AN INVESTIGATION INTO POSSIBLE SOURCES OF PULP WITH PARTICULAR REFERENCE TO THEIR USE IN THE PRODUCTION OF RAYON

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THESIS

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PREFACE

The work herein described was carried out to determine in an empirical way some possibilities for sources of pulp for the production of rayon, and through the empirical information obtained stimulate further research to procure more accurate and definite data.

Information regarding the special phases of the work is very scarce in the literature and the author has been unable to find any which has been of value in the work. Milkweed has been worked on to a certain extent, but not with the ideas in view which accompanied the origin of these problems.

The author wishes to extend thanks to Dr. J. W. Watson for his aid in the writing of this thesis, and to Dr. R. E. Hussey for his help. Especially does he wish to thank Dr. Philip C. Scherer for the suggestion of the problems and his generous advice throughout the investigation.

C.R.W.M., Jr.

GENERAL OBJECT

The purpose of the investigations carried out as described herein was to determine the feasibility of using certain raw materials for the production of various pulps, with particular reference to their use in the manufacture of artificial silk. As originally outlined the purity of the various materials were to be studied, along with their physical characteristics, so that the developments in the processes could be connected more intimately with the properties of the obtained products. As will be shown, this had to be adhered to even more closely than was the original intention.

The idea behind the research was not only the mere production of pulp from hitherto unknown sources, but also to make available certain by-products of various industries and waste materials for the manufacture of a substance of more general benefit than those for which they are now used, and to put to use land which at present has no known value. Reference is here made to milk-weed (Asclepiadaceae) which is seen growing along almost any roadside in the southeastern part of the United States, and which can be

grown abundantly on land which produces profitably no other crop.

In the course of this investigation it became evident that the so-called "beta cellulose" was a hindrance to the production of silk from several of the attempted materials. It was deemed advisable to include a study of this material in the research. It is generally conceded that beta cellulose is not only an "adulterant" in the pulp which is used for the manufacture of rayon, but has detrimental effects upon the character of the final product. However, as no actual data were found available by the investigator on the particular phase which drew attention here a study of this material was carried out.

GENERAL EXPERIMENTAL PROCEDURE

Generally, the first step in the production of pulp from almost any source is the delignification of the material for the removal of substances found to be deleterious to the quality of the final product, and to put it into a form which may be readily handled. This procedure was followed in this work. The materials had to be subjected to

various "cooks" to determine which were the most suitable and would give the higher grade of pulp. In one case, the pulp was obtained in a form pure enough, with the exception of the beta cellulose present, to be used without cooks, though to be obtained in this form cooks were necessary in the initial processes. Acid, basic and neutral cooks were used wherever they appeared to be of value. (The words "cook" and "digestion" are here used interchangeably).

The digester used was one of simple construction, consisting of a single iron cylinder closed at the bottom and placed upon piping so as to allow of a "back and forth" motion to agitate properly the contained material. It was built to withstand a pressure of 200 pounds per square inch and a temperature to vary accordingly. The common practice of using live steam to obtain the proper agitation and temperatures was deviated from, the heat being obtained from resistance wire wrapped around the outside of the digester and properly insulated with asbestos. With this apparatus it was possible to secure temperatures of from 100 to 120 degrees centigrade in approximately thirty minutes time as a maximum. A blow-off valve on the lid of the digester made it possible to collect and examine any volatile substances which might offer a field for research.

The various digestions were carried out under direct observation and times and temperatures noted continually. When the cooks were at an end the contents of the digester were removed after the steam and other volatile ingredients were blown off and collected (where feasible). The pulps were then washed thoroughly with water, sometimes with dilute acids. The latter step was found necessary in certain cases in order to obtain a reasonable rate of washing, as the fibers were generally swollen so as to prevent almost completely the passage of water through the cloth in which the mass was suspended. This filtering medium was a very porous (large weave) cheese cloth.

Methods used for the production of cellulose solutions were those specified for the production of normal "viscose" syrups. This rule was not followed exactly in the investigation of beta cellulose. Reference will be made to this at the proper time. (See appendix for sample calculation for formation of viscose syrup, and for other calculations.)

Filtering of the cooked products was exceedingly difficult and the methods of treating these will be discussed elsewhere.

SOURCES

(A) Milk weed (Asclepiadaceae)

(B) (1) Sheet pulp obtained as a by-product in a certain treatment of chestnut oak chips to obtain the contained tannins.

(2) Chestnut oak chips.

(C) A low grade pulp produced from a process of turpentine extraction on Loblolly pine.

(D) Grapefruit hulls from which most of the edible material had been removed.

(E) Beta cellulose, as produced according to the procedure given herein.

SECTION (A). Milk weed.

Object. To produce a pulp from milk weed which had characteristics suitable for its conversion into artificial silk.

Experimental Procedure. The milk weed had been collected in the early fall before complete maturity of the plant so that the seed pods were still intact. They had been allowed to dry out under normal conditions so as to include the latex and other materials. When ready for use the stalks were in a comparatively dry condition.

It was known that there was present in the seeds of this plant an oil which might be deleterious to the production of a pulp from the remainder of the plant. Consequently, an ether extraction was carried out upon part of the seed and seed hairs with the result that an oil was obtained to the amount of approximately 8% of the original weight of seed and seed hairs. This percentage was considerably reduced when figured on the basis of the entire plant, and was considered not high enough to interfere with the work at hand. No data other than that just mentioned will be given on this phase, as it has no direct bearings, with the exception of that just alluded to, upon this work. The oil was retained and is being kept for future research.

A caustic cook was used on the milk weed. The stalks were cut up into short lengths (approximately $\frac{1}{2}$ to 1 inch) and inserted into the digester. Most of the seed and hairs were included with the stalks, but the pods containing the former were discarded. The appearance of them did not warrant their being treated for pulp formation. The proper amount of dilute caustic (8% NaOH) was then added, enough so that there would be a splashing and "slopping" of the mass to insure a maximum degree of digestion. With the lid securely in place the temperature was quickly raised to 100 degrees and maintained between the limits 100 and 120 degrees for two hours.

At the end of the cooking period the digester was "blown" to get rid of volatile materials which might inhibit the production of a pulp. The lid of the apparatus was removed, the contents taken out and examined. Insufficient breaking up of the stalks had taken place, although there was a certain amount of free fiber distributed throughout the mass. Another digestion was apparently needed, but before this repeat in the process mechanical separation of the fibrous material was attempted, using a 6 H.P. motor connected with a shaft on the opposite end of which was secured a propellor shaped metal blade extending approximately two inches

on either side of the shaft. This shaft was immersed in the suspension and the mass thoroughly beaten up for one-half hour. At the end of this period more disintegration had taken place, but there was still a good deal of untouched stalk.

