A STUDY OF THE PHOTOCHEMICAL CHANGES OCCURRING IN RAYON AND COTTON CURTAINS WHEN EXPOSED TO LIGHT

Thesis for the Degree of M. A.
MICHIGAN STATE COLLEGE
Jane Nagelkirk Lanphar
1952

This is to certify that the

thesis entitled

A Study of the Photochemical Changes Occurring
in Rayon and Cotton Curtains Exposed to Light

presented by

Mrs. Jane Nagelkirk Lanphar

has been accepted towards fulfillment
of the requirements for

M. A. degree in Textiles, Clothing &
Related Arts

Bruce E Hartsuch
Major professor

Date 7/28/52

O-169

A STUDY OF THE PHOTOCHEMICAL CHANGES OCCURRING IN RAYON AND COTTON CURTAINS WHEN EXPOSED TO LIGHT

By

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A THESIS

Submitted to the School of Graduate Studies of Michigan
State College of Agriculture and Applied Science
in partial fulfillment of the requirements
for the degree of

MASTER OF ARTS

Department of Home Economics

1952

10-14-52 [illegible]

ACKNOWLEDGMENT

With deep appreciation to Professor Bruce E. Hartsuch for his patient guidance and inspiration during this investigation, and to Professor Hazel B. Strahan for her aid in acquainting the author with the general problem.

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INTRODUCTION

INTRODUCTION

In 1948 an Experiment Station project was initiated at Michigan State College, which had as its purpose the determination of the rate of degradation of window curtains when exposed to sunlight.

Two types of curtains were selected for the study: cotton voile, and viscose rayon marquisette. They were constructed with a three inch heading which extended above the window, and the length was such that they came just above the window sill. The curtains were hung in the Home Management Houses on campus at Michigan State College, at windows which gave exposure to northern, southern, eastern and western light. Both cotton and rayon curtains were subjected to the four exposures. They were laundered every three months, by graduate students in the Home Economics Department, according to standard laundry procedure. At the end of each six months, one pair of rayon and one pair of cotton curtains was removed from each exposure, and tested. The rayon curtains were exposed to sunlight for a total of twenty-four months, and the cotton curtains for thirty-six months.

Physical tests were performed in the Home Economics Department on the withdrawn curtains. These tests included tensile strength, yarn count, weight, and non-fibrous content.

The purpose of the investigation described in this thesis was to study the chemical changes which had taken place in the curtains during exposure to sunlight for from two to three years. It was thought that this would add to, and explain, some of the results obtained by the physical tests.

HISTORICAL

DeBuccar (13), Henk (18), and Pacini (27), studying the effect of light on textiles, found that the first reaction which took place was polymerization. Scharwin and Pokschew (30) and Barr and Hadfield (3) noted the splitting off of carbon dioxide after this polymerization, others (1,2) noted the splitting off of carbon dioxide and water; Stillings (32) noted the splitting off of carbon dioxide and carbon monoxide.

Mass (24) studied the effect of different weather factors and found that sunlight was the most damaging. Edgerton (15) and Lanigan (22) studied the effect of light, individually, and agree that most of the degradation was due to oxidation. Mass (24), Stillings and Van Nostrand (33), Wagner, Weber and Sui (35) found that the loss of strength of cellulose exposed to sunlight was due to breaking down of chains of the cellulose molecules into smaller and smaller fragments. Williams (36) compared the tensile strength of cotton and viscose after exposure to light, and found they had about the same rate of degradation.

Morrison and Jelnik (25) tested curtains at the end of 4, 8 and 12 months' exposure to sunlight and atmosphere. They found that the tensile strength decreased and the fluidity increased. The gain in fluidity was the greatest during the first months, and rayon fluidities were generally higher than the cotton fluidities.

Harrison (9) studied the effect of sunlight on cellulose and found that it produced oxycellulose and some substances which dissolved in water. His oxycellulose had a strong reducing power on Fehling's solution. Davidson (11,12) found that oxycellulose was characterized by increased fluidity, decreased tensile strength, increased reducing power, and increased methylene blue absorption. He attributed the increased reducing power to the oxidation of the primary and secondary alcohol groups to aldehydes and ketones, and the increased methylene blue absorption to the presence of carboxyl groups. He did not recognize two distinct types of oxycellulose. Heuser (19) and Lomax (21) agree that there are two definite types of oxycellulose, the reducing type and the acidic type. According to Lomax (21), the acidic type of oxycellulose is characterized by loss of strength, increased methylene blue absorption, increased fluidity, no increase in copper number and a small solubility in alkali. The reducing type is characterized by loss in strength, increased copper number, increased fluidity, increased alkali solubility, and no increase in methylene blue absorption. Heuser used only the factors which differed for his distinction between the two types of oxycellulose. He states that the acidic type is characterized by relatively low copper number and high methylene blue absorption, and the reducing type by high copper number and low methylene blue absorption. Lomax (21), Marsh and Wood (23), and Grimes (16) attribute the yellowing of fabrics when exposed to sunlight to the reducing type of oxycellulose. Heuser (19), Lomax (21), Marsh and Wood (23), Hartsuch (17), Cunliffe and Farrow (10), and others agree that the type of oxycellulose produced during bleaching is dependent upon the pH of the bleaching bath.

Grimes (16), Oguri (26), Cunliffe and Farrow (10), Schappi (29) and others studied the effect of sunlight on cellulose and found that the copper number increased with exposure to sunlight. Dorée (14) states that the copper number for carefully bleached native cotton is about 0.2. Lomax (21) says that a copper number higher than 0.25 indicates chemical damage.

Dorée (14), and Birtwell, Clibbens and Ridge (4) agree that methylene blue absorption varies with the ash alkalinity. The ash content is approximately proportional to the ash alkalinity. The methylene blue absorption for normally bleached cotton is about 0.1 gram for 100 grams of cellulose.

Marsh and Wood (23), and Clibbens and Little (7) found that the complete range of fluidities for solutions of cellulose in cuprammonium was from 2 for a solution of pure cellulose to 70 for the cuprammonium solution itself. Marsh and Wood (23), and Dorée (14) agree that normally bleached cotton has a cuprammonium fluidity between 5 and 10. Lomax (21) places the upper limit for properly bleached cotton a little lower, at 8. According to Marsh and Wood (23), and Dorée (14), cotton which has a fluidity of from 20 to 30 is overbleached. Clibbens and Little (7), Marsh and Wood (23), and Dorée (14) agree that when the fluidity reaches a value as high as 40, the cotton has completely disintegrated.

Ridge and Bowden (28), and Lomax (21) agree that properly bleached rayon has a fluidity of 12.5 in a 2% solution. For a 0.5% solution, Dorée (14) found that properly bleached rayon had a fluidity of from 30 to 40. Marsh and Wood (23) consider rayon to be overbleached with fluidities of 40 or more in a 2% solution. Clibbens and Little (7) state that rayon is disintegrated with fluidities from 40 to 60. Dorée (14) found that 60 was the point of complete disintegration.

Ridge and Bowden (28), and Lomax (21) found that a rise of five units in fluidity corresponded to a 10% loss in strength for cotton, and a 16 to 17% loss in strength for rayon. Fluidity of normal rayon will be higher than that for native cotton because rayon suffers some depolymerization (chain shortening) during manufacture.

Marsh and Wood (23), and Heuser (19) agree that when fluidity is plotted against the extent of tendering, the resultant curve is a straight line. Barr and Hadfield (3), and Ridge and Bowden (28) agree that the curves which result when fluidity and tensile strength are plotted against time of exposure to sunlight, should be parallel, assuming that tensile strength changes are due only to chemical damage. Ridge and Bowden (28) state that once past the initial stage, the curves of tensile strength plotted against time should be the same for all fibers.

EXPERIMENTAL METHODS

EXPERIMENTAL METHODS

All samples of curtain material used in these experiments were conditioned by allowing them to stand over sulfuric acid in a desiccator. There was about 1.5 inches of 35.9% sulfuric acid (by volume) on the bottom of the desiccator. This was found by Skinkle (31) to provide an atmosphere of 65% relative humidity at 25° C. Since the relative humidity of the atmosphere changes very little with small changes in temperature, the curtain materials were allowed to condition in the desiccator at ordinary room temperature.

Since all calculations were based on bone-dry weight of the cellulosic materials, the percentage of bone-dry weight in the conditioned materials was determined by heating weighed samples in an oven at 105° C. for 12 hours; the samples were removed from the oven, cooled in a desiccator over calcium chloride, and weighed. This weight divided by the conditioned weight, times 100 is the percentage bone-dry weight in the conditioned material. When these determinations were made, the samples were placed in weighing bottles, which were left open during the drying and cooling, but closed when the bone-dry samples were weighed.

Samples were taken from the central section of each curtain, which had been exposed to sunlight, and from the heading which was unexposed to sunlight. When the curtains were received for chemical testing, samples had been removed for the physical tests. The cutting charts (figures 1 and 2) show the location of the samples for these physical tests, as well as the chemical tests.

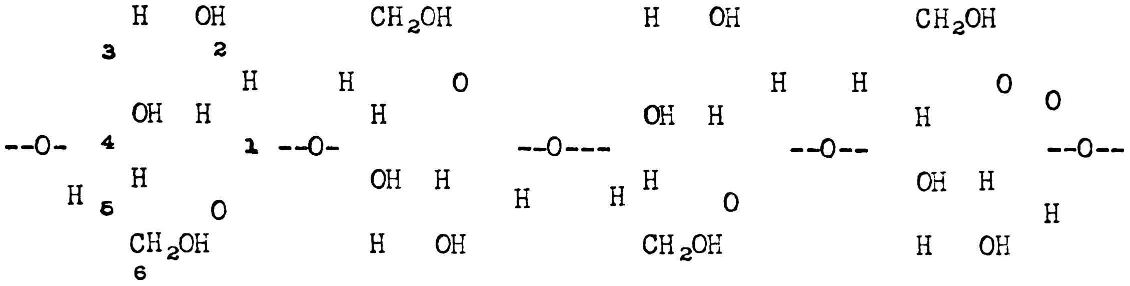
All determinations were run in duplicate, and the averages plotted on curves.

Per cent change for all values obtained by chemical tests were determined by dividing the difference between exposed and unexposed values by the unexposed value.

