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EFFECT OF PURIFICATION TREATMENTS ON COTTON AND RAYON

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ABSTRACT

This paper is concerned with the effect on cotton, and also on cuprammonium and nitrocellulose rayons, of the Corey and Gray modification of the American Chemical Society method for the preparation of "standard cellulose" from cotton. When the fibers were subjected to successive cycles of treatments, each of which consisted in separate extractions with alcohol, ether, and a 1-percent solution of sodium hydroxide, a progressive change in the fibers took place. This was evident from the loss in weight of the fibers and the increase in the fluidity of their cuprammonium solution. Low copper numbers were obtained for all the fibers after the first extraction with alkali. Repeated treatments had no pronounced effect on the alpha-cellulose content of the cotton. Alcohol and ether had no measurable effect other than the removal of soluble material during the first cycle.

CONTENTS

I. INTRODUCTION

Some treatment for the removal of natural noncellulosic materials from cotton is necessary in preparing this fiber for certain studies relating to its use in the textile industry. A method for the removal of these impurities should be one that results in minimum damage to the fiber.

The method for the preparation of "standard" cotton cellulose of the Cellulose Committee, American Chemical Society, as modified by Corey and Gray[1] comprises the successive extractions of raw cotton with alcohol, ether, and a boiling 1-percent solution of sodium hydroxide. Although the resulting product has the characteristics associated with a product of high chemical purity, there is evidence that, aside from the removal of noncellulosic materials, the treatment probably affects certain physical properties of the fiber, as shown by changes in the fluidity of cuprammonium solutions of cellulose fibers caused by treatment with boiling dilute alkali. The measurement of the fluidity of a dispersion of cellulose in cuprammonium solution is particularly

[1] Ind. Eng. Chem. 16, 853, 1130 (1924).

useful in the early stages of degradation for detecting and following slight changes in the fiber before they are evident from direct measurements[2] of strength. Kanamaru[3] found that when cotton is immersed in boiling sodium hydroxide solutions, the viscosities of cuprammonium dispersions of the resulting products decreased rapidly in the first 7 or 8 hours of treatment, increased somewhat or changed but little in the next few hours, and then gradually decreased with further treatment. Somewhat similar results were obtained by Lewis,[4] who, however, used chemically bleached cellulose fibers in the form of rag and purified sulfite pulps.

The present work was undertaken to provide information on the changes effected by the Corey and Gray procedure on cotton and rayon textile fibers. The effects of each step in the procedure and of repetitions of the cycle of treatments were measured with respect to changes in alpha-cellulose content and copper number, tests previously applied to cotton cellulose purified by the method, and in addition by changes in weight and the apparent fluidity of their solution in cuprammonium. The cycle of treatments was repeated to determine the effect of each on the cellulose and thereby indicate the probable effect of the single cycle prescribed by the method, which cannot be measured directly.

Similar data were obtained for cotton digested in hydrochloric acid of sp gr 1.19, in the manner described by Farr and Eckerson.[5] It is recognized, however, that this treatment is for the purpose of preparing cellulose particles from cotton membranes and is not intended to produce pure cellulose in fiber form.

II. MATERIALS

The raw cotton used in these experiments was furnished by the Bureau of Agricultural Economics, United States Department of Agriculture. It was of the Acala variety, grown in 1932 at Blytheville, Ark., and was classed as Strict Middling in grade and was $^{31}/_{32}$ inch in staple length. It had been ginned and twice carded but had received no chemical treatments. It may be considered to represent high-grade natural cellulose.

The rayons were 150 denier commercial products obtained direct from the manufacturers and had received no treatments after spinning. The cuprammonium rayon may be considered to represent regenerated cellulose that has undergone the least drastic treatment in manufacture, the nitrocellulose, the most drastic treatment.[6]

III. TEST METHODS

The alpha-cellulose content was determined by the volumetric method of Launer,[7] and the copper number by the method described by Burton and Rasch.[8]

The fluidity of the cuprammonium dispersion of cellulose was measured in accordance wth the recommendations of the Fabrics

[2] J. Textile Inst. **15**, T157 (1924); **16**, T13 (1925); **17**, T145 (1926); **18**, T277 (1927); Charles Dorée, Methods of Cellulose Chemistry (Chapman & Hall, London) and literature cited therein.
[3] Cellulose Ind. (Tokyo) **7**, 149. Abstracts 33 (English) (1931).
[4] Paper Trade J. **95**, 239 (1932).
[5] Contrib. Boyce Thompson Inst. **6**, 309 (1934).
[6] J. Textile Inst. **22**, T121 (1931).
[7] J. Research NBS **18**, 333 (1937) RP979.
[8] BS J. Research **6**, 613 (1931) RP295.

