

## TANNING STUDIES WITH ALDEHYDES

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## ABSTRACT

Calfskin and cattle hide which had been processed through the conventional pretanning operations were treated with eight different aldehydes. All the aldehydes included in this study underwent interaction with collagen and showed a tanning action as judged by elevation of the shrinkage temperature of collagen and stabilization of its fibrous structure. The shrinkage temperature of the hide substance was increased by treatment at pH about 7.5 to 8.0 to approximately 75°C. for succinaldehyde, 84°C. for glutaraldehyde, 82°C. for 3-methylglutaraldehyde, 78°C. for 2, 4-dimethyl-2-methoxymethylglutaraldehyde, 76°C. for  $\alpha$ -hydroxyadipaldehyde, 80°C. for dialdehyde starch, and 72-74°C. for polymethoxy aldehydes. Formaldehyde and glyoxal (in bicarbonate solution) increased the shrinkage temperature of collagen to approximately 89°C. and 83°C., respectively. In weakly acidic solution glutaraldehyde appeared to be almost as reactive as formaldehyde toward collagen. The tanning action of dialdehyde starch, because of its potential availability at low cost, is of unusual interest.

## INTRODUCTION

The tanning action of certain aldehydes, particularly formaldehyde, has been known for some time, and studies have indicated that tanning action is generally limited to the simpler aliphatic aldehydes (1-4). Formaldehyde, the simplest aldehyde, is the most reactive of this class of organic compounds, and its tanning action has been studied extensively by many investigators. Acetaldehyde, the next higher homologue, has a considerably weaker tanning action, and the higher homologues are lacking in this property (1). Among the unsaturated aldehydes, the simplest member, acrolein, and its next higher homologue, crotonaldehyde, have a tanning action, but this is lost if ethyl or propyl groups are introduced in the 2 and 3 positions of acrolein (4). With regard to dialdehydes, glyoxal, the simplest, is a fair tanning agent, particularly in organic solvents (5-8). Pyruvic aldehyde (methyl glyoxal) also shows tanning power (1,8) and in some solvents is considered comparable to formaldehyde (1). The literature suggests that malonaldehyde and succinaldehyde have tanning power (7,9). Some higher molecular weight dialdehydes, whose structures are equivalent to dialdehydes corresponding to certain polyethylene glycols, also have been investigated (9). These dialdehydes were of the following structure:



and have been conveniently termed monoglycol-, diglycol-, and triglycol-dialdehyde where  $n = 1, 2,$  and  $3$  respectively. The simplest of these

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(monoglycoldialdehyde) was found to be a good tanning agent, increasing the shrinkage temperature ( $T_s$ ) of collagen by 12°C. The tanning power decreased with increasing value of  $n$ , and was essentially absent in the dialdehyde corresponding to the structure where  $n = 3$ .

This paper reports the preliminary examination of several dialdehydes, namely succinaldehyde, glutaraldehyde, 3-methylglutaraldehyde, 2,4-dimethyl - 2 - methoxymethylglutaraldehyde,  $\alpha$ -hydroxyadipaldehyde, and dialdehyde starch. Also examined were some monoaldehydes which may be termed "polymethoxy" aldehydes corresponding to the general structure  $\text{CH}_3\text{-(CH-CH}_2\text{)}_n\text{-CHO}$ . For purposes of comparison glyoxal and formalde-



hyde also have been included.

### EXPERIMENTAL

**Materials.**—Succinaldehyde, glutaraldehyde, 3 - methylglutaraldehyde, and  $\alpha$ -hydroxyadipaldehyde were available as 25 to 50% aqueous solutions and were diluted to a concentration of approximately 5% prior to use. 2,4-dimethyl - 2 - methoxymethylglutaraldehyde polymerizes on standing, and the sample received was the polymer. However, this polymer readily reverted to the monomer on simple Claisen distillation in vacuum as recommended by the manufacturer (10). The monomer, freshly distilled at a pressure of about 5 mm., was dissolved in water to give a stock solution of about 15% aldehyde concentration. This was diluted to 7.5% when used in hide treatments.

Dialdehyde starch, also termed oxystarch, was a sample prepared by the electrolytic periodate oxidation of corn starch (11). Approximately 96% of the anhydroglucose units of the starch molecule were converted into the dialdehyde structure. Dialdehyde starch was solubilized by autoclaving a 10% suspension of this starch derivative in water at 120°C. for one-half hour.