The Degradation of Cellulose

Cellulose may be degraded in two ways, mechanically, and chemically. Mechanical damage results from tearing, stretching, abrasion, etc. Chemical degradation is produced by two types of reactions, acid hydrolysis, and oxidation.

Cellulose is composed of long chains of anhydro-glucose units joined by 1:4 glucosidic linkages.



When cellulose is exposed to acid, the glucosidic linkage is split (the chain is broken) and water is added at the point of cleavage. With continuous attack cellulose is eventually hydrolyzed to glucose. It is the first step of hydrolysis which is of importance in the textile field. The product of this initial step is called hydrocellulose. The result of hydrolysis is twofold. It shortens the chain molecule length, causing loss of strength, and sets up new potential aldehydic reducing end groups. These aldehyde groups increase the alkali solubility of cellulose. If the fabric which has been hydrolyzed is laundered with a soap which is strongly alkaline, a small portion of the cellulose dissolves, the fabric loses weight and becomes weaker.

Although the results of oxidation of cellulose are similar to those of hydrolysis, the mechanism of oxidation is not as well understood as hydrolysis. Probably many reactions are taking place at the same time to form the end product, oxycellulose. Unruh and Kenyon (34) suggest that the oxidation takes place at the following points of attack:

1. Attack at carbons 2 or 3, or both, oxidizing these secondary alcohol groups to ketones, without breaking the ring.
2. Oxidation at both carbon 2 and 3 to form aldehydes, with a simultaneous rupture of the ring.
3. Oxidation of the primary alcohol group at carbon 6 to an aldehyde.
4. Further oxidation of the aldehyde groups at carbon 2 and 3 to carboxyl groups.
5. Oxidation of the carbon 6 alcohol to a carboxyl group.
6. The oxidation may result in oxidation of alcohol groups at carbon 2 and 3 to aldehyde groups, followed by further oxidation of one of them to a carboxyl group, leaving the other as an aldehyde.

Since all of these reactions may take place at the same time, many types of oxycellulose are possible. From the British Cotton Industry Research Association, Birtwell, Clibbens, Geake, Ridge, and others (4,6,8) reported that there are two definite types of oxycellulose, which are the extremes of the many types found. The type of oxycellulose which results from bleaching is determined by the pH of the bleaching bath. The two types are: (1) the acidic type, which is formed with an acidic bleaching bath, and (2) the reducing type which is formed in an alkaline bath. The acidic type is characterized by a large number of carboxyl groups and few aldehyde groups. It results from reactions 4 and 5. The reducing type has a large number of aldehyde groups and few carboxyl groups. It results from reactions 2 and 3. Reaction 6 will produce both types of oxycellulose.

It has been found that the action of light and air on cellulosic material is an oxidative reaction, and the results obtained in this investigation show that the product is an oxycellulose of the reducing type.

Tests Which Show the Presence of Oxycellulose

The presence of carboxyl groups will increase the affinity of cellulose for basic dyes, such as methylene blue, and the methylene blue number determination is a measure of the relative number of carboxyl groups in oxidized cellulosic materials. Ash alkalinity or ash content of cellulose will affect the methylene blue absorption, and therefore it is necessary to determine ash content in order to be certain that variations in methylene blue absorption are due to carboxyl groups rather than differences in ash content.

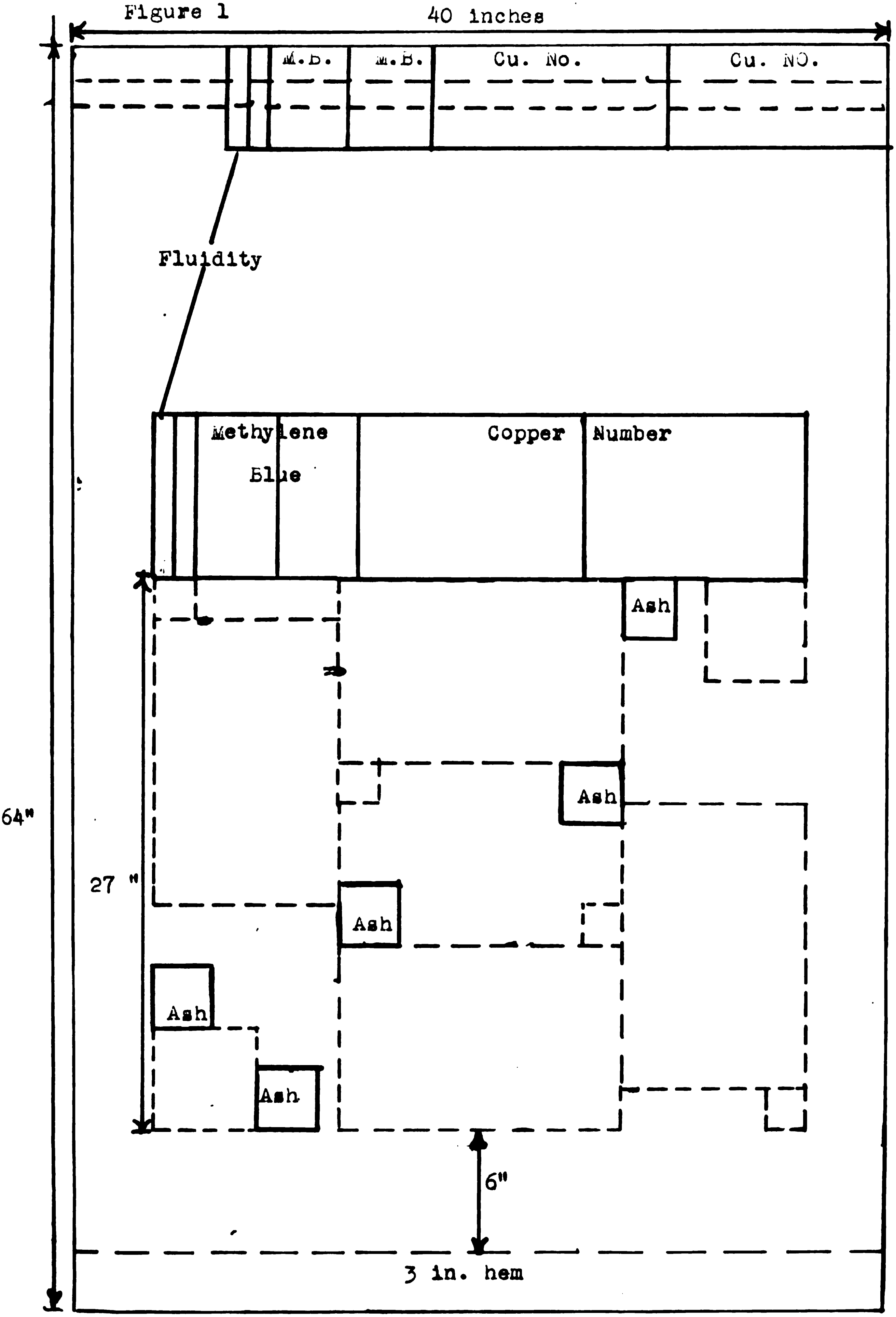
The fluidity of a solution of cellulose in cuprammonium (Schweitzer's reagent) is a measure of chain length. Increase in cuprammonium fluidities indicates chain shortening of the cellulose molecules.

Aldehyde groups have a strong reducing power on Fehling's solution. The copper number determination, which employs a modified Fehling's solution, is a measure of the aldehydic reducing power of oxycellulose. Fluidity and copper number determinations will detect small amounts of degradation in cellulosic materials better than tensile strength tests.

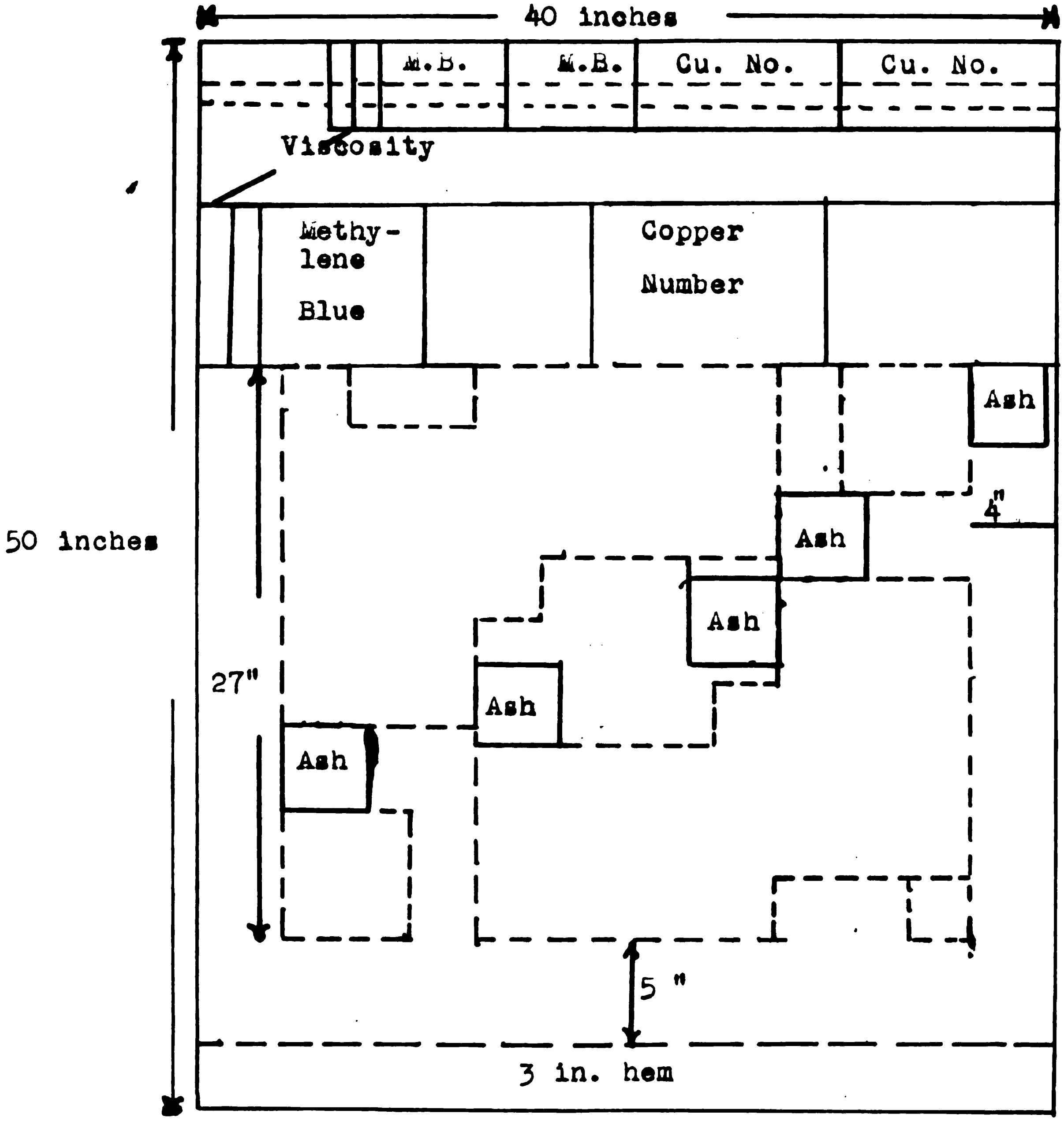
Since fluidity is independent of the type of chemical modification and depends only on chain length, it will show the extent of change due either to hydrolysis or oxidation, or a combination of the two. Decrease in tensile strength may be due to either mechanical or chemical damage, and since increased fluidity is a measure of chemical change, this determination may be used to distinguish between chemical and mechanical damage.

