"SULFATE" LEACH PULPING

Nitrocotton No. 578.....Short fiber
 Weight of soused nitrocotton.....800 g.
 Weight of moist pulp.....261 g. drained
 Weight of dry pulp.....111.3 g.
 Leach changed 3 times in 24 hrs.

Alkalinity of Leach = 12 cc. 0.01 N per 100 cc.

No. of Change	Liquid Drained Off Cc.	Acid per 100 Cc. 0.01N Cc.	Acid Removed Cc.	Acid per 100 G. Dry Cc.
1	2000	453.9	9030	8130
2	2000	370.8	7420	6670
3	2000	41.55	831	746
Total acid removed.....			17281	15546

Residual Acid Left by Sulfate Leach

Inside titration 2 g. dry.....7.2 cc. 0.01 N
 Acid per 100 g. dry.....360 cc.
 Total acid per 100 g. dry.....15,906 cc.
 Per cent acid not removed.....2.32

It will be seen that though the total acidity was considerably higher¹ in the sample used for sulfate pulping the removal of acid, though incomplete with only three leaches, was much better than with "hard" water, only 2.3 per cent of the total acidity being left, as compared with 14 per cent for water. The actual acidities per 1 g. dry were:

1 g. dry, by water	14.7 cc.
1 g. dry, by sulfate	3.6 cc.

One important conclusion from these experiments is this. Although, as already stated, the same degree of mechanical subdivision is reached earlier in water than in sulfate, the acid removal lagged behind that by sulfate. *It appears evident that merely mechanically shortening and destroying the fibers does not greatly facilitate acid removal*, beyond its effect in assisting uniform penetration of large masses. In spite of the fine subdivision of the nitrocotton (see Fig. 9) the latter portions of acid are obstinately retained in water by pulped nitrocotton. In fact, the increased dispersity probably in-

creases this retention, in consequence of the greater surface developed. This acid is, however, readily removed by sulfate leach. This tends to confirm our view that the residual acid is held by selective adsorption, not by mechanical occlusion, and that the sulfate leach acts osmotically on the membrane structure of the fiber primarily, and only secondarily on the cell.

It further appears from these results that if pulping or disintegrating were combined with a sulfate leaching process this would be most desirably effected after acid boiling, stabilizing, leaching out of acid, and washing out of sulfate. Actually, this would correspond with the usual practice where pulping is employed, both for guncotton and for celluloid.¹ Where final boiling in weak alkaline solutions is desired for guncotton, this could be initially effected after pulping in the weakly alkaline water, as this assists the disintegration. In the celluloid industry it is very general to bleach the nitrocellulose after pulping.

We have tested various bleaching methods on sulfate treated cotton, *e. g.*, permanganate followed by bisulfite, "chloride of lime" bleach, sodium hypochlorite, chlorine gas, and hydrogen peroxide, and find them to act at least equally as well on sulfate-leached cotton as on water-washed. Hence, neither the introduction of pulping, nor of pulping and bleaching offers difficulty in the installation of a purification régime utilizing the sulfate leach as the essential deacidifying process.

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The Production of Furfural by the Action of Superheated Water on Aqueous Corncob Extract²

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In a recent paper on the preparation of corncob adhesives by the hydrolysis of field corncocks with hot water under pressure, it was noted that a certain amount of furfural was always produced.³ In the present paper a description is given of a method for treatment of corncocks in such a way that the cellulosic material can be obtained and, in addition, an amount of furfural corresponding to 7.76 per cent of the weight of the original cocks.

The method consists in heating the cocks under pressure for a short time with hot water, a procedure which does not injure the cellulosic material. An amount of furfural corresponding to about 2.8 per cent of the weight of the cocks is formed at the same time and is blown off with a certain amount of water when the pressure is released. The crude cellulosic residue is filtered and pressed, and the aqueous liquors, which contain a considerable amount of soluble carbohydrates, are heated with water under pressure, thus causing hydrolysis and formation of a further amount of furfural, sufficient to make a total weight of 7.76 per cent of the original cocks.

A comparison of this process for the production of furfural with those now described in the literature indicates certain

advantages for the former. Not only is the cellulose saved, but the process has the great advantage of using only water for hydrolysis in place of acid. Moreover it will be noted from the experimental results that the time necessary for handling a given amount of cocks is shorter than is customary by the methods so far described using acid hydrolysis. The method can also be applied to the preparation of furfural from corn husks, corn stalks, and bagasse, and probably from many other plant materials rich in pentosans.

EXPERIMENTAL

One kilo of cocks was heated in an autoclave of about 6-l. capacity with 4000 cc. of water at 180° to 185°. After this temperature had been maintained for three-quarters of an hour, the pressure was released and the vapors were allowed to pass through a condenser. The amount of condensate thus collected was 815 cc. Since 5 cc. of this condensate gave (a) 0.3268 g., (b) 0.3255 g. of phloroglucide, 815 cc. contained 28.0 g. of furfural. The cellulosic residue remaining in the autoclave was filtered with pressure, and 2650 cc. of filtrate containing soluble carbohydrate material capable of further hydrolysis to furfural were obtained. The cellulosic residue was washed with 2000 cc. of water, pressed again, and set aside for other purposes.

The filtrate obtained from the washings was diluted to 4000 cc. with water and used for heating a second batch of 1 kg. of cocks under the conditions given above. In the same

¹ It is almost impossible to obtain uniformity in this respect in small samples of "soused" nitrocotton.

² Presented before the Division of Organic Chemistry at the 61st Meeting of the American Chemical Society, Rochester, N. Y., April 26 to 29, 1921.

