TANNING STUDIES WITH DIALDEHYDE STARCH

PRELIMINARY EVALUATION OF THE LEATHER*

1549

E. M. FILACHIONE, I. D. CLARKE, E. H. HARRIS, JR., J. FEE,
L. P. WITNAUER, AND J. NAGHSKI

Eastern Regional Research Laboratory†
Philadelphia 18, Pennsylvania

and

J. N. BOYD

Biometrical Services, ARS
Beltsville, Md.

ABSTRACT

Calfskin (acetone-dehydrated) was tanned with dialdehyde starch under various conditions. Four tanning variables were investigated. These were: (*a*) dialdehyde starch of three oxidation levels, i.e., 33, 67, and 96%; (*b*) two pH levels, i.e., 8 and 10; (*c*) two methods for dissolving the dialdehyde starch; and (*d*) oiling the leather. The experiments were designed statistically. Tanning with dialdehyde starch, oxidized to the 96% level, at pH 10 and oiling the leather in general resulted in the optimum leather properties and characteristics for this tannage.

INTRODUCTION

Previous publications from this laboratory (1, 2, 3) reported that dialdehyde starch, also referred to as periodate oxystarch or simply oxystarch, was found to effect a tanning action. Dialdehyde starch is a polyfunctional aldehyde derived from ordinary starch by oxidation with periodic acid. The extent of oxidation can be controlled to provide a complete range of aldehyde derivatives of starch in which the level of oxidation varies from 0% to 100%. Our interest in dialdehyde starch was stimulated by recent developments in its preparation (4, 5, 6) which offer promise of making this polyaldehyde commercially available (7, 8).

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†Eastern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

Our previous study (2) was primarily concerned with demonstrating the tanning power of dialdehyde starch. Data on the physical properties of leather obtained from this unusual aldehyde were desirable, and a preliminary evaluation of the leather and correlation with certain tanning variables are reported in this study. This series of tests was made using starch oxidized to three levels, i.e., 33, 67, and 96%. For convenience these dialdehyde starch preparations may be referred to as DAS-33, DAS-67, and DAS-96 respectively. Leffler and Stanko (8) in a recent publication have used the abbreviation "DAS" for dialdehyde starch. The dialdehyde starches were dissolved by two methods, described below, and were used at two pH levels, namely, 8 and 10. The leathers were examined in the unoiled as well as the oiled condition; hence 24 treatments were involved. For convenience, and to facilitate area and thickness measurements, acetone-dehydrated calfskin was used.

EXPERIMENTAL

Hide material.—Five pickled calfskins, weighing between 9 and 12 lb. each, were obtained from a tannery. These were depickled in a laboratory drum with 200% (based on the drained, pickled weight) of a solution 5% with respect to both sodium chloride and anhydrous sodium acetate. After being drummed for 3 hr., at which time the pH was 5.1, the skins were thoroughly washed, drained, and dehydrated by immersion in several changes of acetone. The skins, after being blotted on towels, were tacked out and covered with towels, and the acetone was permitted to evaporate slowly. All manipulations involving acetone were carried out in a fume cupboard. The acetone-dehydrated skins were cut into sides, and each of the 10 sides was cut into 3 strips, 3.25″ in width. Each strip was then divided into 8 squares (3.25″ x 3.25″) for a total of 24 squares from each side. Tanned pieces approximately 3″ square were required for testing, so it was necessary to cut larger pieces from the raw skin to allow for shrinkage during tanning. The squares from each of the 10 sides were assigned at random to 24 piles or lots, and one lot was then assigned at random to each of the 24 treatments. Pilot pieces from the edges of the skins were included with each lot in order to follow the progress of tanning. Before the tanning, the squares were conditioned at 50% relative humidity and 73°F.; then they were subjected to measurements of area, weight, and thickness. For the actual tanning, lots 1 and 13, 2 and 14, etc., were combined. After the tanning, the squares assigned to lots 1 to 12 inclusive were removed from the respective combined lots, and the remaining squares, comprising lots 13 to 24 inclusive, were fatliquored.

