8 hr, and 10 hr) with material to liquor ratio 1:25 at pH 8 adjusted by the addition of sodium silicate which also acts as a stabilizer. In

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another set of experiments, the wool fibres and yarn samples were treated with hydrogen peroxide (2 vol) for 3 hr at different temperatures (30°, 50°, 65° and 80°C) with material to liquor ratio 1:25 at pH 8. After treatment, the samples were washed and dried at room temperature.

Treatment with peracetic acid—Two sets of experiments were conducted. In one, the concentration of peracetic acid was varied, keeping the temperature and duration of treatment constant^{13,14}. In another, concentration and temperature were kept constant and the duration of treatment was varied. The loose wool and yarn samples were immersed in freshly prepared peracetic acid at different concentrations (1,2,3 and 5%) at 25°C for 4 hr with material to liquor ratio 1:25. In the second set of experiments, the samples were treated with 2% peracetic acid at 25°C for different durations (1,3,5,7 and 24 hr) with material to liquor ratio 1:25. After the treatment, the samples were washed repeatedly with cold distilled water and then dried in air.

The following chemical and physical tests were performed on the wool material.

Alkali solubility was determined as the percentage loss in weight by treating the sample with 0.1 N NaOH for 1 hr at 65°C. Urea-bisulphite(UB) solubility was determined by treating the samples with a solution of urea (50%) and sodium metabisulphite (3%) for 1 hr at 65°C. The tenacity and percentage elongation were determined using Uster single yarn tester with breaking time 20 ± 2 sec.

Results and Discussion

Alkali solubility, UB solubility, tenacity and percentage elongation of different samples are given in Tables 1-4. The reducing agents, thioglycollic acid and sodium metabisulphite, primarily attack the disulphide linkages, leading to soluble material. It is evident from the tables that as the concentration of the reducing agents increases, the alkali solubility increases and tenacity decreases. In the case of thioglycollic acid treatment, as the concentration increases from 0.2 M to 1.0 M, the alkali solubility increases gradually from 12.9 to 62.3 and the tenacity decreases from 4.2 to 2.4 in the case of Chokla wool. A similar trend is observed for all other varieties of wool after the treatment with

Table 1—Effect of Oxidizing and Reducing Agents on the Properties of Chokla Wool

Treatment	Alkali solubility %	UB solubility %	Tenacity g/tex	Elongation %
Untreated	12.9	10.8	4.2	17.5
With thioglycollic acid at 35°C at 4.5 pH for 20 hr				
concentration, 0.2 M	27.7	6.5	3.3	10.7
concentration, 1.0 M	62.3	16.1	2.4	13.7
With sodium metabisulphite at pH 5 for 30 min at 25°C and for 30 min at 90°C				
concentration, 1%	17.1	11.1	4.0	29.2
concentration, 7%	19.5	12.1	3.6	8.8
With H ₂ O ₂ (2 vol.) at pH 8 for 3 hr				
temperature, 30°C	20.2	10.0	4.4	20.8
temperature, 80°C	82.7	23.9	3.3	11.2
With H ₂ O ₂ (2 vol.) at pH 8 at 50°C				
duration, 2 hr	33.7	13.5	3.3	15.4
duration, 10 hr	67.9	17.5	3.7	17.6
With peracetic acid at 25°C for 4 hr				
concentration, 1%	79.9	15.2	4.1	21.0
concentration, 5%	84.5	29.1	2.1	20.8
With peracetic acid (conc., 2%) at 25°C				
duration, 1 hr	80.5	20.5	3.1	16.7
duration, 24 hr	88.8	23.3	2.6	14.2

Table 2—Effect of Oxidizing and Reducing Agents on the Properties of Rambouillet Wool

