THE PRODUCTION OF PULP FROM THE ENGLISH PLANTAIN

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By

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INTRODUCTION

Throughout the state there are vast tracts of land that are unfit for normal agriculture purposes, and are of no value to the owner. This land will grow a weed that is called the English, or narrow leaf plantain. These weeds seem to thrive on any type of soil, and are the first to come up in the spring and the last to die in the fall. They also grow as fast as they are cut and due to this fact, the grower may receive several cuttings of the weed each year. These reasons led Dr. P. C. Scherer to suggest the possibilities of preparing from these weeds, a pulp suitable for the manufacture of rayon. This problem was not undertaken primarily with the idea of developing a new method of preparing cellulose but with a view of aiding the agriculturists of Virginia with a possibly paying crop for non-arable lands.

CONTENTS

Historical

No data or material could be found concerning the production of cellulose from the narrow leaf plantain. In 1919, Pefelera Espanola [1] patented a process of making pulp from the plantain or banana tree. In 1919, J. E. Boomer[2] reported work that had been done on the production of pulp from certain materials of the Philippines, such as abaca, banana or plantain, maguey, certain palms and bamboo. Bamboo was found to be the best material for making pulp.

In 1916, B. Cataldi[3] patented a process for the manufacture of cellulose from vegetable fibers. In the extraction of cellulose from vegetable fibers such as wood, cotton straw, esparto, jute, etc., the material is crushed by known mechanical means, and then introduced into digestors lined with acid proof brick and treated with alkali. After a period the liquor is drained off and the pressure is reduced to 50 - 65 cm. Cl_2 gas is then drawn in so that the pressure is again normal, and allowed to stand for several hours. This product is washed and again treated with dilute alkali for a slightly shorter period, after which it is washed and refined. If a perfectly white pulp is desired, further bleaching may be affected by hypochlorite of lime or soda.

A. R. Devain[4] later patented a process for the chlorination of cellulosic materials. In neutralizing the acid set free by the chlorination of ligno or pecto cellulose or similar cellulosic materials, and dissolving out the chlorinated derivatives, an alkali earth metal compound such as $Ca(OH)_2$ or $CaCO_3$ is used for the neutralization, and an alkali compound such as NaOH, NH_4CH, or Na_2CO_3 for dissolving the

chlorinated derivatives. Devain[5] also patented a process of continuous chlorination of cellulose materials. This was brought about by the continuous addition of a chlorinating agent e.g. a Cl solution, and the material to be chlorinated into a chlorination vessel, controlling the supply of chlorinating by the pressure in the chlorination vessel and regulating the supply of cellulosic material in accord with the discharge of chlorinated product.

Theory

The success of this method for the production of pulp depends upon the action of sodium hydroxide and chlorine gas on the weed. Alkalies such as NaOH, at high temperatures attack lignin and form sodium compounds of lignin. These compounds are soluble in water. Caustic soda, however, dissolves only 50 to 75% of the lignin even when under pressure. Caustic soda also has a swelling action on the aggregates of fibers and causes them to break apart so as to form separate fibers or fiber bundles so that the weed breaks down and loses its original form. Chlorine in the presence of water attacks lignin and forms a chloride $C_{19}H_{18}Cl_4O_9$, which is bright yellow in color and soluble in one percent caustic soda solution. By the combination of the two reagents, caustic soda and chlorine, the lignin may be removed from the cellulose and the cellulose liberated in the form of individual fibers.

Apparatus Used

The apparatus used in these experiments consisted of two units. Unit no. I being the "cooking unit" and Unit no. II the Chlorinating unit. The first uhit is pictured in Fig. no. II. This consists of one flask (a) round bottom, 1500 c.c., capacity used as the digestor part. One reflux condenser (b) used for keeping the concentration of the NaOH constant, and one burner (c) for heating purposes. Unit no. II is pictured in Fig. no. I. This consists of water bottle (a) to furnish pressure to force Cl_2 gas out of Cl_2 container (b). The Cl_2 gas passes out of the container (b) through bubble tower (c). By this unit in the apparatus the rate of flow of Cl_2 gas can be regulated by counting the number of bubbles. From this the gas passes into the chlorinating tower (d). The gas enters the bottom, circulates among the material to be chlorinated and excess of the gas passes out the top of the tower to absorption bottle (e) which contains eight percent caustic soda. This absorbs the excess gas. From the absorption bottle the pressure is implied into the manometer (f). This measures the pressure that is involved after the gas has been absorbed by the caustic.