Dialdehyde starch tannage.—Dialdehyde starches of oxidation levels corresponding to 33, 67, and 96% were obtained from the Northern Utilization Research and Development Division. They were prepared for tanning

TABLE I

EFFECT OF TANNING VARIABLES ON DIALDEHYDE STARCH–TANNED CALFSKIN

Lot or Tannage No.	Oxidation of Starch %	Method of Dissolving Starch*	pH of Tan Liquor	Ts °C.†	Finishing	Grade	Area Yield %	Weight Yield %	Thickness Yield %	Stiffness E Kg/cm²	Leather Quality
1	33	a	8	77	No oil	1.0	84	110	76	4780	hard, stiff, untanned
2	33	b	8	76	"	1.2	89	111	77	3930	tinny, undertanned
3	33	a	10	89	"	3.0	99	110	80	1430	stiff, thin, poor
4	33	b	10	88	"	3.0	94	110	88	1040	stiff, thin, poor
5	67	a	8	77	"	1.4	98	113	90	1880	tinny, undertanned
6	67	b	8	79	"	2.0	95	114	92	1660	tinny, undertanned
7	67	a	10	84	"	2.5	95	111	85	1140	poor, some tinny pieces
8	67	b	10	86	"	4.1	99	111	84	940	flat, nonuniform color
9	96	a	8	82	"	3.9	90	112	97	1090	fairly well tanned
10	96	b	8	83	"	3.7	96	111	97	1400	some good pieces; some thin
11	96	a	10	85	"	4.8	92	108	95	910	well tanned, good feel
12	96	b	10	89	"	4.2	91	109	96	580	well tanned, good feel
13	33	a	8	72	Oiled	1.3	92	117	87	1100	flat, tinny, undertanned
14	33	b	8	72	"	2.4	97	118	81	830	flat, tinny, undertanned
15	33	a	10	89	"	4.3	100	122	87	420	fair, rather thin
16	33	b	10	82	"	4.1	104	123	89	360	well tanned, mellow
17	67	a	8	78	"	3.1	102	122	87	530	fair, rather thin and firm
18	67	b	8	78	"	4.1	101	124	96	610	not well tanned
19	67	a	10	84	"	3.7	97	118	88	390	not well tanned
20	67	b	10	84	"	4.4	100	119	89	320	well tanned, mellow
21	96	a	8	80	"	4.4	91	121	103	350	good feel, variable firmness
22	96	b	8	79	"	4.4	93	118	99	490	good feel, slightly firm
23	96	a	10	77	"	4.6	93	118	103	240	good feel, well tanned
24	96	b	10	84	"	4.9	90	117	100	240	good feel, well tanned

* *a* = heating in autoclave; *b* = solid starch added to alkaline tan liquor.
† Ts for lots 1–12 were taken at the end of the 24-hr. tannage; Ts of lots 13–24 were taken after the tanned skins were brought to pH of about 4. Generally there was a drop in Ts upon acidification of these alkaline tannages.

by two procedures. In one series the dialdehyde starch (DAS) was dissolved by heating a dilute aqueous suspension in an autoclave. This method will be referred to hereafter as Method A. In a second series, Method B, the solid DAS was added to, and allowed to dissolve in, the alkaline tan liquor during the tanning process. Details of the tanning are given below. A summary of the tanning conditions for each of the 24 lots is shown in Table I.

Method A.—In this procedure the DAS was first dissolved by autoclaving an aqueous suspension at 120°C. for 30 minutes. A 16% suspension of DAS-33 and 10% suspensions of DAS-67 and DAS-96 were autoclaved.

The lots of acetone-dehydrated calfskin squares to be given the identical tannage were combined, rehydrated in running tap water for 2 hr., and then put through a wringer. Based on the wrung weight the amount of DAS, on a moisture-free basis, taken for tanning was 10, 15.5, and 29% for the levels of oxidation corresponding to 96, 67, and 33% respectively. To the DAS solution prepared by autoclaving was added 26% anhydrous sodium sulfate and 4.5% sodium bicarbonate, each based on the wrung weight of the lots of calfskin, and sufficient water to make a 2:1 float. The wrung skin pieces were then added, and tanning was carried out in vented bottles with agitation provided by rolling the bottles on their sides.