HISTORICAL

Figure 1



CUTTING CHART FOR RAYON CURTAINS



CUTTING CHART FOR COTTON CURTAINS

Determination of Ash Content

A conditioned sample weighing approximately 2.5 gm was cut into pieces, one inch by two inches and placed in a weighed platinum crucible. It was ignited slowly with a Bunsen burner until the sample was completely carbonized, and then with a Meaker burner to a white ash. The crucible was removed and placed in a calcium chloride desiccator, cooled, and weighed. The heating, cooling, and weighing were repeated until the ash had a constant weight.

Calculation of Ash content

The per cent ash is calculated by the following formula:

$$\%\ \text{ash} = \frac{\text{gm ash} \times 100}{\text{gm bone-dry sample}}$$

The results of these determinations are recorded in table I.

TABLE I

PERCENT ASH CONTENT

	Cotton	6 months	12 months	18 months	24 months	30 months	36 months
East		.16	.21	.11	.20	.17	.17
		.14	.17	.11	.20	.14	.16
	Average	.15	.19	.11	.20	.16	.17
South		.16	.20	.13	.21	.20	.13
		.16	.14	.11	.19	.16	.12
	Average	.16	.17	.12	.20	.18	.13
West		.13	.18	.15	.11	.20	.20
		.13	.15	.13	.10	.19	.18
	Average	.13	.17	.14	.11	.20	.19
North		.12	.12	.19	.12	.16	.16
		.10	.13	.17	.11	.14	.12
	Average	.11	.13	.18	.12	.15	.14
	Rayon						
East		.16	.21	.22	.19		
		.16	.16	.21	.17		
	Average	.16	.19	.22	.18		
South		.18	.20	.16	.19		
		.16	.20	.13	.18		
	Average	.17	.20	.15	.19		
West		.21	.18	.20	.18		
		.20	.15	.16	.18		
	Average	.21	.17	.18	.18		
North		.17	.21	.22	.17		
		.17	.16	.20	.15		
	Average	.17	.19	.21	.16		

Determination of Methylene Blue Number

Reagents

Buffered methylene blue solution ($C_{16}H_{18}N_3SCl$)

6.81 gm potassium dihydrogen phosphate

29.63 ml N sodium hydroxide solution

1.279 gm methylene blue hydrochloride

Make up to 1 liter with distilled water

(This solution will be approximately 0.004 M)

Napthol yellow-S solution

0.6 gm napthol yellow-S per liter

Procedure (6)

Samples of curtain material were cut into small pieces, 1/8 x 1/16 in. and conditioned as previously described. A 1.0000 gm sample was placed in a centrifuge tube and 15 ml of the 0.004 M methylene blue solution added. The solution was worked well into the sample with a glass rod and allowed to stand 18 hours at room temperature. The sample was then centrifuged for 5 minutes, 5 ml of the liquid removed with a pipette and transferred to an Erlenmeyer flask, and 20 ml of distilled water was added. This solution was titrated with the napthol yellow-S solution until the liquid turned from blue to yellow. A reddish brown precipitate forms which obscures the endpoint. This can be obviated by placing a drop of the liquid on a white spot plate with a glass rod. By doing this only a small amount of precipitate is transferred to the spot plate, and therefore the color of the solution can be observed much more easily.

Calculations

Methylene blue number is the number of milliequivalents of methylene blue absorbed by 100 gm of cellulosic material.

The methylene blue equivalent of the napthol yellow-S solution was determined by titrating 5 ml methylene blue, (cotton absent) with the napthol yellow-S solution.

The methylene blue numbers were calculated from the following equation:

$$\text{M.B. No.} = \frac{\text{meq. M.B. per liter x ml napthol yellow-S x 100}}{\text{gm bone-dry sample}}$$

The results of these determinations are recorded in tables II, III, IV and V.

TABLE II

COTTON METHYLENE BLUE NUMBERS

Unexposed to sunlight		6 months	12 months	18 months	24 months	30 months	36 months
East		1.72	1.72	1.76	1.76	1.72	1.72
		1.76	1.76	1.80	1.76	1.72	1.76
	Average	1.74	1.74	1.78	1.76	1.72	1.74
South		1.76	1.76	1.76	1.72	1.72	1.72
		1.80	1.76	1.76	1.76	1.76	1.72
	Average	1.78	1.76	1.76	1.74	1.74	1.72
West		1.76	1.76	1.76	1.76	1.76	1.72
		1.80	1.76	1.76	1.76	1.80	1.72
	Average	1.78	1.76	1.76	1.76	1.78	1.72
North		1.76	1.76	1.72	1.72	1.72	1.64
		1.76	1.76	1.76	1.76	1.72	1.68
	Average	1.76	1.76	1.74	1.74	1.72	1.66
Exposed to sunlight							
East		1.80	1.72	1.76	1.72	1.72	1.72
		1.80	1.76	1.76	1.76	1.72	1.72
	Average	1.80	1.74	1.76	1.74	1.72	1.72
South		1.80	1.76	1.72	1.68	1.72	1.72
		1.80	1.80	1.76	1.72	1.76	1.72
	Average	1.80	1.78	1.74	1.70	1.74	1.72
West		1.80	1.76	1.72	1.68	1.72	1.68
		1.80	1.76	1.72	1.68	1.72	1.72
	Average	1.80	1.76	1.72	1.68	1.72	1.70
North		1.76	1.72	1.72	1.76	1.72	1.64
		1.76	1.76	1.76	1.76	1.72	1.68
	Average	1.76	1.74	1.74	1.76	1.72	1.66

TABLE III

COTTON METHYLENE BLUE NUMBERS -- DIFFERENCES BETWEEN EXPOSED AND UNEXPOSED

	6 months	12 months	18 months	24 months	30 months	36 months
East	.06	0	-.02	.02	0	-.02
South	.02	.02	-.02	-.04	0	0
West	.02	0	-.04	-.08	-.06	-.02
North	0	-.02	0	.02	0	0
	PER CENT DIFFERENCES BETWEEN EXPOSED AND UNEXPOSED					
East	3.4	0	-1.1	1.1	0	-1.1
South	1.1	1.1	-1.1	-2.3	0	0
West	1.1	0	-2.3	-4.5	-3.4	-1.1
North	0	-1.1	0	1.1	0	0

TABLE IV

RAYON METHYLENE BLUE NUMBERS

Unexposed to sunlight	6 months	12 months	18 months	24 months
East	1.76	1.72	1.72	1.68
	1.80	1.76	1.76	1.72
Average	1.78	1.74	1.74	1.70
South	1.76	1.72	1.68	1.64
	1.76	1.76	1.68	1.68
Average	1.76	1.74	1.68	1.66
West	1.76	1.72	1.72	1.68
	1.76	1.76	1.72	1.68
Average	1.76	1.74	1.72	1.68
North	1.76	1.68	1.68	1.64
	1.76	1.68	1.72	1.68
Average	1.76	1.68	1.70	1.66
Exposed to sunlight				
East	1.76	1.72	1.76	1.72
	1.80	1.76	1.76	1.72
Average	1.78	1.74	1.76	1.72
South	1.84	1.76	1.72	1.68
	1.84	1.80	1.76	1.72
Average	1.84	1.78	1.74	1.70
West	1.76	1.76	1.72	1.68
	1.76	1.76	1.72	1.72
Average	1.76	1.76	1.72	1.70
North	1.76	1.68	1.68	1.64
	1.80	1.68	1.72	1.68
Average	1.78	1.68	1.70	1.66

TABLE V

RAYON METHYLENE BLUE NUMBERS -- DIFFERENCES BETWEEN EXPOSED AND UNEXPOSED

	6 months	12 months	18 months	24 months
East	0	0	.02	.02
South	.08	.04	.06	.04
West	0	.02	0	.02
North	.02	0	0	0
PER CENT DIFFERENCES BETWEEN EXPOSED AND UNEXPOSED				
East	0	0	1.1	1.1
South	4.5	2.3	3.4	2.3
West	0	1.1	0	1.1
North	1.1	0	0	0

Determination of Copper Number

The original copper number tests were developed by C. G. Schwalbe. He used Fehling's solution for his tests. Clibbens and Geake used his method with modified Fehling's solution as their reagent. Copper number determinations for this investigation were made according to the method of Clibbens and Geake (31).

Reagents

Solution A

$CuSO_4 \cdot 5\ H_2O$ per liter: 100 gm

Solution B

50 gm $NaHCO_3$ plus 350 gm $Na_2CO_3 \cdot 10\ H_2O$ per liter

Ferric alum solution

100 gm ferric alum and 140 ml concentrated H_2SO_4 per liter

Sulfuric acid solution

56.6 ml concentrated H_2SO_4 per liter

Sodium carbonate solution

50 gm anhydrous Na_2CO_3 per liter

Potassium permanganate stock solution

3.25 gm $KMnO_4$ per liter

Potassium permanganate, 0.04 N

Dilute the stock solution 2.5 times with distilled water, and adjust to this normality. Standardize with sodium oxalate.

