

STUDIES ON THE REUSE OF DIALDEHYDE STARCH TANNING LIQUORS IN THE PRETANNING OF HIDES FOR SOLE LEATHER

A. H. KORN, M. L. HAPPICH, J. NAGHSKI, and W. WINDUS

*Eastern Regional Research Laboratory**
Philadelphia 18, Pennsylvania

ABSTRACT

The restrengthening of a dialdehyde starch tanning liquor for repeated reuse as a pretannage for the rapid tanning of sole leather is described. The preparation and stability of a concentrated stock solution of dialdehyde starch is discussed. An analytical method based upon the spectrophotometric determination of the p-nitrophenylhydrazone derivative of dialdehyde starch is given.



INTRODUCTION

Investigations have shown that dialdehyde starch (DAS), a polyfunctional aldehyde derived from starch by periodate oxidation (1-3), is a tanning agent (4-7) and that it can be used as a pretanning agent for the rapid tanning of sole leather (8). Beebe and coworkers indicated from preliminary tests that DAS tanning liquors can be reused by suitable restrengthening. A pilot-plant study of this rapid sole leather tanning process (9) confirmed that the DAS liquor can be restrengthened and reused several times to lower the cost of the tannage.

This paper will describe the conditions for the reuse of the DAS liquor, the preparation and stability of a strong stock solution, and the method for the analysis of the DAS.

EXPERIMENTAL

Materials.—The raw stock was fresh-salted cowhide obtained from a local slaughterhouse. DAS (Blend G), containing 90.6% dialdehyde and 11% moisture was obtained from the Northern Utilization Research and Development Division.

Tanning.—Cowhide sections were limed and unhaired with a lime-sodium sulfide solution in one week. They were washed, cut into 5" x 6" pieces,

*Eastern Utilization Research and Development Division, Agricultural Research Service, United States Department of Agriculture.

and delimed with 1% boric acid based on the white weight of the hide for one hour at 70°F. In all cases only a surface deliming occurred. The pH in the center of the hide was 9.5 or higher.

A 25% stock solution (w/v) of DAS was solubilized with 1.8% borax, based on the weight of DAS, at pH 5. Aliquots of this stock solution were used to make up and restrengthen the dialdehyde starch pretanning solutions.

The pretanning solution was prepared as follows: A volume of the 25% stock solution equivalent to 5% DAS based on the white weight, sufficient sodium bicarbonate to give pH 8.0, and 8% sodium sulfate based on the final solution were made to 1 l. with water. This solution was used for the initial pretanning.

The solution was reused four times, restrengthening with 2½% DAS on the white-weight basis and 2.0 g. of sodium sulfate. When necessary, the pH was brought up to 8.0 by adding sodium bicarbonate.

Studies were also made in which the used tanning liquors were fortified with 3-1/3% DAS. The general tanning steps were similar to those already outlined, but the hide sections were partially delimed with 2½% boric acid and bated with 0.1% Oropon N* based on the white weight. Further, the sodium sulfate level was maintained at 8%, on the solution basis, during the course of these studies.

Effect of buffering agents.—Three 5" x 6" pieces of cowhide were limed, unhaired, and partially delimed as described above. These pieces were tanned with a 5% DAS solution based on the white weight, using an 8:1 float with the following buffer systems:

- (a) 6.3% NaHCO₃ based on the white weight and 8% Na₂SO₄ based on the total solution. The initial pH was 8.6.
- (b) Similar to (a) except that buffered tanning solution was allowed to stand overnight at room temperature, pH 8.2.
- (c) Borax added to give a pH of 8.5.

Samples of the tanning liquor were taken at intervals for the determination of carbonyl content, pH, and specific gravity and of the hide for shrink temperature.

After a pretanning of two days, the DAS-pretanned hide pieces were put into a blend of vegetable tan liquor made up of 50% clarified quebracho extract and 50% chestnut extract, by weight, containing about 11% tannin and having a barkometer of 66° and a pH of 3.7. Approximately seven days were required for complete penetration of this vegetable extract.

