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**A STUDY OF THE RELATIONSHIPS BETWEEN THE
CHEMICAL CONSTITUENTS AND THE RATE AND DEGREE
OF ACETYLATION OF DIFFERENT VARIETIES OF COTTON FIBERS**

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**A STUDY OF THE RELATIONSHIPS BETWEEN THE
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ABSTRACT

The purpose of this investigation was to determine whether or not there is any relationship between the chemical constituents and the rate and degree of acetylation of different varieties of cotton fibers.

Three varieties of scoured and unscoured cotton fibers were chosen to represent a wide range of physical properties and variables such as maturity, fiber fineness, rate and degree of acetylation.

Four different analyses were carried out on the scoured and unscoured cotton fibers.

1. Ash analyses
2. Solvent extraction
3. Alpha cellulose determinations
4. X-ray diffraction pattern examinations

In the ash analysis the per cent ash was first determined, then subjected to spectrographic analysis and the elements determined qualitatively.

In the solvent extraction analyses, a Soxhlet apparatus was used to extract the cotton fibers with chloroform, benzene, ethyl alcohol, water, and glacial acetic acid

respectively. Ammonium oxalate extractions were performed by the reflux method. The time of extraction was chosen to be four hours for each solvent used.

A recent method of extraction was used to determine the exact amount of wax in different varieties of unscoured cotton fibers.

The pattern of the crystalline and amorphous regions were studied with the use of X-ray machine.

From the results of the experimental work, it was found that

1. The ash content and ash constituents had no great effect on the rate and degree of acetylation.
2. Solvent extractable materials had no great effect on the rate and degree of acetylation.
3. Alpha cellulose content had no great effect on the rate and degree of acetylation.
4. As far as the crystalline and amorphous celluloses are concerned, no difference had been found qualitatively between the cotton fibers whether scoured or unscoured.
5. The analysis of scoured cotton fibers gave percentages of the chemical constituents - excluding alpha cellulose - less than the unscoured samples due to the fact that most of the chemical impurities were removed by scouring.

Nevertheless, it was found that the ratios of the same chemical constituent within the three kinds of unscoured cotton fibers were nearly the same compared with those of the scoured cotton fibers.

This means that scouring, which reduced the differences in the rate and degree of acetylation of the cotton fibers, may have caused some physical changes in the fiber structure.

During scouring the fiber is made up more porous, and the surface area of pure cellulose attacked by acetylation is increased to a certain extent due to the breakdown of the chemical impurities but not necessarily removing them completely. This increase is more pronounced in the mature fibers than in the immature fibers.

The results of the study show that the degree of acetylation of cotton fibers is affected by the degree of scouring and the degree of maturity of the fibers. The degree of acetylation of cotton fibers is also affected by the degree of maturity of the fibers.

Summary of the Study.—During scouring, acetylation and maturity of cotton fibers are affected. The degree of acetylation of cotton fibers is also affected by the degree of maturity of the fibers.

CHAPTER I

INTRODUCTION

Partial acetylation of cotton fibers is an important method of modifying cotton cellulose by replacing some hydroxyl groups by acetyl groups. The acetylated cotton has the same appearance of natural cotton but acquires new properties such as resistance to mildew, rotting and heat. Acetylation also reduces the hygroscopicity of cotton fibers, increases electrical resistance, and reduces the affinity to many direct dyes. (1)

Statement of the Problem.--The purpose of this investigation was to determine the relationship between the chemical constituents and the rate and degree of acetylation of different varieties of cotton fibers.

Importance of the Study.--Since partial acetylation produces desirable properties on cotton fibers such as resistance to heat, mildew and rotting, many researches are being undertaken in order to produce this fiber on commercial scales. One of the many problems involving partial acetylation is that different varieties of cotton fibers give different rates and degrees of acetylation when subjected to the same conditions during an acetylation process. (2)

This means, however, that much research work should be done on the chemical and physical properties of cotton fibers.

It has been noted that when cotton fibers are subjected to scouring treatments, the rate and degree of acetylation are brought more closely together and the differences are greatly minimized. (3)

Therefore, a study of the chemical constituents of cotton fibers and their relationships to the rate and degree of acetylation may be of some help in giving the clue as to what causes their differences.

Method of Approach.--These varieties of scoured and unscoured cotton fibers were chosen to represent a wide range of physical properties and variables such as maturity, fiber fineness, tensile strength, and rate and degree of acetylation.

Four different analyses were carried out on scoured and unscoured cotton fibers.

1. Ash analysis of all fibers.
2. Solvent extraction using chloroform, benzene, ethyl alcohol, water, glacial acetic acid and ammonium oxalate solution.
3. Alpha cellulose content determination.
4. X-ray study of all fibers.

The results of these analyses were then studied in relation to the rate and degree of acetylation and with the maturity of the different varieties of cotton fibers, both scoured and unscoured.

CHAPTER II

REVIEW OF THE LITERATURE

Origin of Cotton Fiber.--The English word "cotton" is derived from the Arabic Katan or (Qutn, Kuteen), though it is claimed this name originally denoted flax. (4)

A knowledge of the origin and development of the cotton fiber is an aid in understanding its composition. Shortly after the cotton flower opens, the epidermal cells on the young seeds begin to grow and elongate, forming long, tube-like cells with an ultimate length 1000-4000 times cross-sectional diameter. In about 18 days the cell wall starts to thicken and elongation practically stops. After the ball opens, in 50-60 days after flowering, the fiber is a dry, ribbon-like cell with a thick wall of cellulose. (5)

Cotton requires from 6-7 months of warm or hot weather, sunshine and moisture.

The long fine varieties take longer to mature. The mature fiber is picked as soon as possible after the balls open to minimize deterioration of the fiber by light and moisture. (6)

There are three general types of cotton based on fiber length, fiber fineness, and geographical regions.

Type (1) Long, fine, strong fibers 1 - 2.5 inches staple

Type (2) Intermediate of somewhat coarser

1/2 - 15/16 inches staple.

Type (3) Short coarse fiber 3/8 - 1.0 inch staple. (7)

Physical Properties of Cotton.--Raw cotton fiber is a flattened tube, long twisted ribbon with slightly thickened edges.

The number of twists or half convolutions in raw cotton fibers varies widely. Immature fibers are practically nonconvoluted, while mature fibers of the same variety may be highly convoluted. Thin walled fibers are often called immature fibers.

Cotton fibers are composed of four distinct parts:

1. Cuticle
2. Primary wall
3. Secondary wall
4. Lumen

Cotton cannot be considered a uniform material. Each fiber must be regarded as an individual with its own characteristic length, strength, fineness, etc. For this reason sampling methods are extremely important. (8)

The cotton fiber is somewhat porous and consequently exhibits capillary effects to a high degree. The fibrils themselves are probably dense as a result of the crystalline nature of cellulose and are also nonporous.