The second cook was carried out in the same manner as the previous one with the exception of the pressure's being carried up to 120 pounds per square inch and maintained between the two pressures 120 pounds and 130 pounds per square inch for two hours. After this the digester was "blown" as before, the material removed and examined. Practically no further digestion had taken place. There still remained large particles of stalk which had not been materially affected by the caustic soda.

There was much evidence pointing to the disintegration of the seeds, free hulls being plentifully distributed throughout the mass.

Results. A pulp with satisfactory characteristics was not obtained. There was not sufficient disintegration of the milkweed to allow of a separation of fibrous material from the undesirable lignins. The mass had gelatinous properties, for it was very difficult to drain the mother liquor and obtain the material in a comparatively dry state.

Conclusions. (1) A pulp cannot be made from the stalks of the milk weed by the process outlined above--a digestion with 8% NaOH solution at 130 pounds pressure for a time of two hours. From all appearances it would take a higher pressure and temperature than was obtained in this work maintained for a longer period of time to effect sufficient disintegration.

(2) The gelatinous character of the mass obtained from both cooks can be due to either of two things: (a) What fibers were freed from the lignous material were put into a colloidal form, or (b) there are substances present in the milk weed other than cellulose which result in the gelatinous character of the material. Either or both of these factors may enter in to act as disturbing influences in the production of pulp from milk weed.

(3) The latex present undoubtedly has a deleterious effect. Its "rubbery" character is not completely destroyed by the cook administered herein, and such substances always interfere in the production of pulp.

Recommendations. It is suggested that various other cooks be used upon the stalks of the milk weed to determine whether it is actually possible to obtain a pulp therefrom. It is evident that the gelatinous character of the material obtained when the above given method of digestion was used

DATA ON MILK WEED INVESTIGATION

Weight of extracted seed and seed hairs..... 128 g.

" " ground stalks..... 3163 g.

" " additional seed hairs added..... 7 g.

Stalks removed from digester before digestion..... 1544 g.

Total weight of stalks, seed hairs and extracted seed and hairs (128 + 1619 + 7)..... 1754 g.

Amount of 8% NaOH solution added to digester..... 10 L.

First Cook

Time of digestion..... 2 hrs.

Temperature of digestion..... 100° C. to 130°C.

Second Cook

(The material from the first cook was simply replaced in the digester and a second digestion obtained thereon).

Time of digestion..... 2 hrs.

Pressure of digestion..... 120 # to 130 # sq.in.

Note: a viscosity was run on the material obtained from the second cook, but there were so many large particles of the original material present that nothing of value is to be obtained therefrom, and the viscosity data need not be dealt with here.

will be a hindrance in this work, and a method of cooking which will cause a diminution in this factor will no doubt make for better results. New methods of digestion will probably have to be relied upon, and the determination of these offers another field for research.

SECTION (B) (1)

Object. To investigate a pulp obtained as a by-product in the treatment of chestnut oak chips for the extraction of tannins.

Experimental Procedure. The material was received in the form of pressed sheets which, when torn, showed that the length of the cellulose fibers was unusually small. Previous analyses had shown that there was a low percentage of alpha cellulose present so an "alpha" treat was administered to the pulp. This consisted of suspending the pulp in 18% NaOH solution for 1¼ hours at 18 degrees C. The pulp was removed and thoroughly washed with water after which a slight amount of acid was used to nautralize the base present. The treat raised the alpha content of the pulp considerably. With this product a spinning solution was prepared. (See appendix for normal method of producing a viscose syrup.)

The above process was repeated with a diminution in the time of aging of the soda cellulose.

The process was repeated the third time, but without any alpha treat to determine if a syrup could be spun upon the original pulp.

Results. A silk was spun from the syrups obtained in all three cases, but the characteristics varied. In the first instance, the syrup had a decided tendency to form a thread but the low viscosity would not allow of a continuous one being produced. The filaments broke easily after their formation. There was a tendency for the syrup issuing from the several apertures in the spinnerette to form a mass instead of retaining their individuality after being pulled from the spinning bath. This was attributed to too long a time of aging of the soda cellulose. When the process was repeated and the aging time of the soda cellulose reduced a silk with good characteristics was produced.

Spinning of the syrup from the pulp not treated to remove beta cellulose also produced a silk. The strength of this was at least sufficient to support the weight of its column issuing from the spinnerette up to the removal of strain after it was wound on the spool. However, when the latter was washed and dried it was found impossible to twist the silk thereon. There had been deposition of impurities to such an extent that there was a pronounced tendency for the threads to stick together.

DATA ON ORIGINAL CHESTNUT OAK PULP (AS RECEIVED) *

Alpha Cellulose

Alpha cellulose from previous determinations..... 62.2%

(Low alpha content made it impossible to obtain press ratio of 1:3:33)
Press ratio obtained..... 1:3:95
CS_2 for xanthation taken as 40% on alpha (due to impurities)

Soda Cellulose

Viscosity Time of flow

21.0	21.6
22.0	22.6
22.6	22.4
23.4	23.4

Average time of flow = 22.4

$$\frac{.01055 \times 22.4}{7} \times 100 = 3.38$$

Alpha Cellulose

44.9926	Weight of sample + bottle
39.9842	Weight of bottle
5.0084	Weight of sample
23.4600	Weight of alpha cellulose + bottle
19.9710	Weight of bottle
3.4890	Weight of alpha cellulose

Alpha cellulose in soda cellulose = 68.5

Ripening of Viscose

Time of aging	NH_4Cl number
24 hrs.	18.0
48 "	15.5
72 "	13.4
96 "	13.0
120 "	12.5
144 "	(solution spun, regardless)

* See foot-note page 15

It was impossible in each case to obtain a syrup which, after normal methods of filtration, became completely clear. There remained suspended fine fibers which evidently had not been converted by xanthation. The greatest amount of these was present in the syrup made from original pulp (untreated to remove the beta cellulose).

Conclusions. (1) Artificial silk can be made from chestnut oak chips after they have been subjected to the treatment referred to; namely, for the removal of tannins.

(2) To make a better silk the pulp should be subjected to treatment to remove the beta cellulose as well as other impurities which evidently are partially removed in this treatment.

(3) The fibers of cellulose in the original pulp are shorter than those commonly used in the manufacture of artificial silk. This was attributed to too drastic treatment of the wood chips, and to the size of the chips, which was smaller than that used in the production of ordinary pulp. Regulation of both of these conditions will very likely result in the production of a pulp of excellent quality which can be used in the manufacture of a high grade artificial silk.