Treatment	Alkali solubility %	UB solubility %	Tenacity g/tex	Elongation %
Untreated	18.1	39.7	2.0	23.0
With thioglycollic acid at 35°C at 4.5 pH for 20 hr				
concentration, 0.2 M	38.1	32.7	1.5	16.2
concentration, 1.0 M	77.6	29.4	1.6	13.2
With sodium metabisulphite at pH 5 for 30 min at 25°C and for 30 min at 90°C				
concentration, 1%	19.6	26.3	1.6	19.6
concentration, 7%	25.4	38.9	1.3	13.8
With H ₂ O ₂ (2 vol.) at pH 8 for 3 hr				
temperature, 30°C	30.2	45.3	2.3	27.7
temperature, 80°C	95.1	61.9	1.9	25.2
With H ₂ O ₂ (2 vol.) at pH 8 at 50°C				
duration, 2 hr	40.6	46.1	2.1	23.7
duration, 10 hr	77.0	49.0	2.4	28.7
With peracetic acid at 25°C for 4 hr				
concentration, 1%	75.5	51.0	2.1	30.2
concentration, 5%	89.9	64.7	0.8	11.7
With peracetic acid (conc., 2%) at 25°C				
duration, 1 hr	86.0	56.4	1.4	24.7
duration, 24 hr	84.4	61.3	0.8	11.7

Table 3—Effect of Oxidizing and Reducing Agents on the Properties of Rambouillet × Chokla (50%) White Wool

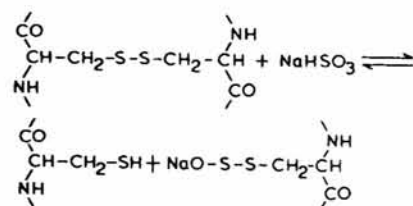
Treatment	Alkali solubility %	UB solubility %	Tenacity g/tex	Elongation %
Untreated	17.6	21.8	3.2	23.3
With thioglycollic acid at 35°C at 4.5 pH for 20 hr				
concentration, 0.2 M	39.5	23.1	1.8	12.8
concentration, 1.0 M	79.8	46.2	1.7	9.2
With sodium metabisulphite at pH 8 for 30 min at 25°C and for 30 min at 90°C				
concentration, 1%	18.3	21.1	1.8	12.6
concentration, 7%	23.1	22.1	2.7	14.4
With H ₂ O ₂ (2 vol.) at pH 8 for 3 hr				
temperature, 30°C	24.5	23.6	3.1	21.4
temperature, 80°C	92.3	43.9	2.4	18.8
With H ₂ O ₂ (2 vol.) at pH 8 at 50°C				
duration, 2 hr	34.6	31.9	2.4	21.6
duration, 10 hr	80.1	36.9	2.4	24.2
With peracetic acid at 25°C for 4 hr				
concentration, 1%	87.5	35.7	2.7	22.7
concentration, 5%	87.3	42.3	1.5	13.9
With peracetic acid (conc., 2%) at 25°C				
duration, 1 hr	87.6	37.5	2.5	14.0
duration, 24 hr	89.0	41.7	—	—

thioglycollic acid. The increase in alkali solubility and reduction in tenacity values are not very significant up to the treatment with 0.4 M thioglycollic acid, but beyond this concentration, there are marked changes in these values. Under similar conditions of treatment, the increase in alkali solubility and deterioration in strength are more pronounced in the case of Rambouillet wool as compared to Chokla wool. Initially, the UB solubility decreases to some extent showing decrease in cystine content, but at higher concentration the UB solubility increases. Increase in UB solubility on treatment with thioglycollic acid of higher concentration may be due to the disintegration of the peptide bonds. Mixed disulphides are formed as intermediates in the reaction of thioglycollic acid with disulphides. These mixed disulphides may participate in the crosslinking reactions with hydroalanine residues. It has been reported in the literature¹² that on treatment with a reducing agent, the tenacity and the percentage elongation of wool decrease. Similar results have been obtained in the present study.

Table 4—Effect of Oxidizing and Reducing Agents on the Properties of Rambouillet × Chokla (50%) Canary Coloured Wool