The crystalline part of the structure may constitute 90 per cent or more of the fiber. (9)

Chemical Properties of Cotton.--The chief constituent of cotton fiber is cellulose ranging from 88 - 96 per cent based on dry weight.

The variation in cellulose content of raw cotton fiber is due to soil, climate, variety of cotton, and other factors which prematurely interrupt its growth. Low cellulose content usually indicates a high proportion of thin walled immature fibers which contain a high proportion of non-cellulosic substances. Diverse values may be due also to uncertainty in the analytical methods for the determination of cellulose. (10)

Cellulose $\text{C}_6\text{H}_{10}\text{O}_5$ is a colloidal substance so that its actual formula is $(\text{C}_6\text{H}_{10}\text{O}_5)_n$, each unit having three hydroxyl groups. (11)

Cellulose may be considered a straight chain of anhydro beta-glucose units whose molecular weight ranges from a very low value to 450,000 or more which also might depend upon the source and previous history of the sample involved. (12)

Alpha, Beta, and Gamma Celluloses, which are terms introduced by Cross and Bevan (1904) and by Jentgen (1911), refer to the fractionation of a cellulose by the action of sodium hydroxide solution of mercerizing strength. The fraction which remains undissolved is the alpha cellulose, the beta and gamma celluloses being dissolved. Of these, the portion which is reprecipitated on acidification is called beta cellulose, while the gamma cellulose remains in solution.

The alpha cellulose is of somewhat the same order of resistance as normal cotton cellulose, while the beta fraction, insoluble in water, is in a less dispersed condition than the gamma fraction which remains in solution. The estimation of alpha cellulose has now become a valuable method for analyzing all types of wood pulp and other technical celluloses. The values of beta and gamma fractions have also acquired significance, e.g., in the manufacture of rayon and as an indication of bleaching treatment in pulps. Their proportions are calculated for analytical purposes as cellulose, but they are not necessarily composed of cellulose at all. (13)

The cellulose chains of cotton fibers are densely packed and regularly oriented. In some regions the chains have reached such a high degree of order that they form crystalline regions which diffract X-rays in the same manner as macrocrystals do and which show numerous other criteria of a high degree of order.

These crystallites are smaller than the total length of the average cellulose molecule. This means that the same chain molecule may pass through several crystalline regions.

Between these regions the chain molecule will be in a so-called "amorphous region." It must be understood, however, that amorphous regions are not necessarily all of the same degree of order. (14)

A low degree of crystallinity is proportional with increased extensibility, increased moisture regain, decreased density, and increased chemical reactivity.

It is precisely upon the degree of crystallinity that the chemical reactivity depends. It is the amorphous region of the cellulose fiber which is the reactive region.

The terms "accessible" and "nonaccessible" regions are usually more correct than amorphous and crystalline in a discussion of chemical reactions. (15)

There are two reasons for making such a distinction. First, not only are the amorphous regions accessible, but the crystalline surfaces are also. The second is that the spaces between chains are larger in some portions of the amorphous regions than in others. In some cases there will not be room enough for very large molecules to enter, so that certain amorphous regions will not be accessible to molecules larger than a certain size. One corollary to this is that accessibility to small particles, such as water or hydrogen ions, will be greater than accessibility to large molecules, such as acetic anhydride.

A chemical method which has been studied in connection with crystallinity is the periodic acid oxidation. The accessibility to the reagent is not proportional with the degree of crystallinity. The nonaccessibility is higher, however, than the crystallinity as determined by X-ray methods. (16)

From the chemical point of view the crystallized and uncrystallized substances are identical.

It is found that beside very highly organized and completely unorganized regions there are other regions having an intermediate state of organization. (17)

In conformity with a paper by Hess and co-workers, cellulose fibers can be transformed into approximately wholly amorphous products by grinding in a vibrating ball mill, and these products partly recrystallize on heating with water. (18)

X-ray diffraction analysis as a research tool for structure determinations has two closely related fields of application. The first is concerned with the form, properties, and three-dimensional arrangement of atoms and molecules within a single crystal; the second is concerned with the form, arrangement, relative amount, and properties of crystalline aggregates in a polycrystalline material.

From the fact that cellulose fibers give continuous diffraction rings, a second important deduction may be made: the crystallinity of the fiber is discontinuous. In other words, a cellulose fiber is not a single crystal; it is a crystalline aggregate.

The X-ray diffraction patterns may be described and differentiated one from the other in terms of the following characteristics:

- A. Number of diffraction rings
- B. Diameter of each ring
- C. Concentration of rings into two or more areas (orientation)
- D. Width of each ring
- E. General scattering or background; amorphous pattern

The number, diameter, and relative intensity of the diffraction rings are associated with the crystalline structure, while the orientation and width of each diffraction ring and the general scattering are more closely associated with the fiber or membrane structure. It is from these six characteristics that the X-ray information regarding the structure and behavior of cellulose fibers must be obtained. (19)

Cellulose Fiber Reactions.--Many of the important chemical reactions of cellulose have a pronounced influence on the physical and chemical properties of the fiber, yet they scarcely affect the X-ray diagram. This indicates that the reaction is intercrystalline in nature and does not change the internal structure of the crystallite.

Other reagents may completely destroy the crystalline pattern, as, for example, when cellulose is oxidized with periodic acid. No new lines are produced, but the original crystalline pattern becomes more diffuse as oxidation proceeds.

With alkaline hydroxides, as a general rule, greater swelling is produced at lower temperatures. At higher temperatures only partial swelling is obtained even with a 20 or 30 per cent solution. (20)

When cellulose is brought into contact with various reagents, there are several possible effects depending upon the nature of the reagent. It is possible that the reagent may merely penetrate the macrocapillary structure and relax the forces holding the microfibrils together so as to bring about a very limited swelling, or dispersion, of the cellulose fiber. Other reagents may be able to penetrate into the microcapillary spaces, thus causing relaxation of the forces holding the chain bundles and a deeper-seated swelling.

Should the reagent be capable of penetrating between the chains of cellulose bundles themselves and breaking the secondary valences, a very marked swelling may occur which might extend to complete dispersion. ~~therefore such reactions~~

In all cases of penetration of the cellulose structure, it is obvious that, with certain reagents, reaction with available hydroxyl groups might take place, or such reactions as hydrolysis or oxidation might occur. Where penetration is limited to the macrocapillary structure, any reaction would be limited to the chains forming the surface of the microfibril. If penetration between the chain bundles takes place, the reagent could bring about a more complete reaction since it could then react with the chains forming the surface of the

chain bundles. When the reagent is capable of penetrating between the chains themselves, the reaction should proceed to completion on all the separate chains of the cellulose fiber. (21)

The reactions of cellulose may be roughly classified into three main divisions:

1. Those which result in a swelling or dispersion of the chains without change in chemical nature.
2. Those which result in a change in the average length of the chains.
3. Those which bring about a complete change in the hydroxyl groups into esters or other groups.