DATA ON CHESTNUT OAK PULP SUBJECTED TO ALPHA TREAT (1) *

Alpha Cellulose

Sample 1		Sample 2
44.9592	Weight of sample + bottle	44.9938
39.9876	Weight of bottle	39.9876
4.9716	Weight of sample	5.0062
44.0684	Weight of sample + bottle	44.1326
39.9876	Weight of bottle	39.9876
4.0808	Weight of sample	4.1450
82.1%	Alpha cellulose	82.8%

Average alpha cellulose = 82.5%

Viscosity

Time of flow

12.5 seconds	11.9 seconds
12.0 "	12.0 "
12.0 "	12.0 "
12.0 "	

Average time of flow = 12.0 seconds

Time of flow of water through same pipette averaged 7 sec.
Viscosity of water at 18 degrees C = .01055

$$\frac{.01055 \times 12}{7} \times 100 = 1.81 \text{ viscosity of treated pulp}$$

Aging of soda cellulose..... 72 hrs.

NH_4Cl number at end of 70 hours..... 11.2

* For the formation of the viscose syrup the normal method was used. See appendix for sample calculations.

DATA ON CHESTNUT OAK PULP SUBJECTED TO ALPHA TREAT (2) *

Alpha Cellulose

45.0246	Weight of sample + bottle
39.9968	Weight of bottle
5.0278	Weight of sample
44.0826	Weight of alpha cellulose + bottle
39.9954	Weight of bottle
4.0872	Weight of alpha cellulose

Alpha cellulose content = 81.3%

Viscosity

11.0	Time of flow	11.0
10.6		11.0
10.6		11.0

Average time of flow = 11.0

Time of flow of water through same pipette averaged 7 sec.

Viscosity of water at 18 degrees C. = .01055

$\frac{.01055 \times 11}{7} \times 100 = 1.62$, viscosity of treated pulp

NH_4Cl number after 40 hours aging of soda cellulose = 10.5

Finished Rayon

Weight of 225 meters ..... 4.183 g.
Weight of 9000 meters (1 Denier).....167.0 g.

Tensile strength (dry)		Elongation (dry)	
202	198	12.5	12.0
200	196	13.0	12.5
198	190	13.0	12.0
190	184	11.0	10.0
196	174	10.8	9.5
Average =	193	Average =	11.6

Tensile strength per Denier = $\frac{193}{167}$ = 1.16

Tensile strength (wet)	Elongation (wet)
60	11.0
58	10.5
54	10.0
58	12.0
54	9.5
Average = 57	Average = 10.6

Tensile strength per Denier = $\frac{57}{167}$ = .34

*See foot-note page 15

SECTION (B) (2)

Object. To produce a pulp suitable for the manufacture of rayon from chestnut oak chips.

Experimental Procedure. Chestnut oak chips were subjected to a sulphite cook in which the ratio of combined SO_2 to free SO_2 was as 1:5.1% CaO was used as the combining medium for the SO_2. The digestion was carried out for $3\frac{1}{2}$ hours at a temperature of 110 to 115 degrees C. The chips came out of the treatment with a jet black color, as did the mother liquor. There was practically no evidence of disintegration. The chips were separated from the liquor and washed well with water, but very little of the color was removed. A small portion of the chips was treated with oxalic acid to attempt a removal of the color. This had some effect, but it was not sufficient. The entire mass was then suspended with oxalic and acetic acids in water and the whole beaten with a motor driven beater for half an hour. Some decolorization took place, but no more than was expected, from the somewhat similar treatment which had been tried before (see immediately above). However, disintegration of the chips was very pronounced, and a mass of fibers obtained in which was distributed some of the untouched wood.

Stronger bleaching was resorted to by the addition at this point of considerable quantities of

chlorine solution (3.5% available chlorine in an 8% NaOH solution). Further treatment of the now pulped chips was anticipated but not resorted to, as this single treatment gave a product which retained only a small quantity of the coloring matter. The disintegrated chips now were colored only a light tan. Dilute sulphuric acid poured over the filtered mass reduced the color still further.

There was still present a considerable amount of unpulped chips. Washing of the material through a fine mesh copper screen removed most of them. Further beating of the unpulped chips failed to produce a pronounced effect, so that the residue was discarded.

The main body of pulp was then washed well and dried. Alpha cellulose tests gave results which indicated that too low a percentage of the former was present to be conducive to the formation of a good pulp. So the fiber mass was immersed in 18% NaOH solution for 2 hours, removed, washed and dried. Analysis of this product gave an alpha content of 85.3%. This was considerably higher than the value for the untreated pulp which ran 74.2%.

A viscose syrup was produced from the treated pulp which had fairly good characteristics. It was of high viscosity, did not contain a large amount of free fibers, and

filtered well. It had, however, a very dark green color--almost too dark for any color to be distinguished. From the character of the original chips this was not altogether unreasonable.

Little difficulty was encountered in the spinning of the syrup. The bath was quickly colored a dark dirty brown due to the separation of colored impurities in the syrup, but a continuous thread was obtained. The silk spun was either dark brown in color itself or had occluded matter to give it a dark brown appearance. This was washed with water and dried.

Attempts to remove the silk from the spool were entirely negative. Too much suspended matter was present, it was assumed, with the consequent sticking together of the threads.

Results. (1) A pulp can be produced from chestnut oak chips which is capable of being converted into artificial silk.

(2) The sulphite cook as administered in this work was insufficient to remove deleterious materials and to break down the chips themselves into fibers of cellulose.

(3) The tannin remaining in the chips unites with the iron from the digester to give a black color.

(4) Mechanical beating of the cooked chips disintegrated a large portion thereof.

(5) The silk produced from the pulp obtained was of poor quality.

Conclusions. There is present in chestnut oak much matter which prevents the formation of a pulp satisfactory for the manufacture of artificial silk. Proper treatment to remove this injurious matter will very likely result in the production of a pulp of high enough quality to be used for this purpose. However, too drastic treatment may be necessary to decolorize the material and as a result produce a silk which has not highly satisfactory characteristics. Application of various varieties of cooks will determine whether or not chestnut oak chips can be satisfactorily used for the manufacture of rayon. This procedure is recommended for more research on the subject.

SECTION(C)

Object. To produce a pulp satisfactory for the production of rayon from a cellulosic by-product (a low grade pulp) of the extraction of turpentine from Loblolly pine.