The polymethoxy aldehydes were prepared from commercially available polymethoxy acetals (12) of the general structure  $\text{CH}_3\text{-(CH-CH}_2\text{)}_n\text{-CH}$



$(\text{OCH}_3)_2$ . Three grades of polymethoxy acetals, designated as PMAC - 5, PMAC - 10, and PMAC - 15\*, were available; these differ in average molecular weight, which increases in the order listed. The acetals were hydrolyzed by mixing 10 g. of the acetal with 60 ml. of a 1% hydrochloric acid solution. The two-phase system was allowed to stand for 2 days or longer with occasional shaking. The PMAC - 5 dissolved almost completely upon hydrolysis, whereas in the case of PMAC - 10 and PMAC - 15 solution was not complete. The hydrolysis mixtures were then neutralized to a pH of 6-7 with about 3 g.

\*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.

of sodium bicarbonate, and sufficient ethyl alcohol was added to the partially solubilized mixtures to effect complete solution of the organic phase. In preparing solutions greater than 10% in concentration, 10 g. of the polymethoxy acetal was hydrolyzed with 30 ml. of the 1% hydrochloric acid solution.

The hide materials were limed cowhide and pickled calfskin obtained from local tanneries. These were converted into acetone-dehydrated stock as described in an earlier publication (13).

**Treatment with Aldehydes.**—The following procedure was typical: Small strips, approximately 1" x 3", were cut from the acetone-dehydrated stock, and several of these, amounting to 5 to 15 g., were used for each treatment. The acetone-dehydrated strips were wet back in water and then blotted on towels. The strips were then placed in 100 ml. of the aqueous aldehyde solution, which generally was about 5% concentration with respect to the aldehyde. In the case of the polymethoxy aldehydes, however, 10 - 15% solutions were used because of their considerably higher molecular weights. The treatments were carried out at room temperature at various pH and salt contents, and agitation was provided by continuously rolling the bottles in which the treatments were made on a low-speed jar mill. Periodically the pH of the solution was determined, and a shrinkage-temperature specimen  $\frac{1}{4}$ " x 2" was cut with a die from each strip. The remainder of the strip was returned to the bottle, and the  $T_s$  specimen was washed in running tap water for 24 hours. The  $T_s$  was determined on the freely suspended specimen mounted in a holder accommodating four samples. After shrinkage, the samples were immersed in cold water for evidence of reversible shrinkage. After 4 days of treatment, the remainder of the strips in the bottle were washed 24 hours in running water, allowed to air-dry, and examined for appearance.

## RESULTS AND DISCUSSION

The data collected are summarized in Tables I and II.

In our studies the shrinkage temperature in the early stages of the reaction was obtained to enable a qualitative judgment of the rate at which the maximum  $T_s$  was attained and thus provide additional data concerning the overall relative reactivity of these dialdehydes toward hide substance. All the aldehydes included in this study showed a tanning action as indicated by elevation of the  $T_s$  of the aldehyde-treated hide material and by the leather-like drying of the products. Among the dialdehydes, as judged by the maximum shrinkage temperature of the treated cowhide and the rate of its attainment under various conditions, glutaraldehyde appeared to be the most reactive, and  $\alpha$ -hydroxyadipaldehyde the least reactive, toward hide substance. The tanning power of 3-methylglutaraldehyde seemed to be almost equal to that of glutaraldehyde. These two glutaraldehydes appeared to be more reactive than succinaldehyde and glyoxal as indicated by the shrinkage temper-

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atures attained after one and three hours of treatment under comparable conditions.

On this same basis 2,4 - dimethyl - 2 - methoxymethylglutaraldehyde appeared to be less reactive than glyoxal, although the products obtained from the trisubstituted glutaraldehyde, particularly in the pH range of 7 to 8, showed good leather characteristics. In the treatments with this dialdehyde at high pH, a gummy insoluble phase, probably a polymer, separated; how-