The tanning was carried out for 24 hr., and the pH at the end was in the range of 7.0 to 7.8. Tanning at pH of about 10 was conducted in the same way except that 2.7% of magnesium oxide in addition to the 4.5% sodium bicarbonate was used. The pH at the end of the 24-hr. tannage was in the range of 9.4 to 9.9. The shrinkage temperatures are shown in Table I (Method A, lots 1–12).

At the end of the 24-hr. tannage, the pieces were washed briefly and then brought to a pH of about 4 by agitation in a 1% acetic acid solution. The pieces were then thoroughly washed and wrung. Ts after acidification is listed in Table I (Method A, lots 13–24).

The pieces to be oiled were removed and fatliquored by the method to be described later, then all were dried in air.

Method B.—In this procedure the solid DAS was added to the skins in an alkaline liquor. Under these conditions the solid DAS dissolved gradually, and tanning was effected by the resulting solution. Details are essentially as follows:

The combined lots of acetone-dehydrated calfskin squares were rehydrated by immersion in water for 2 hr. and then wrung. Based on the wet wrung weight the amount of DAS (MFB) taken for tanning was 10, 15.5, and 29% for the three different oxidation levels, as was done under Method A above. An aqueous solution was prepared from 27% anhydrous sodium sulfate and 4.5% sodium bicarbonate (based on wrung weight) in enough water to make a 2:1 float. The wrung calfskin squares were then added, and the appropriate amount and type of solid DAS was added. Agitation was provided as in Method A above. After 24 hr. the DAS had dissolved completely, and the pH values of the solutions were in the range of 7.1 to 7.7 for the different dialdehyde starches used.

Tanning at pH of about 10 was carried out in the same way as described above, except that 2.7% of magnesium oxide was used in addition to the 4.5% of sodium bicarbonate. The pH at the end of the 24-hr. tannage was in the range of 9.5 to 10.1.

The leather was then brought to a pH of about 4 as described in Method A. The shrinkage temperatures for the leathers immediately after tanning are shown in Table I under lots 1–12 (Method B) and for the acidified leathers under lots 13–24.

Fatliquoring.—The tanned specimens were fatliquored with a blend of 2 parts of sulfated neatsfoot oil and 1 part of 15° cold-test neatsfoot oil. Based on the wrung weight, 5% of oil and 100% of water were used, and fatliquoring was carried out at 55°C. At half-hour intervals two feeds of 1 ml. each of 5*N* acetic acid were added to exhaust the fatliquor, the pH of the exhausted fatliquor being about 4.0.

Drying.—The tanned calfskin squares were first blotted between towels in a conditioned room maintained at 50% R.H. and 73°F. The towels were changed once or twice a day for 2 or 3 days or until the squares were apparently dry. Brass plates, heavy enough to prevent excessive curling, were kept on the squares during the drying period. When removed from the towels and plates, some of the poorly tanned specimens curled or warped excessively in the final stages of moisture adjustment. These were dampened slightly on the surface and put under sufficient weight so that they remained reasonably flat when dry again. The tanned leathers were allowed to reach moisture equilibrium in the conditioned room before testing.

Evaluation of experimental leathers.—The testing procedures were essentially the same as those described in a previous study (9); however, in the present test the comparisons were only between the various tannages and did not involve relations between the tanned and untanned skin.

Before the tanning, each conditioned, acetone-dehydrated square was weighed to 0.01 gram, its thickness was measured at five points and averaged, and the area of the combined 10 squares in each lot was measured with a planimeter. After the tanning, the conditioned leather squares were again measured as before, and yields were calculated.

Before test specimens were cut, the squares were examined by lots for general leather-like characteristics with the results summarized under "Leather Quality" in Table I.