Chlorinating Unit.

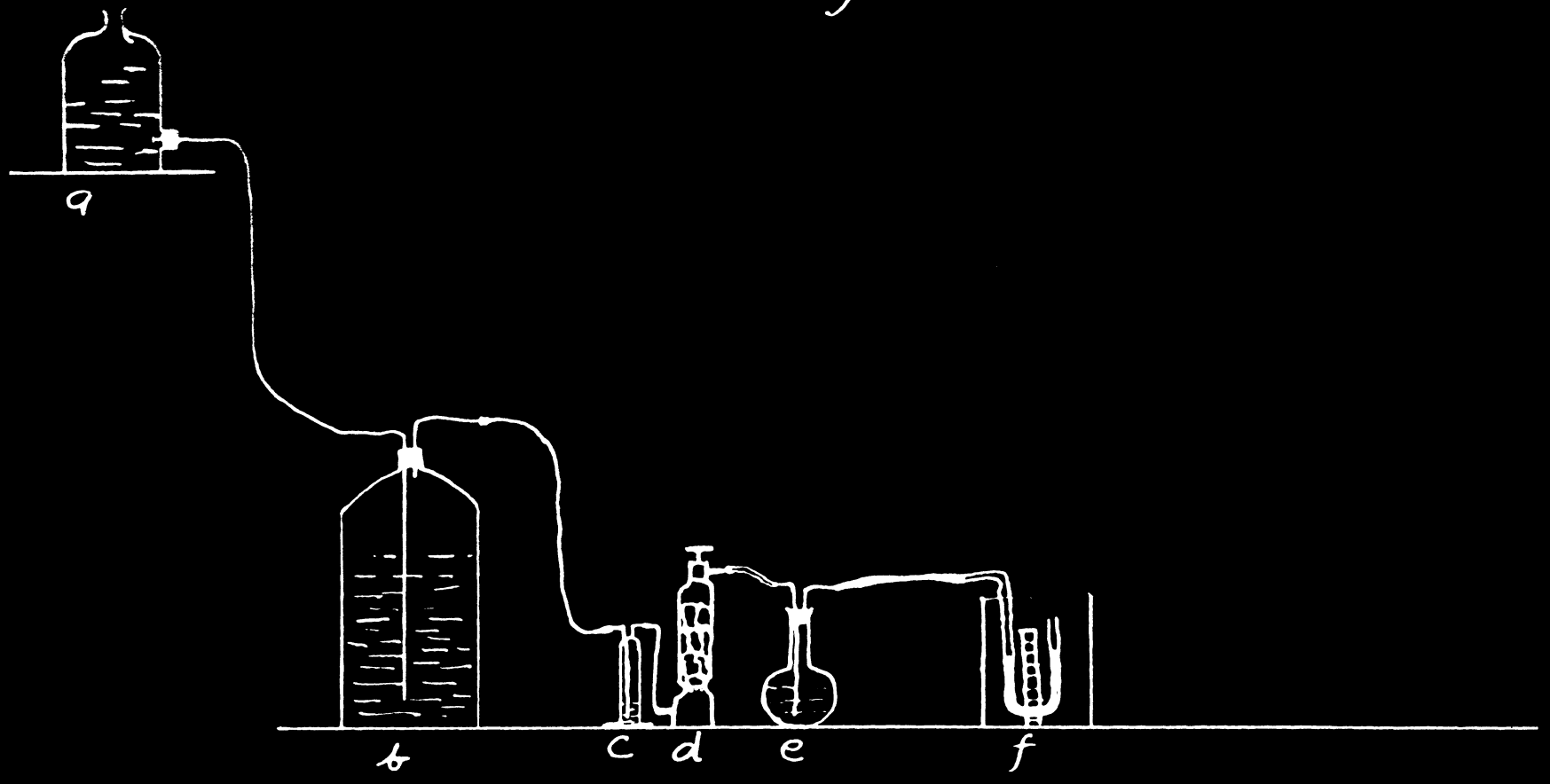

Fig I.

