Part III

PHYSICAL PROPERTIES
EVALUATION OF COMPOUNDS AND MATERIALS

Degradation of Cotton in an Oxygen Atmosphere by Gamma Radiation

FLORINE A. BLOUIN and JETT C. ARTHUR, Jr.
Southern Regional Research Laboratory, New Orleans, La.

CELLULOSE in the form of wood, wood pulp, filter paper, cotton linters, and lint has been irradiated with x-rays, β-rays, cathode rays, γ-rays, and neutrons under various atmospheric conditions to study the effects of high energy radiation (*2, 8–12, 14, 20, 26, 27*). Even though the conditions of irradiation varied widely and the number of chemical and physical properties of the irradiated cellulose, which were studied, was not particularly extensive under any one atmospheric condition, the over-all results have been similar.

The physical and chemical properties of cellulose were not significantly affected until the cellulose had received a total dosage of 10^6 roentgens, after which the affected properties changed rapidly with further increases in dosage. Irradiation of cotton cellulose, as fibers and yarns, produced a decrease in tensile strength, elongation, elasticity, and tenacity (*26*). The major chemical effects produced by high energy irradiation were chain cleavages and the formation of reducing and acid groups, the formation of reducing groups being by far the most predominant chemical change which occurred. These properties were indicated by intrinsic viscosity measurements, copper reducing methods, acid titrations, affinity for basic dyes, and water and alkali solubility measurements.

Gas evolution during the irradiation of cellulose has been observed (*24, 30*). Irradiation increased the amount of easily hydrolyzable material and increased the rate of acid hydrolysis (*24*). The irradiated cellulose exhibited a new absorption band in the infrared at 5.75 microns (*2, 20*). Cellulose irradiated in an inert atmosphere had a residual paramagnetic resonance for several days after the irradiation was concluded (*1, 12*). A marked postirradiation effect on the viscosity of cellulose, which had been dried and irradiated in a nitrogen atmosphere, was produced when the sample was stored in dry oxygen. This effect was terminated by the presence of water (*10–12*). Comparison of cuprammonium and cellulose nitrate viscosity data indicated that irradiated cellulose was not alkali labile as are some types of oxidized cellulose (*27*).

The various types of high energy radiation seemed to produce the same general effects on the cellulose. The total dosage, and not the dose rate, seemed to be the most important factor. The absence or presence of moisture in the cellulose irradiated did, under certain conditions, alter the effect. The gaseous atmosphere under which the irradiation was carried out seemed to produce only small differences in the various properties studied.

Literature data on the irradiation of cellulose with high energy radiation indicated that this was an oxidative degradation reaction, predominantly of the reducing type. As to the specific chemical nature of the oxidized groups formed, very little is yet known.

To determine the mechanism of the radiation-induced reactions of cellulose and to evaluate these chemical alterations of the cellulose molecule with relation to the production of new cotton products, the specific chemical nature of the oxidized groups formed must be known. Even though previous work indicated that only small differences in properties were produced by irradiation in different atmospheres, the atmosphere under which the irradiation is carried out is very important in respect to the exact chemical nature of the groups produced. The differences noted were not particularly significant, because the methods used were too gross in nature, and the conditions of irradiation and analysis were not precise enough to detect these differences.

Investigations of the specific nature of the groups formed on cotton cellulose in an atmosphere of oxygen at a gamma radiation dosage of 10^8 roentgens are reported here.

EXPERIMENTAL

Irradiation of Samples. Two samples of purified Deltapine cotton irradiated under slightly different conditions were used throughout. The differences and similarities of the

Table I. Preparation and Analysis of Irradiated Cotton Cellulose

	Sample A	Sample B
Conditions of Irradiation		
Source	Spent fuel elements	Cobalt-60
γ-energy, m.e.v.	Wide spectrum	1.17 and 1.33
Dose rate, roentgens/hr.	3.0×10^6 (52%); 6.4×10^6 (48%)	0.53×10^6
Dosage, roentgens	10^8	10^8
Cotton/oxygen, g./ml.	1:8.5	1:7.5
Moisture, %	7.24	5.37
Chemical Analyses[a]		
Irradiated sample		
Carbonyl groups, mmoles/g.	3.04	3.01
Carboxyl groups, mmole/g.	0.155	0.177
Degree of polymerization	39	54
Water solubility, %	9.7	9.7
Irradiated sample, water washed		
Carbonyl groups, mmoles/g.	2.63	2.64
Carboxyl groups, mmole/g.	0.069	0.068
Degree of polymerization	48	41

[a] See Blouin and Arthur (2) for methods.

conditions of irradiation and of the resulting evaluations are given in Table I. Sample A was a 75-gram sample of purified cotton which was sealed in an oxygen atmosphere in a water- and air-tight can, and was sent to the National Reactor Testing Station at Idaho Falls, Idaho. The gamma radiation was produced by fission products in spent materials testing reactor fuel elements. This sample was also used in an evaluation of the effects of irradiation on cotton (2).