After examining each lot as a whole, a grade for each lot was determined by mixing all 240 squares, then separating them into 5 piles on the basis of leather-like characteristics. Oiled specimens were, in general, much better than unoiled ones; however, in the grading an attempt was made to minimize the effect of oiling and to judge the pieces on thoroughness of tanning. Grade limits were established during sorting in order to avoid having an excessive number of squares in some grades. Grade 5 was best and Grade 1 poorest. The average grade for each lot is shown in Table I.

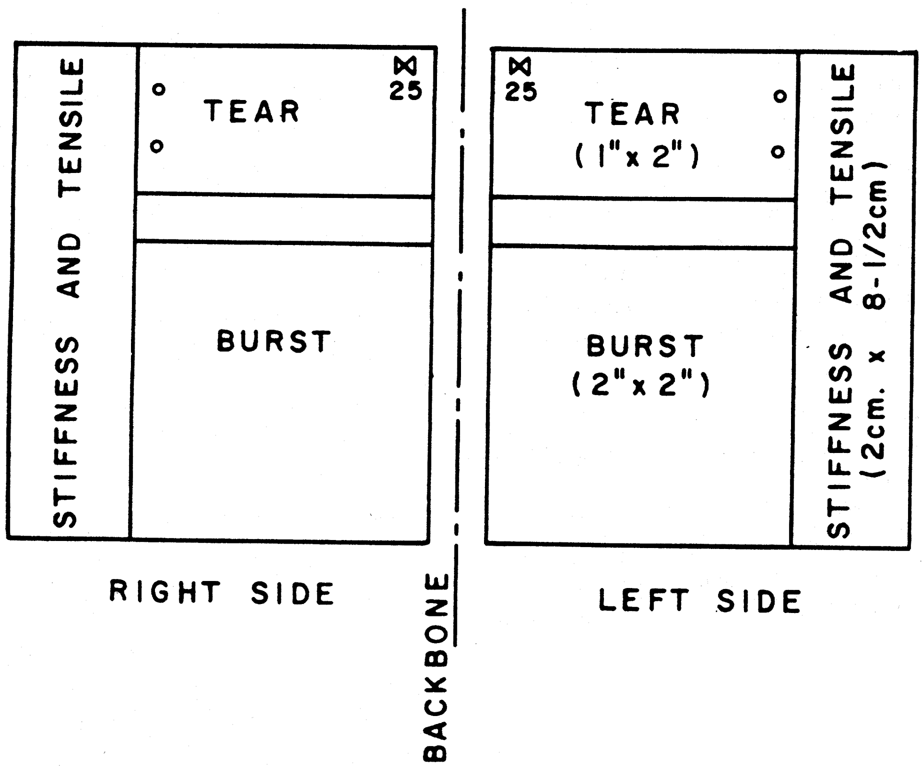

FIGURE 1.—Diagram of squares, from right and left sides, showing location of test specimens.

Test specimens were cut from each square according to the pattern shown in Fig. 1. Tensile, burst, and stitch tear strengths and elongation were determined by means of an Instron Tester, thus enabling calculations to be made of initial tear and energy of rupture as well. Elongation was calculated from plunger rise in the ball burst method as described by Clarke and Harris (10). Results of the physical and chemical tests are shown in Tables I and II for lots. The average values for each level of each main effect or tanning variable appear in Table III.