Experimental Procedure. The pulp as received was colored an ordinary brown. It was first subjected to a basic cook using 8% NaOH solution. The purpose of this cook was to determine the empirical nature of the material. It was found from this that there was resinous material present which gave the pulp a "gummy" feel. The caustic had not affected the fibers as far as could be ascertained at the time.

DATA ON CHESTNUT OAK CHIPS

Sulphite Cook

Desired amount of CaO in initial solution..... 1%

Ratio of combined SO_2 to free SO_2 ..... 1:5

10 liters of sulphite solution used.

$\frac{202 \times 100}{128}$ = 158 g. $Ca(HSO_3)_2$ to be present.

$\frac{CaO \times 158}{Ca(HSO_3)_2}$ = 43.8 g. CaO to be used in order to obtain a solution containing 100 g. (1%) combined SO_2.

Free SO_2 determined volumetrically to obtain 1:5 ratio.

Pulp Obtained

44.9834	Weight of sample + bottle
39.9820	Weight of bottle
5.0014	Weight of sample
28.4940	Weight of alpha cellulose + bottle
24.7850	Weight of bottle
3.7090	Weight of alpha cellulose

Alpha cellulose content = 74.2%

Viscosity

Time of flow
17.0 sec.
17.0
17.0
17.0

Average = 17.0

Absolute visc. water (18° C.) = .01055

$\frac{.01055 \times 17}{7} \times 100 = 2.56$

Where 7 is the value for water when run through same pipette.

Pulp Obtained After Alpha Treat

Alpha Cellulose

44.9874	Weight of sample + bottle
39.9804	Weight of bottle
4.0070	Weight of sample

44.2374	Weight of alpha cellulose + bottle
39.9800	Weight of bottle
4.2574	Weight of alpha cellulose

Alpha cellulose content on treated pulp = 85.3%

Viscosity

Time of flow

28.6 sec.
29.0 "
29.6 "
29.8 "
30.4 "
30.6 "

Absolute visc. water (18° C.) = .01055

$$\frac{.01055 \times 29.6}{7} \times 100 = 4.46,$$

where 7 is the value for water when run through same pipette.

Soda Cellulose

Alpha cellulose

48.0834	Weight of sample + bottle
43.0832	Weight of bottle
5.0002	Weight of sample

44.5770	Weight of alpha cellulose + bottle
40.6774	Weight of bottle
3.8996	Weight of alpha cellulose

Alpha cellulose on soda cellulose = 78.0%

Viscosity
(no determinations)

Viscose Syrup

Ripening

Age	NH_4Cl
48 hrs.	13.3
72 "	11.4
96 "	10.5 (solution spun)

Viscosity
(Solution too dark. No determinations)

The original material was then subjected to a sulphite cook* for a period of 2 hours at 135° C. After this time it was removed and thoroughly washed with water. Practically none of the color was lost in the digestion so that the next step was an attempt at bleaching. This was carried out with the use of chlorine water containing about .75% available chlorine** for a duration of 45 minutes. A good deal of color was removed in this manner, but not enough. The material was then treated with a mixture of oxalic and acetic acids at 80° C. for ten minutes, with the result that most of the color disappeared.

A viscose syrup was made from the pulp obtained from the washing and drying of the bleached material. Fine particles of suspended matter were thickly distributed throughout and the solution in general had a poor appearance. Its viscosity was several times that of the normal viscose made from a high grade pulp. Attempts made at filtration all failed, and the syrup had to be discarded.

A third digestion was then run on the material, this time with an SO_2 solution containing no CaO. The time

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* The sulphite solution used here was the same as that used on the chestnut oak chips. See pp.17 and 21.

** The chlorine solution was the same as that used before after diluting to .75% available Cl. See p. 17.

of cooking was 1 hour, the temperature 110° C. This procedure took away some of the color and a small amount of the "gummy feel".

The alpha cellulose determination on the original pulp ran comparatively high (86.7%) so no alpha treat was administered at this time. Soda cellulose was made from the pulp and from this the normal syrup.

The viscose obtained was little better in characteristics than that made with the pulp from the former treat. Fibers were still present in abundance and although attempts at filtration met with better success they were still negative. The syrup was abandoned.

Results. (1) Digestions of the pulp carried out with both acidic and basic solutions produced a pulp which had a gummy feel, with very little diminution in color.

(2) There is an abundance of material not soluble in a solution of $Ca(HSO_3)_2$ containing an excess SO_2, or in dilute NaOH solution, under the conditions worked with.

(3) The process to which the Loblolly pine had been subjected would have to be changed so as to remove more of the foreign material in the pulp produced.

Conclusions. Artificial silk cannot be manufactured from the pulp which is at present produced in the

DATA ON PULP FROM LOBLOLLY PINE

First Digestion

(no data)

Second Digestion

Alpha Cellulose

45.0000	Weight of sample + bottle
39.9834	Weight of bottle
5.0166	Weight of sample

44.3362	Weight of alpha cellulose + bottle
39.9830	Weight of bottle
4.3532	Weight of alpha cellulose

Alpha cellulose present in treated pulp = 86.77%

Viscosity

Time of flow

19.0 sec.
18.6 "
18.6 "
19.6 "
19.8 "
19.6 "
19.4 "

Average = 19.3

Absolute visc. water (18° C.) = .01055

Abs. Visc. = $\frac{.01055 \times 19.3}{7} \times 100 = 2.90$,

where the time for water through same pipette is 7.

Soda Cellulose

Alpha Cellulose

44.9844	Weight of sample + bottle
39.9816	Weight of bottle
5.0028	Weight of sample

44.5470	Weight of alpha cellulose + bottle
39.9810	Weight of bottle
4.5560	Weight of alpha cellulose

Alpha cellulose content on soda cellulose = 91.1%

Viscosity

Time of flow

218.6 sec.
226.4 "
248.0 "

(Viscosity entirely too high for normal syrup)

Aging of soda cellulose, 65 hours.

