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EVOLUTION OF CARBON DIOXIDE AND WATER FROM VEGETABLE-TANNED LEATHERS AT ELEVATED TEMPERATURES

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ABSTRACT

The rates of evolution of carbon dioxide and water from untanned-hide powder and from chestnut-, quebracho-, cutch-, and sumac-tanned leathers in the presence of oxygen or air or of one of the inert gases, nitrogen or helium, in the temperature range 60° to 140° C were determined. Hide powder evolves much less carbon dioxide and water than the leathers. Chestnut leather evolves carbon dioxide at the greatest rate, and the order of decreasing rate of evolution of carbon dioxide by the leathers is chestnut, sumac, cutch, and quebracho. Cutch and quebracho leathers in the presence of air and oxygen generally give off more water than sumac and chestnut leathers. The rates of evolution of carbon dioxide from all the leathers heated in the presence of oxygen or air increase in the majority of cases by a multiple of approximately 3 for every 20° C rise in temperature. The changes in the rates at which water is evolved under the same conditions are smaller. The ratio of carbon to hydrogen oxidized to carbon dioxide and water, respectively, is approximately 1 to 3. In the presence of helium, the amounts of carbon dioxide found are small, a fact which indicates that the mechanism of the reaction in oxygen is principally an oxidation. The ratios of the amounts of carbon dioxide and water produced in the presence of air to those amounts produced in the presence of oxygen are different from the ratio of the partial pressures of oxygen in the two gases. The amounts of carbon dioxide emitted from the leathers correlate linearly with the percentages of the total nitrogenous materials extractable by a 0.1 *N* solution of sodium carbonate from leathers treated under the same conditions.

CONTENTS

I. INTRODUCTION

The oxidation of vegetable tannins has been associated with the darkening of the colors of solutions and of materials containing tannin, with the difficulty in determining the moisture content of leather, and with the deterioration of vegetable-tanned leather in storage. J. Jany [1] [1] and E. W. Merry [2] measured the rates of absorption of

[1] Figures in brackets indicate the literature references at the end of this paper.

oxygen by tannins and assumed that these rates were proportional to the rates of oxidation. Merry [2] made a thorough study of the amounts of oxygen absorbed by tanning materials and by ordinary and treated tannin solutions.

The results obtained in a series of investigations at the National Bureau of Standards on the stability of vegetable-tanned leathers at elevated temperatures have been presented in previous papers [3, 4, 5]. In those investigations the change in stability of the leathers under the various conditions studied was determined from chemical changes occurring in the hide substance and from physical tests of the leather. In two of those papers [3, 4] it was shown that carbon dioxide and water were evolved from leathers in the presence of oxygen and that the rates at which carbon dioxide was evolved at a constant temperature varied directly with the rates of deterioration of the leathers when aged in oxygen under pressure. The deterioration of the leathers aged under these conditions was measured by the percentage of the total nitrogenous materials extractable by a 0.1 N solution of sodium carbonate.

In the present investigation a further study has been made of the amounts and rates of evolution of carbon dioxide and water from leathers at different temperatures and in the presence of different gases. The purpose was to obtain additional information which could be used in developing a suitable aging test for leather. This work, which involves principally changes occurring in the tannins, is correlated with other work in which chemical changes in the hide substance were studied.

II. APPARATUS AND PROCEDURE

The leathers used in this investigation were tanned in the experimental tannery at the National Bureau of Standards. Four types were prepared, namely, chestnut, quebracho (ordinary), cutch, and

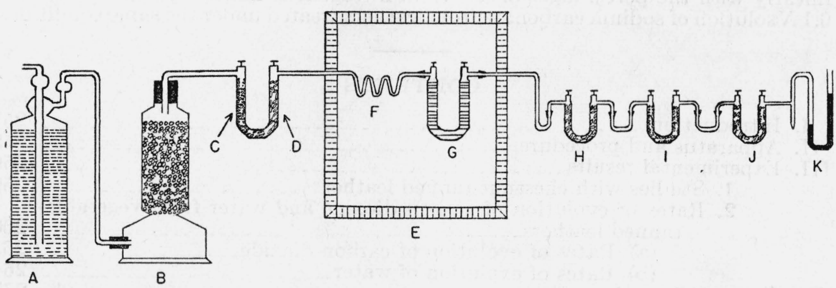

FIGURE 1.—*Diagram of apparatus used in determining the amounts of carbon dioxide and water evolved from leather.*

A, sulfuric acid; *B*, soda lime; *C*, Ascarite; *D*, magnesium perchlorate; *E*, oven; *F*, preheating coil; *G*, leather sample; *H*, water absorbed; *I*, carbon dioxide absorbed; *J*, safety tube; *K*, flowmeter.

sumac. These leathers were analyzed to determine their tannin contents, then degreased, and conditioned at 65-percent relative humidity and 70° F before the experiments were made.