It should be recognized that no reaction belongs entirely to any one of the above groups but that all reactions partake, to some extent, of all three classes.

In the third division, the type of reaction involved is that of a normal organic alcohol and therefore such reactions depend upon the alcoholic nature of the hydroxyl groups of cellulose. Cellulose should then be capable of undergoing esterification, etherification, or xanthation. (22)

However, in the case of cellulose, all of the hydroxyl groups are not readily available for reactions, as in the case of ordinary alcohols, since many of them are bound by secondary valences to other hydroxyl groups of other chains.

Any typical reaction of cellulose can therefore only proceed to a degree, and at a rate, depending upon the availability of the hydroxyl groups. Any reagent not able to penetrate between the separate chains is not able to bring about a complete conversion but is limited by the degree of penetration. (23)

Partial Chemical Derivatives of Cotton.---The reactions of cellulose, as stated above, are usually those that take place at hydroxyl groups, such as formation of esters and ethers. Hence, the new properties obtained may be due to blocking some of the hydroxyl groups, thus interfering with the normal absorption capacity of cotton, or to the introduction of new substituent groups.

Acetylated cottons are available commercially containing 30 and 60 per cent of combined acetic acid. At about 30 per cent acetylation all amorphous material and crystal surfaces are believed to be acetylated while beyond this point the reaction is believed to extend into the crystalline cellulose. (24)

Impurities.---The natural impurities in the raw cotton consist chiefly of pectic matter, coloring matter, cotton wax, albuminous matter, and inorganic salts. There is also a small amount of oil which appears to be identical with cotton seed oil, and is probably obtained from the seed to which the hair was attached. The albuminous or nitrogenous matter in cotton

is very small and probably consists of protoplasmic residue. Purified and bleached cotton cellulose contains no nitrogen. (25)

Cotton Wax.---The crude wax material extracted from raw cotton fibers by chloroform, carbon tetrachloride, or benzene is called wax. It may be classed with the plant cuticle waxes. Presumably most of the wax is located in the cuticle which lies on the outside of the fiber, but the difficulty of its removal suggests that at least part is located inside the fiber or bound to the cellulose. (26)

The amount of wax in native cotton is usually 0.5 per cent and varies according to the type of cotton. The wax appears to serve as a protective layer and resists wetting; hence, in the purification of cotton it is necessary to remove the wax either by extraction with a solvent or more commonly by boiling with dilute alkali. (27)

According to Guthrie, the usual alkaline kier boil to which raw cotton fabric is subjected prior to bleaching and dyeing does not remove all the wax. (28)

Among a group of 62 essentially unweathered fiber samples from American Upland Cotton plants of different inherent and environmental background, per cent wax was found to be rather closely proportional to surface area per unit weight of fiber as determined by the air flow method of Sullivan and Hertel. (29) The weight of wax per unit of fiber surface was thus a relatively constant quantity, although not an absolutely constant one, among these samples.

In general, a relationship exists between percentage of wax in cotton fibers and fiber maturity, and it is possible quantitatively to explain the relationship by relating the percentage of wax to the specific surface of the fiber (surface area per unit weight) or the reciprocal wax percentage to the amount of cell wall material per unit surface (average maturity). (30)

Pectins.--Pectins, or materials closely related to them, are often found with cellulose. Pectin in plants is not a single substance but a complex series of carbohydrate derivatives containing galacturonic acid, associated with arabinose and galactose. It may exist either as the free acid, or in the form of metal salt, or as the methyl ester. Pectic substances are further divided into protopectin, which is water-insoluble in the plant but is rendered soluble by treatment with water, and salt solution.

Pectic acid may be obtained by hydrolysis of pectin, resulting in the complete removal of the methyl ester group. In the plant cell wall pectin exists in the form of an insoluble calcium salt, or the salts of other metals. (31)

Protein.--The protein occurs chiefly in the central cavity or lumen of the fiber. The nitrogen is readily removed from cotton by bleaching.

The total protein content of American cotton is 1.3 per cent and Egyptian cotton is 1.9 per cent. (32)

Pigment.--The coloring matter in cotton is thought to consist of two organic pigments, one of which is readily soluble in alcohol and the other is dissolved only by boiling alcohol. The pigment matter is found chiefly in the lumen, but is also in association with the cellulose itself.

The coloring matter of cotton is not immediately soluble in alkali, as air and light or chlorine are necessary for its complete removal. (33)

Ash Constituents.--The approximate composition of a typical cotton ash is as follows:

K_2O	34 per cent
CaO	11 per cent
MgO	6 per cent
Na_2O	7 per cent
Fe_2O_3	2 per cent
Al_2O_3	2 per cent
SiO_2	5 per cent
$S O_3$	4 per cent
P_2O_5	5 per cent
Cl	4 per cent
CO_2	20 per cent
Cu, Mn	Trace

Recorded variations may be due to the presence of sand, soil and dust in the cotton, to faulty methods of analysis, and to variations arising from soil, climate, and variety of cotton. (34)

Effect of Various Solvents on Cotton Fibers

Water.---Raw cotton loses 1.4 - 4.2 per cent of its dry weight when extracted with water at 20° C. and somewhat larger amounts at higher temperatures.

The amounts of ash constituents, nitrogenous substances and sugars extracted do not account for all of the weight loss of raw cotton when it is extracted with water. This indicates that substances of an unknown nature are present in the water extract.

Other solvents like ethyl alcohol, chloroform, carbon tetrachloride, etc., have different effects from water. (35)

After extraction with alcohol, cotton yarns, when subjected to distilled water extraction, yielded a large amount of extract.

In the dry state the extracts are of brown color, similar in appearance to the alcoholic extracts. They are not so hygroscopic as the latter, nor do they reduce Fehling's solution so readily. Like the alcoholic extracts, they are faintly acid to litmus. The proportion of mineral matter was found to be even greater than in the alcoholic extract. (36)

Alcohol.---After extracting raw cotton fiber with benzene then subjected to extraction with alcohol, the extracts consisted of amorphous brown very hygroscopic substances, which exert

a powerful reducing action on Fehling's solution. They are faintly acid to litmus and contain high percentage of mineral matter. (37)

Chloroform and Benzene.--Hot chloroform is used for the extraction of the fat, wax, and resinous matter.

The properties of the extracts obtained with hot benzene show somewhat difference from chloroform extract. Chloroform is recommended for wax determination. (38)

Ammonium Oxalate Solution.--Hot ammonium oxalate or citrate solution is used for the extractions of pectin from the cotton fiber. (39)

Ammonium oxalate solution extracts nearly all pectic substances which form most of the impurities in cotton fibers.