Stability of DAS.—Experiments were carried out to test the stability of stock solutions containing varying quantities of DAS, since it was necessary to prepare DAS tanning solutions well in advance of the actual pilot tanning runs.

*The mention of specific brands or companies is not to be construed as an endorsement by the U. S. Department of Agriculture of these brands or companies over those not mentioned.

Five, ten, and twenty-five percent stock solutions of DAS were prepared by dissolving 1.8% borax based on DAS weight in distilled water heated to 70°C. and adding the DAS in one feed with vigorous agitation. Heating was continued for ½ hour. The solution was cooled and made up to volume with distilled water. All stock solutions showed varying degrees of opalescence. The pH values for the 5%, 10%, and 25% stock solutions were 5.1, 5.0, and 4.9, respectively.

A separate 25% stock solution of DAS was prepared as just described but using 2.8% borax based on the DAS weight as a solubilizing agent.

All stock solutions were aged at room temperature, and aliquots were taken at intervals and analyzed for carbonyl content by the method described below.

The results are tabulated in Table I.

TABLE I
ANALYSIS OF STOCK SOLUTIONS OF DAS*

Conc. of DAS in Soln., %	Theory	Carbonyl Content (mg/ml) after						
		0 day	1 day	2 days	4 days	10 days	16 days	32 days
5 (1.8% borax)	40.5	45.3	44.5	45.3	44.1	42.9	43.1	42.6
10 (1.8% borax)	81.0	88.2	90.8	91.8	90.0	86.2	85.8	82.5
25 (1.8% borax)	202.5	216.9	220.6	210.6	210.6	215.7	219.3	—
25 (2.8% borax)	202.5	206.3	206.3	—	—	204.4	210.6	—

*The dialdehyde starch (Blend G) used in this study had an oxidation level of 90.6% and a moisture content of 11.0%.

Determination of carbonyl content of tanning liquors.—A colorimetric method (10) was used with slight modification for analyzing tanning liquors. This general method is based on the reaction of p-nitrophenylhydrazine with a carbonyl group to form the corresponding highly-colored hydrazone. The p-nitrophenylhydrazone is precipitated from an acidic aqueous solution, dissolved in methyl cellosolve, and determined spectrophotometrically. This rapid method is particularly suited to the precise estimation of low percentages of carbonyl groups in periodate-oxidized starch tanning solutions. The dialdehyde content of the DAS powder, however, can be determined more accurately by the borohydride reduction method (11).

Five-ml. samples are taken from the tanning liquors and the controls and made up to volume in 10-ml. volumetric flasks. Samples above pH 5 are brought to this pH with glacial acetic acid before being made up to volume to prevent further degradation of the DAS before analysis. One-ml. aliquots are then pipetted into 25-ml. volumetric flasks and made up to the mark with distilled water. Aliquots containing approximately 5 mg. of DAS are then removed for analysis.

The sample to be analyzed is placed in a 25 mm. x 200 mm. test tube, and distilled water is added to make a total volume of 20 ml. One and one-half ml. of the reagent consisting of .50 g. p-nitrophenylhydrazine in 15 ml. of glacial acetic acid is added and the solution is thoroughly mixed and then heated one hour on the steam bath with occasional agitation. After cooling, 0.4 g. of filter aid is added, and the precipitated p-nitrophenylhydrazone is filtered off in a fritted-glass funnel under suction. The reddish precipitate is transferred from the test tube to the funnel by washing two times with 5-ml. portions of 7% acetic acid followed by two 5-ml. portions of water. In washing, the acid and water are poured through the funnel. These washings are discarded, and the receiver is replaced with a clean, dry 250-ml. filter flask. The test tube and the funnel are treated repeatedly with hot methyl cellosolve until all the p-nitrophenylhydrazone has been dissolved and collected in the receiving flask. This solution is transferred to a 100-ml. volumetric flask and made up to the mark with methyl cellosolve. For analysis, a 2-ml. aliquot is diluted to 100 ml. with methyl cellosolve in a volumetric flask, and the absorbance is measured at a wave length of 445 m μ against a water blank. The absorbance obtained is compared with that produced by a standard DAS curve.