Sample B was made up of two 10-gram samples of purified Deltapine cotton, which after irradiation, were ground and thoroughly mixed. Sample B was irradiated in an oxygen atmosphere with gamma radiation from a cobalt-60 source. The samples were contained in a glass cylinder, the top of which was tightly closed with a sealing agent. The cylinder had a side arm containing a stopcock, so that the gas pressure in the cylinder could be measured, and the gases and B, given in Table I, indicated fairly good reproducibility of results under the two different conditions of irradiation.

Gas Analysis. The cotton was sealed in a known volume of oxygen at 26° C. and atmospheric pressure at the time of sealing. After irradiation of the sample, the cylinder was connected to a manometer, and the pressure in the cylinder was measured at constant temperature, 26° C., and volume, about 85 ml. The pressure in the cylinder was 110 mm. of mercury above the original pressure in the cylinder. From other work, it was known that the system had passed through a minimum pressure well below that of the original pressure in the cylinder and then increased to above the original pressure. Based on the known volume of the cylinder, the volume of cotton present, the change in atmospheric pressure, and the dilution of pressure on connecting the cylinder to the manometer, the volume of gas in the cylinder after irradiation was determined. A sample of the gas in the cylinder was removed by connecting the cylinder to an evacuated bulb. The gas contained in the bulb was analyzed in a cycloidal-focusing type mass spectrometer (Consolidated Engineering Corp., Model 21-620). The composition of the gas in the cylinder after irradiation was carbon monoxide, 60%; carbon dioxide, 20.2%; hydrogen, 9.3%; and oxygen, 10.7%. Based on the original volume of oxygen, it was calculated that 88% of the oxygen had been consumed in the reaction. The magnitude of amount of oxygen consumed indicates that this is an important effect of the irradiation of cellulose.

Fractionation. The irradiated sample was fractionated into compounds of different molecular size, and they were subsequently examined. The water-soluble fraction was obtained by refluxing the irradiated sample with water (1 gram of cotton per 100 ml. of distilled water) for 1 hour. The water-soluble materials were filtered from the residues. The weights of the residues were determined by drying in an air-convection oven at 105° to 110° C. for about 16 hours. The water-soluble materials were solidified by freeze drying and dried to constant weight in a vacuum over phosphorus pentoxide. They were further fractionated by five extractions with 90% ethyl alcohol (100 mg. of material to 1 ml. of alcohol per extraction). The residue of the extractions, a light tan powdery material, was then dried to constant weight in vacuum over phosphorus pentoxide. The alcohol-soluble fraction was, for chromatographic purposes, concentrated to a 0.5 to 1-ml. volume by air evaporation of the alcohol. For quantitative work, the fraction was first vacuum distilled to remove most of the alcohol, solidified by freeze drying, and then dried to constant weight in vacuum over phosphorus pentoxide. The relative percentages of the different fractions (Table II) were determined by weighing the dried residues in each case.

Acid Groups. The acid groups in the total irradiated sample and the water-insoluble residue were determined by the calcium acetate method as described by Davidson and Nevell (4). One-gram samples were used. The acid content of the water-soluble fractions was determined by potentiometric titration using a Beckman Model G pH meter. The results of the analysis of the various fractions are given in Table II. These analyses were done on sample B. In spite of the marked dissimilarity of the physical state of the materials analyzed and the differences in the methods used, the results were comparable. The number of acid groups increased as the molecular weight of the fractions decreased,

Table II. Distribution of Acid and Reducing Groups in Fractions of Irradiated Cotton

	% of Total Sample	Acid Groups, Mmoles/G.	Acid Groups to Glucose Units	Reducing Groups, Mmoles/G.	Reducing Groups to Glucose Units	Degree of Polymerization
Total sample	100	0.177[a]	...	3.01[b]	...	...
Water-insoluble	90.27	0.068[a]	1:91	2.63[b]	1:2.3	41
Water-soluble, calcd. (calcd.)	...	1.192	...	6.47	...	...
Water-soluble	...	0.933[c]	...	2.69[d]	...	...
Alcohol-insoluble (90% ethyl alcohol)	5.97	0.317[c]	1:19	2.38[d]	1:2.6	~8[e]
Alcohol-soluble (90% ethyl alcohol)	3.76	1.721[c]	1:4	3.22[d]	1:1.9	~3[e]

[a] Calcium acetate method (4).
[b] Copper number method (3).
[c] Potentiometric titration method.
[d] Somogyi reducing sugar method (15).
[e] Estimated by solubility and chromatography.

indicating that the acid groups were present on the ends of the chains, at least in the water-insoluble fraction and in the alcohol-insoluble fraction.