A diagram of the apparatus used in making the experiments is shown in figure 1. Samples of the leathers, each weighing approximately 5 g, were placed in U-tubes equipped with side arms having ground-glass connections. The U-tubes were placed in the oven and connected to the gas train, as shown in the figure. The temperature of the oven was maintained constant within ±1.5° C. A continuous stream of either dry oxygen, air, or one of the inert gases, helium or nitrogen, was passed over the samples, then led outside the oven and through a series of U-tubes. The water evolved was absorbed in anhydrous magnesium perchlorate in the first U-tube and the carbon dioxide was absorbed in Ascarite in the second U-tube. The rates of evolution of these gases were determined by weighing the U-tubes at regular intervals. The rate of flow of the gas stream was 8 to 12 cm^3 per minute.

III. EXPERIMENTAL RESULTS

The amounts and rates of evolution of carbon dioxide and water from leathers tanned with chestnut, quebracho, cutch, and sumac, when heated at 60°, 80°, 100°, 120°, and 140° C in the presence of oxygen or air, or of one of the inert gases, helium or nitrogen, were measured. No study of the rates of evolution of carbon dioxide or water was made below 60° C because this was the lowest temperature at which measurable quantities of carbon dioxide were evolved in short periods of time. The study was not continued above a temperature of 140° C because at this point small quantities of organic materials condense on the cold walls of the glass tubing, just outside of the oven, an indication that a breakdown, other than the formation of carbon dioxide and water, began at this temperature. The experiments made possible not only determinations of the rates of evolution of carbon dioxide and water at a constant temperature but also permitted determinations of the increases in the rates of evolution of these gases with increase in temperature.

1. STUDIES WITH CHESTNUT-TANNED LEATHER

The amounts of carbon dioxide and water evolved from chestnut leather heated in oxygen are shown in figure 2. Each curve represents the amount evolved, during the specified time at the specified temperature expressed as a percentage of the weight of the tanned leather. At all temperatures the evolution of carbon dioxide and water is most rapid during the first 4 or 5 days. After this the rate decreases slowly with increase in time. The rates of evolution are greatest at higher temperatures, particularly above 100° C. The curves showing the rate of evolution of water have been arbitrarily extrapolated to 14.6 percent. This value is very close to the values obtained by the usual method of determining the water content of leathers, namely, drying at 100° C in the presence of air for 16 hours, and may be assumed to be that water reversibly adsorbed by the leather. Values above 14.6 percent are considered to be water resulting from oxidation or dehydration reactions. It may be noted in the figure that only one point, that representing a percentage evolved at 60° C, is lower than this percentage for the adsorbed water.

When chestnut leather was heated in the presence of air at different temperatures, the trends with regard to the rates of evolution of carbon dioxide and water were similar to those shown when it was heated in oxygen. However, much smaller amounts of the two gases were produced. The amount of carbon dioxide evolved from chestnut leather in the presence of air at any temperature was approximately one-half of that evolved in the presence of oxygen.

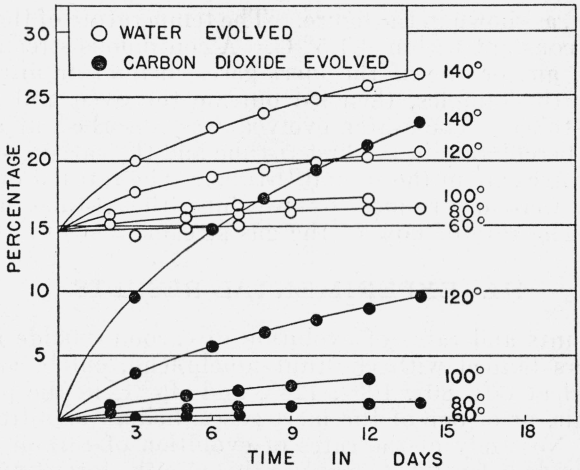

FIGURE 2.—*Rates of evolution of carbon dioxide and water from chestnut-tanned leather heated in oxygen at various temperatures.*

Percentages are based on the weight of the conditioned leather.