DATA ON PULP FROM LOBLOLLY PINE (Cont'd)

Ripening

(Solution discarded before ripening tested)

Third Digestion

Alpha Cellulose

(Figures not available)

Alpha cellulose content of soda cellulose = 84.6%

Viscosity
(not determined)

Soda Cellulose

Alpha Cellulose

44.9874	Weight of sample + bottle
39.9860	Weight of bottle
5.0014	Weight of sample

44.6761	Weight of alpha cellulose + bottle
39.9865	Weight of bottle
4.6896	Weight of alpha cellulose

Alpha cellulose content on soda cellulose = 93.76%

Viscosity

Time of flow
291.2 sec.
280.0 "
303.2 "
326.0 "

(Viscosity entirely too high for normal syrup)

Ripening

Time	NH_4Cl
20 hrs.	9.9

extraction of turpentine from Loblolly pine by the Hummel-Ross method. The coagulation of the syrup after practically no time had been allowed for ripening points to the fact that there are substances already present in the original wood which are not removed in the present process, or that others are introduced somewhere along the line which have this coagulating effect. Variation in this process, or the adoption of a new method, might result in the production of a pulp from which a high grade of rayon could be produced. The length of the fibers in the original material seemed satisfactory from this point of view. The alpha cellulose content was comparatively high. Characteristics other than these could not be readily determined because of the foreign material already noted as being present.*

SECTION(D)

Object. To produce a pulp from the hulls of the grapefruit which can be converted into artificial silk.

Experimental Procedure. The hulls from the grapefruit were obtained from a mess hall where most of the edible material had been removed, so that only the fibrous material was dealt with. Any effect which might be produced

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* It was apparent that xanthation was not complete. This is probably due to the presence of some substances in the pulp not convertible to soda cellulose. It is possible that lignous, resinous, or waxy remains from the turpentine process may cause such a phenomenon;

from a large portion of the edible material was not investigated in this work.

(A) A series of four cooks was run on the hulls with variations in the conditions and methods of treatment. No attempt was made to separate the seeds which remained, though the number was small.

In the first digestion, the hulls were chopped by a mechanical device to smaller pieces and inserted directly into the digester. Enough 8% NaOH solution was then added to cover completely the material and the digestion carried out at a temperature of 100° C. for approximately 1 hour. After this time* the lid was taken off, the contents removed and examined.

Considerable disintegration had taken place, the unaffected material being made up mostly of the hulls from the seeds present. The mass was drained from the mother liquor**, well washed with water and subjected to decolorizing processes. To this end the material was treated with a mixture of oxalic and acetic acids, but little decolorization

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* The digester was blown into a condenser and the gases collected. The distillate was black, very oderiferous and upon standing for several weeks gave up by precipitation a sediment of crystalline material. This was reserved for further investigations.

** From the filtrate a precipitate, similar to that from distillate mentioned above, was obtained. It was saved along with the former.

took place. A test sample subjected to the same process but heated to boiling and allowed to remain at this point for several minutes showed signs of losing its color. The mass of pulp was then thoroughly washed and subjected to a chlorine treat, using a solution of 3.5% available chlorine containing 8% NaOH. Steam was passed into the container holding the mixture so as to raise the temperature to 30° C. for ½ hour. This treatment produced a decided bleaching effect, only a small amount of color remaining (a light tan). The filtered and washed mass was then inserted into a dryer (heated by steam) to remove most of the water. Pronounced shrinking accompanied the loss of water. Complete dehydration was not resorted to at this time, but a hard horny mass was procured which proved to be very resistant even to the blows of an ordinary hammer, complete dehydration would have probably given a product practically incapable of being treated in any way.

No tests were run on the dried pulp, as no chopping device which could put such material into a form suitable for testing was available. 70% alpha cellulose was taken as a basis and viscose syrups produced therefrom. Due to the large amount of impurity a greater amount of CS_2(45% on alpha cellulose) was used for xanthation, and a characteristic xanthate obtained. A sogginess was present, however,

which is not characteristic of normal xanthates.

The syrup obtained appeared to be normal except for an opaqueness which is usually not present. Spinning was carried out with little difficulty, the thread had strength and retained some of the original color of the dried pulp. It was dark brown as it came out of the bath, but washing with water removed the color so that only a light tan remained.

The spool of silk was next dried and attempts made at twisting.

Results of (1). (1) A pulp was produced from the grapefruit hulls, a viscose solution made therefrom, and the resulting syrup spun to give a cellulosic thread.

(2) Filtration of the contents of the digester after treatment was poor. A porous cheese cloth was used as the filtering medium, but in spite of this the character of the pulp was such as to make filtration and subsequent washing very slow--practically speaking, impossible.

(3) The pulp itself when subjected to drying at a low temperature was formed into a hard horny mass which resisted to a high degree attempts at disintegration.

(4) The syrup produced from the dried pulp was normal in appearance but had an opacity which is usually absent in syrups produced from normal pulp.

DATA ON FIRST GRAPEFRUIT

Amount of material volatile at 105° C..... 77.5%

Amount of material added to digester..... 12,000 g.

Amount of 8% caustic solution added..... 6,600 g.

Viscose

Amount of alpha assumed (taken as a basis)..... 70.0%

Ripening

Age	NH_4Cl	
72 hours	18.0	
96 "	9.5	(solution spun)

Cellulose* present in viscose solution..... 3.39%

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* For determination of cellulose in viscose solutions, see appendix.

(5) The threads on the spool were cemented together by some material present originally. They were very brittle so as to resist all attempts at twisting, in spite of their apparent tensile strength.

Conclusions to (1). (1) It is possible to make a pulp from the hulls of the grapefruit which will give a viscose syrup with fair characteristics and with spinning qualities.

(2) There were present originally substances deleterious to the production of a satisfactory pulp to be used for the purpose at hand.

(3) The fibers are naturally of short length, to which was attributed, in part, the formation of the tough, hard horny mass obtained with the drying of the digested material.

(B) Results of the first digestion showed that a syrup could be obtained from the hulls of the grapefruit which would spin into an artificial silk. The pulp produced from this, however, gave upon drying, such a hard tough product that the remainder of the work on grapefruit was confined to the production of a workable pulp.

The second digestion was carried out with the use of a 5.8% NaOH solution over a period of four hours, while the initial temperature of 15° C. was caused to rise

slowly to one of 90° C. at the end of this period. The material was then removed, after blowing the digester, and examined. Not so much disintegration was found to have taken place, there was less depth of color to the mass. It was subjected to a few minutes beating with the mechanical beater, poured into a cheese cloth filter and allowed to drain. Filtering of this mass as well as subsequent attempts at washing were just as difficult as after the first digestion. The gelatinous condition still remained.

The third digestion was carried out only in the presence of water. Seven hours was the time of cooking, with the initial temperature 15° C. and the final one 100°C. Heat was applied so that the hulls were raised gradually to the final temperature. A smaller amount of disintegration had taken place than in the second cook, there was little change in color from that of the original material. Attempts were made at filtration and washing, but the same difficulty was met with here as before. The liquor, being highly basic and therefore a natural hindrance to the filtration of any pulp, was treated before filtration with dilute acetic acid. This made very little difference.

