

THE ADSORPTION OF CHROMIUM OXIDE BY HIDE POWDER

BY A. W. DAVISON

The question as to the constitution of leather is still a widely debated one. The adherents of the chemical compound theory on the one hand are pitted against the supporters of the physical adsorption theory on the other. Neither faction is ready to accept, in their entirety, the claims of the other. As a representative of those supporting the chemical compound viewpoint, Fahrion¹ points out that leather is a salt, in which the oxidized hide, being amphoteric in character, may play the role of either acid radical or basic radical; and the tanning agent, that of basic or acid radical. Whether the hide functions as acid or base will depend solely upon the character of the tanning agent.

The adherents of the physical adsorption theory believe that the changes wrought in hides by tanning are of a physical, rather than a chemical nature; and that they are analogous to those brought about in cotton by mercerization; rubber by vulcanization; or in cellulose by nitration; all of which are now regarded as adsorption phenomena.

Some authors go a step farther, and claim that although the process of tanning is one of adsorption, pure and simple, further slow changes may take place with time. Stiasny² holds that since in the majority of cases tan stuffs are taken up from their colloidal solutions, the adsorption becomes immediately irreversible. He does not deny that slow chemical reactions may later take place between the hide fiber and the tanning agent.

As a preliminary to some extended work on the theory of tanning which is to be carried on in this laboratory, it was deemed desirable to substantiate, if possible, the claims of the physical theorists that the first process in tanning is one

¹ Zeit. angew. Chem., 22 (2) 2083, 2135, 2187 (1909).

² Zeit. Kolloid Chem., 2, 257 (1908).

of straight adsorption. Further, and later changes, of whatever nature, are without the province of this paper.

The author has chosen the phase rule method of attack, because it so readily lends itself to the solution of problems of this character. Chromium has been selected as the tanning agent, since it, as a typical metallic tan, affords ease and certainty of analysis.

Although chromium salts are known to harden gelatine,¹ it was believed to be more advisable to use hide powder as the adsorbing agent, for the reason that one would thereby be working nearer to actual tanning conditions; and he could be more certain of dealing with a uniform, readily replaceable material. The hide powder used was the variety known as American Standard, obtained from Daigger and Company, Chicago. Although this product is somewhat coarse, it was found to be sufficiently porous to be thoroughly permeated by the tanning solutions. The powder was kept in a tightly closed metal can, and was weighed directly, without previous treatment, into the shaking flasks.

The tanning solution was made after a "single bath" formula by Flemming.² Transposed into the metric system, this formula calls for: Solution A Chrome alum, 120 g in 1000 cc water; Solution B Sodium carbonate, 30 g in 100 cc water. Solutions A and B are to be slowly mixed, and any resulting precipitate removed by filtration. Throughout the remainder of this article, the resulting solution is called "strong tan solution."

The final solution in which hides are to be tanned consists, for, say, ten kilograms of wet skin:

Strong tan solution	2.5 liters
Water	66.3 liters
Salt	70.0 grams

After the tanning process has been going on an hour, two and a half additional liters of strong tan solution should be added: this addition of strong tan solution should be con-

¹ Neuner: *Zeit. Kolloid Chem.*, 8, 144 (1911).

² "Practical Tanning," p. 225.

tinued until the hides are fully tanned. In all, about eight liters of strong tan solution are said to be required for ten kilograms of skin.

In order that conditions in all of the tanning flasks might be perfectly uniform, it seemed desirable to complete the impregnation of the hide fibers at one operation. The usual method of "strengthening up" the solution after each hour leaves entirely too much uncertainty of equilibrium. Then, too, when one is dealing with powdered hide, which has previously been soaked in salt water, there is no tendency toward "case hardening," or uneven tanning, because the solution so easily permeates the entire fibrous mass. At least, in these experiments, microscopic examination of the tanned powder failed to reveal uneven tanning.