Cooking Unit

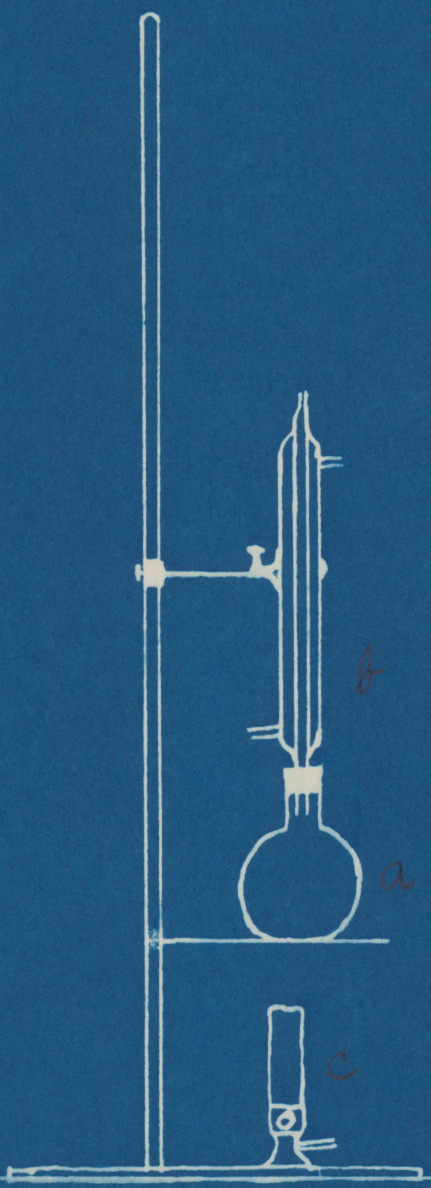

Fig II.

Procedure

The material used in these studies was the stem of the English or narrow leaf plantain. This material is a long slender stalk, green in color and at the top is the seed in clusters forming the head. The first difficulty encountered was that the seeds would not disintegrate on cooking and had to be removed. The first method tried to accomplish this was to run the dried stems through a washing machine wringer. The rolls were too soft to crush off the heads. The matter was temporarily dropped at this point and the heads were removed by hand. After the heads had been removed, the weed was broken up into small pieces of about one inch long. These were put into the flask of the cooking unit and caustic soda added in the amount of twelve and one-half c.c. to each gram of weed. This product was cooked for a definite length of time. After this, the product was transfered to the stirrer, and stirred very vigorously until the weed was more or less disintegrated. From the stirrer the weed was placed in the chlorinating unit and treated with Cl_2 gas until the weed was a bright yellow. This material was then treated with one percent caustic soda and again stirred vigorously, at this point most of the disintegration took place. At this point, the material was transfered to the wash box and thoroughly washed until the material no longer tasted of alkali or salts. This material was subjected to another caustic cook, chlorination and washing. At the end of this procedure the material was found to be well disintegrated. If pure white pulp was desired, the material was bleached with liquid soda bleach at 30°C. until the product was white. This product was then

washed with water until no taste of caustic or salts was present. The pulp was given an antichlor treatment of one-half percent Na_2S. If higher alpha cellulose content was desired the pulp was given an alpha treatment consisting of a boil with eight percent caustic for thirty minutes. This product was washed very thoroughly and made into test sheets. This was done by making a water-pulp suspension, which was poured into a Buchner funnel until the top of the funnel was completely filled. Then the suction was gradually applied and the pad of cellulose was evenly drawn down. This pad was put in the press and two thousand pounds per square inch pressure applied. Steam heat was turned on and the pad dried under pressure. The pulp in this form was the final product. The above is not a definite program but gives a generalized procedure which was used in most of the experiments. The details of each run are given below.

The first preliminary batch run was as follows: a quantity of weed was broken up and put into the flask of the cooking unit. To this was added one percent caustic soda, approximately 12.5 c.c. per gram of air dried weed or enough to cover it. This was cooked for two hours and the product washed with water. It was then treated with Cl_2 gas (85% Cl_2 and 15% air) for two hours. The product was washed with one percent NaOH, washed with water and cooked again with one percent NaOH, for two hours; again treated with Cl_2 gas for two and one-half hours; washed with one percent NaOH and then washed with water. The product had a greyish white color and was hard and brittle. No alpha cellulose determination was made on this pulp.

The second preliminary batch was run in the same way as the first except four percent NaOH was used for the cook liquor. The product was somewhat on the order of the first, greyish in color, hard and brittle. No determination for alpha cellulose was made on this product.