Reducing Groups. The reducing groups in the total irradiated sample and in the water-insoluble fraction were determined by Braidy's copper number method (*3*), using 0.25 gram of sample. The water-soluble fractions were analyzed by Somogyi's reducing sugar method (*15*). In previous work (*2*), the copper number data, on irradiated cotton, were presented in terms of carbonyl groups per gram, based on a calculation assuming that one reducing group reduced two moles of copper(II) to copper(I). The analyses on the lower molecular weight fractions were, at first, calculated by the more classical method which expressed the reducing power in terms of weight of glucose which gave the same amount of reduction when done under the same heating conditions and with the same reagents. To compare this with the copper number data, the results were then calculated in terms of milliequivalents of glucose per gram. The results were: water-soluble fraction, 1.48; alcohol-insoluble fraction, 1.32; alcohol-soluble fraction, 1.72 meq. per gram. These results were so similar in magnitude to those calculated from the copper number data that the data obtained by the Somogyi method were calculated similarly. The results by the methods, one involving a 3-hour heating time and the other a 20-minute heating time, are presented in Table II.

Apparently, the majority of reducing groups was produced along the cellulose chain. The data also indicated that there was a stoichiometric relationship between the reducing groups produced in the cellulose and the amount of copper reduced: Either one reducing group reduced two moles of copper(II) to copper(I) or based on the glucose equivalents, one reducing group reduced one mole of copper(II) to copper(I).

Paper Chromatography. The chromatographic work (*17*) was done with Whatman No. 1 chromatography sheets using a 16-hour descending technique. The reagents used were:

Developers	Proportions
1. Ethyl acetate–acetic acid–formic acid–water	18–3–1–4
2. *n*-Butyl alcohol–acetic acid–water	4–1–5
3. *n*-Butyl alcohol–pyridine–water	6–2–3
4. *n*-Butyl alcohol–ethyl alcohol–water	4–1–5
Spray Reagents	
A. Aniline hydrogen phthalate	
B. 0.2*M* $AgNO_3$–0.1*N* NH_4OH (room temperature)	1–1 (*23*)
C. Alcohol chlorophenol red	0.04%
D. *o*-Phenylenediamine (HNO_3)	

The R_G values given were the ratio of the distance traveled by the "spot" from the starting line compared with the distance traveled by a standard glucose spot from the starting line.

Most of the chromatographic work was done using sample A. Sample B, examined chromatographically, was similar in almost all respects to sample A. The carbohydrates used as standards were obtained from the National Bureau of Standards, Nutritional Biochemicals Corp., and Eastman Kodak Co. Other chemicals used were C.P. grade materials.

ALCOHOL-SOLUBLE FRACTION. This fraction of the irradiated cellulose gave chromatograms which, after development, exhibited yellow-white fluorescence under ultraviolet light the entire length of the development. Developer 1 produced a distinctly stronger fluorescent spot at R_G = 0.83. In developers 2 and 3, distinct fluorescent spots were occasionally observed. When the chromatograms were sprayed with various color reagents, almost the entire length of the development was streaked. The intensity of the streaking varied with the reagents used from only a slight hindrance of color detection to complete obliteration of all distinct spots. This streaking was partly due to the presence of glyoxal in the fraction. Detection of the components in the alcohol-soluble fraction with sprays A and D was considerably enhanced by examination under ultraviolet light.

The R_G values of the components of this fraction are given in Table III. The identity of the first four components listed was chromatographically established. The identity of component 5 was almost definitely glyoxal. There was some uncertainty, as glyoxal produced a streak rather than a distinct spot. The rate and character of the reaction of glyoxal with the ammoniacal silver nitrate reagent B were distinctive.

Using only developers 2 and 3 and sprays A, B, and C, the 2-ketogluconic acid (component 3) would be difficult to distinguish from glucuronic acid. With developer 1 there was a definite difference in R_G between the two standards. With spray reagent D, 2-ketogluconic acid gave a yellow color in daylight and under ultraviolet light gave an extremely strong yellow fluorescence. This spray reagent easily distinguished between 2-ketogluconic acid and glucuronic acid in all three developers.

