acetic acid and insoluble in methyl alcohol, ethyl alcohol, ligroin and aqueous alkalies. It gave no depression of the freezing point in benzene. The substance slowly melts at 151–156° (corr.) without decomposition.

Anal. Subs., 0.2021, 0.2209, 0.1939: CO_2, 0.6028, 0.6591, 0.5743; H_2O, 0.1392, 0.1496, 0.1320. Calcd. for $C_{19}H_{22}O_2$: C, 80.81; H, 7.86. Found: C, 81.32, 81.37, 80.78; H, 7.70, 7.58, 7.52.

Some other work bearing on the question discussed in this paper is in progress and will be given later.

We extend our thanks to Dr. W. C. Geer, Vice-President of the B. F. Goodrich Company, for his interest in this work and for permission to publish this paper.

Summary

1. Weber's "tetroxyphenyl-polyprene," formed by the action of phenol on rubber "tetrabromide," is shown not to have the ether structure, $R(OC_6H_5)_2$, but the hydroxy structure, $R(C_6H_4OH)_2$. The name is changed to rubber di(hydroxyphenyl).

2. The rubber di(hydroxyphenyl) has been methylated, forming rubber di(methoxyphenyl) and its properties have been studied. The formation of this compound verifies the new structure assigned to the first compound.

AKRON, OHIO

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF COLUMBIA UNIVERSITY, No. 509]

DOES CHROMIUM COMBINE WITH THE BASIC OR ACIDIC GROUPS OF HIDE PROTEIN?[1]

BY ARTHUR W. THOMAS AND MARGARET W. KELLY

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The chemical mechanism of the union between hide protein and chromium in the production of chrome leather is in doubt. Wilson[2] has suggested the possibility of the interaction of the carboxyl radicals of the protein with the chromium cations. Since chrome tanning occurs in solutions which are decidedly on the acid side of the iso-electric point of collagen, the amount of ionized carboxyl groups would be exceedingly slight while the degree of ionized amino groups would be correspondingly great. This would point to the possibility of chrome fixation involving the nitrogen-containing radicals of the protein. It must be conceded, however,

[1] From data reported to the Division of Leather Chemistry at the 66th Meeting of the American Chemical Society, Milwaukee, Wisconsin, September 10–14, 1923, and at the 67th Meeting, Washington, D. C., April 21–26, 1924, under the titles "Combination of Chrome with Vegetable-Tanned Leathers" and "Chrome Tanning of Quinone-Collagen."

[2] Wilson, *J. Am. Leather Chem. Assoc.*, **12**, 108 (1917).

that, due to the very pronounced insolubility of chrome leather, fixation of chrome at the carboxyl groups could take place, even though the amount of ionized carboxyl were extremely small; but, inasmuch as chromium forms ammino compounds, the possibility of chrome tanning involving the nitrogen radicals merits consideration.

Since the hide protein is decidedly positively charged (that is, is cationic) in chrome-tanning solutions, recent literature[3] contains hints of the possibility that the presence of negative chrome complexes in chrome liquors is responsible for chrome tanning. Gustavson,[4] in one of a series of very noteworthy papers on the chemistry of chrome-tanning solutions, has experimentally demonstrated that anionic chromium, in the form of sodium dioxalatodiaquochromiate, $Na[(H_2O)_2Cr(C_2O_4)_2]$, tans hide. Gustavson and Widen[5] postulate that upon concentration of ordinary basic chrome liquors containing cationic chromium, the valence of the cation is expected to increase "gradually by transference of completely coördinately saturated chrome complex into an anion, where the gain in charges by the cation is balanced by the formation of negative chrome." They also suggest the possibility of the univalent chrome cation $\left[Cr\begin{matrix}(OH)\\ {}_1/_2H_2SO_4\end{matrix}\right]$ which predominates in liquors of high basicity and low concentration, combining with hide substance through the nitrogen groups.

While the present status of our knowledge of the constitution of proteins does not permit an exact description of the mechanism of the chrome-protein combination, the idea of combination between chrome and nitrogen radicals is not unwarranted speculation in view of the fact that chromium forms ammino compounds of the type $\left[Cr\begin{matrix}(NH_3)_n\\ (OH_2)_m\end{matrix}\right]X_3$, where $n + m = 6$ and X is an anion here expressed as univalent. Further, an advance in this sense has been made by Pfeiffer[6] in the preparation of a series of tetra-aquo-dipyridine chromic salts and their derivatives.