Procedure

A sample weighing 2.5 gm was cut into pieces approximately 0.5 by 1 in. and placed in a 125 ml glass stoppered iodine flask. Five ml of solution A was mixed with 95 ml of solution B, (measured with burettes) heated to boiling, and poured over the sample in the flask. The flask was placed in a constant level water bath which was adjusted to maintain the water just below the top of the flask. The temperature of the bath was maintained at 90 to 100° C. and the flask left in the bath exactly three hours. The flask was removed from the bath and the sample filtered immediately by suction through a Gooch crucible, into a filter flask. The sample was washed with approximately 50 ml of the sodium carbonate solution, followed by 50 ml of hot distilled water. The original filtrate and the washings were discarded. Using a clean 250 ml filter flask, the residue was washed with 50 ml of ferric alum solution in four portions, followed by 50 ml of the sulfuric acid solution. The combined ferric alum and sulfuric acid washings were heated and titrated with 0.04 N $KMnO_4$. A blank determination was run by mixing 50 ml of the sulfuric acid solution and 50 ml of the ferric alum solution, heating and titrating with 0.04 N $KMnO_4$. The figure obtained in this blank titration was subtracted from each copper number titration.

Calculation

Copper number is the number of grams of copper reduced by 100 grams cellulosic material from Fehling's solution or a modification of it.

The copper numbers were calculated from the permanganate titrations, by the following equation:

$$\text{Cu. No.} = \frac{\text{ml } KMnO_4 \times N\ KMnO_4 \times 0.0636 \times 100}{\text{gm bone-dry sample}}$$

(0.0636 is the milliequivalent weight of copper)

The results of these determinations are recorded in tables VI, VII, VIII and IX, and the values are plotted as curves in graphs 1, 2, 3 and 7.

TABLE VI

COTTON COPPER NUMBER

Unexposed to sunlight		6 months	12 months	18 months	24 months	30 months	36 months
East		.20	.22	.21	.22	.23	.24
		.20	.20	.22	.22	.23	.23
	Average	.20	.21	.22	.22	.23	.24
South		.20	.21	.21	.22	.23	.24
		.20	.21	.21	.21	.22	.24
	Average	.20	.21	.21	.22	.23	.24
West		.19	.19	.20	.22	.22	.23
		.19	.19	.20	.20	.22	.23
	Average	.19	.19	.20	.21	.22	.23
North		.19	.19	.21	.21	.23	.23
		.17	.18	.19	.21	.21	.21
	Average	.18	.19	.20	.21	.22	.22
Exposed to sunlight							
East		.66	.71	.77	.82	.89	.96
		.64	.71	.76	.82	.89	.94
	Average	.65	.71	.77	.82	.89	.95
South		.71	.79	.82	.91	.98	1.06
		.70	.77	.82	.89	.98	1.05
	Average	.71	.78	.82	.90	.98	1.06
West		.54	.58	.60	.64	.66	.69
		.51	.56	.60	.64	.65	.68
	Average	.53	.57	.60	.64	.66	.69
North		.42	.47	.50	.55	.61	.64
		.42	.44	.49	.54	.59	.64
	Average	.42	.46	.50	.55	.60	.64

TABLE VII

COTTON COPPER NUMBER -- DIFFERENCES BETWEEN EXPOSED AND UNEXPOSED

	6 months	12 months	18 months	24 months	30 months	36 months
East	.45	.50	.56	.60	.66	.71
South	.51	.57	.61	.68	.75	.82
West	.34	.36	.41	.46	.51	.56
North	.24	.27	.30	.34	.38	.42
PER CENT DIFFERENCES BETWEEN EXPOSED AND UNEXPOSED						
East	225	238.1	254.5	272.7	286.9	295.9
South	255	271.4	290.5	309	326.8	341.7
West	178.9	189.4	205	219	231.9	243.4
North	133.3	142.1	150	161.8	174.7	190.9

TABLE VIII

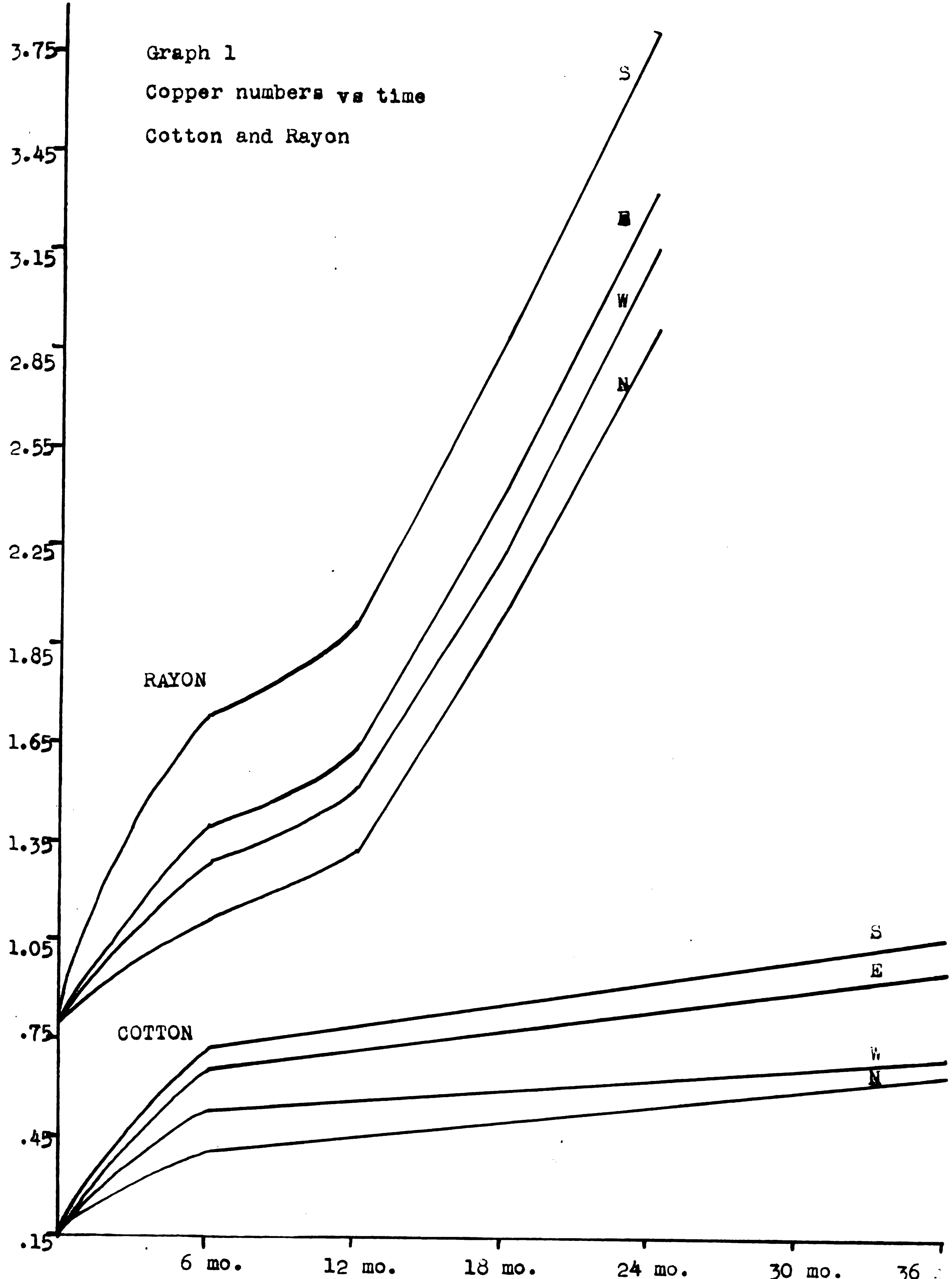
RAYON COPPER NUMBERS

Unexposed to sunlight		6 months	12 months	18 months	24 months
East		.87	.93	.99	1.06
		.86	.93	.99	1.06
	Average	.87	.93	.99	1.06
South		.90	.97	1.03	1.09
		.90	.96	1.02	1.08
	Average	.90	.97	1.03	1.09
West		.86	.93	.99	1.06
		.86	.91	.97	1.05
	Average	.86	.92	.98	1.06
North		.84	.91	.97	1.05
		.83	.90	.97	1.05
	Average	.84	.91	.97	1.05
Exposed to sunlight					
East		1.39	1.63	2.41	3.33
		1.38	1.63	2.44	3.32
	Average	1.39	1.63	2.43	3.33
South		1.72	2.03	2.88	3.81
		1.72	2.01	2.88	3.81
	Average	1.72	2.02	2.88	3.81
West		1.28	1.51	2.18	3.15
		1.28	1.51	2.17	3.13
	Average	1.28	1.51	2.18	3.14
North		1.11	1.32	2.07	2.91
		1.10	1.32	2.05	2.91
	Average	1.11	1.32	2.06	2.91