Research Committee (London),[9] except that the concentration of 240 g of ammonia per liter, originally recommended by Clibbens and Geake,[10] was used. The measurements were made at 21°±0.1° C. The results are expressed as fluidity in cgs units (reciprocal poises or rhes) for 0.5-percent solutions of cotton and for 2-percent solutions of rayon.

The percentage loss in weight was calculated on the basis of the weight of the dry sample before the first treatment,[11] which was taken as 100 percent.

IV. EXTRACTION WITH ALCOHOL, ETHER, AND 1-PERCENT SOLUTION OF SODIUM HYDROXIDE

The fibers were first immersed in water at 60° C. and conditioned to constant weight in an atmosphere of 65-percent relative humidity and 21° C. Determinations of the moisture content, fluidity of their cuprammonium solution, copper number, and alpha-cellulose content were made on the conditioned, untreated material.

The three kinds of fibers were subjected five times to a cycle of treatments, each cycle being divided into three steps. Samples were analyzed at the end of each step.

In the first step, the fiber was extracted in a Soxhlet apparatus for 6 hours with alcohol, was air-dried at room temperature, immersed in water at 60° C. for about 5 minutes, and again conditioned to constant weight. The second step was similar to the first except that ether was substituted for the alcohol. In the third step, the material was extracted for 6 hours with a boiling 1-percent solution of sodium hydroxide, thoroughly washed with distilled water, steeped for 2 hours in a 1-percent solution of acetic acid at room temperature, washed with distilled water, and conditioned to constant weight.

This is the Corey and Gray procedure, except for slight modifications of the equipment used for the extractions with alkali and the immersion in water following the extractions with alcohol and ether. These immersions were intended to remove any adsorbed solvent and to permit the specimens to approach a constant weight from a wet condition.

The apparatus shown in figure 1 was used for the extractions with alkali. The fiber was placed in the cheesecloth bag, *D*, and agitated in the cylinder, *A*, which contained about 10 liters of a 1-percent solution of sodium hydroxide. This solution was freshly boiled before the material was introduced, and was kept boiling during the period of the extraction. The position and amplitude of the plunger, *C*, were adjusted so that the cellulose was immersed in liquid at all times. A boiling 1-percent solution of sodium hydroxide was siphoned continually from the cylinder, *B*, to *A* at the rate of about 2.5 liters per hour for 6 hours. The tube, *G*, which was connected to a pump, maintained a constant level in *A* by removing the old solution as rapidly as the fresh was introduced.

With the exception of the first cycle of treatments, alcohol and ether had no significant effect on either the weight of the fibers or on

[9] Report of the Fabrics Research Committee, Department of Scientific and Industrial Research. His Majesty's Stationery Office, London (1933).

[10] J. Textile Inst. **19**, T77 (1928).

[11] Calculated from the moisture content and the weight after coming to equilibrium in an atmosphere of 65-percent relative humidity at about 21° C. The moisture content was determined by heating specimens of the conditioned cotton or rayon in a drying oven at 105° to 110° C to constant weight.

their measured properties. Cotton lost 1.7 percent of its weight in the first cycle, as a result of extraction with alcohol; cuprammonium rayon, 0.1 percent; and nitrocellulose rayon, 0.0 percent. Subsequent extractions with ether had no further effect on the cotton, but the cuprammonium and nitrocellulose rayons lost 0.4 and 0.2 percent in