TABLE II

CHEMICAL AND PHYSICAL PROPERTIES OF DIALDEHYDE STARCH–TANNED CALFSKIN*

Lot or Tannage No.	Elongation at Rupture Tensile Method %	Elongation at Rupture Burst Method %	Tear 2-hole Stitch Maximum Kg.	Tear 2-hole Stitch Maximum Kg/cm	Tensile Strength Kg	Tensile Strength Kg/cm^2	Burst Strength Kg	Burst Strength Kg/cm	Hide Substance %	Fat %	Water Solubles %	Combined Tannin %
1	36	28	26	140	43	251	77	456	92.4	0.4†	2.3	4.7
2	32	30	25	131	38	206	74	404	87.7	.4†	3.0	8.7
3	36	33	17	81	36	173	71	346	92.2	.4†	1.5	5.6
4	36	37	17	86	28	136	65	307	93.0	.4†	1.6	4.9
5	26	30	23	103	32	150	63	295	90.8	.4†	2.3	6.4
6	25	31	20	86	32	151	63	286	90.4	.4†	2.5	6.5
7	41	36	21	94	29	132	66	329	94.0	.4†	1.5	3.8
8	40	37	21	85	31	138	70	324	91.3	.4†	1.6	6.4
9	39	34	20	81	32	138	64	264	92.9	.4	1.9	4.7
10	37	35	18	79	28	133	59	280	93.3	.3	1.6	4.7
11	39	40	23	85	36	138	69	272	94.6	.4	1.2	3.6
12	51	43	22	86	33	141	65	294	93.7	.3	1.2	4.6
13	36	34	24	118	39	181	63	305	86.6	7.7	1.9	3.5
14	29	32	26	139	33	176	63	356	87.3	7.9	2.0	2.5
15	57	45	26	126	40	207	68	372	83.8	9.1	1.6	5.2
16	48	47	28	122	43	193	70	338	83.2	9.4	1.6	5.3
17	48	35	27	121	40	174	70	317	85.2	8.6	2.2	3.7
18	43	39	24	113	40	184	64	311	83.0	8.6	2.3	5.8
19	52	47	28	122	50	245	76	383	86.0	8.4	1.3	3.9
20	59	46	27	130	45	210	75	376	83.5	8.6	1.6	5.9
21	65	54	29	114	44	186	69	305	83.3	8.3	2.2	5.8
22	53	49	28	115	47	187	73	292	86.8	7.6	1.5	3.8
23	76	58	30	118	49	202	75	301	85.4	8.2	1.7	4.2
24	71	60	33	131	48	196	83	333	87.7	7.7	1.6	2.4

*Ash (not shown) was difference between values shown and 100; values were usually between 0.1 and 0.3; highest value 0.6.
†Assumed values.

TABLE III

PHYSICAL TEST MEAN VALUES FOR DIALDEHYDE STARCH TANNAGES

Physical Property	Oxidation of Starch, %			Method of Dissolving Starch*		pH of Tannage		Fatliquor	
	33	67	96	a	b	8	10	Unoiled	Oiled
Grade	2.5	3.2	4.4	3.2	3.5	2.8	4.0	2.9	3.8
Area yield, %	95	98	92	94	96	94	96	93	97
Weight yield, %	115	117	114	115	115	116	115	111	120
Thickness yield, %	83	89	99	90	90	90	91	88	92
Stiffness, kg/cm²	1740	930	660	1190	1030	1550	670	1730	490
Elongation at grain crack, tensile, %	21	30	46	34	31	25	40	14	51
" " " ", burst; %	18	18	23	20	20	16	23	8	32
Load at grain crack, tensile, kg.	26	27	29	28	27	27	28	19	36
" " " " , burst, kg.,	32	30	30	31	30	29	32	18	44
Elongation at rupture, tensile, %	39	42	54	46	44	39	51	37	53
" " " , burst, %	36	38	47	40	41	36	44	35	46
Tear, 2 hole, initial, kg.	22	22	23	23	22	22	22	20	25
" , " ", " , kg/cm	106	98	92	99	99	102	96	88	110
" , " ", maximum, kg	24	24	25	25	24	24	25	21	28
" , " ", " , kg/cm " "	118	107	101	109	109	112	106	95	122
Tensile strength, kg.	37	37	39	39	37	37	39	33	43
" " , kg/cm²	190	173	165	181	171	176	176	157	195
Burst strength, kg.	69	68	70	69	69	67	71	67	71
" " , kg/cm	360	328	293	329	325	323	331	321	323
Energy of rupture, tensile, kg.	30	32	41	35	34	31	38	26	43
" " " , " , kgcm/cm²	150	148	173	161	153	143	171	120	194
" " " , burst, kgcm	21	21	23	22	21	21	22	21	22
" " " , " , kgcm/cm	110	98	95	102	100	101	101	98	104
Modulus of elasticity, kg/cm²	1460	680	280	890	720	1310	300	340	1270

* *a* = heating in autoclave; *b* = allowing to dissolve in buffered tan liquor.