TABLE I  
TANNING OF COWHIDE WITH ALDEHYDES

Exp't. No.	TREATMENT*					SHRINKAGE TEMPERATURE, °C., AFTER				
	Aldehyde	Conc., %	Buffer	Salt	pH**	1 hr.	3 hr.	6 hr.	1 day	3 days
1.	Succinaldehyde	•5	None	None	3.2-3.3	68	72	72	77	76
2.	"		None	NaCl	3.5-4.0	72	78	79	80	80
3.	"		NaHCO <sub>3</sub>	None	6.9-7.4	68	71	71	73	75
4.	"		MgO	NaCl	9.1-8.8	68	75	74	75	78
5.	Glutaraldehyde	5	Lactic	NaCl	2.5-3.1	73	79	81	83	84
6.	"		None	None	3.4-4.2	70	81	—	84	86
7.	"		None	NaCl	3.8-4.7	77	82	82	83	—
8.	"		NaHCO <sub>3</sub>	None	8.8-7.8	75	82	84	84	84
9.	"		MgO	NaCl	9.8-9.4	78	83	84	86	86
10.	3-Methylglutaraldehyde	5	Lactic	NaCl	2.7-3.1	72	77	79	81	82
11.	"		None	None	3.7-4.0	76	81	81	81	80
12.	"		None	NaCl	4.0-4.6	77	80	81	82	81
13.	"		NaHCO <sub>3</sub>	None	8.0-7.7	75	81	82	82	81
14.	"		MgO	NaCl	9.4-9.0	77	80	80	81	81
15.†	2,4-Dimethyl-2-Methoxy-methylglutaraldehyde	7.5	None	None	4.6-4.4	65	65	66	70	69
16.†	"		NaHCO <sub>3</sub>	None	8.2-7.7	65	69	71	75	78
17.†	"		MgO	NaCl	9.9-9.4	62	64	65	68	73
18.	α-Hydroxyadipaldehyde	5	None	None	4.5-5.1	62	65	—	69	72
19.	"		NaHCO <sub>3</sub>	None	8.5-7.8	65	66	—	72	76
20.	"		MgO	NaCl	9.3-8.9	—	64	—	69	70
21.	Glyoxal	3	None	None	3.0-3.3	63	63	62	69	70
22.	"		None	NaCl	3.9-4.4	65	67	68	75	78
23.	"		NaHCO <sub>3</sub>	None	8.1-7.3	71	77	78	76	81
24.	Formaldehyde	3	None	None	5.2-4.7	73	80	82	87	89
25.	"		NaHCO <sub>3</sub>	None	9.2-8.9	75	83	86	86	88
26.‡	PMAC - 5	10	NaHCO <sub>3</sub>	None	7.1-7.6	—	—	—	74	77
27.‡	"		MgO	Na <sub>2</sub> SO <sub>4</sub>	11.1-10.9	—	—	—	73	74
28.‡	PMAC - 10	10	NaHCO <sub>3</sub>	None	7.3-7.7	—	—	—	70	72
29.‡	PMAC - 15	10	NaHCO <sub>3</sub>	None	7.3-7.7	—	—	—	70	73

\*Two or three strips (1" x 3") of cowhide (*T<sub>s</sub>* about 63°C.) were treated with 100 ml. of the aqueous aldehyde solution. Where indicated, the salt content was 5%, the NaHCO<sub>3</sub> was 0.25 *M*, the MgO was 0.5%, and lactic acid 0.02 *M* on the solution basis.

\*\*Range of pH from 1 hour to 3 days.

†*T<sub>s</sub>* of raw hide in these experiments was 60°C.

‡The polymethoxy acetal was hydrolyzed to the corresponding aldehyde prior to the experiment. The aqueous solutions contained 10-25% alcohol.