The fourth cook was carried out in the presence of dilute H_2SO_3. SO_2 was bubbled into water placed in the digester to saturation. The digestion was carried on until a rise in temperature to 75° C. had been accomplished, and at

this point the process was interrupted and the contents examined. The same state of affairs that had previously been found to exist was obtained here. $NaHSO_3$ to the amount of 5% of the original amount of water was then added and the digestion continued for 2 hours at 120° C. Then the material was removed and beaten for several minutes with the mechanical beater. Attempts to filter and wash it were as negative as before.

Results of (2). With the cooks used it was not possible to remove the foreign material present in the grapefruit hulls to an extent which would allow of the production of a satisfactory pulp.

Conclusions of (2). (Conclusions from (1) simply corroborated.*)

SECTION(F)

Object. To study the effects of "beta cellulose" upon artificial silk.

Experimental Procedure. It was first necessary to produce a sufficient amount of beta cellulose to carry on

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* There is a possibility that the pulping process caused hydrolytic degradation of the cellulose to form beta cellulose or similar substances which produced the gelatinous condition. Though this does not seem very probably considering the character of the cooks, it is entirely possible.

DATA ON SECOND, THIRD, AND FOURTH DIGESTIONS OF GRAPEFRUIT

Second Digestion

Digesting solution.....	5.8% NaOH
Temperature at start.....	15° C.
Temperature at finish.....	90° C.
Time of digestion.....	4 hours
Final pressure...(initial pressure,0#).....	20 # sq.in.

Third Digestion

Digesting solution.....	H_2O
Temperature at start.....	15° C.
Temperature at finish.....	100° C..
Time of digestion.....	7 hours.
Final pressure....(initial pressure, 0#).....	40# sq.in.

Fourth Digestion

Digesting solution.....	sat.soln.SO_2
Temperature at start.....	15° C.
Temperature at finish.....	75° C.
(Process interrupted and 5% $NaHSO_3$ added)	
Final temperature.....	120° C.
Time of digestion (total).....	4 hours
Final pressure.....	60# sq.in.

the investigation. There is only one method for its production known at the present time, and was arrived at through the definition of "beta cellulose" which states that it is that cellulosic material found accompanying alpha cellulose, and which is soluble in 8%, or better, NaOH solution and is precipitated in the form of fibers upon dilution or with the addition of acid (to reduce the NaOH below 8%) to the caustic solution.

Alpha, or resistant, cellulose is known to degrade into this type of material when allowed to remain for some time in contact with caustic soda solution. It has been found that its production is increased when the amount of NaOH present is small, approaching that present in the soda cellulose crumbs used in the formation of a normal viscose syrup.

Sheets of spruce wood pulp were dipped in 18% NaOH solution for 1 hour, removed, allowed to drain and pressed to a ratio of 1:4 (alpha cellulose:soda cellulose). The soda cellulose thus formed was ground to give the proper fluff test (see appendix for this test) and then allowed to remain at ordinary room temperature for a period of seven days. After this time portions of the material were treated in the following manner.

A portion was placed in cheese cloth and subjected to pressure which was increased to approximately 4,000# sq. in. The liquor squeezed out was collected and treated with dilute

sulphuric acid to neutralize most of the NaOH, but the process was carried over the point of neutrality with acetic in order to prevent as much hydrolysis as possible. There precipitated out fine fibers of beta cellulose. The newly formed suspension was filtered through a linen filter, the residue washed well with water and removed. This process was repeated until a sufficient amount of beta cellulose was obtained. To prevent any possible hydrolyzing degradation which might result, further drying of the material was not resorted to.

No satisfactory method for determining the amount of cellulose present in this material was available and no tests, with the exception of that to determine moisture content, were run. The amount of dry material was assumed to be made up entirely of cellulose and subsequent calculations made upon this basis.

In order to study the effects upon viscose syrup, varying amounts of beta cellulose were substituted for the 7% alpha cellulose present in the normal syrup. That is, the normal syrup was made containing 7% alpha. The next contained 6% alpha and 1% beta, the next 5% alpha and 2% beta, and so on.

The ripening of the syrups was based upon the NH_4Cl numbers for the normal syrup, and when this was ready for spinning the remaining syrups were also spun. In this way it was thought to obtain a general empirical relationship between the various solutions.

Xanthation of the beta cellulose was carried out by inserting the proper amount of CS_2 into each flask together with the right amounts of beta cellulose and enough dilute caustic to make a fluid mixture. But it was kept in mind that the total amounts of water and caustic required for the formation of the normal syrups were to be used, no more and no less. The normal pulp (made from spruce pulp), was treated in the ordinary manner, the xanthate mixed in with that of the beta cellulose and the whole allowed to ripen along with the normal syrup at 20° C.

Only the syrup produced from normal pulp was very characteristic. All of the others were very dark and not at all clear, there being an abundance of suspended matter contained therein. When the former was ripe for spinning all of the others had solidified with the exception of three, those which contained 1%, 2% and 3% beta cellulose respectively. Attempts were made at filtering. It was found impossible to filter the most "dilute", that is, the one which contained 3% of beta cellulose. But "forcing" of the process resulted in enough of the remaining syrups being obtained to spin.

From here on two different procedures were used:

(1) The normal syrup was spun to a thread with only fair apparent characteristics. That containing 1% beta produced a very brittle thread, having very little strength and colored a dark brown. Attempts to remove it from the spool

resulted in failure. The third syrup, containing 2% beta, coagulated in the feed stem connected to the spinnerette, owing, apparently, to the coagulating effects of the heated spinning bath which was kept at a temperature of 40° C.

(2) Syrups were made in exactly the same manner as before.* They were spread out, when ripe, upon glass plates containing a rim of rubber and, to insure the production of a film of uniform thickness, allowed to stand at room temperatures on level surfaces for 1 hour. When dry, and after being treated according to the directions given, attempts were made to remove the films from the plates. Failure resulted in every case except with that made from normal cellulose. The films were not substantial enough to withstand attempts at removal from the glass.

Results. (1) Attempts at filtration of the various syrups were failures except in the case of those containing 0%, 1% and 2% beta cellulose respectively.

(2) Viscose films could be formed only from one syrup; namely, that which contained 0% beta cellulose.

Conclusions. (1) Beta cellulose has a decidedly detrimental effect upon the production of a normal viscose syrup.

(2) Rate of ripening of viscose is increased by the presence of beta cellulose, the greater the amount of the

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* See appendix for production of viscose film.

latter present, the less time is required for the syrup to ripen.