TABLE IX

RAYON COPPER NUMBER -- DIFFERENCES BETWEEN EXPOSED AND UNEXPOSED

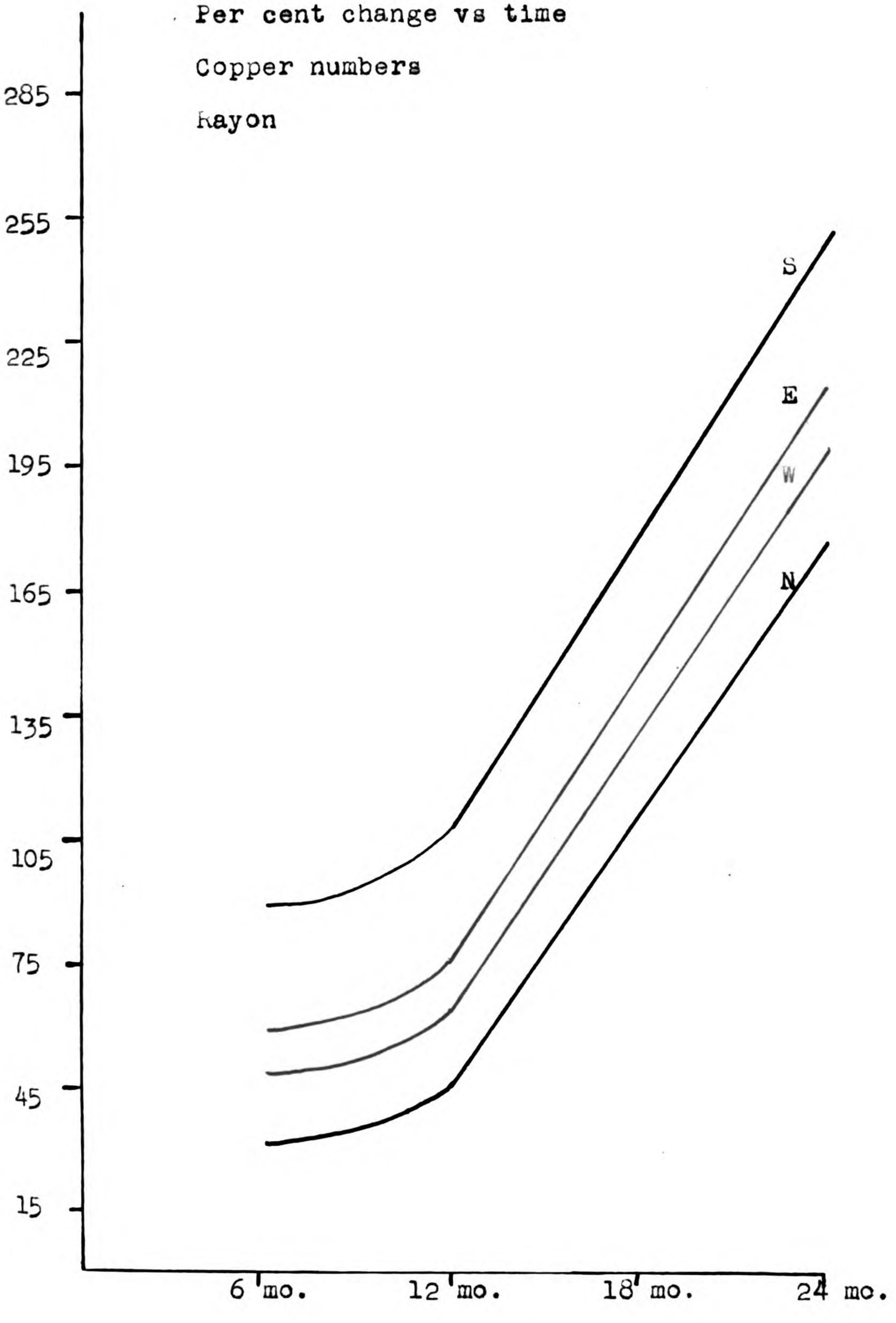
	6 months	12 months	18 months	24 months
East	.52	.70	1.44	2.27
South	.81	1.05	1.85	2.72
West	.42	.59	1.20	2.08
North	.27	.41	1.09	1.86
	PER CENT DIFFERENCES BETWEEN EXPOSED AND UNEXPOSED			
East	59.8	75.3	145.4	214.1
South	90.0	108.3	179.6	249.5
West	48.8	64.5	132.6	196.2
North	30.9	45.0	112.4	177.1



Graph 1

Copper numbers vs time

Cotton and Rayon

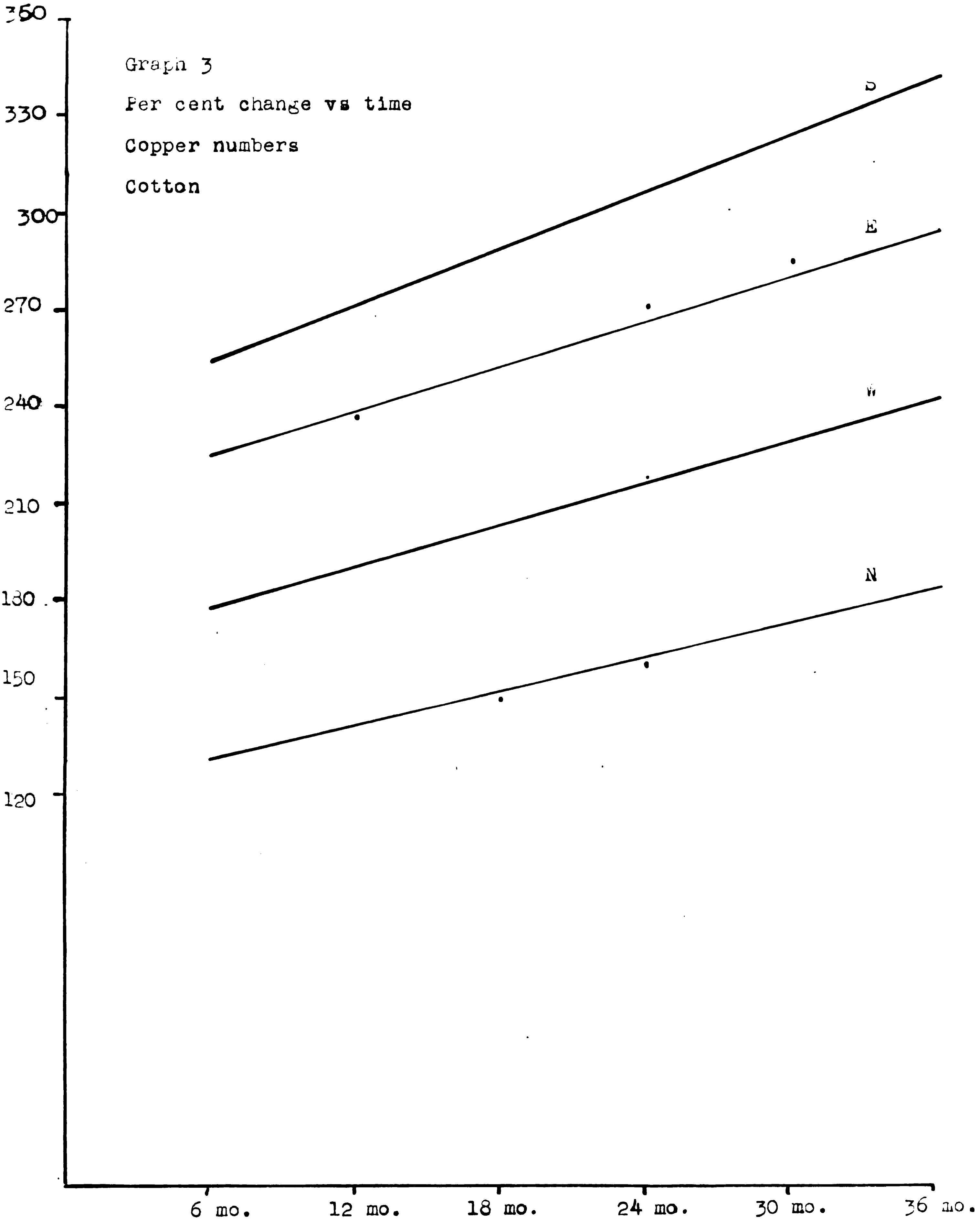


Graph 2

Per cent change vs time

Copper numbers

Rayon



Graph 3

Per cent change vs time

Copper numbers

Cotton

Determination of Fluidity

The rate of flow method of fluidity determination used in this problem was first used by Ost. His method was improved by Clibbens and Geake. Gibson, Joyner, Farrow and Neale used a falling sphere method for fluidity determinations. Howlett and Belward (20) experimented with shortened methods of fluidity measurement. They report two methods, one of which requires one-half hour, and the other two hours. Both methods require strict laboratory techniques which make them impractical for the average textile laboratory.

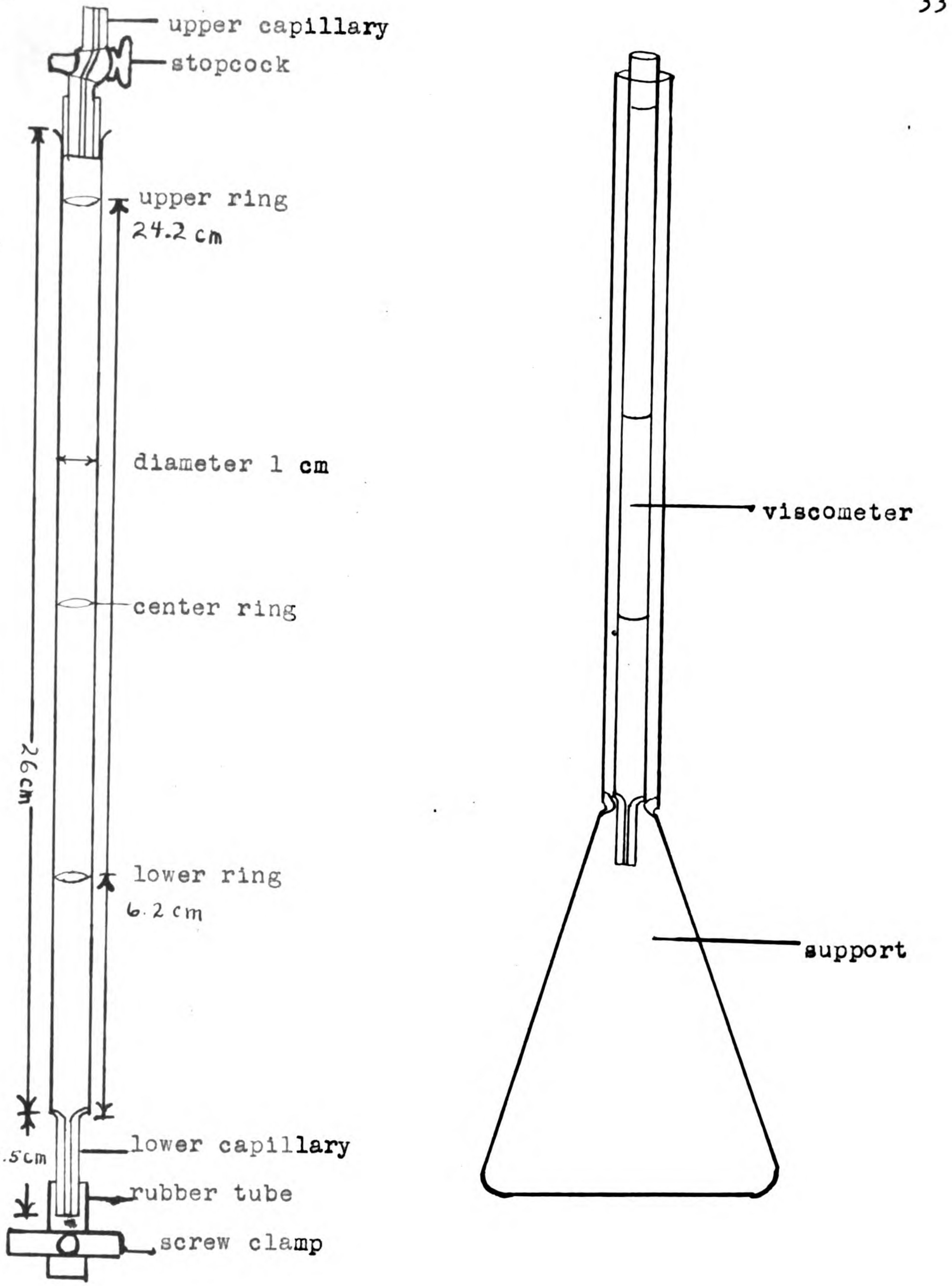
Fluidity measurements in this study were made according to the method of Clibbens and Geake (5). The viscometer used was no. 27220 from the catalogue of the Central Scientific Company, Chicago, Illinois. This viscometer is shown in figure 3.