Treatment	Alkali solubility %	UB solubility %	Tenacity g/tex	Elongation %
Untreated	14.3	10.6	3.8	14.3
With thioglycollic acid at 30°C at 4.5 pH for 20 hr				
concentration, 0.2 M	20.2	9.0	3.3	14.4
concentration, 1.0 M	44.5	19.1	2.2	11.4
With sodium metabisulphite at pH 8 for 30 min at 25°C and for 30 min at 90°C				
concentration, 1%	13.0	9.0	3.7	14.2
concentration, 7%	14.9	9.5	3.7	15.4
With H ₂ O ₂ (2 vol.) at pH 8 for 3 hr				
temperature, 30°C	20.8	10.4	3.7	16.2
temperature, 80°C	62.2	16.3	3.1	18.2
With H ₂ O ₂ (2 vol.) at pH 8 at 50°C				
duration, 2 hr	26.0	13.8	3.3	21.2
duration, 10 hr	42.3	12.8	3.4	20.8
With peracetic acid at 25°C for 4 hr				
concentration, 1%	68.7	18.2	3.2	17.8
concentration, 5%	76.4	21.1	1.9	16.2
With peracetic acid (conc., 2%) at 25°C				
duration, 1 hr	65.8	21.8	2.8	20.0
duration, 24 hr	81.2	19.4	2.1	13.0

The main reaction of wool with sodium metabisulphite involves disulphide bond breakdown. The disulphide bond is probably not significantly attacked when a dilute solution of sodium bisulphite is used¹⁰. But under average conditions, 50% of the total cystine can be reduced by this reagent according to the equation:

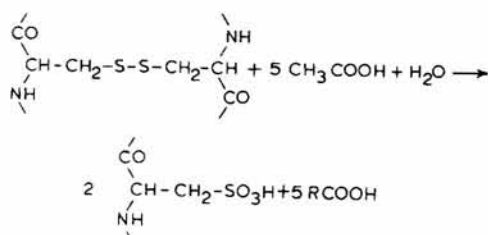


The alkali solubility increases and the tenacity values decrease to a small extent. Damage to the fibres even at higher concentration is not appreciable.

In the study with hydrogen peroxide on varying the temperature and duration of treatment, keeping all the

other variables constant, the alkali solubility and UB solubility increase and the tenacity and percentage elongation decrease as the temperature is varied from 30° to 80°C. The alkali solubility increases from 12.9 to 20.2 on treating Chokla wool with hydrogen peroxide at 30°C. As the temperature of the reaction mixture is increased from 30° to 50°C, the alkali solubility increases from 20.2 to 24.0. Beyond 50°C, there is a sharp increase in the alkali solubility without further deterioration in strength. This type of behaviour is exhibited by all varieties of wool. Increase in temperature causes more degradative effect on wool as compared to the increase in duration of treatment with hydrogen peroxide. A number of protein groups like thiol, disulphide, thioether, imidazole, phenolic, indole, etc. are susceptible to oxidative attack. In the reaction with hydrogen peroxide, several intermediate oxidative products may be formed between disulphide and sulphuric acid.

It was considered that all the disulphide groups were readily accessible and could be oxidized completely with peracetic acid. It was shown that the attack of peracetic acid is specific for the oxidation of cystine, methionine and tryptophan. In the present experiments, two different sets of treatments were given. The alkali solubility was found to be very high due to the solubilization of wool with peracetic acid; simultaneously, the tenacity falls considerably. The tenacity values decrease with increase in concentration as well as the duration of treatment. As the concentration of peracetic acid increases from 1 to 5%, the alkali solubility increases from 17.6 (untreated Ramb. × Chokla white wool) to 87.3 and tenacity decreases from 3.2 to 1.5. A similar behaviour is exhibited by other varieties of wool. The following reaction takes place. The cystine disulphides are converted to cysteic acid groups which may facilitate electrophoric separation of the peptides.



In the case of peracetic acid treatment, the UB solubility increases and the percentage elongation decreases with increase in the severity of the reaction.

Comparing the damage to different wools under the same conditions of treatment, it is observed that the damage to Chokla wool is comparatively less than the damage to Rambouillet and crossbred wools. This may be due to the difference in the diameters of fibres of the four varieties of wool. Rambouillet wool having the least average diameter (14.70 ± 0.2015) is damaged to a greater extent than Chokla (average diameter, 26.21 ± 0.61) and Ramb. × Chokla (average diameter, 21.23 ± 0.44) wools.

Conclusion

The deterioration in strength and the chemical damage are maximum in the case of thioglycolic acid and peracetic acid treated wools as compared to hydrogen peroxide and sodium metabisulphite treated wools. Chokla wool has greater capacity to withstand chemical attack as compared to Rambouillet and other crossbred wool; its strength is not affected markedly.

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