Carbon dioxide and water evolved in the presence of helium may be considered to originate from direct decomposition. That the amounts coming from this source are very small is shown by figure 3, where the amounts of carbon dioxide and water evolved from chestnut leather when heated at 120° C in the presence of either oxygen, air, or helium are recorded.

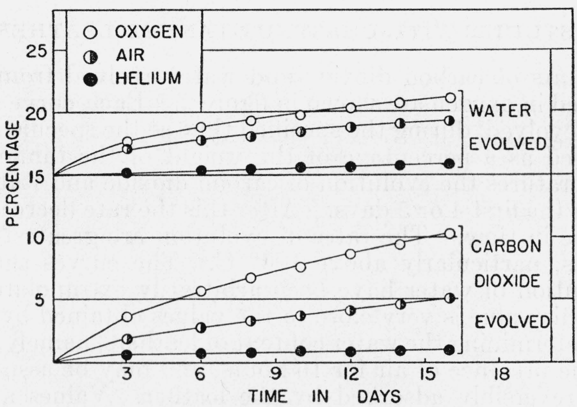

FIGURE 3.—*Rates of evolution of carbon dioxide and water from chestnut-tanned leather heated at 120° C in the presence of either oxygen, air, or helium.*

Percentages are based on the weight of the conditioned leather.

2. RATES OF EVOLUTION OF CARBON DIOXIDE AND WATER FROM VEGETABLE-TANNED LEATHERS

The method originally used in making the studies with chestnut leather required considerable time because it was necessary to continue the experiments for 2 weeks and to change samples for each experiment. A new method was therefore introduced in which one sample of leather was used throughout the entire range of temperatures and the time of heating at any one temperature was reduced to 7 days. Thus a sample was heated at 60° C for 1 week. At the end of this period the temperature was raised to 80° C and the same sample heated for another week. This procedure was repeated at 20-degree intervals throughout the range of temperatures studied. These results are recorded in figure 4, where the percentages of carbon dioxide evolved at different intervals at the specified temperatures are given. At each temperature the rate of evolution of carbon dioxide was first rapid, after which it slowly diminished. This is similar to the result

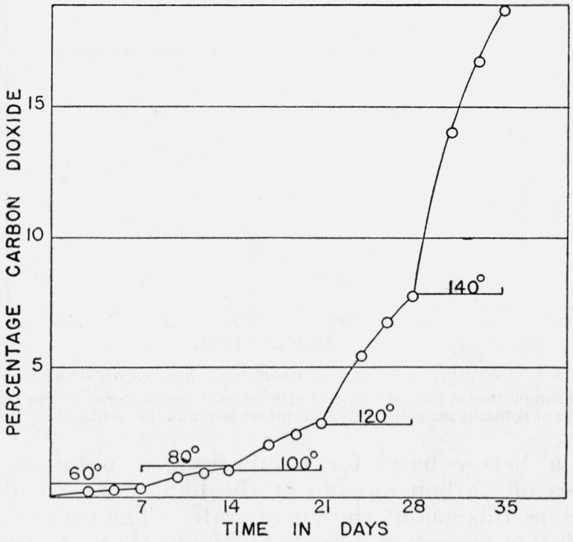

FIGURE 4.—*Evolution of carbon dioxide from a single sample of chestnut-tanned leather heated for 35 days, 7 days at each indicated temperature.*

Percentages are based on the weight of the conditioned leather.

obtained when separate samples were used at each temperature as was previously shown in figure 2. The results obtained by this method are compared in figure 5 (curve *A*) with the results obtained when separate samples were heated for 7 days at the specified temperature (curve *B*). The new method gives slightly higher results than the original because the samples remain heated for a longer period. At the highest temperature, the difference is, however, no greater than 2.5 percent, which appears to be sufficiently accurate. This method was therefore used in comparing the stabilities of the different vegetable-tanned leathers.