Reagents

Cuprammonium solution

Concentrated ammonium hydroxide (2.6 liters, sp. gr. 0.88), of water, and 3 gm cane sugar were placed in a flask of about 5 liters capacity and stirred at 4 r.p.m. with 180 gm of copper which had passed a 60-mesh sieve. Air was passed through the solution for five hours at the rate of 10 liters per hour. This air had previously been washed and saturated with ammonia by passing it through ammonium hydroxide (sp gr 0.88). The solution was syphoned off and stored in 200 ml bottles. It was found that 200 ml was the amount of the cuprammonium solution needed for one day's testing. The bottles were corked, sealed with paraffin, and

Figure 3



Capillary:
Inner diameter o.088 cm
External diameter 0.6 cm

wrapped in brown paper to prevent light from affecting the solution.

Glycerine-water mixture, sp gr 1.1681

This is the specific gravity of a mixture containing 64.4% glycerine by weight.

Standardization of viscometers

Since the viscometers had slightly different dimensions, it was necessary to standardize the instruments individually, thus determining a constant for each one. The glycerine-water solution was used for this standardization. The viscometer was filled with the glycerine-water solution, and the time in seconds required for the meniscus to fall from the top ring to the bottom ring measured with a stopwatch.

A constant for each instrument was calculated from the following equation:

$$C = 1.075\ (dFt)$$

1.075 = a constant

d = specific gravity of the solution (1.1681)

F = fluidity of the glycerine (6.81)

t = time in seconds

Procedure

About 5 ml of the cuprammonium solution was placed in the viscometer, the lower clamp opened, and the capillary filled, after which the clamp was closed. The conditioned sample which had been cut into pieces not more than 1/8 by 1/16 in. was placed in the viscometer with the metal wedge. The cotton sample was approximately 0.1 gm and the rayon sample

0.2 gm bone-dry weight. The exact weight of the samples must be adjusted for each determination so as to give a 0.5% solution of cotton and a 1.0% solution of rayon.* The viscometer was filled to the top, the stopcock inserted, and the excess solution allowed to run out through the upper capillary. The stopcock was closed and the viscometer wrapped in dark cloth to eliminate the effect of light on the solution. The solution of the sample in the cuprammonium was accomplished by rotating the viscometer in such a way that the metal wedge slid from end to end. This was done by attaching the viscometer to a wheel and rotating for 12 hours. The speed of the rotation was 4 r.p.m. The stopcock was opened and the solution allowed to run out. The time in seconds required for the meniscus to fall from the top ring to the bottom ring was measured with a stopwatch.

Calculation

The fluidity of the solution was calculated from the following equation:

$$F = \frac{C}{dt}$$

C = the constant of the instrument

d = density (the density may be taken as 0.94)

t = time in seconds

The results of this determination are recorded in tables X, XI, XII and XIII, and the values plotted as curves in graphs 4, 5, 6 and 7.

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* The directions given by Glibbens and Geake call for a 2.0% rayon solution. This was found to be difficult to dissolve and was changed to a 1.0% solution.

TABLE X

COTTON FLUIDITIES

Unexposed to sunlight		6 months	12 months	18 months	24 months	30 months	36 months
East		6.10	6.43	6.78	7.15	7.43	7.75
		6.23	6.48	6.81	7.06	7.36	7.66
	Average	6.17	6.46	6.80	7.11	7.40	7.71
South		6.16	6.49	6.83	7.13	7.37	7.71
		6.26	6.47	6.81	7.08	7.45	7.68
	Average	6.21	6.48	6.82	7.11	7.41	7.70
West		6.18	6.57	6.74	7.11	7.38	7.73
		6.22	6.46	6.83	7.12	7.41	7.69
	Average	6.20	6.52	6.79	7.12	7.40	7.71
North		6.24	6.41	6.78	7.09	7.40	7.72
		6.13	6.51	6.79	7.11	7.42	7.69
	Average	6.19	6.46	6.79	7.10	7.41	7.71
Exposed to sunlight							
East		7.56	9.77	11.93	14.09	16.54	18.46
		7.43	9.74	11.96	14.21	16.57	18.59
	Average	7.48	9.76	11.95	14.15	16.56	18.53
South		7.63	9.87	12.13	14.67	16.99	19.28
		7.59	9.80	12.23	14.54	16.83	19.19
	Average	7.61	9.84	12.18	14.61	16.91	19.24
West		7.31	9.63	11.35	13.65	15.49	17.77
		7.38	9.59	11.48	13.70	15.46	17.95
	Average	7.35	9.61	11.42	13.68	15.48	17.86
North		7.29	9.47	10.83	12.11	14.04	15.79
		7.25	9.52	10.95	12.30	14.13	15.94
	Average	7.27	9.50	10.89	12.21	14.09	15.87

TABLE XI

COTTON FLUIDITIES -- DIFFERENCES BETWEEN EXPOSED AND UNEXPOSED

	6 months	12 months	18 months	24 months	30 months	36 months
East	1.31	3.30	5.15	7.04	9.16	10.82
South	1.40	3.36	5.36	7.50	9.50	11.54
West	1.15	3.09	4.63	6.56	8.08	10.15
North	1.08	3.04	4.10	5.11	6.68	8.16

PER CENT DIFFERENCES BETWEEN EXPOSED AND UNEXPOSED

	6 months	12 months	18 months	24 months	30 months	36 months
East	21.2	51.1	75.7	99.0	123.8	140.3
South	22.5	51.9	78.6	105.5	128.2	149.9
West	18.5	47.3	68.2	92.1	109.2	131.7
North	17.4	47.0	60.4	71.9	90.1	105.9

TABLE XII

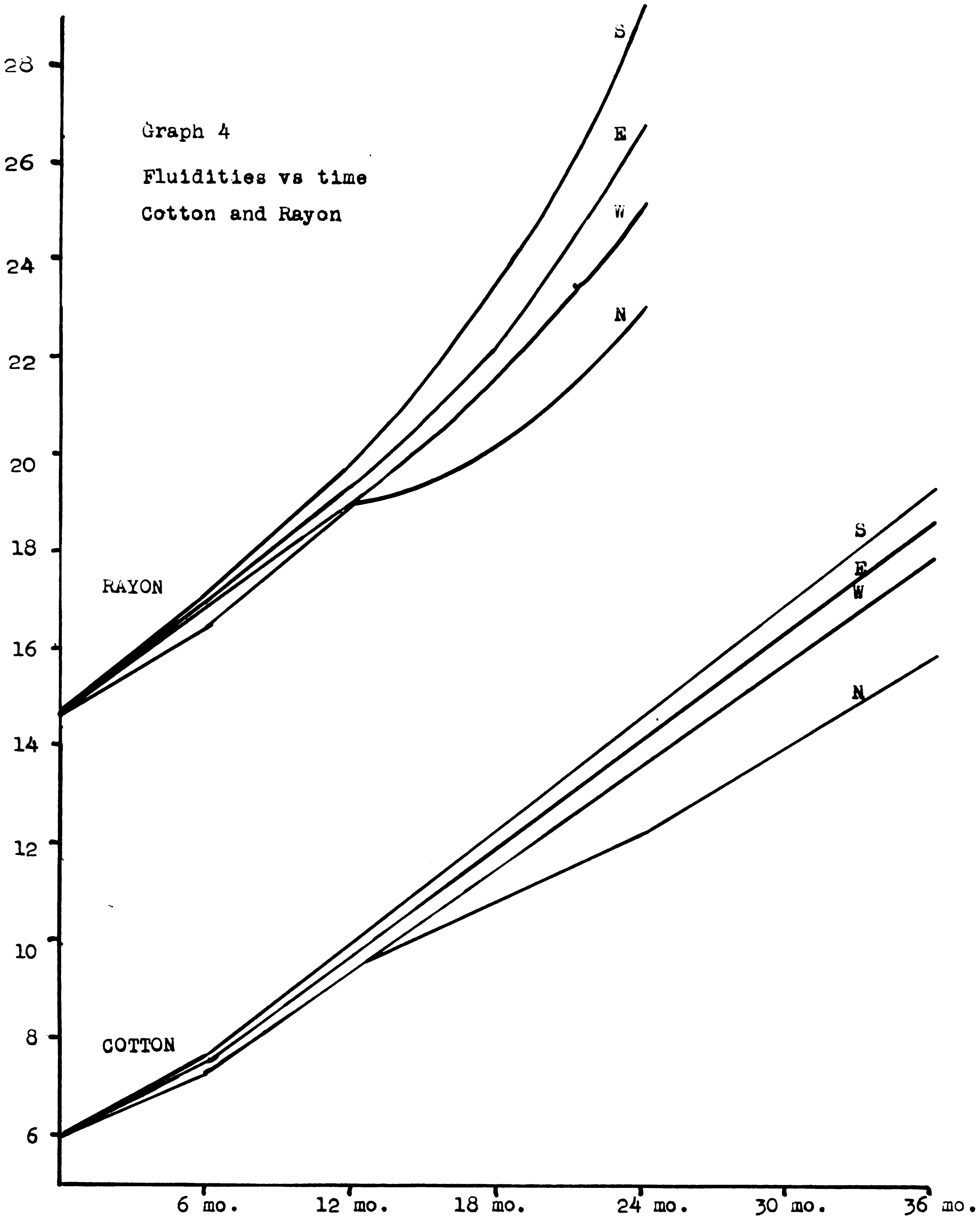
RAYON FLUIDITIES

Unexposed to sunlight	6 months	12 months	18 months	24 months
East	14.93	15.51	15.94	16.55
	15.05	15.47	16.03	16.51
Average	14.99	15.49	15.99	16.53
South	15.02	15.53	15.98	16.54
	14.96	15.46	16.01	16.48
Average	14.99	15.50	16.00	16.51
West	14.97	15.50	15.95	16.53
	15.04	15.51	16.05	16.49
Average	15.01	15.51	16.00	16.51
North	15.01	15.54	15.97	16.50
	14.99	15.47	16.05	16.52
Average	15.00	15.51	16.01	16.51
Exposed to sunlight				
East	16.97	19.45	22.31	26.84
	16.97	19.48	22.27	26.77
Average	16.97	19.47	22.29	26.81
South	16.98	19.75	23.52	29.31
	17.09	19.69	23.50	29.27
Average	17.04	19.72	23.51	29.29
West	16.85	19.34	21.59	26.19
	16.83	19.27	21.62	26.23
Average	16.84	19.31	21.61	26.21
North	16.54	19.17	20.06	23.05
	16.47	10.12	20.20	22.96
Average	16.51	19.15	20.13	23.01