TABLE II  
TANNING OF CALFSKIN WITH ALDEHYDES

Exp't. No.	TREATMENT*				pH**	SHRINKAGE TEMPERATURE, °C., AFTER				
	Aldehyde	Conc., %	Buffer	Salt		1 hr.	3 hr.	6 hr.	1 day	3 days
1.	Succinaldehyde	5	None	NaCl	3.3-3.4	73	77	77	78	78
2.	"		NaHCO <sub>3</sub>	Na <sub>2</sub> SO <sub>4</sub>	7.4-7.9	71	72	72	74	77
3.	"		Na <sub>2</sub> CO <sub>3</sub>	Na <sub>2</sub> SO <sub>4</sub>	9.2-9.1	71	75	74	77	77
4.	Glutaraldehyde	5	None	NaCl	3.9-4.3	80	82	83	83	83
5.	"		NaHCO <sub>3</sub>	None	7.6-8.0	80	80	80	81	81
6.	"		NaHCO <sub>3</sub>	Na <sub>2</sub> SO <sub>4</sub>	7.6-8.0	83	83	83	82	82
7.	"		Na <sub>2</sub> CO <sub>3</sub>	Na <sub>2</sub> SO <sub>4</sub>	9.6-9.5	70	75	78	83	83
8.	3-Methylglutaraldehyde	5	None	NaCl	4.1-4.3	78	80	80	80	80
9.	"		NaHCO <sub>3</sub>	Na <sub>2</sub> SO <sub>4</sub>	8.3	82	82	82	82	82
10.	"		Na <sub>2</sub> CO <sub>3</sub>	Na <sub>2</sub> SO <sub>4</sub>	9.3-9.1	81	80	81	81	81
11.	†,2,4-Dimethyl-2-Methoxy-Methylglutaraldehyde	7.5	None	NaCl	5.2-5.0	64	65	66	64	64
12.†	"		NaHCO <sub>3</sub>	Na <sub>2</sub> SO <sub>4</sub>	7.9-8.3	69	75	76	74	72
13.†	"		Na <sub>2</sub> CO <sub>3</sub>	Na <sub>2</sub> SO <sub>4</sub>	10.3-9.6	74	79	79	78	76
14.†	Dialdehyde Starch	5	None	NaCl	5.1-5.3	68	72	73	76	79
15.†	"		NaHCO <sub>3</sub>	Na <sub>2</sub> SO <sub>4</sub>	8.1-7.8	72‡	—	75	79	81
16.†	"		Na <sub>2</sub> CO <sub>3</sub>	Na <sub>2</sub> SO <sub>4</sub>	9.4-8.6	70‡	—	70	74	77
17.†	"		MgO	Na <sub>2</sub> SO <sub>4</sub>	10.1-9.8	68‡	—	71	75	78
18.	Glyoxal	3	None	NaCl	3.3-3.5	59	61	62	73	77
19.	"		NaHCO <sub>3</sub>	Na <sub>2</sub> SO <sub>4</sub>	7.6-7.4	73	77	79	80	83
20.	"		Na <sub>2</sub> CO <sub>3</sub>	Na <sub>2</sub> SO <sub>4</sub>	9.4-9.1	72	79	82	84	88
21.	Formaldehyde	3	None	NaCl	5.5-5.0	74	78	81	84	85
22.	"		NaHCO <sub>3</sub>	Na <sub>2</sub> SO <sub>4</sub>	8.3-8.5	82	85	87	88	89
23.	"		Na <sub>2</sub> CO <sub>3</sub>	Na <sub>2</sub> SO <sub>4</sub>	10.2	82	84	85	87	89
24.††	PMAC-5	10	NaHCO <sub>3</sub>	None	7.3-7.9	—	—	—	73	74
25.††	PMAC-10	15	NaHCO <sub>3</sub>	None	7.6-8.0	—	—	—	68	72
26.††	PMAC-15	15	NaHCO <sub>3</sub>	None	8.0-8.3	—	—	—	61	71

\*Several strips (1" x 3") of calfskin (*T<sub>s</sub>* about 65°C.) were treated with 50-100 ml. of the aqueous aldehyde solution. Where indicated, the salt content was 5%, and the NaHCO<sub>3</sub> and Na<sub>2</sub>CO<sub>3</sub> were 0.25 *M* on a solution basis.

\*\*Range of pH from 1 hour to 3 days.

†*T<sub>s</sub>* of raw stock was 58°C. in these experiments.

††The polymethoxy acetal was hydrolyzed to the aldehyde. The aqueous solution contained 10-25% alcohol.

‡*T<sub>s</sub>* after 2 hours of treatment.

ever this gradually dissolved during the course of the treatment. The air-dried specimens treated for the full length of time with the dimethylmethoxymethylglutaraldehyde yielded an almost white fibrous product.

In mildly acidic solution (pH about 4), the reactivity of glutaraldehyde toward cowhide approached that of formaldehyde. In contrast to the saturated aliphatic monofunctional aldehydes, which exhibit a rapid decrease in tanning power with increasing molecular weight, the tanning power of the saturated aliphatic dialdehydes appears to be maintained, at least in the series from glyoxal to the glutaraldehydes.

The tanned specimens obtained on treating cowhide or calfskin with succinaldehyde, glutaraldehyde, and 3-methylglutaraldehyde showed to a cer-

tain extent the property of reversible shrinkage, i.e., the heat-shrunk  $T_s$  specimen recovered a major portion of its shrinkage upon immersion in cold water. The reversibility of shrinkage was not as complete as that shown by formaldehyde-tanned specimens. In this property the behavior appeared to be similar to that of the glycolaldehydes reported by Gustavson (9).