In an attempt to elucidate the question of the significant radicals of the collagen molecule in chrome tannage, the authors have measured the combining capacities for chromium of vegetable-tanned, quinone-tanned and deaminized hide powder, respectively. The first two methods are based on the hypothesis that both vegetable tannin and quinone combine with the nitrogen groups in hide protein.

Wilson[2] suggested the probable chemical mechanism of vegetable tannage to be the union between the amino groups of the protein and the tannic

[3] Burton, *J. Soc. Leather Trades' Chem.*, **6**, 164 (1922); *J. Am. Leather Chem. Assoc.*, **18**, 110 (1923). Thompson and Atkin, *J. Soc. Leather Trades' Chem.*, **6**, 207, 244 (1922); *J. Am. Leather Chem. Assoc.*, **17**, 571 (1922).

[4] Gustavson, *J. Am. Leather Chem. Assoc.*, **20**, 382 (1925).

[5] Gustavson and Widen, *Ind. Eng. Chem.*, **17**, 577 (1925).

[6] Pfeiffer, *Z. anorg. Chem.*, **31**, 401 (1902); *Ber.*, **39**, 1864 (1906).

acid to form compounds such as substituted ammonium tannates. Presumptive evidence for such a mechanism has been provided,[7] while a study of the combining capacity of deaminized collagen for vegetable tannins by Thomas and Foster[8] apparently proved it. This study revealed the fact that the removal of amino nitrogen from hide protein resulted in a decrease in its tannin-combining capacity just as the neutralizing power of gelatin toward hydrochloric acid is diminished when it is deaminized.

Quinone (and its polymerization products) is a very active tanning agent in alkaline solution.[9] Meunier,[10] the first to note the tanning power of quinone, postulated its action on hide to be similar to that on primary amines, that is, part of it oxidizes the amino groups (quinol resulting) and the remainder adds on to these oxidized nitrogenous groups. Strong evidence for the validity of Meunier's theory has been offered.[8,9]

It is apparent, then, that the combining capacity for chromium of vegetable- or quinone-tanned leathers or of deaminized hide powder should be less than that of pure hide substance if the nitrogen groups are involved in the combination with chromium. If "chrome collagen" is sufficiently less soluble than "collagen tannate," it might be argued that the chromium would replace the tannin, but even so, the rate of chrome tannage would be retarded.

Before describing the experimental procedure, it should be noted that Wood[11] measured the combining capacity of chromed gelatin for tannin, finding that it combined with as much tannin as pure gelatin. This led him to believe that chrome and vegetable tanning do not involve the same groups of the protein molecule. In the light of our present knowledge, his experiments were not conclusive.

I. Chrome Tannage of Vegetable- and Quinone-Tanned Leathers

Materials Used.—The "vegetable leathers," designated as "V_1" and "V_2", were prepared by tanning hide powder with wattle bark extract at P_H = 2 and 5. These Sörensen (P_H) values were selected because at P_H = 2 a much higher degree of tannage is obtained than at P_H = 5. A portion of defatted hide powder equal to 200 g. of absolutely dry substance was agitated in 10 liters of wattle bark solution (containing 60 g. of dry extract per liter) at P_H = 4.93 for 24 hours, when it was filtered off, washed to complete the removal of uncombined substances and air dried. The composition of these is given in Table I.

Two varieties of "quinone leather" were prepared. One designated as "Q_1" was made by stirring fat-free hide powder equal to 150 g. of dry substance in 12 liters of a 0.0667 *M* phosphate buffer solution of 205 g. of quinone at P_H = 8.0 for 24 hours. The quinone-tanned hide powder was then washed with water to remove extraneous

[7] Thomas and Kelly, (a) *Ind. Eng. Chem.*, **15**, 1148 (1923); (b) **16**, 800 (1924).

[8] Thomas and Foster, THIS JOURNAL, **48**, 489 (1926).

[9] Ref. 7 b, p. 925.

[10] Meunier, *Compt. rend.*, **146**, 987 (1908); *Collegium*, **1908**, 195; **1909**, 58, 319; **1914**, 523.