The intensity of color reactions and the reproducibility of detection indicated that components 6 to 9 were the remaining major low molecular weight components of the alcohol-soluble fraction. Some tentative identifications are given in parentheses in Table III. Using the acid indicator, spray C, the major acid components of this fraction were components 3, 6, 7, and a streak at the top of the chromatograms (oligosaccharides). A number of the other components gave very weak acid reactions with this spray and with spray B. Component 6 was thus a major acid component of the mixture. This component was an oblong spot which on occasions gave indications of being two spots. Its movement somewhat resembled that of cellobionic acid. However, it gave a spot with the reducing sugar reagent A, which most of the time was brown but occasionally gave a pink color (acid reaction). Since 2-ketogluconic acid was a major acid component of the fraction, component 6 was tentatively identified as 2-ketocellobionic acid and possibly its lactone.

Component 7 gave a strong fluorescence in ultraviolet light before spraying, and a fairly strong acid spot with spray C. When a large quantity of the standard 2-keto-

Table III. Chromatographic Evaluations of the Alcohol-Soluble Fraction of Irradiated Cotton

Component Number	R_G in Developer 1	2	3	Spray Reagent	Identification[a]
1	0.33	0.55	0.56	ABD	Cellobiose
2	0.98	1.02	1.01	ABD	Glucose
3	1.21	0.79	0.40	ABCD	2-Ketogluconic acid
4	1.45	1.21	1.21	ABD	Arabinose
5	0–1	2–3.5	2–3.5	B	Glyoxal
6	0.48	...	...	ABC	(2-Ketocellobionic acid)
7	0.83	...	...	C	(2-Ketogluconic acid lactone)
8	1.67	1.46	1.49	ABCD	
9	2.96	2.62	2.78	AB	
10	...	0.36	...	B	(Acid)
11	...	0.63	...	B	(Acid)
12	...	0.92	...	B	(Acid)
13	...	2.12	...	B	
14	...	2.39	...	A	
15	...	3.05	...	B	
16	...	3.64	...	B	
17	...	With front	...	C	(Acid)

[a] Parentheses indicate tentative identification.

gluconic acid was spotted on the chromatogram, the streaking extended to the region of the chromatogram where component 7 was observed. No fluorescence was observed with the standard 2-ketogluconic acid before spraying. However, the fluoresence of 2-ketogluconic acid before spraying has been reported (*22*). The equilibrium between a sugar lactone and its free acid is strongly affected by the acidity of the medium (*13*). The alcohol-soluble fraction was highly acid. This could produce a different equilibrium between 2-ketogluconic acid and its lactone than would exist in standard 2-ketogluconic acid. On the basis of these facts, component 7 is probably a lactone of 2-ketogluconic acid.

Component 8 gave a very weak yellow-brown color with the reducing sugar spray A, but exhibited a strong yellow-orange color under ultraviolet light. It also gave a very faint acid reaction with sprays C and B. Component 9 gave a strong reaction with silver nitrate. No other distinctive reactions were obtained.

The other components of the alcohol-soluble fraction, with the exception of components 11 and 12, were in very low concentrations and were undoubtedly minor secondary degradation products. The color reactions given by components 10 to 17 were never very distinctive, and reproducibility of R_G values was not good. Glyoxal and arabinose were considered to be secondary degradation products of the reaction.

ALCOHOL-SOLUBLE FRACTION AS PHENYLHYDRAZINE DERIVATIVES. To get chromatographic movement of the high molecular weight components of this fraction, it was necessary to form phenylhydrazine derivatives of the compounds. Two drops of phenylhydrazine were added to 0.1 ml. of the alcohol-soluble fraction and to similar standard solutions. The mixtures were placed on a steam bath for ½ hour. These reaction conditions would favor phenylhydrazone formation rather than phenylosazone formation (*21*). The acids present under these conditions form phenylhydrazides (*5*). The samples were then chromatographed using solvent 4, and were sprayed with reagent B. The data are given in Table IV. There was evidence of degradation, particularly of the monosaccharides; glucose in the standard solution and in the unknown gave two spots. Although some tentative identifications of the monosaccharides were made, the spots were very close together, and the rates of reaction were not very distinctive.

Components 8, 10, 12, and 13 gave a strong and fast reaction with the ammoniacal silver nitrate spray reagent. Scott and Senti (*25*) and Whelan, Bailey, and Roberts (*29*) have shown that members of a homologous series of oligosaccharides exhibit R_F values directly proportional to their molecular weight and that when the log $(1/R_F - 1)$ for such a series is plotted against the degree of polymerization of the oligosaccharide involved, a straight-line relationship is obtained for all members of the series except the monosaccharide. The disaccharide rather than the monosaccharide was considered the first member of the series because it was the first to contain the glycosidic linkage. Components 8, 10, 12, 13, 15, and 16 plotted in this manner indicating that this was a homologous series of cellulodextrins.