The third preliminary batch was identical with the first two, using four percent NaOH for the cook liquor. This product was subjected to an alpha cellulose cook. Such a cook consisted of heating the product with nine percent NaOH for thirty minutes and then washing with water until free from caustic. The product was fairly white and was well disintegrated. An alpha cellulose determination was made on this product and an alpha cellulose content of eighty-six percent was found.

Since the chief difficulty appeared to be the disintegration of the weed, a new procedure was used on the fourth preliminary batch. The weed was put into the disintegrating machine (Werner and Pfludera), and ground with three percent caustic for four hours. It was then cooked with four percent caustic for two hours, washed, treated with Cl_2 gas for three hours, washed with one percent caustic and then with water. The product was given an alpha cellulose cook, and a determination of the alpha cellulose was run. The percentage of alpha cellulose was 81.3. The ash content was also determined and found to be 0.76%. The pulp had a greyish color and was hard and brittle.

The first batch was run in a manner different from these described. It was thought possibly that the first two caustic cooks could be eliminated. The procedure followed was to put fifty-four gram weed in the ball mill, then two liters of three percent caustic soda were added and the

weed ground for four hours. The mass was chlorinated until the product was as white as it would get. It was washed with one percent caustic and then washed with water. The product was hard and tough on drying. It was then given an alpha cellulose cook with eight percent caustic. The hardness and brittleness remained after the alpha cook. The product was subjected to an alcohol extraction, as it was thought that the hardness and brittleness was due to fats and waxes present in the weed. But this was not the case as the hardness and brittleness were still present after the extraction. An alpha cellulose determination was run on the product which was found to be 83.8% alpha. The product was greyish in color and was very short fibered. It was also hard and brittle. Yield of rough alpha cellulose was 10.35%. Yield of pure alpha cellulose was 8.89% based on dried weed.

The second run was on the same plan as that of the first, second and third preliminary batches. Forty grams of air dried weed were cooked with 500 c.c. of four percent NaOH for two hours and forty minutes. This was stirred vigorously with the stirrer and washed well with water. The product was then put into the chlorinating tower and treated with five and onepfourth liters of Cl_2 gas. It was then washed with one percent NaOH and stirred very vigorously and washed with water. The product was fairly well disintegrated but had a brownish color. It was then cooked with four percent caustic for one hour and thirty-five minutes. It was washed, chlorinated with four and one-fourth liters Cl_2 gas, treated with 500 c.c. of one percent NaOH, stirred vigorously and then washed with water. The product was not given an alpha cellulose cook but the product was steeped in cold eighteen percent NaOH for thirty minutes, washed with

water, acetic acid and then water. An alpha cellulose determination was made on this pulp and was found to be 95.03%. The ash content showed 0.46% and the copper number 1.647. Yield of alpha cellulose was 20% based on dry weed. Its viscosity was 11.44 poise for a one percent Dudley solution. Pulp sheets were made up by making a water pulp suspension, filling a Buchner funnel full with the suspension and by applying suction the cellulose was drawn down evenly. The pads of cellulose were put between two pieces of flannel and put into a hydraulic press and subjected to 2000 pounds in pressure. Heat was applied and the sheets dried. The product was soft and pliable and had fairly good color.

The third batch was nearly the same as the first. Forty grams air dried weed were cooked with four percent caustic soda for one hour and thirty-five minutes, washed with water and stirred vigorously with stirrer. They were chlorinated, until all stems changed color and then treated with one percent caustic and stirred vigorously and they were washed thoroughly with water. The pulp was brown and partially disintegrated. It was cooked again with four percent caustic soda for one hour and fifteen minutes, washed and chlorinated until no more color changes appeared. It was then washed with one percent caustic, stirred and washed with water. The pulp was white and very well disintegrated. It was then given an eight percent caustic alpha cook. The product was then made into test sheets. This pulp was very white but hard and brittle. No alpha cellulose content was determined or yield of product calculated.

The fourth run was similar to the first preliminary run except the first NaOH cook was for two hours and fifteen minutes and the second was for one hour. After the second cook the product was given a liquid

caustic bleach. The product would not whiten. It was then given the regular Cl_2 treatment, treated with one percent caustic soda, stirred and washed with water. A liquid caustic bleach containing 1.5% available Cl_2 was then used. The product was white, very well disintegrated and with long fibers. The alpha cellulose content was determined and found to be 89.92%. The ash content was 0.22% and the copper number .715. The viscosity was 11.44 poise for a one percent Dudley solution. Percent yield, 16.5 based on dried weed. This product was very white and well disintegrated. It was soft and pliable. This was the best pulp produced.