Glacial Acetic Acid.--It is considered that glacial acetic acid itself is a swelling agent for cellulose. On acetylation in the presence of benzene it was found that cotton which had been preswollen with 200 per cent its weight in glacial acetic acid reacted about ten times faster than without pre-treatment. (40)

Organic acids, such as acetic acid, by virtue of their low ionization, have much less action on cotton than inorganic acids, but acetic acid at 0.1N, or about 0.6 per cent, caused five per cent tendering in 15 minutes at 212°F. (41)

The Effect of Scouring on Raw Cotton Fibers.--The action of boiling sodium hydroxide solution serves to saponify the waxes and fats. By using some detergents the impurities will be emulsified and maintained in a dispersed state during the scouring and washing. (42)

Acetylation.--An examination of the cellulose formula shows three hydroxyl groups free to react in each glucose residue. By virtue of their positions in the residue and their primary and secondary natures, it might be expected that they would show significant differences in reactivity. (43)

However, in acetylation reactions it appears that there is no difference in the functional value of the hydroxyl groups, but rather that their physical accessibility in the fibrous structure determines their preference for reaction. (44)

CHAPTER III

INSTRUMENTATION AND EQUIPMENT

Soxhlet Extraction Apparatus.

Reflux Extraction Apparatus.

ARL - Dittert 1.5 Meter Grating Spectrograph.

Forced Circulation, Electrically Heated Oven.

Muffle Furnace, "Multiple Unit", Type 62.

X-Ray Machine, North American Philips Co., Inc., New York, N.Y.

Type 41000.

Acetylation Machine.--Morton one-pound package Dyeing Machine
modified with cooling devices for acetylation.

Analytical Apparatus.--Standard laboratory equipment such as
platinum dishes, Erlenmeyer flasks, beakers, pipettes,
weighing bottles, separatory funnels, desiccators,
water bath, and analytical balances were used.

List of Reagents Used.--

Chloroform.

Benzene.

Ethyl Alcohol, 95%.

Ammonium Oxalate Solution 0.5%.

Glacial Acetic Acid.

Sodium Hydroxide Solution 17.5%.

Duponal RA 1%.

Tetrasodium Pyrophosphate 1.5%.

Acetic Anhydride.

Perchloric Acid 60%.

Diphenyl Fast Red 5BL Supra I (Geigy).

Chlorantine Fast Green BLL (Ciba).

Standard Chemical Laboratory Reagents.

CHAPTER IV

EXPERIMENTAL PROCEDURE

Three varieties of cotton fibers -- Memphis, Empire Bale 92, and Lockett 140 -- were selected for analyses. These were chosen to represent a wide range of physical properties and behavior toward acetylation.

The moisture content was determined prior to analysis.

Maturity.--The per cent maturity of each variety of raw cotton fibers was determined by the Southern Regional Research Laboratory by the caustic swelling method. The results are shown in Tables 2 and 5. Another method to determine maturity is the Differential Dye Test method. In this method, mature fibers are dyed a red color while the immature fibers acquire a greyish-green to distinct green color.

Scouring.--A one-pound package dyeing machine subsequently used for acetylation was used for scouring all cotton samples. Seventy-five grams of each variety of the cotton fibers were placed in separate layers in the cylindrical reaction chamber of the machine. Each layer was separated from adjacent layers by circular stainless steel screens which allowed free passage of the scouring liquor, but prevented admixture of the different cottons. The cottons were scoured using 1 per cent Duponol RA and 1.5 per cent tetrasodium pyrophosphate at 212°F. for thirty minutes. (45)

Acetylation.---The raw and scoured cotton fibers were acetylated in the one-pound package dyeing machine. (46) The cotton fibers were first presoaked in glacial acetic acid at room temperature, then acetylated by using a mixture of three parts of glacial acetic acid, one part of acetic anhydride, and 0.15 per cent of perchloric acid catalyst.

After the reaction had continued for the specified length of time, the acetylating reagents were drained, and the samples were then washed in water and dilute ammonium hydroxide until neutral. These samples were then dried and brought to standard conditions at 65 per cent relative humidity and 70°F.

The acetyl contents of scoured and unscoured cottons were determined. (47) The results are shown in Table 1.

Ash Determination.---An exact weight of dry cotton fiber -- between 5 - 10 grams -- was placed in a platinum dish and ignited gradually in an electrically heated muffle furnace. The ashing was completed by heating in the furnace to a dull red heat. Finally the dish and contents were cooled in a desiccator and weighed. The results were calculated on the percentage of the dry weight of the cotton used. (48)

Analysis of Ash.---The ash samples were dissolved in 0.1N HCl and the solution of each sample was evaporated on pure copper electrodes. The sample was then excited by the use of a high voltage spark. The spectra, which were produced by

a 1.5 meter grating spectrograph, were photographed on 35 mm. film. These films were then examined for the lines of the elements. (49) From these lines the elements found in the ash were reported as trace, weak, fair, or strong.

Extraction Analyses

Soxhlet Extraction.--An exact weight of about five grams of the dry cotton sample was placed in a thimble in the extraction tube, and the solvent to be used was placed in the flask. On heating, the vaporized solvent passed up through the vapor tube and was condensed to a liquid in the condenser from which it dripped down on the sample in the extraction tube. When enough solvent had condensed and fallen on the sample to fill the extraction tube up to the top of the siphon, it siphoned over into the flask and the cycle repeated again. While the solvent was in contact with the sample, it dissolved some of the impurities which passed down into the flask. Another lot of pure solvent then condensed and removed more impurities. (50)

The kind and amount of impurity extracted depended on the kind of solvent used. By this method the solvents used were water, ethyl alcohol, benzene, chloroform, and glacial acetic acid.

The time for extraction was chosen to be four hours, at the end of which the contents of the flask were removed and the solution was evaporated to dryness, then placed in

the electrically heated oven at a temperature of 200-210°F. for two hours to insure complete drying. Finally the flask, which had been weighed before extraction, and the impurities were cooled in a desiccator and weighed. The result was calculated to percentage of the dry weight of the cotton used.

Alcohol Extraction Method.--(51) An exact weight of around five grams of the cotton sample was placed in a coarse thimble in a large Soxhlet extractor. About 250 ml. of 95 per cent ethyl alcohol was added to the extraction flask and the temperature was adjusted until the liquid siphoned over at 3 - 4 minute intervals. The extraction was continued for six hours at the end of which the alcoholic extract was transferred to a 500 ml. separatory funnel. The Soxhlet flask was washed with several 5 ml. portions of hot 95 per cent ethyl alcohol and additional alcohol was added to make the final volume 100 ml. One hundred ml. of pure chloroform was added in the separatory funnel and the solution mixed thoroughly. Seventy-five ml. of distilled water was added to the alcohol-chloroform solution and agitated somewhat to cause mixing and separation of two distinct layers, the chloroform layer being at the bottom. The two layers were allowed to stand overnight for complete separation. The chloroform layer was drawn off and set aside in a 250 ml. Erlenmeyer flask. A fresh 50 ml. of chloroform was added to the separatory funnel, agitated gently, and allowed to stand overnight after which the chloroform was

drawn off again. The chloroform solution was washed once with distilled water in the separatory funnel. When separation was completed the chloroform layer was drawn off into an Erlenmeyer flask. Two 5 ml. portions of fresh chloroform were successively added to the separatory funnel, shaken well, allowed to separate, and drawn off each in turn into the Erlenmeyer flask containing the main body of chloroform solution. The chloroform was removed from the flask by evaporating in tared 100 ml. beakers on a steam bath. After drying, the wax residue was cooled in a desiccator and weighed. The weight was calculated as the percentage of the dry weight of the original cotton used.