Table IV. Chromatographic Evaluations of Phenylhydrazine Derivatives of Alcohol-soluble Fraction of Irradiated Cotton

Component Number	R_F[a]	Identification[b]
1	0.91	Phenylhydrazine reagent
2	0.87	Phenylhydrazine reagent
3	0.79	Arabinose
4	0.74	Glucose
5	0.69	Glucose
6	0.63	(Erythrose)
7	0.58	(2-Ketogluconic acid)
8	0.52	Cellobiose
9	0.38	(Oligosaccharide)
10	0.31	Cellotriaose
11	0.21	(Oligosaccharide)
12	0.16	Cellotetraose
13	0.08	Cellopentaose
14	0.07	(Acid)
15	0.04	Cellohexaose
16	0.02	(Celloheptaose)

[a] Developer 4 and spray reagent B were used.
[b] Parentheses indicate tentative identification.

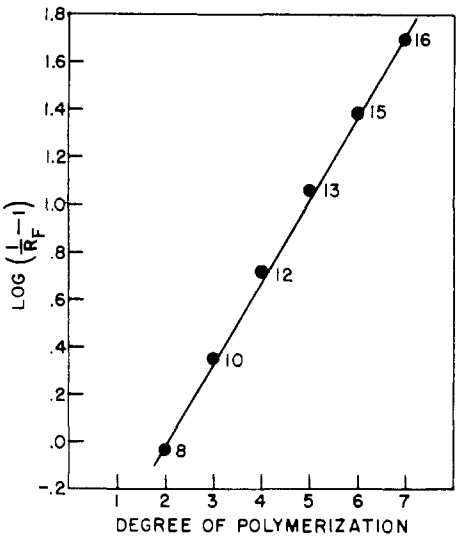

Figure 1. Homologous series of phenylhydrazine derivatives of cellulodextrins from the alcohol-soluble fraction of irradiated cotton
Numbers refer to components in Table IV

By hydrolysis of purified cotton and by fermentation of the glucose, a solution containing appreciable quantities of cellobiose and cellotriaose was prepared. This solution reacted with phenylhydrazine in the same manner as the test solution. The spots produced by the cellobiose (R_F = 0.52) and the cellotriaose (R_F = 0.31) on an average moved at the same rate as components 8 and 10 of the test solution.

Glucose and cellobiose had been chromatographically proved to be in the alcohol-soluble fraction by other chromatographic techniques. The standard cellobiose and the cellobiose and cellotriaose obtained by hydrolysis of cellulose corresponded in movement, as their phenylhydrazine derivatives, to components 8 and 10 of this series. This fraction would seem to contain the cellobiose series molecules having degrees of polymerization of at least six. But the movement of cellobionic acid, as its phenylhydrazide (R_F = 0.52), was the same as that for cellobiose and for component 8 of this fraction. This would indicate that the series of cellulodextrins of which cellobionic acid is the first member, would also have the same chromatographic movement as the series in question. This would probably hold equally true for the similar series of which 2-ketocellobionic acid is the first member. Also, the reducing power of the various fractions indicated that at least one out of every three glucose units contained a reducing group along the chain. Therefore, the cellulodextrin series from this fraction could not be an unaltered cellobiose series. The presence of these reducing groups along the chain could also account for the strong reaction of the series with the ammoniacal silver nitrate reagent. This strong reaction never occurred with the cellulodextrins produced by hydrolysis of unaltered cellulose. The characteristic rate of movement of the series

of cellulodextrins from this fraction was due principally to the character of the glycosidic linkage and to the number of monomer units involved.

ALCOHOL-INSOLUBLE FRACTION AS PHENYLHYDRAZINE DERIVATIVES. The alcohol-insoluble fraction was treated in the same manner to form the phenylhydrazine derivatives. The chromatograms were developed using solvent 4 as before, but were allowed to develop for 64 hours. The first component of this mixture, which was in appreciable concentration and moved from the origin, corresponded to the movement of the hexaose in the alcohol-soluble fraction, when it was developed in this same manner.

Ultraviolet Spectra. The ultraviolet spectra of the alcohol-soluble and the alcohol-insoluble fractions were determined over the 220 to 350 mμ range, in 0.01*N* hydrochloric acid and in 0.01*N* sodium hydroxide. The maxima obtained and the absorptivity at this maximum wave length are given in Table V. Sample B was used in this work. Absorptions of the type exhibited by these fractions in this ultraviolet spectral range are characteristic of the presence of an ionizable chromophore group, such as enediols or enols (*6, 16, 18*). The spectra of these compounds shift with increasing pH to longer wave lengths and/or exhibit an increase in absorptivity. 2-Ketogluconic acid is an enediol of this type. It has been reported to exhibit a maximum in acid solution at 230 mμ and in alkaline solution at 275 mμ (*16*). The components present in the alcohol-soluble and alcohol-insoluble fractions exhibited maximum absorptivity in 0.01*N* hydrochloric acid at 259 mμ and in 0.01*N* sodium hydroxide at 278 mμ. These data indicated the presence of 2-ketogluconic acid and the homologous series of cellulodextrins. The ratio of these components in the alcohol-insoluble fraction to those in the alcohol-soluble fraction was 1 to 4.3, compared to the ratio of titrated acid groups in these same fractions of 1 to 5.5.