TABLE XIII

RAYON FLUIDITIES -- DIFFERENCES BETWEEN EXPOSED AND UNEXPOSED

	6 months	12 months	18 months	24 months
East	1.98	3.98	6.30	10.28
South	2.05	4.22	7.51	12.78
West	1.83	3.80	5.61	9.70
North	1.51	3.64	4.12	5.50
PER CENT DIFFERENCES BETWEEN EXPOSED AND UNEXPOSED				
East	13.2	25.6	39.4	62.2
South	13.7	27.2	46.9	77.4
West	12.2	24.5	35.1	58.7
North	10.1	23.5	25.7	33.3



Graph 4

Fluidities vs time

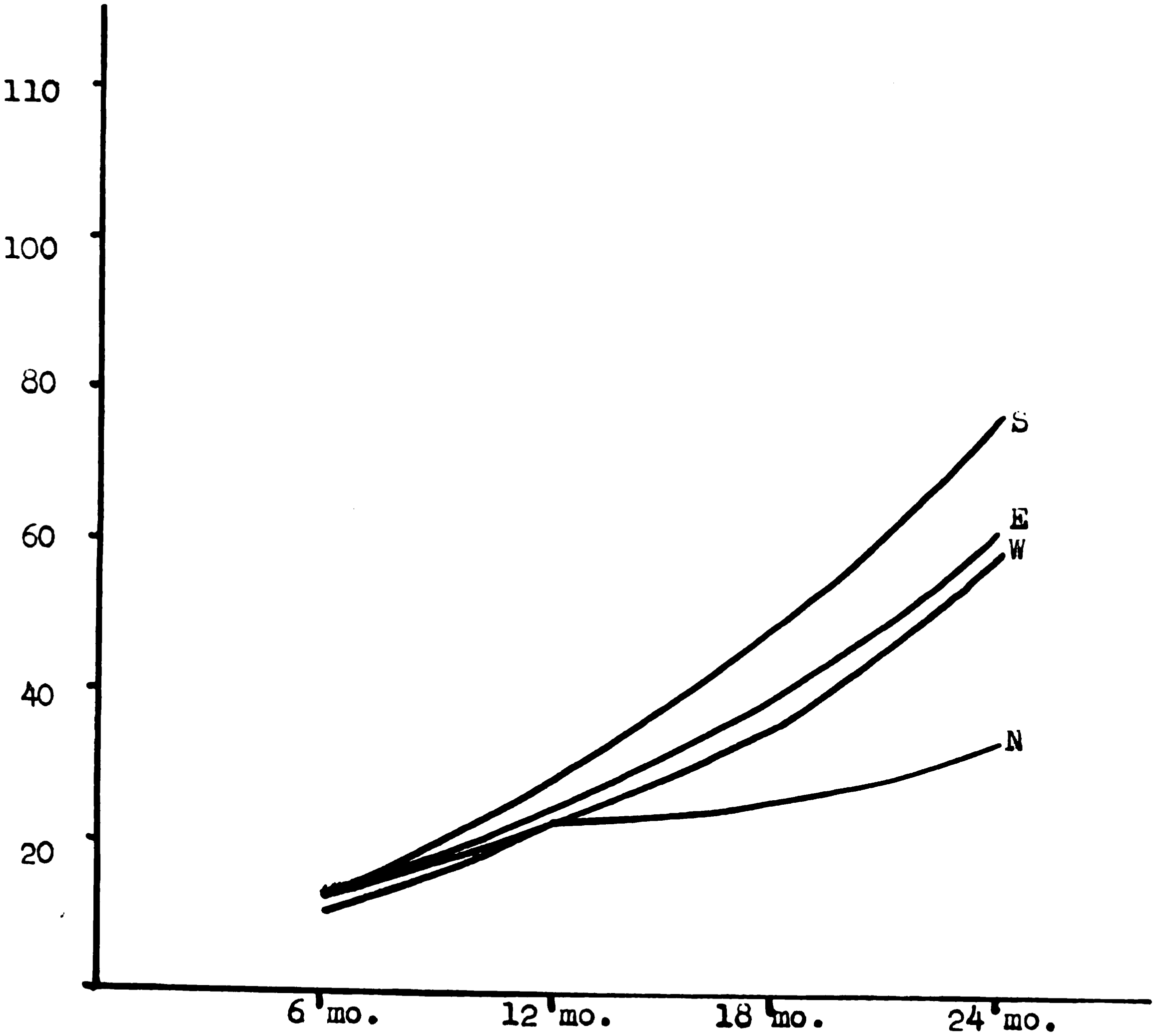
Cotton and Rayon

Graph 5

Per cent change vs time

Fluidities

Rayon

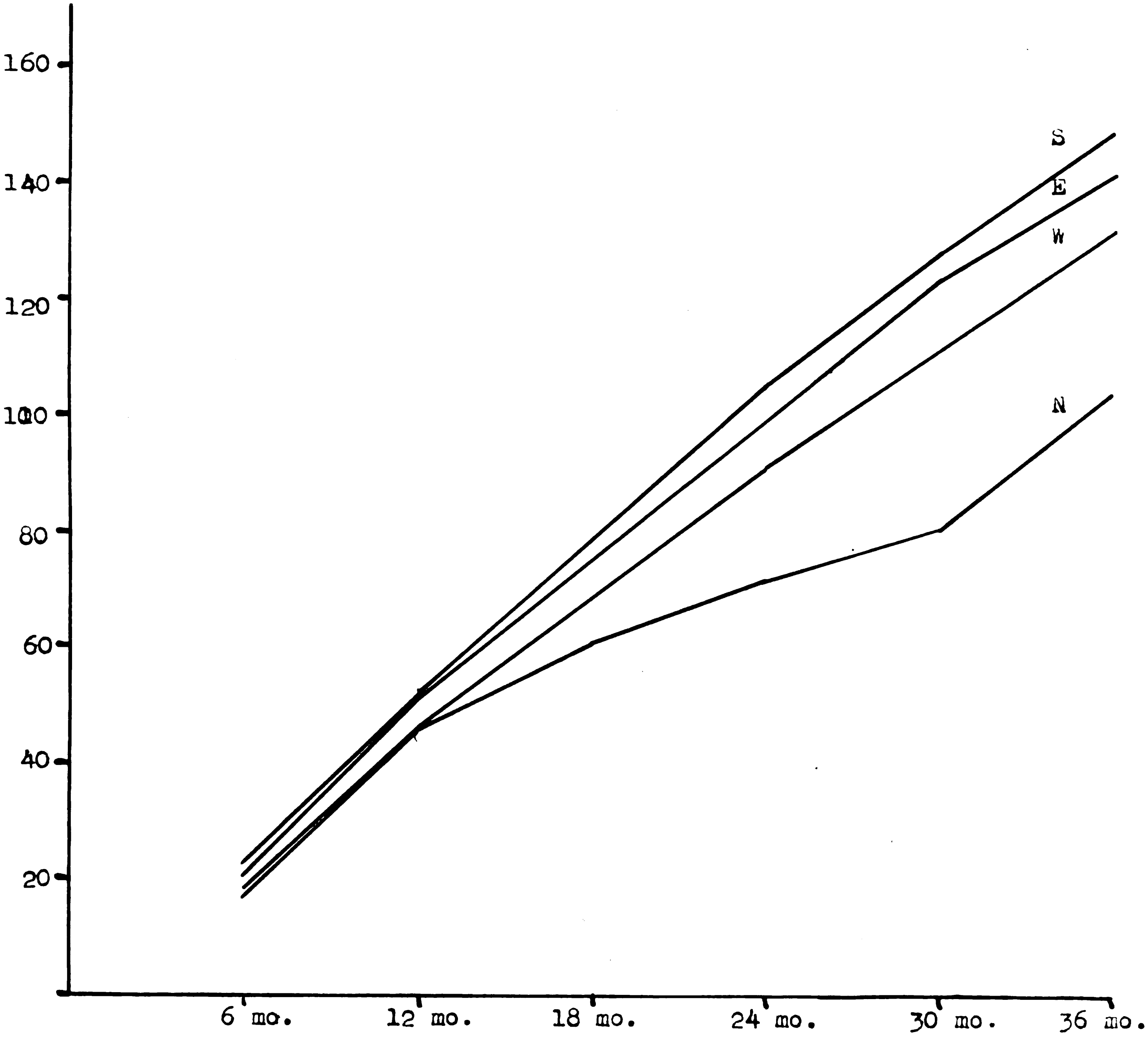


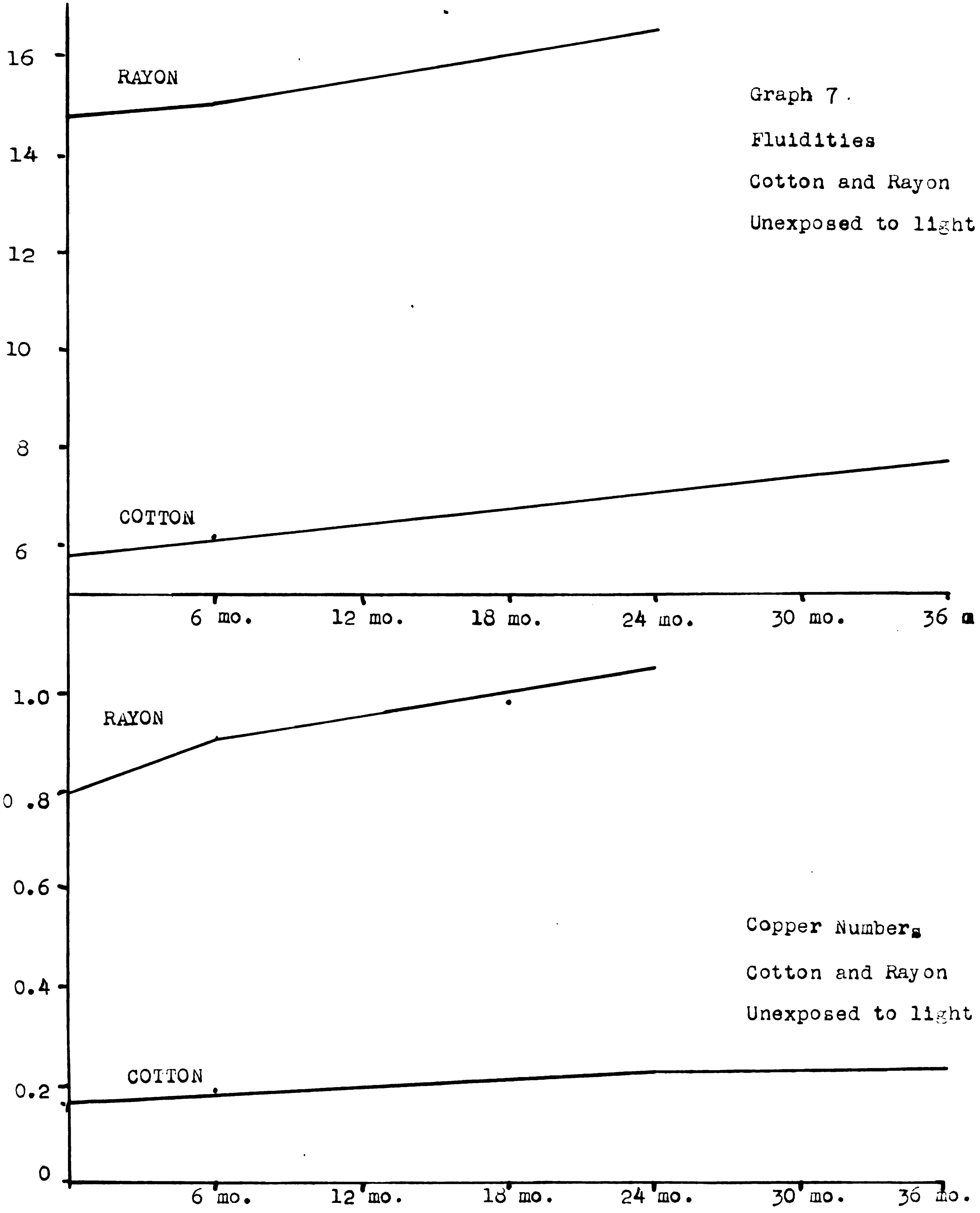
Graph 6

Per cent change vs time

Fluidities

Cotton





Graph 7.

Fluidities

Cotton and Rayon

Unexposed to light

Copper Numbers

Cotton and Rayon

Unexposed to light

DISCUSSION

DISCUSSION

As a result of the present investigation, it has been found that the oxycellulose which is formed when rayon and cotton are exposed to sunlight, is composed principally of the reducing type and contains practically no oxycellulose of the acidic type. This is known to be true because all of the rayon and cotton samples tested showed considerable increase in copper number (with increased time of exposure) which indicates the reducing type of oxycellulose, whereas the methylene blue number (which shows the presence of the acidic type) did not increase appreciably.

Since the changes in methylene blue number are approximately the same for the portions which were exposed and unexposed to sunlight, they can not be due to the effect of light. It was brought out previously that variations in ash content would produce variation in methylene blue absorption, but the ash content of samples tested in this work did not change beyond what would be expected because of experimental error, and therefore the methylene blue numbers may be considered a true measure of the methylene blue absorption.

The copper number of cotton showed the greatest increase during the first six months. After that the change in copper number was small. In fact, the change during the last 30 months was only a little more than half the increase during the first six months.

The original copper number of rayon was four times the original copper number of cotton. This is due to the modification of the rayon during manufacture. At the end of six months, the rayon copper numbers were greater than the cotton copper numbers after three years. When the rayon curtains were withdrawn from the study, after two years, they had copper numbers which were four times as great as the cotton curtains which had been exposed for the same length of time.

The most interesting thing learned from copper number determinations was the difference between the rate of change for rayon as compared with cotton. This is shown on Graphs 2 and 3. These curves show that, during the second six-month period the increase in copper number was approximately the same for each material. However, after that time the rate of increase in copper number for all the rayons was very much greater than for the cotton curtains.

This may be due to the orientation of the cellulose molecules during the spinning process in the manufacture of rayon. It may be entirely possible that during the spinning (particularly if any cold drawing process is carried out) the cellulose molecules are oriented in such a way that a much larger proportion of primary alcohol groups are exposed than is the case with native cotton. This would increase the chances for more reducing aldehydic groups to be formed.

The rayon fluidities increased at progressively greater amounts during each period. During the last six months period, the increase was about twice that of the first six months period, with the exception of the northern exposure. After the first six months, the amount of increase of the cotton fluidities was constant during the remainder of the three years exposure.

The original rayon fluidities were more than twice the original cotton fluidities. For each six months period, the rayon fluidities remained approximately twice the cotton fluidities, and at the end of one year, the rayon fluidities were greater than the cotton fluidities at the end of three years.

The rates at which the fluidities increased are illustrated by graphs 5 and 6, in which per cent change is plotted against time.

The rate of the change in fluidities of rayon increased progressively during the entire two year period. The cotton fluidity maintained the same rate of increase throughout the three years of exposure and was similar to the rayon rate of change. Not only was the rate of change practically the same up to two years, but the actual magnitude of the difference between the original and exposed material was also the same.