Reflux Extraction.---In this method a reflux apparatus was used instead of Soxhlet apparatus. The cotton sample was placed in the flask with a sufficient amount of 0.5 per cent ammonium oxalate solution and refluxed for four hours at the boil. The cotton sample was then taken out of the flask and washed thoroughly with cold distilled water, squeezed, dried in the oven, cooled in a desiccator, and weighed. The weight lost was then calculated to the percentage of the dry weight of the original cotton used.

Alpha Cellulose Determination.---An exact weight of about three grams of each cotton fiber under investigation was covered at 20°C. with 35 ml. of carbon-dioxide free sodium hydroxide

solution made up to contain 17.5 grams of the base in 100 grams of solution. (52) A total of 40 ml. more of the alkali was added in 10 ml. volumes over a period of ten minutes, during which time the mass was occasionally agitated with a glass rod. After a total mercerization time of 45 minutes, 75 ml. of distilled water was mixed thoroughly into the mass, which was promptly filtered through a Gooch crucible and washed with 750 ml. of distilled water at 25°C. The mat of alpha cellulose on the Gooch crucible was then soaked for ten minutes in 10 per cent acetic acid to remove absorbed alkali and was finally washed quite free from acid with distilled water. The sample was then dried in the oven for overnight at a temperature of exactly 105°C. After cooling in a desiccator and weighing, the weight was calculated to percentage of the dry weight of the original cotton fiber.

X-Ray Diffraction Pattern.--In these studies a flat-plate diffraction camera was used. (53) A copper anode was used and the X-ray machine was operated at 40 kilovolts and 20 milliamperes. The collimation was provided by two pinholes, the second being 0.025 inches in diameter. A bundle of cotton fibers of the order of 2 millimeters in diameter was placed over the second pinhole. The photographic plate was placed approximately 5 centimeters from the specimen. The experimental arrangement was kept fixed for all samples. Exposure time for each sample was approximately two hours. The developing procedure for the various films was the same.

CHAPTER V

RESULTS AND DISCUSSION OF RESULTS

Each chemical analysis was done in duplicate. The individual result of each trial and the average are shown in Tables 7, 8, and 9 of the Appendix.

The varieties of cotton fibers used for wax, pectin, ash, etc., analyses were Memphis, Empire Bale 92, and Lockett 140. The other cottons, Acala 4-42 (Greenville, Texas), Acala 5675 (Florence, S. C.), Coker 100W (Weslaco, Texas), Coker 100W (Florence, S. C.), Sea Island (St. Vincent), and Sealand 1 47-295 were used for the exact determination of wax by the alcohol extraction method.

The summary of the physical and chemical analyses of scoured and unscoured cotton fibers under investigation are shown in Tables 1 through 6 on the following pages.

Effect of Scouring on Acetylation.--The results of acetylation are presented in Table 1, page 28. (54)

In Table 1 it is also shown that scouring prior to acetylation tends to reduce the differences in the rate and degree of acetylation of the different varieties of cottons. An examination of the 60-minute acetylation of the unscoured cottons reveals a variation in acetyl content much higher than that of scoured samples. This increase in the rate and hence in the degree of acetylation was true for all scoured cottons under investigation.

Table 1. The Effect of Scouring on the Rate and Degree of Acetylation of Various Cottons

Cotton	Per cent Acetyl after acetylation at 64°F. for:		
	30 minutes	60 minutes	90 minutes
Memphis Unscoured	14.0	19.5	23.5
Scoured	18.3	20.8	26.1
Empire Unscoured	8.0	13.5	18.8
Bale 92 Scoured	16.3	20.9	24.2
Lockett Unscoured	6.3	10.8	13.5
140 Scoured	15.6	19.8	24.4

Table 2. Physical Properties of Scoured and Unscoured Cottons Selected for Experimentation

Cotton	NaOH* Maturity (Per Cent)	Fiber Fineness (Micronaire Reading)	Strength (Pressley Index)
Memphis Unscoured	38	2.45	7.15
Scoured	--	2.50	6.98
Empire Unscoured	72	3.70	7.30
Bale 92 Scoured	--	3.71	6.80
Lockett Unscoured	92	5.67	7.51
140 Scoured	--	5.65	7.13

*Data furnished by Southern Regional Research Laboratory.

Table 3. Average Percentages of the Chemical Constituents of Scoured and Unscoured Cottons

Cotton		Ash	Alpha Cellulose	Chloroform Extract	Benzene Extract	95% Ethyl Alcohol Extract	Distilled Water Extract	0.5% Ammonium Glacial Acetic Acid	
								Solution Extract	Extract
Memphis	Unscoured	0.87	95.3	0.93	1.00	2.2	2.6	4.50	6.1
	Scoured	0.25	98.5	0.80	0.84	1.00	1.5	0.74	2.8
Empire Bale 92	Unscoured	0.90	97.1	0.51	0.63	1.4	2.4	3.50	5.3
	Scoured	0.36	99.0	0.38	0.43	0.71	1.2	0.48	2.0
Lockett 140	Unscoured	0.96	97.4	0.38	0.51	1.2	2.2	3.80	5.1
	Scoured	0.37	99.2	0.31	0.35	0.52	1.1	0.41	1.9

Table 4. Spectrographic Analysis for Cotton Ash Constituents

Element	Cotton Variety					
	Unscoured			Scoured		
	Empire		Lockett:	Empire		Lockett
	Memphis	Bale 92	140	Memphis	Bale 92	140
Calcium	*f	f	f	s	s	s
Strontium	-	-	-	f	f	f
Aluminum	t	-	-	w	w	w
Potassium	f	w	f+	-	-	-
Sodium	f+	f	f	f	f	f
Magnesium	f-	f+	f-	f	f-	f+
Silicon	w-	w	w-	w	w	w
Boron	w	w-	w	w-	t	w-
Phosphorus	t	-	-	-	-	-

*s= strong; f= fair; w= weak; t= trace; -- not found

Table 5. Physical Properties and Wax Content of Different Varieties of Cottons

Cotton	Source	NaOH* Maturity (%)	Fineness (Micronaire Reading)	Pressley Index	X-Ray* Angle (40%)	Wax Content Per Cent
Memphis	--	38	2.5	7.15	37.92	1.400
Empire Bale 92	--	72	3.7	7.3	34.05	0.770
Lockett 140	--	92	5.6	7.51	36.18	0.555
Acala 4-42	Greenville, Texas	77	3.9	9.24	28.8	0.610
Acala 5675	Florence, S.C.	81-82	4.2	8.22	32.6	0.570
Coker 100W	Weslaco, Texas	77	4.5	6.96	33.6	0.640
Coker 100W	Florence, S.C.	86	4.6	5.91	35.5	0.555
Sea Island St. Vincent	--	80	1.8	10.1	00	1.000
Sealand 1 47-295	Florence S.C.	81-82	3.4	7.71	31.6	0.670

*Data furnished by Southern Regional Research Laboratory.