Infrared Spectra. The infrared data were obtained using the potassium bromide disk technique described by O'Connor, Du Pré, and McCall (*19*). The absorption in the 5.5 to 6.0-micron range for the control cotton, the water-insoluble, water-soluble, alcohol-insoluble, and alcohol-soluble fractions are presented in Figure 2. These data indicated that the new band at 5.75 microns produced by irradiation of cellulose, was C = O which was predominantly present in the alcohol-soluble fraction. Based on the acid titrations and the reducing group analyses, this new absorption at 5.75 microns was a carboxyl group absorption, rather than a reducing group.

Other Qualitative Tests. The water-soluble fraction and a distillate obtained from this fraction gave negative results when testing for the presence of formaldehyde, formic acid, and methanol. The water-soluble and the water-insoluble fractions gave negative results, when tested for liberation of iodine from potassium iodide, indicating the absence of peroxide groups (*12*). These two fractions gave a weak positive reaction with an acid Tillman's reagent. The water-insoluble fraction gave a slow but strong positive reaction in weakly alkaline solution with this reagent. This test indicated the presence of reductones (*6*).

DISCUSSION

High energy irradiation produces oxidative degradation of the cellulose molecule. The penetrating power of γ-rays, and probably most other kinds of high energy radiation, makes this oxidative reaction of cellulose unique when compared to ordinary chemical oxidations. The ionizations induced in the cellulose by high energy radiation are not hindered by the crystalline-amorphous nature of the cellulose structure (*24*). The irradiation of a polymer, such as cellulose in a solid state, induces an interesting type of radiochemical reaction, in that the polymer molecules are more or less in a fixed lattice and ordinary collision mechanisms can no longer hold (*28*).

Table V. Ultraviolet Spectra of Water-Soluble Fractions of Irradiated Cotton

	Solvent			
	0.01*N* HCl		0.01*N* NaOH	
	Max. wave length, mμ	Absorptivity	Max. wave length, mμ	Absorptivity
Alcohol-soluble	259	3.55	278	4.57
Alcohol-insoluble	252	0.67	278	1.06
			252	1.38

The transfer of energy on interaction of high energy radiation with matter occurs by many processes depending upon the atomic number of the elements of the material being irradiated. Irradiation produces excited or ionized atoms. Cellulose consists of long linear chains made up of repeating anhydroglucose units, which contain carbon, oxygen, and hydrogen atoms. Each anhydroglucose monomer unit has an equal probability of being affected by the irradiation, and each carbon and oxygen atom which makes up this unit has at least a similar probability of being ionized. The nature of the adjustment resulting from this ionization is belived to be dependent upon the particular carbon atom ionized or the particular carbon atom to which the ionized atom is bound, the position of this carbon atom in the basic glucose unit, and the atmosphere under which the material is irradiated or the atmosphere to which it is thereafter exposed.

Gamma irradiation of cellulose produces chain cleavage, reducing groups, and acid groups. A reducing group at the C_1 position of the glucose unit would not be produced by the same mechanism as a reducing group at the C_6 position. One of these positions is already a potential aldehyde group, whereas the other is a primary hydroxyl group. Each carbon atom of the glucose unit would thus have to be considered individually wherever possible, when discussing the mecha-