DISCUSSION AND RESULTS

The results of the stability study show that DAS solubilized with borax is stable for periods of at least one month at room temperature in concentrations as high as 10% in aqueous solutions at pH 5, and the data indicate that this would also be true for 25% solutions.

The data in Fig. 1 show the effect of various buffering agents at pH 8.5 on the uptake of DAS by cowhide. After three days the borax-buffered hide had taken up only 50% of the DAS, while the hide buffered with NaHCO₃ had consumed 80% of the tanning agent.

The analytical data obtained from DAS tanning liquors restrengthened four times are tabulated in Tables II and III. Initially, a make-up of 2½% DAS, based on the white weight, was thought to be adequate. However, the analyses (Table II) showed that the dialdehyde content of these restrengthened tanning liquors became progressively lower. This indicated that the fresh hide pieces were removing more than the added amount of DAS. When the make-up with DAS was increased to 3⅓% (Table III), the DAS level remained almost constant throughout the experiment. In the latter case an average of 55% of the total DAS present was consumed by the hide during each restrengthening cycle.

The data show that DAS can be used successfully as a pretanning agent to shorten the time required to produce heavy sole leather and that DAS tanning

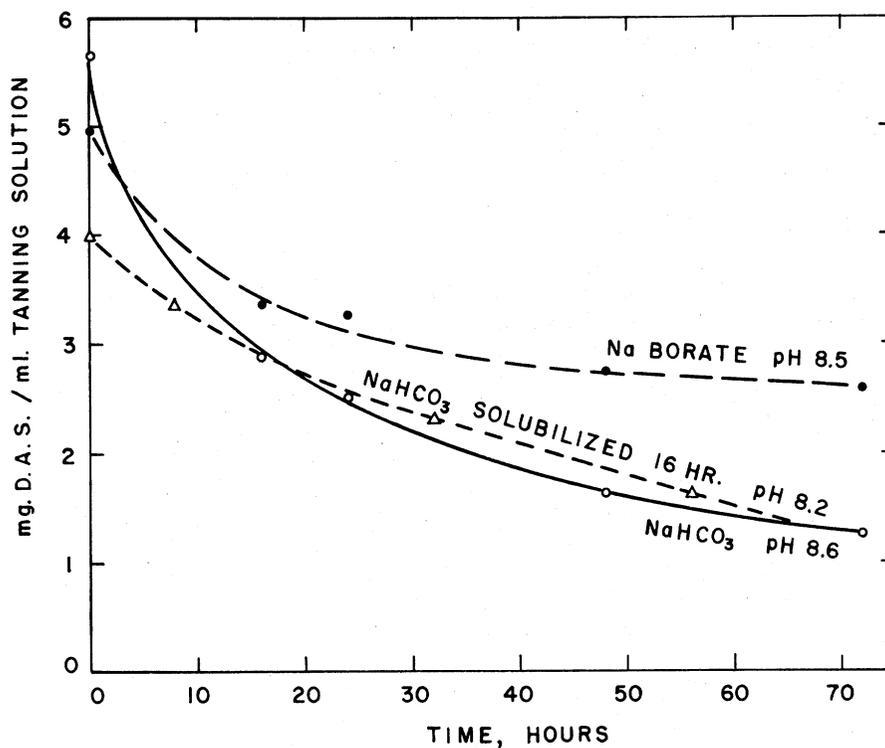


FIGURE 1.—Effect of buffering agents on the uptake of DAS by unhaired and partially delimed cowhide.