The fifth run differed from the others in that water was used instead of four percent caustic as the cook liquor. The Cl_2 treatments were the same as any of the other runs. No disintegration occured. The regular four percent caustic cooks and chlorination treatments were applied but even with these the pulp would not disintegrate. No alpha cellulose content or yield of pulp was run on this product.

The sixth batch was run on weeds that had been out in the weather all winter. The procedure was the same as in the eighth run. The weed would not disintegrate very well and the pulp would not take the bleach. It behaved in somewhat the same manner as the weeds cooked in the water. No alpha cellulose content or yield of pulp was determined.

The seventh batch was run on new weeds gathered in the early spring. These weeds were gathered before the seed was hard or just as it began to flower. The weed was put into the cooker without removing the heads and it was subjected to identically the same treatments as the fourth batch. The product was white and well disintegrated. No determinations were made on this pulp.

Results

First and Second Preliminary Runs

The products were hard and brittle and possessed a greyish color. No alpha cellulose determination was run on these products.

Third Preliminary Run

The product was soft and fairly white. It had an alpha cellulose content of 86.%. This was after it had received an eight percent caustic cook.

Fourth Preliminary Run

The product was hard and brittle, had short fibers, possessed a greyish color. It had an alpha cellulose content of 81.3%

First Batch

The product was hard and brittle, greyish in color and possessed very short fibers. It had an alpha cellulose content of 83.8%.

Second Batch

The product was very soft, but possessed a slight brownish color. The fibers were long and well suited for making pulp sheets. It had an alpha cellulose content of 95.03%, ash content of .46%, copper number 1.647, viscosity 11.44 poise for a 1% Dudley solution, an average fiber length of 3.019 m.m., and gave a yield of 20% based on dried weed stems.

Third Batch

The product was very white but was hard and brittle. No alpha cellulose content was made on this product.

Fourth Batch

The pulp was very white and soft. It possessed long fibers and made up into pulp sheets well. It had an alpha cellulose content of 89.92%, ash content of .22%, viscosity of 11.44 poise for a 1% Dudley solution, copper number of .715, average fiber length of 3.56 m.m., and gave a yield of 16.5%.

Fifth Batch

The product was dark grey in color and the stems were not disintegrated.

Sixth Batch

The product was brown in color and the stems were not disintegrated.

Seventh Batch

The product was soft and white and showed no signs of the seed as all were disintegrated.

Data Obtained

Third Preliminary Run

Alpha Cellulose

Weight of weighing dish plus sample	36.0580
Weight of weighing dish	34.7858
Weight of sample	1.2722
Weight of sample after treatment	1.1064

$\frac{1.1064}{1.2722} \times 100 = 86.00\%$ alpha cellulose

Fourth Preliminary Run

Ash

Weight of crucible plus sample	10.0090
Weight of crucible	9.8660
Weight of sample	.1430
Weight of ash	.0011

$\frac{.0011}{.1430} \times 100 = .76\%$ ash

Alpha Cellulose

Weight of weighing dish plus sample	36.8562
Weight of weighing dish	34.5783
Weight of sample	2.0709
Weight of sample after treatment	1.6849

$\frac{1.6849}{2.0709} \times 100 = 81.83\%$ alpha cellulose

First Batch

Alpha Cellulose

Weight of weighing dish plus sample	40.3746
Weight of weighing dish	34.7829
Weight of sample	5.5917
Weight of sample after treatment	4.6882

$\frac{4.6882}{5.5917} \times 100 = 83.8\%$ alpha cellulose

Yield of Pulp

Weight of pulp 5.5917
Weight of weed 54.0000

$\frac{5.5917}{54.0000} \times 100 = 10.35\%$ yield

Second Batch

Alpha Celluouse

Weight of weighing dish plus sample 37.0591
Weight of weighing dish 34.7847
Weight of sample 2.2744
Weight of sample after treatment 2.1615

$\frac{2.1615}{2.2744} \times 100 = 95.03\%$ alpha cellulose

Ash

Weight of crucible plus sample..... 10.5925
Weight of crucible 10.2684
Weight of sample ..... .3241
Weight of ash ..... .0015

$\frac{.0015}{.3241} \times 100 = .46\%$ ash

Copper Number

Weights of duplicate samples ..... .25
First titration with $KMnO_4$ ..... 2.16 c.c.
Second titration with $KMnO_4$ ..... 1.08 c.c.
3.24 c.c.