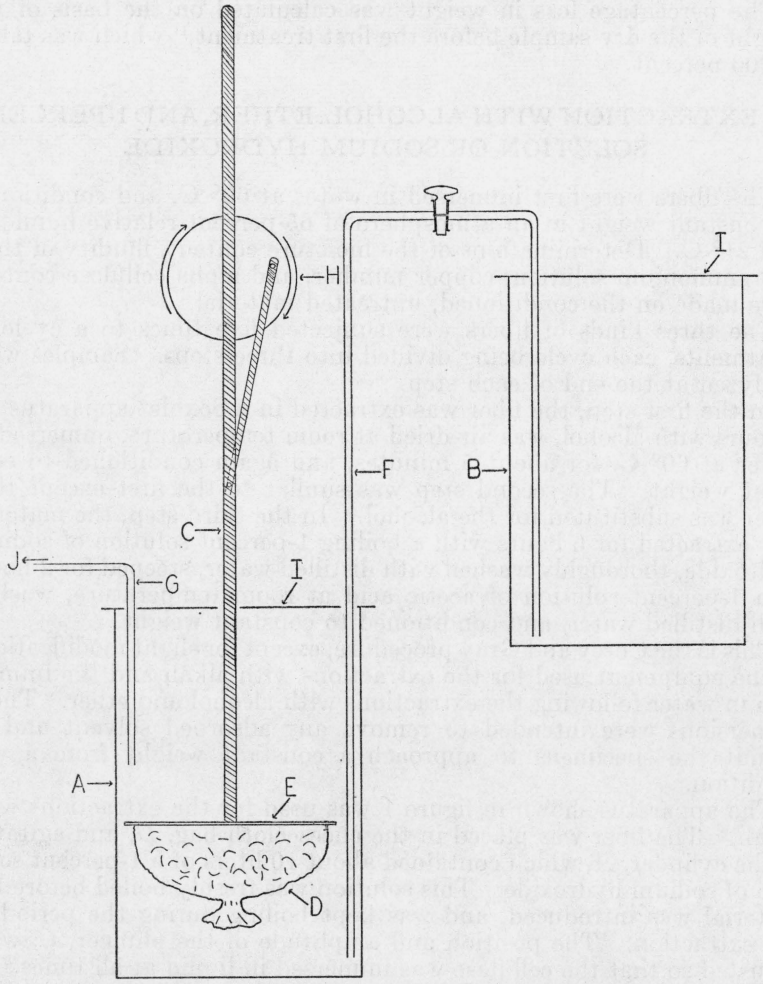

FIGURE 1.—*Apparatus for extracting fibrous materials with a sodium hydroxide solution.*

A and *B*, 16-liter Monel-metal vessels; *C*, Monel-metal plunger; *D*, cheesecloth bag; *E*, perforated disk; *F*, siphon; *G*, overflow tube; *H*, drive-wheel for plunger; *I*, Monel-metal covers; and *J*, to pump.

weight, respectively. The fluidities of dispersions in cuprammonium solutions of the untreated fibers and of the fibers after extraction with alcohol and ether were the same. Except for the losses in weight resulting from extraction with alcohol and ether in the first cycle, all the changes that occurred in a cycle of treatments may be attributed to the action of a boiling 1-percent solution of sodium hydroxide.

The over-all effects of one and five cycles of treatments on the properties of the three kinds of fibers are shown in table 1. At the end of

TABLE 1.—*Effect on cotton, cuprammonium rayon, and nitrocellulose rayon of 1 and 5 cycles of treatments, each including extraction with alcohol, ether, and hot 1-percent solution of sodium hydroxide*

Treatment	Cotton				Cuprammonium rayon			Nitrocellulose rayon		
	Fluidity (0.5% solution)	Copper number	α-Cellulose content	Loss in weight	Fluidity (2% solution)	Copper number	Loss in weight	Fluidity (2% solution)	Copper number	Loss in weight
	Rhes		*Percent*	*Percent*	*Rhes*		*Percent*	*Rhes*		*Percent*
Untreated	1.1	0.01	97.4	-------	4.3	0.5	-------	14.9	2.4	-------
One cycle	2.4	.01	95.7	4.5	5.8	.2	4.5	18.8	.5	16.9
Five cycles	14.9	.01	94.6	12.7	14.7	.1	17.7	25.6	.1	33.6

the first cycle of treatments the fluidities of the treated fibers are somewhat higher than those of the untreated. At the end of the five cycles, all three kinds of fibers have very different properties from the