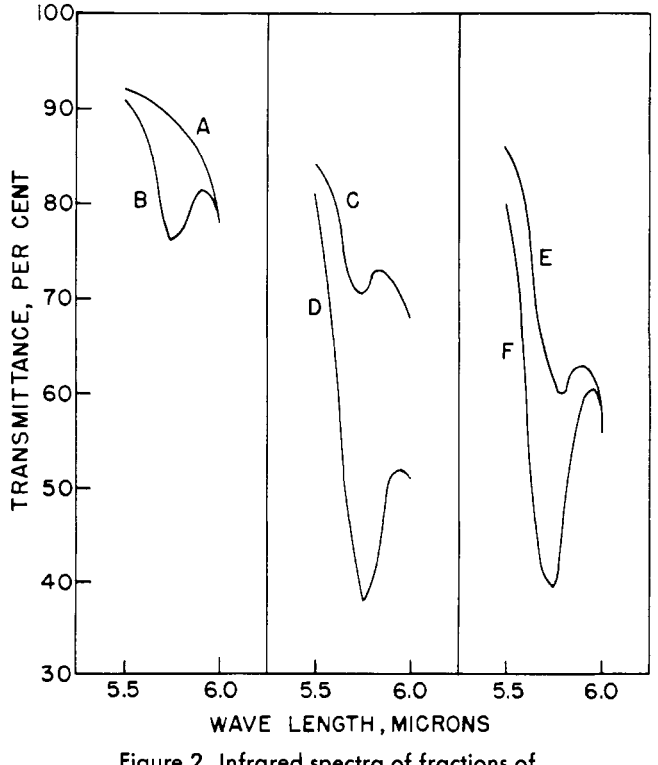

Figure 2. Infrared spectra of fractions of irradiated cotton in 5.5 to 6.0 micron range

A. Control. B. Total sample. C. Water-insoluble. D. Water-soluble. E. Alcohol-insoluble. F. Alcohol-soluble. Concn. of A-E, 6 mg.-sample/1000 mg.-KBr disk. Concn. of F, 2.5 mg./1000 mg.

nism of the reactions of cellulose produced by radiation. The data are considered in terms of the activation of a particular carbon atom in the glucose unit. This activation was produced by ionization at the carbon atom itself or by ionization of one of the atoms or groups of atoms bound to it.

The data presented are consistent with the following mechanism of chain cleavage. When the C_1 position is activated, chain cleavage occurs forming 2-ketogluconic on the reducing end of the chain utilizing 1 mole of oxygen, leaving an unaltered glucose unit on the nonreducing end of the other chain. Activation of the C_4 position results in chain cleavage, liberating the reducing end of the chain as an unaltered glucose unit and producing a ketone group in the C_4 position on the nonreducing end of the other chain.

Gamma irradiation of cellulose over a wide range of dosages, in either nitrogen or oxygen atmospheres, has been reported to form carbonyl and carboxyl groups, and cause chain cleavage in the approximate ratio of 20:1:1 (2). In an oxygen atmosphere at a dosage of 10^6 roentgens, this ratio was more accurately found to be 19:0.5:1. This indicated that for every two chain cleavages one acid group was produced. The two carbon atoms which are involved in the glucosidic linkage are the C_1 and the C_4 positions. Thus, activation of these two positions would be the most likely to produce chain cleavage.

The distribution of acid groups between the various fractions of the irradiated cellulose indicated that acid group production was principally a chain-end effect and that one acid group was produced per every two chains formed. The chromatographic data established the presence of glucose, cellobiose, and a homologous series of cellulodextrins. 2-Ketogluconic acid was one of the major acid monosaccharide units produced. The other major acid components were at least partially identified as the lactone of 2-ketogluconic acid and 2-ketocellobionic acid. It was also concluded that a homologous series of cellulodextrins, of which 2-ketocellobionic acid was the first member of the series, was not inconsistent with the homologous series found. The ultraviolet spectral data also indicated that 2-ketogluconic acid was present in the low molecular weight fraction and the higher molecular weight fraction, in approximately the same ratio as was found by acid titration of these fractions. The infrared spectra also showed a similar pattern for the distribution of acid groups.

The data also suggested that activation of the C_2, C_3, C_5, and C_6 positions caused reducing group formation with evolution of hydrogen and without chain cleavage.

The distribution of reducing groups in the various fractions of the irradiated cellulose indicated that these groups were equally distributed along the cellulose chain, suggesting the C_2, C_3, C_5, and C_6 positions. The gas consumption and evolution studies showed that considerable quantities of oxygen were consumed. The oxygen consumed in the reaction could go into formation of acid groups or carbon dioxide, but this would account for only a small fraction of the oxygen. Peroxide groups could be formed in the cellulose, but the qualitative test for the presence of peroxides was negative. The most logical explanation of oxygen consumption was by reaction with hydrogen, liberated in the formation of reducing groups, to form water. Apparently the predominant reaction on irradiation of cellulose was dehydrogenation with the production of reducing groups, either ketones or aldehydes. The data suggested, but did not adequately establish this mechanism. There is also evidence in the literature of similar effects produced when crystalline sugars were irradiated with γ-rays (*18*) and when cellulose was irradiated in vacuum with ultraviolet light (*7*).

The carbon monoxide and carbon dioxide evolved in the irradiation are considered to be secondary degradation products formed by decomposition of aldehydes and/or ketones in the case of carbon monoxide and by decarboxylation of carboxyl groups in the case of carbon dioxide (*7*). Irradiation produced a much greater quantity of reducing groups than carboxyl groups; thus more carbon monoxide than carbon dioxide is found. The quantity of carbon monoxide formed is high; however, rate of carbon monoxide formation data would be required to associate definitely this end product with the secondary degradation process. This work is now being carried out at this laboratory.