[11] Wood, *J. Soc. Chem. Ind.*, **27**, 384 (1908).

tanning solution and air dried. Another specimen designated as "Q_2" was prepared in a similar manner. It was tanned in a solution at $P_H = 10.5$ (phosphate and sodium hydroxide) and in addition to the original 205 g. of quinone, 100 g. was added when partial exhaustion of the original amount permitted. The composition of "quinone leathers" Q_1 and Q_2 is given in Table I.

TABLE I

COMPOSITION OF EXPERIMENTAL LEATHERS

Kind	Vegetable	Vegetable	Quinone	Quinone
Designation	V_1	V_2	Q_1	Q_1
Moisture, %	11.5	11.5	11.1	10.5
Hide substance, %	72.3	54.5	68.8	49.8
Ash, %	0.2	0.6	1.7	1.2
Tannin, %	16.0	33.4	18.4	38.5

Method.—Portions of the leathers equal to 3.75 g. of hide substance were placed in contact with 150 cc. portions of basic chrome solutions prepared from commercial "chrome" crystals (composition approximately $2Cr(OH)SO_4.1Na_2SO_4$) at the dilutions noted in Tables II and III, the concentrations given being those obtained by analysis of each solution. One series was rotated for 48 hours, while another series was allowed to stand for eight weeks and a third for 16 weeks; the last two were shaken at least once a day. At the ends of the time intervals the mixtures were

TABLE II

FIXATION OF CHROME BY VEGETABLE-TANNED LEATHERS

Cr_2O_3 per liter of tanning soln., g.	Cr_2O_3 fixed by 1 g. of hide substance, mg.					
	48 hours		8 weeks		16 weeks	
	V_1	V_2	V_1	V_2	V_1	V_2
0.537	15	12	20	18	17	19
3.08	49	30	92	78	87	79
7.63	65	38	122	119	137	(113)?
15.3	70	45	130	124	153	130
30.6	75	48	129	117	163	134
50.0	64	40	118	116	147	126
80.9	42	31	92	87	(105)?	104
117.9	22	21	62	59	76	73
153.5	12	9	32	25	41	35

TABLE III

FIXATION OF CHROME BY QUINONE-TANNED HIDE POWDER

Cr_2O_3 per liter of tanning soln., g.	Cr_2O_3 fixed by 1 g. of hide substance, mg.			
	48 hours		16 weeks	
	Q_1	Q_2	Q_1	Q_2
0.501	16	18	15	16
2.94	55	39	74	72
7.35	63	32	102	84
14.8	62	30	99	84
29.5	55	28	99	82
48.8	50	21	95	76
77.4	32	16	78	61
109.6	21	10	66	41
142.1	16	8	51	29

filtered through bags and washed with kneading until all uncombined chrome had been removed, when they were air dried.

The amount of nitrogen in each air-dried sample was determined by the Kjeldahl method and the amount of chromium by the Eschka mixture method. From these values the amounts of "chrome fixed by 1 g. of hide substance" were calculated.

The results are shown in Tables II and III and in Figs. 1 and 2.

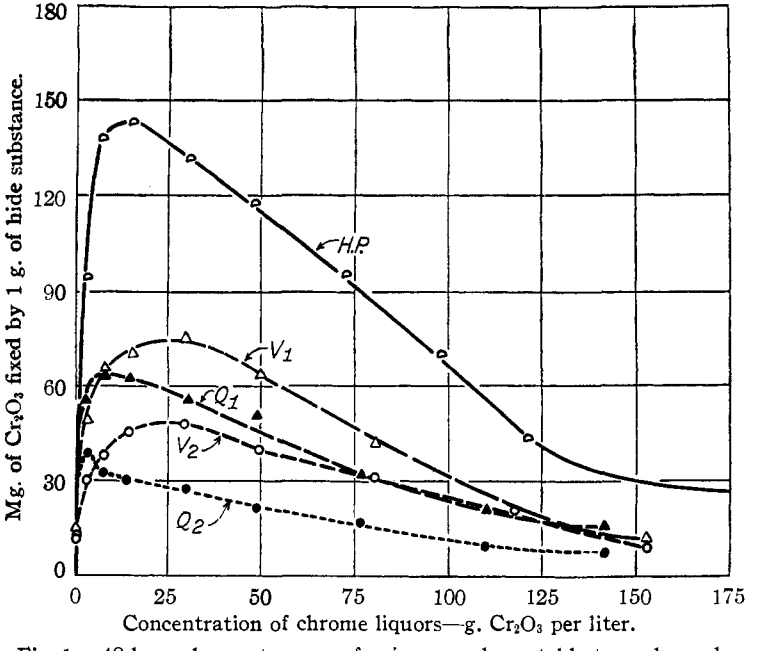

Fig. 1.—48-hour chrome tannage of quinone and vegetable-tanned powders. H.P. = raw hide powder. V_1, V_2, Q_1 and Q_2 are vegetable- and quinone-tanned leathers of low and high tannin content, respectively, as given in Table I.