After being tested, the specimens were combined by lots and ground for chemical analysis (9). The analytical data are shown in Table II.

RESULTS AND CONCLUSIONS

Statistical analyses.—The objective of these analyses was to determine the effect of a number of tanning variables on certain properties or characteristics of the leather. The variables and levels for each variable were constant from one property to another. There were in all 24 characteristics or properties; however, some of the tests presumably measured the same property.

The statistical design used in each of these 24 experiments is referred to as a factorial experiment. In each experiment the main four variables or main effects were as follows: oxidation or dialdehyde content of the starch, method of its solution, pH of tanning, and oil. As there are six combinations of four variables taken two at a time, we have six two-factor interactions. Similarly we have four three-factor interactions and one four-factor interaction. A significant interaction simply means that a combination of two or more of the four mentioned main effects or variables is more important than any single main effect for a particular property.

TABLE IV

ANALYSIS OF VARIANCE FOR GRADE

Source	Degrees of Freedom	Sum of Squares	Mean Square	F
Total	239	493	—	—
Replication	9	41	4.56	1.30
Oxidation (X)	2	138	69.00	19.71*
Solubility (S)	1	8	8.00	2.29
pH (P)	1	90	90.00	25.7*
Oiling (O)	1	49	49.00	14.0
XS	2	12	6.00	1.71
XP	2	26	13.00	3.71
XO	2	8	4.00	1.14
SP	1	1	1.00	.28
SO	1	1	1.00	.28
PO	1	3	3.00	.86
XSP	2	2	1.00	.28
XSO	2	1	.50	.14
XPO	2	6	3.00	.86
SPO	1	1	1.00	.28
XSPO	2	7	3.50	7.29†
Error	207	99	.48	

*Significant at the 5% level.
†Significant at the 1% level.

TABLE V

SIGNIFICANT F VALUES*

Test	Source of Variation† and Degrees of Freedom X 2	S 1	P 1	O 1	XS 2	XP 2	XO 2	SO 1	PO 1	XSO 2	XOP 2	XSP 2	XSPO 2
Grade	20	—	26	—	—	—	—	—	—	—	—	—	7
Area yield													
Weight yield	—	—	—	71	—	—	—	—	—	—	8	—	—
Thickness yield	20	—	—	—	—	—	—	—	—	5	—	7	—
Stiffness	—	—	—	—	3	—	—	—	—	—	26	—	—
Stretch at grain crack, tensile	19	—	—	63	3	—	—	—	—	—	3	—	—
Stretch at grain crack, burst	—	—	—	54	—	—	13	—	15	—	—	—	—
Load at grain crack, tensile, kg.	—	—	—	46	—	—	—	—	—	—	—	—	6
Load at grain crack, burst, kg.	—	—	—	36	—	—	—	—	10	5	—	—	—
Elongation at rupture, tensile	—	—	—	—	—	—	—	—	—	—	4	—	—
Elongation at rupture, burst	—	—	—	—	—	—	11	—	4	—	—	—	—
Tear, 2 hole, initial kg.	—	—	—	—	—	—	—	4	—	—	11	—	—
Tear, 2 hole, initial kg/cm	—	—	—	—	—	—	—	9	—	—	16	—	—
Tear, 2 hole, maximum kg.	—	—	—	—	—	—	—	—	—	—	7	—	—
Tear, 2 hole, maximum kg/cm	—	—	—	47	—	—	—	—	—	—	—	—	3
Tensile strength kg.	—	4	—	20	—	—	—	—	—	—	5	—	—
Tensile strength kg/cm^2	—	—	—	—	3	—	—	—	—	—	10	—	—
Burst strength kg.	—	—	—	—	—	—	10	—	4	—	—	—	—
Burst strength kg/cm	—	—	—	—	—	—	—	—	—	—	—	—	3
Energy of rupture, tensile kgcm	—	—	—	22	—	—	—	—	—	—	7	—	—
Energy of rupture, tensile kgcm/cm^2	—	—	—	20	—	—	—	—	—	—	7	—	—
Energy of rupture, burst kgcm	—	—	—	—	—	5	15	—	5	—	—	—	—
Energy of rupture, burst kgcm/cm	—	—	—	—	—	—	—	—	—	—	12	—	—
Modulus	—	—	—	—	—	—	—	—	—	4	25	—	—