$\frac{3.24}{2.00} = 1.62$ c.c. $KMnO_4$ used in the titration

$1.62 \times .04 \times .06753 = .00411966$ grams of copper

$.00411966 \times 4 \times 100 = 1.67$ copper number

Viscosity

Time for 69.98% glycerol solution to run out of pipette = 1.5 sec.
69.98% glycerol solution at 30° C = 14.30 poise
1.5 grams pulp + 1.5 grams copper hydrate + 150 grams
26° Be. NH_4OH = 1% Dudley solution

Time it took for 1% Dudley solution to run out of pipette 1.2 sec. at 30° C.

$\frac{1.5}{14.30}, \frac{1.2}{x}$, x = 11.44 poise on 1% Dudley solution

Yield of Cellulose

Weight of cellulose obtained	8.00
Weight of weed	40.00

$\frac{8.00}{40.00} \times 100 = 2.0\%$

Length of fibers

Average length of fiber = 3.019 mm.

Fourth Batch

Alpha Cellulose

Weight of weighing dirt plus sample	37.2467
Weight of weighing dish	34.7842
Weight of sample	2.4615
Weight of sample after treatment	2.2136

$\frac{2.2136}{2.4165} \times 100 = 89.92\%$ alpha cellulose

Ash

Weight of crucible plus sample.....	10.2078
Weight of crucible	9.9852
Weight of sample	.2226
Weight of ash	.0005

$\frac{.0005}{.2226} \times 100 = .22\%$ ash

Viscosity

Time in seconds	1.2 sec.
1.5 in sec.	14.30 poise
1.2 sec.	11.44 poise on 1% Dudley solution

Copper Number

Weight of sample no. 1	.2513
Weight of sample no. 2	.2506
Titration with .04 N $KMnO_4$	
No. I	.77 c.c.
No. II	.66 c.c.

.77 x .04 x .06753 x .2513 x 3.97 x 100 .77 copper no.
.66 x .04 x .06753 x .2506 x 3.99 x .00 .66 copper no.

$$\begin{array}{r} .77 \\ \underline{.66} \\ 1.43 \end{array} \qquad \frac{1.43}{2} = .715 \text{ average copper number}$$

Fiber length

Average length of fiber = 3.56 mm.

Discussion of Results

The preliminary runs were made to set up a general method for preparing a pulp from the weed.

The products from preliminary runs I and II were hard and brittle. This fact was attributed to the lack of washing that the pulp received. Because of this deficiency in washing some of the compounds of lignin and free sodium hydroxide were not removed from the pulp. The difficulty in disintegrating the weed was due to the lack of stirring. No determinations of any kind were made on this product as quantative results were not desired. The product of the third preliminary run was soft, fairly white and well disintegrated. It was not understood why this product was soft and white and the product from the second preliminary run was not. It was finally thought that it was due to the 8% alpha cook that it received. If this product had been washed better it would have been whiter and softer than it was. The alpha cellulose content was rather high, being 86%. This is fairly high for a pulp.

In preliminary run IV and the first batch, the main reason that these products were not good was the length of time it took to carry out the process. The material dried after the first two cooks in the fourth preliminary run, and after the treatment with Cl_2 gas in the first batch it could not be disintegrated again after such drying. The shortness of the fibers was due to the grinding that the weed received in the ball mill. It may be possible that the reason why the pulp would not disintegrate after it had dried was due to some sort of fats and waxes present in the weed. At first it

appeared that the dried weed could not be used since it was thought that the dried weed contained fats and waxes and that they had hardened in the weed so that disintegration could not occur. This fear was allayed in the next determination. It was also found that the initial four percent caustic cook was essential to the process.