Treatment of cowhide in the presence of sodium bicarbonate with the dialdehydes investigated in our studies resulted in elevation of the shrinkage temperature to 84°C. for glutaraldehyde, 82°C. for 3-methyl glutaraldehyde, 81°C. for glyoxal, 75°C. for succinaldehyde, 76°C. for  $\alpha$ -hydroxyadipaldehyde, and 78°C. for 2,4-dimethyl-2-methoxymethylglutaraldehyde. Treatment of calfskin with these aldehydes gave similar results except that maximum  $T_s$  was generally reached in a shorter time than in the case of cowhide. Seligsberger and Sadler (14), in a paper also appearing in this number of the Journal, reported that smooth-grained, soft, and pliable leather was obtained by tanning with formaldehyde or glyoxal in the presence of 2*N* sodium carbonate solutions. These authors found that malonaldehyde and succinaldehyde tanned best on the acid side, and that glutaraldehyde was effective over a wide pH range.

The data in Table II also show the tanning action of dialdehyde starch (oxystarch). Dialdehyde starch may be considered to be a polyfunctional aldehyde derived from the oxidation of the anhydroglucose units of the starch molecule to a dialdehyde structure. This material was of much interest in view of the recent development of an efficient electrolytic periodate oxidation process (11), which promises to make available a large variety of polyfunctional aldehyde derivatives from starch at potentially low cost. This process may be readily controlled to produce any given extent of oxidation of anhydroglucose units in the starch chain to dialdehyde structure. It was found that dialdehyde starch, 96% oxidized and solubilized by autoclaving at 120°C., readily interacted with calfskin, effecting a tanning action. The reaction appeared to proceed most rapidly in the pH region of about 8. Under these conditions, the shrinkage temperature of the calfskin was increased to about 80°C., and the reactivity of the dialdehyde starch appeared to be comparable to that of glyoxal.

The polymethoxy acetals, which have recently become available, are mixed methoxy acetals produced from methyl vinyl ether and methanol. The aldehydes derived from the acetals did show some tanning power, which was surprising since previous investigators have shown that the tanning action of the monofunctional aliphatic aldehydes decreases very rapidly with increasing molecular weight. Tanning action with these polymethoxy aldehydes was tested only in the neutral or alkaline pH range. The aldehydes from PMAC-5 appeared to be more active than those from the higher molecular weight polymethoxy acetals, increasing the  $T_s$  of cowhide by 14°C. The tanned specimens were quite stiff. By occasional working of the sample during the

latter stages of air-drying, however, a reasonably flexible leather-like material resulted, particularly from the treatment of calfskin with the aldehydes corresponding to PMAC-5.

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#### REFERENCES

1. Gustavson, K. H., in *Advances in Protein Chemistry* (New York: Academic Press, Inc., 1949), **V**, 353; *The Chemistry of Tanning Processes* (New York: Academic Press, Inc., 1956), 244, 278.
2. McLaughlin, G. D., and E. R. Theis. *The Chemistry of Leather Manufacture* (New York: Reinhold Publishing Corp., 1945), 332.
3. Bowes, J. H., in *Progress in Leather Science: 1920-1945* (London: British Leather Manufacturers' Research Association, 1948) chap. 25.
4. Gustavson, K. H. *J. Intern. Soc. Leather Trades' Chem.*, **24**, 377 (1940).
5. ———, *Svensk. Kem. Tid.*, **59**, 98 (1947).
6. Winheim, A. H., and E. E. Doherty. *JALCA*, **45**, 122 (1950).
7. ———, ———, U. S. Patent 2,516,283, July 25, 1950.
8. Kremen, S. S., R. L. Southwood, and B. L. Lucas, Jr. *JALCA*, **49**, 437 (1954).
9. Gustavson, K. H. *Svensk. Kem. Tid.*, **61**, 114 (1949).
10. Shell Development Co., Emeryville, California.  $\alpha, \gamma$ -Dimethyl -  $\alpha$ -methoxymethylglutaraldehyde Data Sheet.
11. Dvonch, W., and C. L. Mehlretter. *J. Am. Chem. Soc.*, **74**, 5522 (1952); U. S. Patent 2,648,629, August 11, 1953.
12. General Aniline and Film Corp., New York. *PMACs (Polymethoxy Acetals)*, Data Sheet No. P - 117, July, 1953.
13. Filachione, E. M., and E. H. Harris, Jr. *JALCA*, **51**, 160 (1956).
14. Seligsberger, L., and C. Sadlier. *JALCA*, **52**, 2 (1957).