*All values rounded to whole numbers. Critical values of F for an error term with 207 degrees of freedom and greater mean squares with degrees of freedom of 1, 2, and 9 respectively are as follows: 5% point 3.9, 3.0, and 1.9; 1% point 6.8, 4.7, and 2.5; 0.1% point 11.3, 7.2, and 3.4; dash (—) indicates nonsignificant value of F.

†Letters have the following significance: X = degree of oxidation of starch; S = method of dissolving starch; P = pH of tan liquor; O = oiling method; XS, XP, etc. = interactions. Two interactions, SP and SPO, are not shown, since none of the F values were significant.

Table IV is the analysis of variance table for grade of leather and illustrates how the data were handled. A similar table was computed for all the other properties but is not included here for sake of brevity. The complete analysis of variance tables will be published elsewhere. Areas were determined by lots and not on individual squares, so an analysis of variance was not made. From the analysis of variance tables the F values that were significant at the 5% level or less were obtained, and these are summarized in Table V.

Best tanning conditions for dialdehyde starch.—From the analysis of variance tables and from the significant F values (Table V) the best tanning conditions, as shown by the various tests, were selected and are indicated in Table VI. The optimum tanning factors were considered to be those

TABLE VI

BEST* TANNING CONDITIONS AS SHOWN BY VARIOUS TESTS

Test	DAS Oxidation %	DAS Method of Solution†	pH of Tanning	Oil‡
Grade	96	—**	10	+
Area yield††	67	b	10	+
Weight yield	67 (33)	—	8 (10)	+
Thickness yield	96	b	10	+
Stiffness	96	b	10	+
Elongation at grain crack, tensile	96	a	10	+
Elongation at grain crack, burst	96	—	10	+
Load at grain crack, tensile	96	—	—	+
Load at grain crack, burst	96 (67)	—	10	+
Elongation at rupture, tensile	96	—	10	+
Elongation at rupture, burst	96	—	10	+
Tear, 2 hole, initial, kg.	96 (67)	—	—	+
Tear, 2 hold, initial, kg/cm	33	a	8	—
Tear, 2 hole, maximum, kg.	96	—	10	+
Tear, 2 hole, maximum, kg/cm	33	—	8	—
Tensile strength, kg.	96	a	10	+
Tensile strength, kg/cm²	33	a	8	—
Burst strength, kg.	96	—	10	+
Burst strength, kg/cm	33	a	8	—
Energy of rupture, tensile, kgcm	96	—	10	+
Energy of rupture, tensile, kgcm/cm²	96	—	10	+
Energy of rupture, burst, kgcm	96	—	10	+
Energy of rupture, burst, kgcm/cm	33	—	8	—
Modulus of elasticity, kg/cm²	96	—	10	+

*Best values were considered to be high values for all tests except stiffness and modulus, for which low values were best.

†*a* denotes dissolving DAS by autoclaving; *b* denotes allowing the solid DAS to dissolve in the buffered tan liquor.

‡ + indicates presence of oil and — absence of oil.

** — denotes that factor was not significant.

††From data in Tables I and III (not treated statistically).

that gave the highest values for all the properties or tests, except stiffness and modulus. It should be borne in mind that the optimum or best conditions which result from these analyses are not necessarily the true optimum conditions. That is, these optimum conditions are only optimum for the four different variables and the levels of each used in these experiments. For example, in general, the condition with oil was greatly superior to that with no oil, although in each of these 24 analyses only one type of oil was used and only one amount of this particular type of oil. Therefore, no inference can be made about all types of oil or different amounts of oil. In addition, the raw stock used for this study was acetone-dehydrated; however, the influence of this factor was not evaluated.