(3) Due to the inability to form either a thread of artificial silk or a film of dried viscose it was impossible to study further effects of this material.

(4) It is recommended that the above procedures be repeated using for an upper limit of beta cellulose content 1% instead of 7%, and to vary the amounts between this figure and 0% beta in the syrups produced.

GENERAL DISCUSSION OF RESULTS

The production of a pulp suitable for the manufacture of rayon from milkweed will depend upon application to the stalks of a cook which will break down the lignified celluloses and destroy the foreign materials, or remove them by solution, so that the desirable fibers can be obtained in a pure enough form. The latex in the stalks does not seem to be entirely removed by simply drying, and the presence of this tends to produce a non-workable mass. A preliminary extraction may be necessary to remove this latex.

Rayon can be produced from the pulp obtained in the extraction of tannins from chestnut oak chips, even with the extraction process now used, but a variance in this procedure will

probably allow the manufacture of much better pulp and may produce a high grade of artificial silk.

Proper cooks will have to be discovered for the treatment of grapefruit hulls in order to obtain a pulp suspension which can be readily filtered and handled. Those obtained by the cooks used in this investigation were too gelatinous to be used for the production of a good pulp.

Loblolly pine would possibly serve as a source of pulp production for rayon if the present procedure was varied considerably. The resinous materials present in the pine wood (or else introduced in the present process somewhere) interfere greatly and would have to be removed. It would seem as though the procedure would at best be expensive and not to be recommended as a commercial source of rayon pulp except in the case of dearth of pulps from other sources.

Beta cellulose has a detrimental effect upon viscose syrups. This effect is empirical at present, but the recommendations referred to under the previous discussion of this topic would give results of a more definite nature. The effects of minute quantities of beta cellulose might be found to be non-injurious or even beneficial.

APPENDIX

APPENDIX

SAMPLE CALCULATION FOR VISCOSE SYRUP

(The following stoichiometry is that used for the production of the normal viscose syrup):

Weight of pulp as received..... 600 g.

% moisture in pulp..... 7.41%

"Alpha" cellulose content.....(dry basis)..... 95.25%

Press ratio to be obtained..... 1:3:33

(a) $600 \times \frac{7.41}{100} = 44.46$ total moisture in 600 g. pulp

$600 - 44.46 = 555.54$ grams bone dry stock

$555.54 \times \frac{95.25}{100} = 529.15$ g. alpha cell.in 600 g. pulp

$529.15 \times 3.33 = 1762.08$ g. soda cellulose (press weight)

(b) $1762.08 - 100 = 1662.08$ g. soda cellulose to xanthate after removal of 100 g. for analysis.

$\frac{1662.08}{3.33} = 500$ g. cellulose to be xanthated.

37% of the weight of alpha cellulose used is the weight of CS_2 to be used for xanthation.

$500 \times \frac{37}{100} = 185$ g. CS_2 , specific gravity 1.25

$\frac{185}{1.25} = 148$ cc. CS_2 for xanthation.

(c) $1662 \times \frac{31.5}{100} = 523.5$ g. stock for syrup

523.5 = 7% of the total weight of solution desired.

$\frac{523.5}{7} \times 100 = 7479$ g., weight of total solution

Solution should contain 6.5% NaOH

$7479 \times \frac{6.5}{100} = 486.1$ g. NaOH desired in final solution.

Titration of a sample of the soda cellulose gave 13.95% NaOH present.

$1662 \times \frac{13.95}{100} = 132.7$ g. NaOH already present in soda cellulose.

486.1 - 132.7 = 353.5 g. NaOH to be added.

NaOH solution already made up contains 17.5% NaOH by weight

$353.5 \times \frac{100}{17.5} = 2019.2$ g. 17.5% NaOH solution to be added

Specific gravity of 17.5% NaOH solution = 1.2

$\frac{2019.2}{1.2} = 1683$ cc. 17.5% NaOH solution.

2019 - 1662 = 3681 g. NaOH solution and soda cellulose to be added to form syrup.

Total weight of final solution is to be 7479 g.

7479 - 3681 = 3798 g. (cc.) water to be added

Amounts of substances necessary:

Soda cellulose	1662.08	g.
CS_2	148	cc.
NaOH solution (17.5%)	1683	cc.
Water	3798	cc.

METHOD FOR THE DETERMINATION OF ALPHA CELLULOSE

Bone dry the pulp as received. Weigh out a 5-gram sample, accurately to the third place at least. Transfer the weighed sample into a 400 cc. beaker and add 50 cc. of 18% NaOH solution, noting carefully the time when the caustic is added. Pound this to a mush with a glass rod. In pounding comparable samples this time of pounding should be the same. Add 50 cc. more caustic solution, stir it up and allow to stand for exactly 30 minutes. Temperature should be kept between 20 and 25 degrees Centigrade. At the end of this 30-minute period, dilute with 250 cc. distilled water, stir, and filter through a linen filter on a Buchner funnel. While residue is still on filter wash with 750 cc. cold distilled water, remove suction and cover sample in funnel with 100 cc. of 20% acetic acid. Allow this to stand for about a minute. Apply suction and wash with 1 liter boiling distilled water. Dry in an over at 105 degrees Centigrade to constant weight (3 to 6 hours).

METHOD FOR DETERMINATION OF VISCOSITY OF PULP

Take some pulp, put in distilled water, and beat it to a mush. Filter on a Buchner funnel (linen filter), suck down loosely and wash with alcohol or acetone. Tear pulp apart,

dry at 105 degrees Centigrade in an over, put back into dry container and beat up again. Dry in an over at 105 as before.

Weigh into a 300 cc. Erlenmeyer flask, fitted with rubber stopper, exactly: 6.0000 g. of sample, 9.0000 g. $Cu(OH)_2$, and add 225 cc. NH_4OH (sp. gr. 0.90). Shake flask for 4 minutes. Place in a thermostat at 25 degrees Centigrade for 1 hour. Solution is now ready for viscosity determination.

To make the determination, suck (slowly) the solution up into a pipette (100 cc. capacity) for which the rate of flow of pure glycerine at a definite temperature is known. Time the efflux of solution. From the glycerine's absolute viscosity and the comparative rates of flow of this and the unknown solution, the absolute viscosity of the pulp can be determined. The viscosity of the copper solution is taken as the "viscosity of the pulp".

METHOD FOR PRODUCTION OF SODA-CELLULOSE

When pulp is immersed in the caustic solution there is, of course, marked swelling. Allowance must be made for this in the quantity of pulp immersed.