Previous results reported from this Laboratory[12] showed that when the combination of chrome with hide substance is followed as a function of the concentration of the basic chrome liquors (composition approximately $2Cr(OH)SO_4.1Na_2SO_4$) in contact with hide substance, the curve rises rapidly to a maximum in liquors containing 15 g. of chromium sesquioxide per liter and then abruptly descends. The maximum fixation of chrome was 143 mg. of chromium sesquioxide per gram of hide substance (corresponding to a little greater than what might be termed "tetrachrome collagen") in 48 hours, 239 mg. in 13 weeks, and 266 mg. in 8.5 months ("octachrome collagen"). The curves for the fixation of chrome as a func-

[12] Thomas and Kelly, *J. Ind. Eng. Chem.*, **13**, 31 (1921); **14**, 621 (1922).

tion of the concentration of the chrome liquors by hide powder in 48 hours and 13 weeks[12] are plotted in the figures for comparison.

The fixation of chromium is seen to be pronouncedly inhibited by the presence of fixed tannin, whether it be vegetable or quinone tannin.

It is also evident, especially in Fig. 2 which depicts the amount of chrome fixation during a long period of time, that quinone-tanned hide powder has much less affinity for chromium than the vegetable-tanned specimens. For example, the maximal amount of chromium fixed by leather "Q_2"

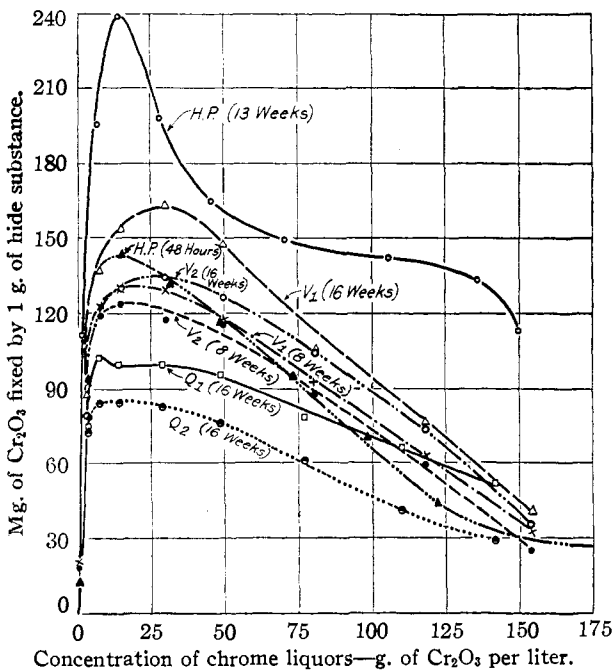

Fig. 2.—Chrome tannage of quinone- and vegetable-tanned leathers. The designations are the same as those in Fig. 1, the remarks in parentheses indicating the duration of the chrome tanning.

in 16 weeks is 84 mg. of chromium sesquioxide per gram of hide substance while in 8 and 16 weeks, leather "V_2" fixed a maximum of 124 and 134 mg., respectively. This has an interesting bearing upon the question raised, since a given weight of quinone should combine with and thus mask a greater number of nitrogen groups than the same weight of vegetable tannin, due to the lower molecular weight of the former. Of course, the fact that polymerization products of quinone may be the actual tanning bodies in quinone tannage must be taken into account, but it is rather unlikely that such products approach the natural vegetable tannins in molecular magnitude.