The soaking and tanning operations were carried out in five hundred cubic centimeter, rubber stoppered, Erlenmeyer flasks. These were clamped to a rotating device in such a manner that the flasks were turned about a horizontal shaft perpendicular to their axis of symmetry. The radius of rotation was twelve inches; the flasks revolved fifty times per minute. This insured perfect agitation, since the total volume of solution in each five hundred cubic centimeter flask was only two hundred and seventy-five cubic centimeters. The whole device was immersed in a thermostat at 28° C.

Two grams of hide powder were weighed directly into each flask, and two hundred and fifty cubic centimeters of salt solution, containing ten grams of sodium chloride per liter, added. The flasks were then rotated for one hour, in order to insure perfect and uniform soaking of the material. Then the strong tan solution was introduced. The actual amount of tan liquor added is of little import, since interest centers only around concentrations at equilibrium, and the solutions were all to be analyzed at a later stage. The volumes varied roughly from one to twenty-five cubic centimeters. Since it was highly necessary to hold the salt concentrations in the various flasks constant, the tan liquor added was in every instance diluted to twenty-five cubic centimeters. Thus

in the case of the flask to which ten cubic centimeters of strong tan solution were to be added, fifteen cubic centimeters of distilled water were mixed with the chrome liquor before the latter was added to the tan flask. The conditions in all flasks were, therefore, the same, except for varying amounts of tan liquor.

The tanning process proper was run for four hours. Preliminary experiments showed that equilibrium was fully established in that time: Two gram portions of hide powder were soaked one hour, then tanned for varying times, using in each instance twenty cubic centimeters of strong tan solution. At the end of each hour, a flask was removed, and the solid phase analyzed. The results are shown in Table I.

TABLE I

Hours in contact with tan liquor	Weight Cr_2O_3 in solid phase
1	0.1795
2	0.2038
3	0.2093
4	0.2120
5	0.2115
6	0.2117

It will be noticed that after four hours there was a loss in the weight of Cr_2O_3 found. This may be attributed to experimental error, or it may be caused by disintegration and solution of the finer particles of tanned powder after so long a time in the rotating device.

The separation and analysis of the different phases under consideration presented by far the most difficult and perplexing problem. In order to obtain concordant results, there must be no solution adhering to the tanned powder, and the latter required quantitative treatment. Once tanned, however, hide powder is not difficult to operate upon; it does not tend to stick to chemical glassware, neither does it present serious difficulties in filtration. However, the removal of adhering solution requires the utmost care. Washing with any solvent whatever is entirely impossible; hence some simple

method of mechanical separation was desired. The author believes that the problem was solved, within reasonable limits of error, by first filtering off the solid phase, then removing the adhering liquid with a centrifuge. Had it been possible to use the centrifuge alone, more accurate results might have been secured, because the uncertain amount of chromium adsorbed from the solution by the filter paper would have been eliminated. Unfortunately, when one attempted to run the solution containing the tanned powder directly into the centrifuge while it was rotating, small particles of leather clogged the orifice.

A number of methods for obtaining a rough separation, giving a solid-liquid mixture of sufficiently small volume to be introduced into the stationary centrifuge, were tried; but the only successful one consisted in filtering off the solid phase on small four centimeter Büchner funnels, using hardened filter paper, and removing the last particles of tanned powder from the Erlenmeyers by washing with some of the solution which had already been through the filter. This rough separation could easily be effected in twenty minutes. The liquid at this point was saved for analysis. The solid phase still contained considerable solution, but the maximum amount of this could now be removed with the centrifuge. The latter was the usual Dulin Rotarex laboratory type. Each sample, after being carefully separated from the small disc of filter paper, was centrifuged thirty minutes, at the maximum speed; and at the end of that time the assumption had to be made that they were uniformly dry. It has been pointed out by Leighton¹ that where one is dealing with dilute solutions, the nature of an adsorption curve is changed but little, when there is a marked difference in the amount of water adsorbed by the solid phase at different concentrations of the liquid phase. Since extreme care was exercised in the centrifugal process in order to secure uniformity of drying, it was not deemed advisable or necessary to determine the actual amount of water taken up in every instance.