Table 6. Wax Content and Rate and Degree of Acetylation of Different Varieties of Cotton Fibers

Cotton	Source	Wax	Per cent acetyl after acetylation at 64°F. for:*		
			30 minutes	60 minutes	90 minutes
Memphis	--	1.400	14.1	20.2	23.9
Empire Bale 92	--	0.770	8.48	15.4	18.5
Lockett 140	--	0.555	6.65	12.0	16.5
Acala 4-42	Greenville, Texas	0.610	8.30	14.2	19.6
Acala 5675	Florence, S.C.	0.570	10.4	16.4	21.4
Coker 100W	Weslaco, Texas	0.640	8.83	14.5	20.6
Coker 100W	Florence, S.C.	0.555	8.88	13.9	19.1
Sea Island St. Vincent	--	1.000	12.5	21.4	24.2
Sealand 1 47-295	Florence S.C.	0.670	12.4	20.4	24.8

*Data was taken from Progress Report No. 6 Project No. 208-156, "Partial Acetylation of Cotton", by Taylor, J. L., and Colcord, A. R., Jr. Engineering Experiment Station of the Georgia Institute of Technology, September 20, 1953.

Effect of Physical Properties.---Fiber fineness and fiber strength determinations of Memphis, Empire Bale 92, and Lockett 140 cottons were reported by Holloway. (55) Table 2 reveals that there is a considerable difference between the unscoured cottons in maturity, fiber fineness, and strength.

After scouring the cotton fibers, there was no appreciable change in the fiber fineness nor in the fiber strength.

Ash Content and Ash Constituent.---In the scoured cotton samples the ash content was reduced in all the three cottons under examination, but still there was a slight difference between them. Nevertheless, the rate and degree of acetylation of these cottons as shown in Table 3 were brought closer together by the scouring treatment.

Analysis of the ash of both scoured and unscoured cottons -- Memphis, Empire Bale 92, and Lockett 140 -- by the spectrographic method showed slight difference in the elements present as indicated in Table 4. Unscoured cotton Memphis shows some traces of aluminum and phosphorus in addition to the elements found in the other two cottons, Empire Bale 92 and Lockett 140. Scoured cottons, however, showed the absence of potassium which must have been removed by scouring. The amounts of sodium, magnesium, silicon, and boron are not changed after scouring but a new element has been added which is strontium which may be due to the scouring ingredients. Scouring appears to increase the amounts of calcium and aluminum. This increase may possibly come from the scouring ingredients.

These results indicate that the constituents found in the ash may have no great effect on the rate and degree of acetylation.

Solvent Extractions.---The average results of the solvent extractions of scoured and unscoured cottons under examination are summarized in Table 3. These extractions were made on cotton fibers by using chloroform, benzene, 95 per cent ethyl alcohol, distilled water, 0.5 per cent ammonium oxalate solution, and glacial acetic acid.

It is shown that chloroform and benzene extracts have the lowest percentages compared with the other solvent extracts. Their extracts are composed of mostly wax and some fats and resinous matter. Ethyl alcohol extracts not only wax, fats, and resinous matter but also all the reducing substances. This extract is faintly acid to litmus and contains a high percentage of mineral matter giving a percentage higher than both benzene and chloroform. Water removes most of the substances soluble in alcohol and some more mineral matter insoluble in alcohol. Ammonium oxalate solution extracts nearly all pectic substances which form a great part of the impurities in cotton. Glacial acetic acid gives the highest percentage of extract compared with the other solvents.

Scouring treatments reduce the amount of extracts of all kinds of solvents as shown in Table 3, but the ratios of the same extract within the three kinds of the scoured cotton

fibers are nearly the same compared with that of the unscoured cottons. Therefore, it appears that these extractable materials do not play a great role in minimizing the differences between the rate and degree of acetylation of these varieties of cotton fibers.

The exact amount of wax of the original three varieties of raw cottons and six other varieties were determined by the new ethyl alcohol extraction method. The ethyl alcohol removed all the wax from the cottons along with the other reducing and nonreducing substances. The ethyl alcohol extract was again extracted by the use of chloroform in the presence of distilled water so that all the wax was transferred to the chloroform layer, and by draining the chloroform layer and evaporating it, the wax was determined quantitatively.

The average results of wax content and the physical properties of the cottons extracted by the new alcohol-chloroform method are shown in Table 5. It is shown that cottons, Memphis, Empire Bale 92, and Lockett 140 have higher percentages of wax compared with the ordinary method applied by chloroform extraction which is shown in Table 3 as (Chloroform Extract). The reason is that in the ethyl alcohol extraction method all the cotton wax is extracted and also the time of extraction is six hours while in the ordinary method it was chosen to be four hours. Nevertheless, the ratios of the wax percentages by this method within the three cottons are nearly the same as compared with that of the chloroform method.

There is a considerable decrease in wax content between Memphis, Empire Bale 92, and Lockett 140 cottons respectively corresponding to an increase in maturity, fiber fineness, and Pressley index.

These results of exact wax content are valuable when used to determine the maturity of cotton fibers of the same variety.

An examination of Table 5 reveals that both Acala 4-42 (Greenville, Texas) and Acala 5675 (Florence, S. C.) cottons are of the same variety, and it is shown that there is some increase in wax content corresponding to a decrease in maturity and fiber fineness. The same could be said about cottons Coker 100W (Weslaco, Texas) and Coker 100W (Florence, S.C.) since both of them are of the same variety.

As discussed before, the more immature fiber yields a higher acetyl content when acetylated. Scouring greatly reduces the differences in acetyl content between the three varieties of cottons, Memphis, Empire Bale 92, and Lockett 140. For this reason a maturity test was made on the scoured samples, Memphis and Lockett 140, to determine whether maturity test was affected by scouring or not. The test was made by the differential dye test method which showed that maturity was not affected by scouring.