ACKNOWLEDGMENT

The authors thank Dan A. Kirkley for the mass spectrometer analyses, Robert A. Pittman for the ultraviolet absorption analyses, and Donald Mitcham for the infrared curves.

LITERATURE CITED

(1) Abraham, R.J., Whiffen, D.H., *Trans. Faraday Soc.* **54**, 1291–9 (1958).
(2) Blouin, F.A., Arthur, J.C., Jr., *Textile Research J.* **28**, 198–204 (1958); Authur, J.C., Jr., *Ibid.*, **28**, 204–6 (1958); Arthur, J.C., Jr., Blouin, F.A., Demint, R.J., *Am. Dyestuff Reptr.* **49**, 383–8 (1960).
(3) Clibbens, D.A., Geake, A., *J. Textile Inst.* **15**, T27–38 (1924).
(4) Davidson, G.F., Nevell, T.P., *Shirley Inst. Mem.* **21**, 85–100 (1947); *J. Textile Inst.* **39**, 102–117 (1948).
(5) Dyfverman, A., *Acta Chem. Scand.* **7**, 280–4 (1953).
(6) Euler, H.v., Eistert, B., "Chemie und Biochemie der Reduktone und Reduktonate," Ferdinand Enke, Stuttgart, 1957.
(7) Flynn, J.H., Wilson, W.K., Morrow, W.L., *J. Research Natl. Bur. Standards* **60**, 229–33 (1958).
(8) Gilfillan, E.S., Linden, L., *Textile Research J.* **25**, 773–7 (1955).
(9) *Ibid.*, **27**, 87–92 (1957).
(10) Glegg, R.E., *Radiation Research* **6**, 469–73 (1957).
(11) Glegg, R.E., Kertesz, Z.I., *J. Polymer Sci.* **26**, 289–97 (1957).
(12) Glegg, R.E., Kertesz, Z.I., *Science* **124**, 893–4 (1956).
(13) Green, J.W., in "The Carbohydrates—Chemistry, Biochemistry, Physiology," W. Pigman, ed., p. 304, Academic Press, New York, 1957.
(14) Harmon, D.J., *Textile Research J.* **27**, 318–24 (1957).
(15) Hodge, J.E., Davis, H.A., "Selected Methods for Determining Reducing Sugars," U.S. Dept. Agr., Bur. Agr. and Ind. Chem., Mimeo Circ. Ser. **AIC-333** (April 1952).
(16) Laurent, T.C., *J. Am. Chem. Soc.* **78**, 1875–7 (1956).
(17) Lederer, E., Lederer, M., "Chromatography—A Review of Principles and Applications," Elsevier, New York, 1953.
(18) Liggett, R.W., Feazel, C.E., Ellenberg, J.Y., *J. Agr. Food Chem.* **7**, 277–80 (1959).
(19) O'Connor, R.T., DuPré, E.F., McCall, E.R., *Anal. Chem.* **29**, 998–1005 (1957).
(20) Pan, H.-P., Proctor, B.E., Goldblith, S.A., Morgan, H.M., Naar, R.Z., *Textile Research J.* **29**, 415–21 (1959).
(21) Pigman, W., in "The Carbohydrates—Chemistry, Biochemistry, Physiology," W. Pigman, ed., pp. 452–62, Academic Press, New York, 1957.
(22) Rabson, R., Tolbert, N.E., *Nature* **181**, 50–1 (1958).
(23) Ranson, S.L., in "Modern Methods of Plant Analysis," K. Paech and M.V. Tracey, eds., Vol. **II**, p. 554, Springer, Berlin, 1955.
(24) Saeman, J.F., Millett, M.A., Lawton, E.J., *Ind. Eng. Chem.* **44**, 2848–52 (1952).
(25) Scott, T.A., Jr., Senti, F.R., *J. Am. Chem. Soc.* **77**, 3816–21 (1955).
(26) Teszler, O., Kiser, L.H., Campbell, P.W., Rutherford, H.A., *Textile Research J.* **28**, 456–62 (1958).
(27) Teszler, O., Wiehart, H., Rutherford, H.A., *Ibid.*, **28**, 131–5 (1958).
(28) Weiss, J., *J. Polymer Sci.* **29**, 425–32 (1958).
(29) Whelan, W.J., Bailey, J.M., Roberts, P.J.J., *J. Chem. Soc.* **1953**, pp. 1293–8.
(30) Winogradoff, N.N., *Nature* **165**, 72 (1950).

RECEIVED for review August 24, 1959. Accepted January 25, 1960. Trade names are given as part of exact experimental conditions and not as endorsement of products over those of other manufacturers.