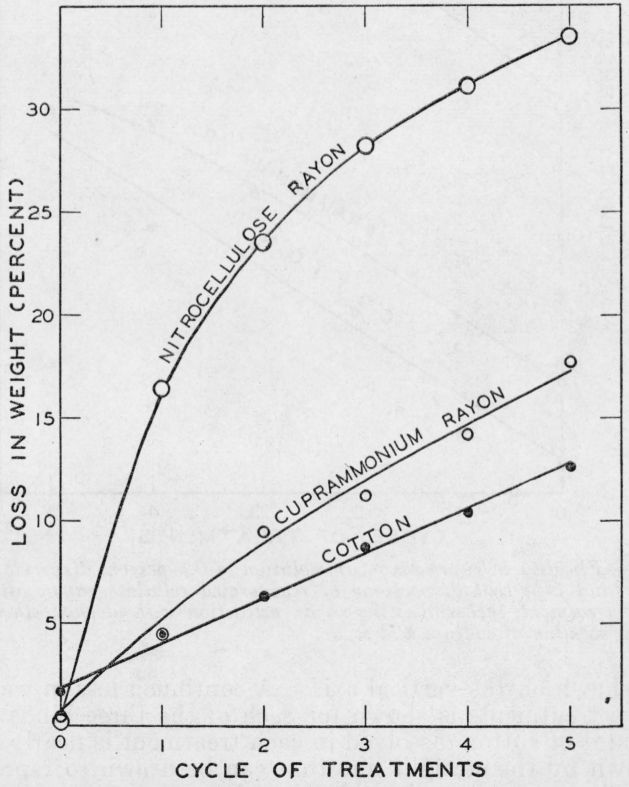

FIGURE 2.—*Loss in weight of cotton, cuprammonium rayon, and nitrocellulose rayon in repeated extractions with alcohol, ether, and 1-percent solution of sodium hydroxide.*

The values given for the 0-cycle represent the loss after the first extraction with alcohol and ether, but before the first extraction with 1-percent solution of sodium hydroxide. The other values represent the cumulative loss at the end of each cycle of treatment.

untreated fibers. It was also noted that the treated fibers were weaker than the untreated.

Low copper numbers were found for all the fibers after the first extraction with alkali, for the reducing substances in cellulose responsible for its copper number are removed by boiling with alkali.[12]

The values for the alpha-cellulose content of the cotton after one and five cycles are nearly the same, whereas the fluidities are very different.

The loss in weight at the end of each cycle is shown in figure 2, in which the combined effect of the first extractions with alcohol and

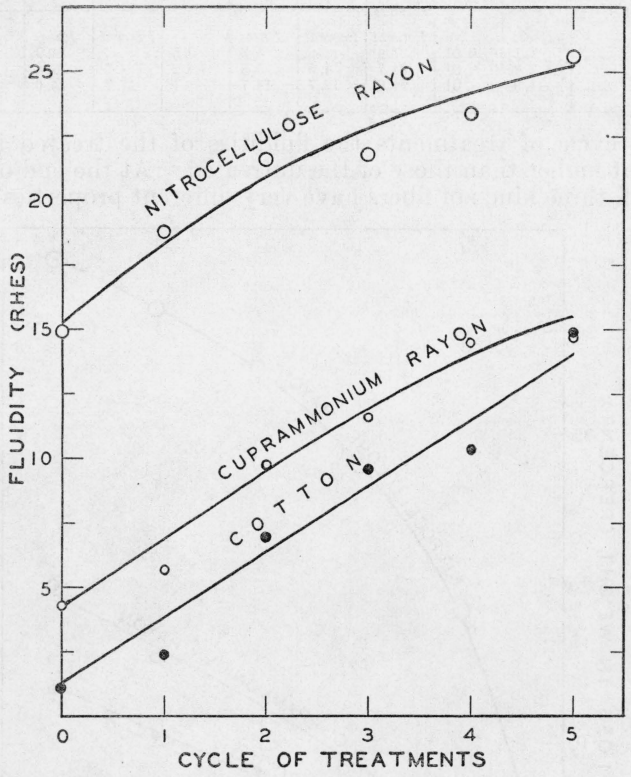

FIGURE 3.—*Fluidity in cuprammonium solution of 0.5-percent dispersions of cotton cellulose and 2-percent dispersions of regenerated cellulose rayon after repeated cycles of treatment, each consisting in an extraction with alcohol, ether, and with 1-percent solution of sodium hydroxide.*

ether is shown on the vertical axis. A continued loss in weight with successive treatments is shown for each of the three kinds of fibers. The amount of cotton dissolved in each treatment is nearly the same as is shown by the straight line that can be drawn to represent the losses. The rayons, particularly the nitrocellulose, lost rapidly in weight during the first cycle, and less rapidly thereafter.