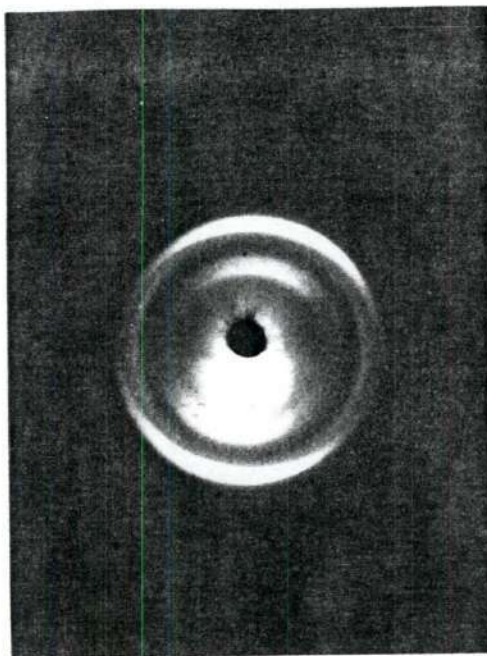
Alpha Cellulose.--The difference in alpha cellulose content between the three varieties of cottons, Memphis, Empire Bale 92, and Lockett 140, whether scoured or unscoured, is rather small as shown in Table 3. Scoured cottons show slightly higher percentages of alpha cellulose compared with the unscoured cottons due to the fact that some of the impurities are removed by scouring. It seems that alpha cellulose does not play a great role in regard to the rate and degree of acetylation.

X-Ray Diffraction Pattern.--It had been observed that, while the reactivities of the three varieties of cottons Memphis, Empire Bale 92, and Lockett 140 before scouring were different, scoured samples had reactivities which were more nearly the same as observed by the acetylation results. The purpose of the X-ray studies was to determine whether this effect was related to easily observable changes in the diffraction patterns of the three kinds of cottons both scoured and unscoured. The photographs of the X-ray films of these samples are shown on the following pages.

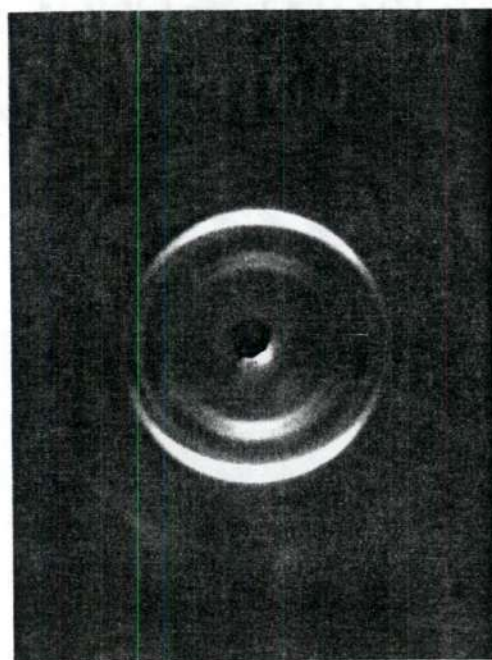
The variation in the amount of diffracting material in the various samples plus slight variations in exposure time and developing procedure caused some films and photographs to be generally darker than others. Relative intensities rather than absolute intensities must therefore be considered in examining the photographs.

The following characteristics of the diffraction patterns are related to the fiber structure: number, diameter, and relative intensity of the diffraction rings; concentration of the rings into arcs; diffuseness of the rings and amount of the general scattering. Changes in these characteristics would indicate changes in the fiber structure.

The films had been examined qualitatively before the photographs were made, and no changes had been observed.

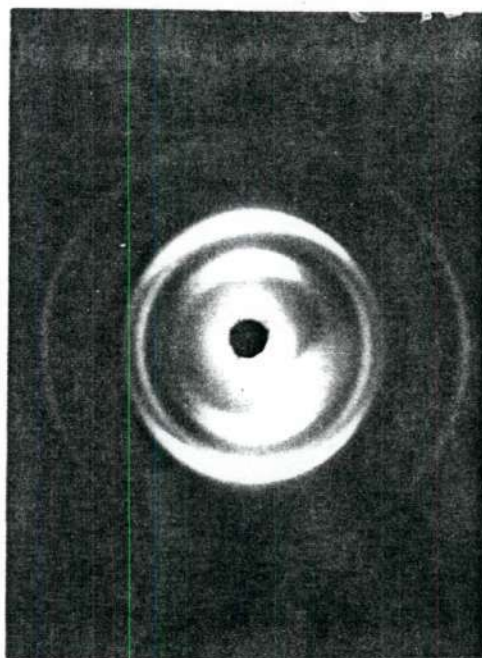


Unscoured

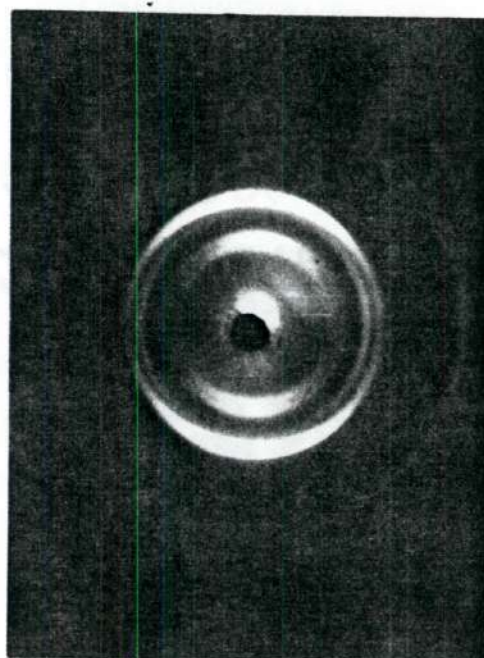


Scoured

Figure 1. X-Ray Diffraction Patterns of Scoured and Unscoured Memphis Cotton.

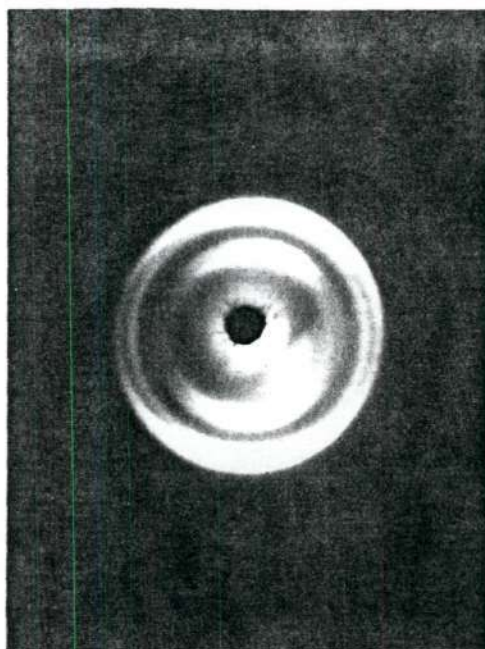


Unscoured

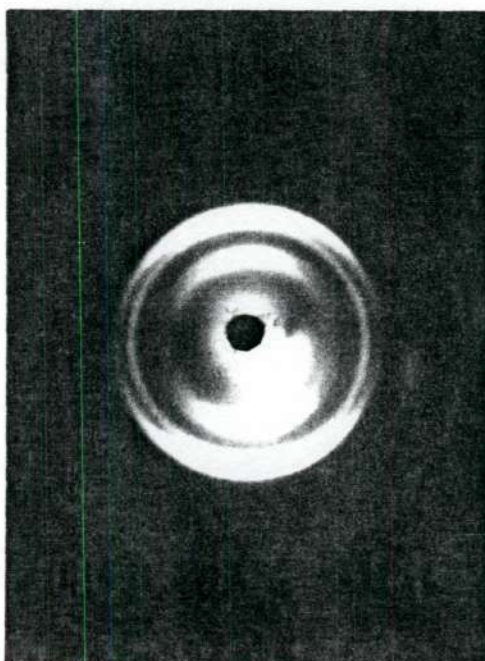


Scoured

Figure 2. X-Ray Diffraction Patterns of Scoured and Unscoured Empire Bale 92 Cotton.