For both the rayon and cotton curtains, the rate of increase for the northern exposure was the same as the other exposures up to the end of the first year. At that time, the rate of increase dropped off decidedly. Since the northern light did not vary, the change must be due to something in the fabric itself. In some way the fabric which had been exposed to northern light had become resistant to the chain shortening effect of sunlight. It has long been thought that reactions such as oxidation attack first the surface of the cellulose, and then work progressively inward. It is possible that northern light is strong enough to produce shortened chains on the surface of cellulose, but is unable to penetrate past the surface, into the inner portion of the fibers.

As was expected, the southern light was the most damaging to the curtains, and the northern light the least damaging. This is shown by the high copper numbers and fluidities of both the cotton and rayon curtains exposed to southern light, and the lower copper numbers and fluidities of the curtains exposed to northern light. Apparently morning sunlight is more damaging than afternoon light. Evidence for this is found in the fact that the curtains exposed to eastern light have higher copper numbers and fluidities than those exposed to western light.

It is obvious that the effect of light on rayon is different from the effect of light on cotton, particularly with respect to increased reducing power, as illustrated by graphs. Since the light to which the cotton and rayon curtains were exposed was constant, the difference must be due to the fabrics. Reducing power (copper number) may be considered a measure of the oxidative attack on the alcohol groups of cellulose. It is possible that, during the manufacture of rayon, the cellulose molecules are oriented in such a way as to expose more alcohol groups, and therefore provide a greater chance for oxidation of these groups, and a higher rate of increase in reducing power.

This same relationship between the effect of light on rayon and cotton was not found in respect to chain shortening action, as shown by graph 4 of cotton and rayon fluidities. The difference between rayon and cotton fluidities was the same after two years exposure to light as before exposure to light. This indicates that, although there was chain shortening during manufacture (illustrated by the greater original fluidity of rayon), the orientation of the cellulose molecules did not provide a means for the rate of chain shortening to increase.

It was thought at the beginning of this investigation that there would be a proportionality between tensile strength decrease and the chemical changes which were measured. However the tensile strength results were too erratic to make any comparison possible.

An interesting point may be noted in connection with the wet tensile strength of cotton. Native cotton has a higher wet tensile strength than dry tensile strength. However, the tensile strength figures obtained during a study of the physical properties of these curtains show that after cotton is chemically modified, the wet tensile strength is lower than the dry tensile strength. It appears that, as chain shortening progresses, the wet tensile strength changes (decreases) at a faster rate than the dry tensile strength. The reason for this is not apparent at the present time.

Tensile strength results may be found in an Experiment Station Bulletin to be published by Michigan State College.

SUMMARY

SUMMARY

1. Sunlight produces the reducing type of oxycellulose.
2. Methylene blue absorption showed no appreciable change.
3. The increase in rayon copper number was greatest during the third and fourth six months periods.
4. The cotton copper number increased more during the first six months than during the remainder of the three years.
5. The original rayon copper number was four times the original cotton copper number.
6. After six months, the rayon copper numbers were greater than the cotton copper numbers after three years.
7. The cotton copper number increased at the same rate for the entire three year period.
8. The rayon copper numbers increased at a greater rate during the second year than during the first year.
9. The rayon fluidities increased by progressively greater amounts each period.
10. The cotton fluidities increased at a constant rate after the first six months.
11. Rayon fluidities were twice the cotton fluidities.
12. After one year, the rayon fluidities were greater than the cotton fluidities after three years.
13. The cotton fluidity maintained a constant rate of increase.

14. For both rayon and cotton, the rate of increase of fluidity for the northern exposure was the same as for the others up to one year, and then dropped off decidely.
15. Rayon showed greater increase of reducing power than cotton.
16. The chain shortening effect was similar in the two fabrics.
17. Southern light was the most damaging to the curtains.
18. Northern light was the least damaging to the curtains.
19. Morning light was more damaging than afternoon light.
20. There was no proportionality found between decrease in tensile strength and change in chemical properties.

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