Another noteworthy fact brought out by the curves is the shift in the point of maximum fixation of chrome. Hide powder shows a very decided maximal fixation of chrome from the type of liquor used when the concentration of the basic chromic sulfate is equivalent to 15 g. of chromium sesquioxide per liter, which fact Gustavson[4,5] attributes to the predominance of the univalent ion $\left[\mathrm{Cr}\begin{smallmatrix}(\mathrm{OH})\\ {}_{1/2}\mathrm{SO_4}\end{smallmatrix}\right]^{+}$ in such a liquor at the stated concentration. It is seen that the point of maximal fixation by the "vegetable leathers" is from liquors of greater concentration (about 30 g. of chromium sesquioxide per liter), while the maximum obtained with the "quinone leathers" was from weaker liquors (of about 7 g. of chromium sesquioxide per liter).

II. Chrome Tannage of Deaminized Hide Powder

For the experiments described in this section, chromic sulfate solutions of a basicity of 52%[5] were employed, the stock solution having been prepared by addition of the calculated amount of 2 *M* sodium hydroxide to a concentrated solution of C.P. chromic sulfate crystals, and the actual basicity determined by analysis of the resulting solution. Deaminized hide powder was prepared as described in an earlier paper.[8] Analysis of the original and deaminized hide powders gave the following values calculated to the moisture-free basis.

TABLE IV
COMPOSITION OF HIDE POWDERS

	% fat ($CHCl_3$ extract)	Ash, %	Nitrogen, %
Original hide powder	1.05	0.31	17.91
Deaminized hide powder	0.34	.81	17.64

Samples equivalent to 5.000 g. (dry basis) of ordinary and of deaminized hide powders were treated with 200cc. portions of the basic chromic sul-

TABLE V
FIXATION OF CHROME BY DEAMINIZED HIDE POWDER

Cr_2O_3 per liter of tanning solution, g.	*P*H value of original solution	Cr_2O_3 fixed by 1 g. of hide substance and *P*H value of final tanning solutions, mg. Ordinary hide powder Cr_2O_3 fixed, mg.	Ordinary hide powder *P*H of filtrate	Deaminized hide powder Cr_2O_3 fixed, mg.	Deaminized hide powder *P*H of filtrate
3.00	3.32	90	3.70	70	3.58
7.08	3.27	160	3.38	79	3.43
10.9	3.23	198	3.36	85	3.37
15.0	3.17	195	3.33	92	3.33
19.9	3.18	179	3.29	94	3.28
24.9	3.17	167	3.26	89	3.24
34.6	3.13	163	3.20	90	3.20
49.9	3.05	153	3.13	89	3.12
75.3	2.98	138	3.00	77	3.02
125.3	2.82	102	2.87	43	2.88

fate solution prepared as described above, at the dilutions given in Table V, the concentration at each dilution having been determined by analysis. After rotating for 48 hours, the samples were filtered off, washed, air dried and analyzed for nitrogen and chromium as described above; from the values thus obtained, together with the percentages of nitrogen in the untanned powders, the "milligrams of chromium sesquioxide fixed by 1 g. of hide substance" were calculated. The results are summarized in Table V and Fig. 3.

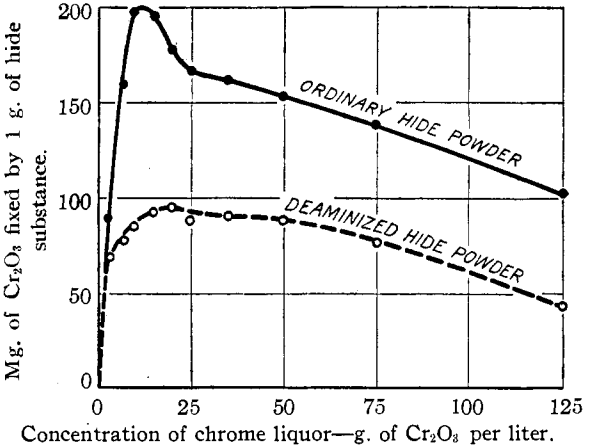

Fig. 3.—Chrome tannage of deaminized and ordinary hide powder. The time of tannage was 48 hours.

It is apparent that the removal of nitrogen groups from the collagen molecule inhibits to a marked degree the rate of fixation of chromium from solutions of basic chromic sulfate.

The authors are indebted to A. F. Gallun and Sons Company for their aid in this, one of a series of investigations of the chemistry of leather formation.

Summary

The rate of combination of chromium with hide substance is greatly inhibited if the hide substance contains either combined quinone or vegetable tannin. Further, deaminized hide powder fixes less chromium in a given time than untreated hide powder. This would seem to indicate that the nitrogen groups of the protein play a significant role in chrome tanning.

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