³ *Chemical Age (N. Y.)*, 28 (1920), 332; see also *Z. angew. Chem.*, 27 (1914), 654; *This Journal*, 13 (1921), 133.

¹ Schrimpf, *Loc. cit.*, 96.

way, 825 cc. of distillate were obtained, which contained about 28 g. of furfural. The cellulosic material was filtered by pressure and washed with 2000 cc. of water, and again pressed. The filtrate and wash waters from this second kilo of cobs were mixed and concentrated to their original volume of 3175 cc. (the 4000 cc. minus 825 cc. blown off when the pressure was released). This solution, with the 2650 cc. obtained from the first kilo of cobs, contained the carbohydrate material from 2 kg. of cobs.

Forty-five hundred cc. of this solution, which represented the soluble extracts from 1540 g. of cobs, were heated in the autoclave at 180° to 185°. After 15 min. the autoclave was blown off through the condenser as before. The amount of condensate was noted and an equal volume of water was added to the contents of the digester and it was again heated for 15 min. at 180° to 185°. This was then blown off, the volume of the condensate noted, an equal volume of water added to the digester, and the heating repeated. This was carried out five times, after which so little furfural was being produced that it was not worth while to carry the process further.¹ The following table denotes the results obtained by five successive heatings of 4500 cc. of soluble

extractives obtained by the method described above.

No.	Condensate Cc.	Phloroglu- cide G. from 5 Cc.	Furfural G. in 5 Cc. (Av.)	Furfural in Condensate Grams	Furfural in Con- densate Per cent
1	750	(a) 0.2770 (b) 0.2738	0.1454	21.8	2.91
2	775	(a) 0.2610 (b) 0.2625	0.1388	20.9	2.70
3	755	(a) 0.2137 (b) 0.2180	0.1146	17.3	2.29
4	725	(a) 0.1310 (b) 0.1240	0.0691	10.2	1.38
5	725	(a) 0.0752 (b) 0.0760	0.0420	6.1	0.84

If it is desired merely to prepare furfural and not to save the cellulose, the process could be made continuous from the start, following the general procedure just described for the hydrolysis of the soluble carbohydrate extractives. Under these conditions the cellulosic material would be allowed to remain in the digester during the complete process. It should be emphasized, however, that the cellulose may have as great value as the furfural in technical operations and it is of great importance to preserve it from injury by over-heating.

The Color Value of a Tan Liquor as a Function of the Hydrogen-Ion Concentration^{2,3}

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In judging the value of a vegetable tanning extract, tanners often place much weight upon the color imparted to skin by solutions of the extract. This has given rise to a movement to try to devise some satisfactory method for measuring the color value of an extract. In Europe the tendency has been toward matching a solution of the extract with standard colored glasses, but apparently the preparation of absolutely standardized glasses is a serious problem. Moreover, the color of a tan liquor is not necessarily a measure of the color it will give to a skin. In this country preference seems to have been given to a method involving the observation of the color of strips of sheep or calf skin tanned in a standard solution of the extract. A strip of tanned skin accompanying the analysis report is apt to find greater favor with the tanner than figures on an arbitrary scale, but this method has sometimes been deceptive, because a given tan liquor may impart different colors to samples of skin from different sources. The present paper does not deal with the question of measuring color values, but with factors powerfully affecting such measurements which in the past have been uncontrolled and apparently often quite unappreciated.

It has long been known that the presence of lime in a tanned skin will cause a darkening of the color. If the skin is treated with mineral acid soon after tanning, the color brightens, but the effect of acid becomes less pronounced the longer the skin is previously allowed to stand exposed to air. In our studies on the effect of change of hydrogen-ion concentration upon tanning, we obtained leather differently colored for each different pH value of the tan liquor. It was immediately apparent that the color of a tan liquor as well as that of the leather is a function of the hydrogen-ion concentration.

¹ In large-scale practice the process may be made continuous by keeping the temperature constant and maintaining a constant level in the digester by continuous addition of water or steam.

² Presented before the Section of Leather Chemistry at the 62nd Meeting of the American Chemical Society, New York, N. Y., September 6 to 10, 1921.

³ Received August 22, 1921.

INDICATOR EFFECT

Two tan liquors were prepared, one from gambier and the other from quebracho extract. To each was added sufficient phosphoric acid to bring the pH value to 2.5, as determined by the hydrogen electrode. The phosphoric acid was added to act as a buffer in preventing large changes in pH value upon long standing. To equal portions of each, sodium hydroxide was added to give series of tan liquors ranging in pH value from 3.0 to 12.0 and all having a tannin content of 1 per cent, as determined by the authors' new method.¹ The gambier series varied in color from light straw at pH = 3.0 to a very deep red at 12.0. The quebracho series was similar in color excepting that the liquors of lower pH value had a touch of violet. Either series resembled a standard series of colors used in the indicator method of determining hydrogen-ion concentration, except for the fact that a light precipitate formed in all liquors having a pH value of 4.0 or less. The difference in color was evidently a true indicator effect, for any member of the series could be made to match any other member simply by bringing it to the same pH value. All members of either series appeared practically identical when brought to a pH value of 3.0. This complete reversibility of color change, however, was not found when liquors at higher pH values were allowed to stand long exposed to air.

OXIDATION EFFECTS

Two complete series of each extract were poured into test tubes; the tubes of one series of each were tightly stoppered, while the others were left uncovered. Next day the liquors in the stoppered tubes showed practically no change, but the others had become darker in color, the more so the higher the pH value. When the liquors in a series not exposed to air were all brought to a pH value of 3.0, they all assumed practically the same color. But when those of a series that had been exposed to air were all brought to 3.0, they did not assume the same color, but were darker the higher the pH

¹ THIS JOURNAL, 12 (1920), 465, 1149.