The procedure for the second batch was exactly the same as used in preliminary run three. This proved that the dry weed could be disintegrated and the product be soft and white. The complete disintegration was brought about by the use of a high speed stirrer that had just been installed in the laboratory. The softness was due to the intensive washing that the product received in the process. The high alpha cellulose content was attributed to the severe alpha cellulose treatment that the pulp received, this treatment being the same as used in determining the alpha cellulose content. The ash content was rather high which might have been due to the presence of salts not removed in the washing. The copper number indicated that the treatments the pulp received had not degraded the material to any great extent. This number is not as high as for some commercial pulps. The length of the fiber was high enough to be used in the manufacture of rayon, but the yield was low because of the smallness of the sample. This method could not well be used commercially on account of the difficulty in handling eighteen percent caustic soda in commercial plants.

The product of the third batch was nearly pure white yet it was very hard and brittle. It will be noticed that the length of the first cook was only one hour and thirty-five minutes, while all the rest had an initial cook of at least two hours or more. It was observed that

all pulps which had received the nine percent caustic alpha cook were hard and brittle. It may be that the nine percent caustic cook breaks down the cellulose into products which are not easily washed out.

The product of the fourth batch was the best that had been obtained. It was pure white and soft. This was attributed to the wash box that had been used for the first time. This allowed the pulp to be washed free from all alkalies and salts that were present. The alpha cellulose content of the pulp was also increased. The copper number was exceedingly low, much lower in fact than most pulps manufactured commercially. The fiber length was just a little larger than the pulp of the white spruce. The ash content was unusually low. The yield of the pulp, however, was low, which was due to the mechanical loss in the procedure. The pulp also took the bleach exceedingly well.

The product of the fifth batch was useless. This run was made to see if water could be used instead of caustic soda in the initial cooks of the weed. It was found that this could not be done since the weed would not take the Cl_2 gas. It appeared that water either had some hardening effect on the weed or lacked the power to disintegrate them.

The product of the sixth run was also useless. The run was made on weathered weed that had been out-doors all winter, and was made to determine the possibility of using such a material. All the other weed had been gathered in the fall while still wet with the sap. This weathered weed gave somewhat the same results as the weed cooked in water.

The product of the seventh run was white and well disintegrated. This experiment was made chiefly to determine whether the head of the weed would disintegrate if it were gathered before it hardened. This was found to be the case and this fact leads us to believe that the problem of a mechanical means for removing the heads is solved.

Recommended Procedure

Forty grams of deheaded dried weed are broken up into pieces about one inch in length. These are put into the flask of the cooking unit and 500 c.c. of four percent caustic soda is added. This is put into the reflux condenser and boiled for two and one-half hours. After this the cook liquor is drained off and the weed is placed in the wash box and washed until free of salts and caustic. Remove the product from the wash box and place in the chlorinating tower. Pass the Cl_2 gas through the tower until the product is a bright yellow. The gas is shut off, product removed and placed in a beaker of 1000c.c. size, Add to this product 500 c.c. of one percent NaOH, place under a high speed stirrer and stir until all the product shows signs of disintegrating. This product is washed in the wash box until free from caustic and salts. This pulp is then put back into the cooking flask and 500 c.c. of four percent caustic soda is added and boiled for one and one-half hours. This is then washed and put into the chlorinating tower. This time the product will not give a yellow color, but will turn white, The Cl_2 gas is passed through until the product shows no more color change. This product is then treated with 500 c.c. of one percent caustic and stirred until it is completely disintegrated. This is then washed free from caustic and salts. If the pulp is not white it is given a liquid caustic bleach containing 1.5 to 3% available Cl_2. This is then washed with water and treated with 500 c.c. of one-half percent Na_2S, and then washed again.

This product will be white and soft and is then ready for the determination. It is made into a pad by pouring into a Buchner funnel and applying suction.

Conclusions

The author draws these conclusions from the results.

1. That the initial caustic soda cooks must be for at least two hours.
2. That the product must be chlorinated until all stems of the weed are of a light yellow color.
3. That the product must be beaten well after the initial cooks and after treating the chlorinated material with one percent caustic soda.
4. That four percent caustic soda is the best concentration to use in the initial cooks.
5. That the pulp must be washed well after the cooks and after the caustic treat on the chlorinated material.
6. That gaseous chlorine is not enough to give white pulp, but a bleach must be used.
7. That the weed should be harvested just as the plant is flowering as this eliminates the problem of removing the heads.

This problem is not solved by any means, but the author thinks that it is a good working basis for following work.

However, if the recommended procedure is followed, it is believed that pulp suitable for the manufacture of rayon can be produced. Lack of material prevented the preparation of pulp from plantain in a large enough quantity to attempt the preparation of viscose and rayon from it.

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