Immerse the desired number of grams of pulp in the form of sheets in a tank containing 18% NaOH solution. Enough of the latter should be present to cover completely the pulp so as to allow of good contact. The temperature of the caustic should be 18 degrees Centigrade and remain close to that for the period of immersion. Allow the pulp to remain in the solution for exactly 1 hour, remove and press to obtain the correct weight. Press ratio of 1 pulp to 3.33 soda-cellulose is to be obtained using the alpha content of the material for the calculation.

The material is then set away, after being ground sufficiently, for from sixty to one hundred twenty hours, depending upon the original characteristics of the pulp.

FLUFF TEST

This test is run on the soda cellulose to determine if sufficient grinding has taken place. Find the weight of one liter of pulp. Sufficient grinding should give this weight

as approximately 300 grams. If much greater than this more grinding is necessary.

DETERMINATION OF ALPHA CELLULOSE IN SODA CELLULOSE

Take enough of the pulp after it has been ground and wash with water until no caustic "feel" can be obtained. Cover with 20% acetic acid for a minute or so and wash thoroughly with water until free from the acid. Pulp is then beaten up in water (this is usually unnecessary if the pulp was sufficiently ground beforehand), filtered and dried. This is used without any further fluffing. On this product the alpha cellulose is determined exactly as given before.

VISCOSITY OF SODA CELLULOSE

This test is run in the same manner as that given for the original pulp with the substitution of the following weights of materials: 12 g. $Cu(OH)_2$, 8 g. sample, 150 cc. 0.90 sp. gr. NH_4OH.

RIPENING OF THE VISCOSE SYRUP

"Ripening" is the term applied to the changes of the syrup which make it the more suitable for spinning, and is

measured by the cubic centimeters of a 10% NH_4Cl necessary to produce coagulation.

Weigh out exactly 20 g. viscose into a small beaker or Erlenmeyer flask of approximately 400 cc. capacity. Run in 30 cc. distilled water and mix thoroughly by shaking with a rotary motion. From a burette run into the container 10% NH_4Cl solution until coagulation takes place. The number of ccs. required is taken as a measure of the ripeness of the syrup and should be between 9 and 11 ccs.

PRODUCTION OF THE VISCOSE SYRUP

The weight of pulp to be used depends upon the amount of syrup to be produced, of course, and upon the size of the apparatus available. The normal weight for experimental work is approximately 80 g. of high grade pulp, although larger quantities are often used. A smaller amount than this is not to be recommended.

The pulp (usually in the form of sheets) is cut up into the most convenient size for handling, immersed in 18% caustic soda solution for one hour at 20 degrees Centigrade, removed and pressed to previously calculated press weight (taken from the press ratio of 1:3.33 : Amount of alpha cellulose used : desired press weight). It is necessary to determine the amount of alpha cellulose present in the pulp, the amount of moisture, viscosity, etc. before proceeding with the formation of soda cellulose. After

the latter is produced it is ground in a suitable machine to get the proper fluff test. At this point a sample is removed and the various tests run thereon. The aging of the soda cellulose is determined by the viscosity of the original pulp. A normal pulp is aged about 72 hours. A high viscosity means a short aging period, and vice versa.

After aging, the soda cellulose is removed and inserted with the correct amount of CS_2 into a xanthating machine (drum), and allowed to remain until completion of the reactions. This is determined by a decrease in the pressure within the drum as measured by a gauge. The apparatus must be hermetically sealed. If no gauge is available allow $1\frac{1}{2}$ hours for complete xanthation.

The yellow crumbs are now removed and placed in a suitable container together with the amount of caustic soda and water necessary to bring the final syrup up to its final strength. This is stirred until solution has taken place and then set away at constant temperature (close to 20 degrees C.) until the ripening process has proceeded far enough. Filtering of the syrup follows and then spinning (filtering may come at any time during the ripening period).

(Refer to SAMPLE CALCULATION FOR VISCOSE SYRUP).

DETERMINATION OF VISCOSITY OF VISCOSE SYRUP

(The method given here is not the only one in use, but is that which was used by the investigator).

The viscosity of the syrup is a comparative value and is taken as the number of seconds it takes a steel ball of 5/32 in. diameter to fall from mark to mark in a glass tube which has an inside diameter of 1.8 cm., the marks being 15 cm. apart. A good spinning viscosity by this method gives 20 seconds.

SPINNING BATH

(There are other baths in use than the one mentioned below. The latter was used exclusively in this work).

The bath consists of a solution of 9% H_2SO_4, 16% Na_2SO_4 (anhydrous), 30% $MgSO_4.7H_2O$ (measured as such) and 45% (by difference) of water. This is known as the Verhave bath.

TESTS ON FINISHED PRODUCT

There are a number of tests which can be applied here, both chemical and physical. The only properties sought in this investigation were the two most important, however, and were the only ones used to any extent. They are the strength (wet and dry) and the elongation of the rayon. Both wet and dry

strengths are reported as "grams per Denier". (1 Denier is the weight of 9000 meters of silk). A good strength runs from 1.5 to 1.9 grams per Denier. A standard testing machine was used for this purpose.

TREATMENT OF SPUN SYRUP

Desulphurization. Use a .5 to 1% Na_2S solution at 80 degrees Centigrade for from $\frac{1}{2}$ to 1 hour. Wash after this treatment in pure water.

Acid Treatment. Treat the washed silk with a .1% HCl solution. Wash with pure water.

Bleaching. Oxidizing substances are used for this purpose. The best all round substance is NaOCl, which contains .2% available chlorine. Treat at 20 to 25 degrees Centigrade. The time of treatment depends upon the rate of bleaching of the material. Rarely more than 2 minutes is necessary, or actually used. Wash after this treatment with cold water.

Antichlor Treatment. Dip the silk into a solution of .2% $NaHSO_3$ at 20 to 25 degrees for 5 minutes. SO_2 water is just as good. Wash once more and treat with .1% HCo solution.

Wash for the last time and do it in a thorough manner. The silk (which should be in the form of skeins by now) are dried and prepared for the final tests (strength, elongation, etc.,).

DETERMINATION OF TOTAL CELLULOSE IN VISCOSE SOLUTION

Weigh out 2 to 3 grams of viscose syrup and spread into a thin film on a watch glass by air pressure. Dry for 2 hours at 105 degrees C. Immerse in a 0.5% Na_2S at 80 degrees C., then in warm water (any temperature up to 80 degrees C.), and then in 0.2% HCl solution at 25 degrees C., for fifteen minute periods each. Wash the film well with water, dry and weigh. The latter is the amount of total cellulose present.