Inspection of Table VI clearly shows that the best properties resulted from particular combinations of usually more than two tanning variables. In most cases the manner of dissolving the dialdehyde starch did not appear to be significant; thus this factor can be safely ignored because of its slight influence on leather properties. This conclusion was based on a constant time factor of 24 hours for the tannage, which permits sufficient time for solution of the DAS by Method B and tanning by the dissolved material. It has been noted that several hours were required for solid DAS to dissolve at room temperature in the tanning liquor at pH about 8. Hence in tanning for short periods of time the rate of solution of the solid DAS (Method B) may become the dominant factor. Solution of the material beforehand, either by autoclaving or by warming with alkaline agents (borax, bicarbonate, etc.), would be preferred for a rapid tannage with dialdehyde starch.

The use of Table VI is best illustrated by an example. Thus in the case of thickness yield the thickest leather resulted when dialdehyde starch of 96% oxidation was used at pH 10, allowing the solid to dissolve in the alkaline tan liquor, and oiling of the leather. Although not shown in the table, the flattest or thinnest leather came from tanning with 33% oxidized dialdehyde starch, at pH 8, without oiling. This explains why the strength properties on a unit thickness or area basis were highest for the leathers made with this combination of tanning variables. Since the 33% oxidation level dialdehyde starch in general produced the poorest quality leather (except tannage No. 16 in Table I), it can be eliminated as a satisfactory agent for tanning. With but few exceptions all the other properties were at a maximum when dialdehyde starch of 96% oxidation (DAS-96) was used at pH 10, with oiling. This particular combination of tanning factors, i.e., DAS-96, pH 10, and oil, was found to give the optimum with respect to the following characteristics: grade of leather, thickness yield or plumpness, flexibility, grain crackiness, stretch, tear strength, breaking load (tensile), burst strength, and energy of rupture. In two cases, load at grain crack (burst) and initial tear (kg), both the 96% and the 67% oxidation levels produced optimum values. The area yield was highest for the tannage with DAS-67 added as the solid to the tanning liquor at pH 10, and oiled. The best weight yield was noted under two sets of conditions. One was tannage with DAS-67 at pH 8 after oiling, and the other with DAS-33 at pH 10 after oiling.

It is noted in Table VI that there is a high degree of correlation between the tensile and burst methods for measuring the strength, elongation, and energy of rupture of the leather.

SUMMARY

Pickled calfskins were dehydrated with acetone and cut into 3¼″ squares. These were combined randomly into lots of 10 squares each. A lot was then assigned at random to each of 24 tannages. The tanning variables included: (*a*) dialdehyde starch of three oxidation levels, namely 33, 67, and 96%; (*b*) two procedures for dissolving the dialdehyde starch; (*c*) tanning at two pH levels, namely 8 and 10; and (*d*) oiled and unoiled condition. After being tanned, the leathers in each lot were dried and evaluated. The data were treated statistically. In general the procedure for dissolving the dialdehyde starch did not appear to be significant in a 24-hr. tannage. The dialdehyde starch oxidized to the 33% level produced the flattest leather, which was of poor quality. Maximum leather quality was obtained with dialdehyde starch of the highest oxidation level, i.e., 96%. Tanning with DAS-96 (dialdehyde starch oxidized to the 96% level) at pH 10 and oiling the leather was optimum with respect to the following leather characteristics: grade, thickness yield, flexibility, grain crackiness, stretch, tear strength, breaking load (tensile), burst strength, and energy of rupture. Area yield was highest for tannage with DAS-67, added as the solid to the tanning liquor, at pH 10 and oiling of the leather. Optimum weight yield was noted in tannages with DAS-67 at pH 8 or DAS-33 at pH 10 after oiling.

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