TABLE II
EFFECT OF RESTRENGTHENING WITH 2½% DAS*
ON THE REUSE OF DAS TANNING LIQUORS

Tanning Liquor	Time	pH	Carbonyl Content		DAS Uptake %	Ts
			Theory mg/ml	Found mg/ml		
Original	0 hr.	7.9	6.90	7.32	—	60°–61°C.
"	48 hr.	8.6	—	3.17	57	80°C.
1st Restrengthening	0 hr.	8.5	6.37	6.54	—	—
"	48 hr.	8.6	—	2.06	68	83°C.
2nd Restrengthening	0 hr.	8.5	5.50	5.71	—	—
"	72 hr.	8.6	—	2.04	64	79°C.
3rd Restrengthening	0 hr.	8.4	5.08	5.34	—	—
"	48 hr.	8.0	—	2.50	53	79°–80°C.
4th Restrengthening	0 hr.	8.0	5.40	5.68	—	—
"	48 hr.	7.8	—	2.38	59	82°C.
Av. 60						

*On white hide weight

liquors can be reused at least four times. Hide pieces pretanned in a solution reused for the fifth time after restrengthening were retanned rapidly in concentrated vegetable extract with as good results as those pretanned in solution used for the first time.

TABLE III
EFFECT OF RESTRENGTHENING WITH 3½% DAS*
ON THE REUSE OF DAS TANNING LIQUORS

Tanning Liquor	Time	pH	Carbonyl Content		DAS Uptake %	Ts
			Theory mg/ml	Found mg/ml		
Original	0 hr.	7.8	6.48	6.62	—	60°C.
"	48 hr.	8.4	—	2.59	61	84°C.
1st Restrengthening	0 hr.	8.2	6.74	6.66	—	—
"	66 hr.†	8.6	—	2.31	65†	85°C.
2nd Restrengthening	0 hr.	8.2	7.17	7.50	—	—
"	48 hr.	8.3	—	3.38	55	80°C.
3rd Restrengthening	0 hr.	7.8	7.23	6.89	—	—
"	48 hr.	8.3	—	3.64	47	82°C.
4th Restrengthening	0 hr.	8.1	7.69	7.34	—	—
"	66 hr.	8.0	—	3.96	46	80°C.
					Av. 55	

*On white hide weight

†Some spillage occurred over the weekend.

The positive results of this study were confirmed by the Armour Leather Company in the final stages of its contract (9). The reuse of the DAS solution was carried out successfully in the pilot tannery through ten consecutive pretannages, and commercially acceptable sole leather was produced using this process.

SUMMARY

It has been shown that a DAS tanning solution can be restrengthened and reused for the pretanning of hides to permit a rapid vegetable retannage with strong liquors. A 25% stock solution of DAS with a pH of 5 is stable for at least 16 days. The spectrophotometric determination of the p-nitrophenylhydrazone derivative of DAS is suitable for the analysis of DAS in the tanning solution.

REFERENCES

1. Dvonch, W., and Mehlretter, C. L. *J. Am. Chem. Soc.*, **74**, 5522 (1952). U. S. Pat. 2,648,629, August 11, 1953.
2. Mehlretter, C. L., Rankin, J. C., and Watson, P. R. *Ind. Eng. Chem.*, **49**, 350 (1957).
3. ———. U. S. Pat. 2,713,553, July 19, 1955.
4. Fein, M. L., and Filachione, E. M. *JALCA*, **52**, 17 (1957).
5. Filachione, E. M., Harris, E. H., Fein, M. L., Korn, A. H., Naghski, J., and Wells, P. A. *JALCA*, **53**, 77 (1958).
6. Wells, P. A., Filachione, E. M., and Fein, M. L. U. S. Pat. 2,886,401, May 12, 1959.
7. Filachione, E. M., Clarke, I. D., Harris, E. H., Jr., Fee, J., Witnauer, L. P., and Naghski, J. *JALCA*, **56**, 200 (1961).
8. Beebe, C. W., Happich, M. L., Naghski, J., and Windus, W. *JALCA*, **54**, 628 (1959).
9. Wagoner, J. F., Stemososki, J. C., Windus, W., and Witham, W. C. *JALCA*, **57**, 302 (1962).
10. Wise, C. S., and Mehlretter, C. L. *Anal. Chem.*, **30**, 174 (1958).
11. Rankin, J. C., and Mehlretter, C. L., *Anal. Chem.*, **28**, 1012 (1956).

Received September 12, 1962.