The fluidities of dispersions of each of the three kinds of fibers in cuprammonium solution at the end of each of the cycles are shown in

[12] J. Textile Inst. **19**, T349 (1928).

figure 3. Like the loss in weight, the fluidity increased about an equal amount for each cycle of treatment. There is indication that the fluidity of the cuprammonium rayon, and particularly of the nitrocellulose rayon, is increased more rapidly in the first cycles of treatments than in the last.

Since the loss in weight and increase in fluidity of the cotton are about the same in all cycles of treatment, there does not appear to be any "optimum" time of boiling for the preparation of a "standard" cotton fiber, and there is no indication that the properties would become constant with further treatment.

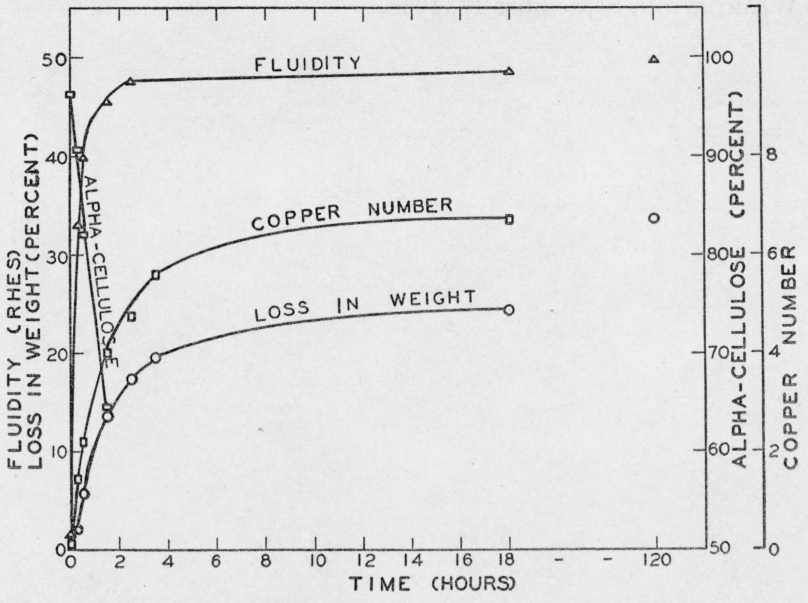

FIGURE 4.—*Changes in weight, fluidity in cuprammonium solution, copper number, and alpha-cellulose content of cotton cellulose when digested in a hydrochloric acid solution of specific gravity 1.19.*

V. DIGESTION WITH HYDROCHLORIC ACID

Ten-gram samples of cotton that had previously been subjected to one complete cycle of extractions with alcohol, ether, and dilute alkali, were placed with 250-ml portions of hydrochloric acid (sp gr 1.19) in each of seven 500-ml Pyrex glass-stoppered bottles, which were then kept at a temperature of 21° ±2° C. At intervals of ¼, ½, 1½, 2½, 3½, 18, and 120 hours, the contents of a bottle were centrifuged, the residue thoroughly washed with distilled water, dried to constant weight, and specimens tested.

The residues varied in physical form from weak fibers for the shorter periods of treatment to a powdery mass for the longer treatments. The change was first apparent in the fibers treated for 2½ hours. These fibers were brittle and could readily be reduced to a powder. The dry residues from the 18- and 120-hour treatments were tough, horny masses that were difficult to pulverize.

Figure 4 shows the effects of digestion in acid on the weight of the cotton, the fluidity of its cuprammonium solution, its copper number, and its alpha-cellulose content. A very rapid loss in weight, an increase in fluidity and in copper number, and a decrease in alpha-cellulose content occurred during the first 3½ hours. The subsequent changes took place more slowly. The products differ from those obtained with the alkali extractions in having higher copper numbers than the original fiber and much higher fluidity for the same loss in weight. They are, of course, no longer to be considered textile fibers because of the loss of fiber structure.

WASHINGTON, September 17, 1938.