¹ Jour. Phys. Chem., 20, 47 (1916).

The concentration of chromium in the solutions at equilibrium was determined volumetrically. The chromium in aliquot portions of each solution was oxidized by boiling with sodium peroxide, and converted into sodium dichromate, with acid. A measured excess of tenth normal ferrous ammonium sulphate was run in, and the unoxidized iron determined with tenth normal dichromate, using diphenylcarbazine for indicator.¹

These concentrations represent true values at equilibrium, except for the small amounts of chromium solution adsorbed by the filter papers in the Büchner funnels. Analyses of these papers showed the amount of water, and chromium, taken up by so small a disc to be entirely negligible when compared to the large volume of solution (two hundred and seventy-five cubic centimeters) dealt with.

In Table 2, concentrations of the solutions are expressed in terms of the number of cubic centimeters of tenth normal ferrous ammonium sulphate equivalent to the dichromate from one hundred cubic centimeter portions of the liquid phase.

At first the chromium in the solid phase was determined as follows: The tanned hide powder was dried at 80°, pulverized, and fused with sodium peroxide, in nickel crucibles. The resulting mass was next dissolved in boiling water, acidified, and filtered. The chromium, now present as sodium dichromate, was determined by titration, as in the case of the liquid phase samples. But the quantitative fusion of so large a mass of tanned hide powder was found to be entirely too uncertain and troublesome, so a more simple method of analysis was devised. The dried product from the centrifuge was treated with a few cubic centimeters of nitric acid, placed in porcelain crucibles, and ignited at dull red heat in an electric furnace. This treatment burned out the gelatine of the hide, leaving behind the chromium oxide, sodium chloride, potassium sulphate, and the ash of the hide powder. The sodium chloride and potassium sulphate were washed out, and the residue weighed. This, minus the weight of the insoluble ash from two grams of

¹ Jour. Am. Chem. Soc., 35, 156 (1913).

hide powder, was called Cr_2O_3 . In Table 2, the concentration of chromium in the solid phase is given in grams of Cr_2O_3 taken up by two grams of hide powder.

Concentration values for both the liquid and the solid phase are given in Table 2.

TABLE 2

Concentration in liquid phase cc $n/10$ FeSO_4 equivalent to dichromate produced by chromium in 100 cc solution	Concentration in solid phase gm Cr_2O_3 adsorbed by 2 gm hide powder
0.08	0.0743
0.17	0.0873
0.43	0.1093
0.78	0.1238
1.49	0.1421
2.09	0.1591
3.12	0.1740
4.78	0.1940
6.29	0.2041
8.05	0.2120
11.37	0.2244
14.90	0.2352

When plotted, the results appear in Fig. 1.

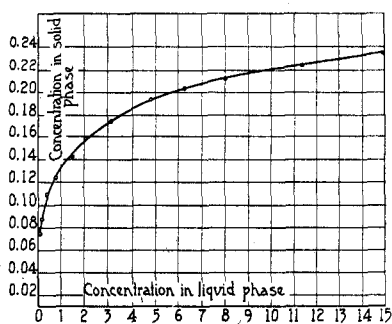


Fig. 1

Adsorption of chromic oxide by hide powder

An inspection of the curve will reveal the fact that no breaks, horizontal, or vertical portions, exist. The phase

rule, therefore, tells us that we are dealing with an adsorption isotherm; and that no compounds between the hide powder and the tanning agent have been formed. In the case of chrome tanning, therefore, the contention of the physical theorists, that the first step is one of pure adsorption, has been verified.

The author desires to express his appreciation to Professor W. D. Bancroft for certain suggestions; and to Mr. E. K. Files, of this laboratory, for carrying out the analyses of the solid phases.

*Laboratory of Physical Chemistry
University of Cincinnati*