Unscoured



Scoured

Figure 3. X-Ray Diffraction Patterns of Scoured and Unscoured Lockett 140 Cotton.

CHAPTER VI

CONCLUSIONS

1. It was found that the amount of ash and ash constituents had no great effect on the rate and degree of acetylation of the different varieties of cottons.

2. The data indicate that solvent extractable materials have no great effect on the rate and degree of acetylation.

3. It was found that maturity tests were valid for both scoured and unscoured cottons.

4. Alpha cellulose content apparently has no great effect on the rate and degree of acetylation.

5. The X-ray diffraction pattern of both scoured and unscoured cottons shows no distinct differences which indicates that scouring treatment does not affect the pattern of the crystalline cellulose of the different varieties of cotton fibers.

6. It is concluded that scouring treatment may have caused some physical changes in the fiber which make it more porous by breaking down the impurities without necessarily removing them completely. Hence, the surface area of pure cellulose is increased giving a better chance for cotton to react with the acetylating reagents. This increase in reactivity is more pronounced in the mature fibers than in the immature fibers.

CHAPTER VII

RECOMMENDATIONS

It is recommended that this investigation should be carried out on a greater number of cotton varieties to give more definite conclusions.

Further study of X-ray analysis is recommended. The qualitative study which has been made in this investigation by no means precludes the possibility that observed changes in reactivity are related to changes in fiber structure. However, a more quantitative method seems necessary. This study would involve a more satisfactory method of sample preparation and photometer measurements of films. This would require more time and accuracy than the qualitative method used in this investigation.

It is also recommended that physical properties should be thoroughly investigated on both scoured and unscoured cottons, especially those investigations which could tell whether or not the surface area of pure cellulose has been increased by the scouring treatment.

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APPENDIX

Table 7. Chemical Analyses of Unscoured Cotton Fibers.

Kind of Test	Cotton Variety		
	Memphis	Empire Bale 92	Lockett 140
Moisture (per cent)	7.00	6.80	6.80
	7.00	6.80	6.80
	Average	7.00	6.80
Ash (per cent)	0.870	0.90	0.96
	0.860	0.90	0.96
	Average	0.865	0.90
Alpha Cellulose (per cent)	95.30	97.00	97.40
	95.30	97.10	97.30
	Average	95.30	97.05
Chloroform Extract (per cent)	0.930	0.500	0.380
	0.940	0.520	0.370
	Average	0.935	0.510
Benzene Extract (per cent)	1.00	0.63	0.510
	1.00	0.63	0.500
	Average	1.00	0.63

Table 7. (Continued) Chemical Analyses of Unscoured Cotton Fibers

Kind of Test	Cotton Variety		
	Memphis	Empire Bale 92	Lockett 140
Ethyl Alcohol Extract (per cent)	2.20	1.40	1.20
Average	2.20	1.40	1.20
Distilled Water Extract (per cent)	2.60	2.40	2.20
Average	2.70	2.40	2.20
Ammonium Oxalate Extract (per cent)	2.65	2.40	2.20
Average	4.50	3.50	3.80
Glacial Acetic Acid Extract (per cent)	4.50	3.50	3.80
Average	4.50	3.50	3.80
Glacial Acetic Acid Extract (per cent)	6.10	5.30	5.10
Average	6.10	5.30	5.10

Table 8. Chemical Analyses of Scoured Cotton Fibers

Kind of Test	Cotton Variety		
	Memphis	Empire Bale 92	Lockett 140
Moisture (per cent)	6.70	6.50	6.40
	6.70	6.50	6.40
Average	6.70	6.50	6.40
Ash (per cent)	0.24	0.35	0.37
	0.26	0.37	0.37
Average	0.25	0.36	0.37
Alpha Cellulose (per cent)	98.50	99.00	99.30
	98.60	99.00	99.20
Average	98.55	99.00	99.25
Chloroform Extract (per cent)	0.800	0.380	0.310
	0.810	0.380	0.310
Average	0.805	0.380	0.310
Benzene Extract (per cent)	0.840	0.430	0.350
	0.850	0.430	0.350
Average	0.845	0.430	0.350

Table 8. (Continued) Chemical Analyses of Scoured Cotton Fibers

Kind of Test	Cotton Variety		
	Memphis	Empire Bale 92	Lockett 140
Ethyl Alcohol	1.00	0.70	0.51
Extract			
(per cent)	1.10	0.72	0.53
Average	1.05	0.71	0.52
Distilled Water	1.50	1.20	1.10
Extract			
(per cent)	1.50	1.20	1.10
Average	1.50	1.20	1.10
Ammonium Oxalate	0.73	0.49	0.42
Extract			
(per cent)	0.75	0.47	0.40
Average	0.74	0.48	0.41
Glacial Acetic	2.70	2.10	1.80
Acid Extract			
(per cent)	2.80	2.00	1.90
Average	2.75	2.05	1.85

Table 9. Wax Determination by the New Ethyl Alcohol
Extraction Method

Kind of Test	Cotton Variety		
	Memphis	Empire Bale 92	Lockett 140
Moisture (per cent)	7.00	6.80	6.80
	7.00	6.80	6.80
	Average 7.00	6.80	6.80
Wax (per cent)	1.42	0.75	0.550
	1.38	0.79	0.560
	Average 1.40	0.77	0.555
	Acala 4-42 Greenville, Texas	Acala 5675 Florence, S.C.	Coker 100 W Weslaco, Texas
Moisture (per cent)	6.2	6.1	6.0
	6.2	6.1	6.0
	Average 6.2	6.1	6.0
Wax (per cent)	0.61	0.57	0.64
	0.61	0.57	0.64
	Average 0.61	0.57	0.64

Table 9. (Continued) Wax Determination by the New Ethyl Alcohol Extraction Method

Kind of Test	Cotton Variety		
	Coker 100 W Florence, S.C.	Sea Island St. Vincent	Sealand 1,47-295 Florence, S. C.
Moisture (per cent)	6.3	6.4	6.3
	6.3	6.4	6.3
Average	6.3	6.4	6.3
Wax (per cent)	0.550	0.99	0.67
	0.560	1.01	0.67
Average	0.555	1.00	0.67