(a) RATES OF EVOLUTION OF CARBON DIOXIDE

The amounts of carbon dioxide evolved from single samples of chestnut, sumac, cutch, and quebracho leathers and hide powder on heating for 7 days at each successive temperature in the presence of oxygen are shown in figure 6. The amounts of carbon dioxide are expressed as percentages of the weight of tannin substance, including both tannin and nontannin. Since hide powder as shown in the figure gives off comparatively small amounts of carbon dioxide, the source of this gas is apparently the tannin substance. Therefore, if the results are calculated on the basis of equal contents of tannin

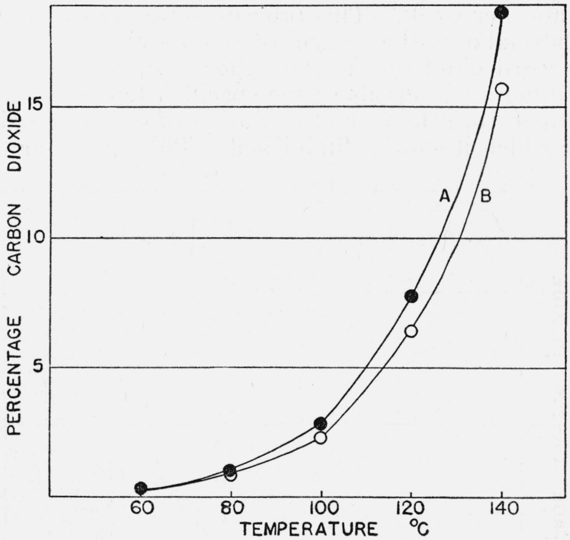

FIGURE 5.—*Evolution of carbon dioxide from chestnut-tanned leather.*

Curve *A*, single sample heated 35 days, 7 days at each constant temperature. Curve *B*, separate samples, each heated 7 days at constant temperature. Percentages based on the weight of the conditioned leather.

substance, a better basis for comparison is obtained. Chestnut leather gives off carbon dioxide at the highest rate and quebracho leather evolves this gas at the lowest rate. The order of decreasing rate of evolution of carbon dioxide by the leathers at every temperature studied is chestnut, sumac, cutch, and quebracho.

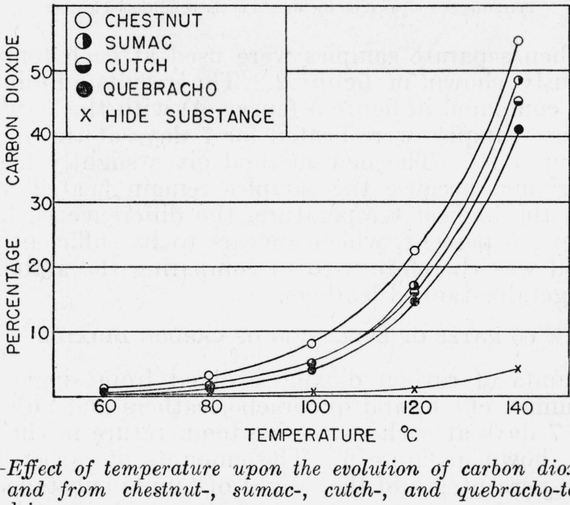

FIGURE 6.—*Effect of temperature upon the evolution of carbon dioxide from hide substance and from chestnut-, sumac-, cutch-, and quebracho-tanned leathers when heated in oxygen.*

Percentages for the leathers are based on the weight of tannin substance in the conditioned leathers. Percentages for hide substance are based on the weight of conditioned hide substance.

The comparative stabilities in the presence of oxygen, air, helium, or nitrogen with increase in temperature, as shown by the rates of evolution of carbon dioxide, are presented in figure 7, where average results for all the leathers are plotted. The results for each leather are given in table 1. The average results in the figure indicate that the increase in the amounts of carbon dioxide evolved for each 20-degree rise in temperature in either air or oxygen is in the majority of cases a multiple of approximately 3. The ratio of the amount given off in air to that evolved in oxygen is less than 1 to 3 and is therefore not proportional to the partial pressure of oxygen. The results for the individual leathers in the table indicate that in the case of chestnut leather the ratio of the amount of carbon dioxide evolved in air to that evolved in oxygen is almost exactly 1 to 2 for every temperature studied, while for the other leathers it is more nearly 1 to 3. Since only small amounts of carbon dioxide are produced in the presence of helium, it is evident that the reaction is an oxidation.

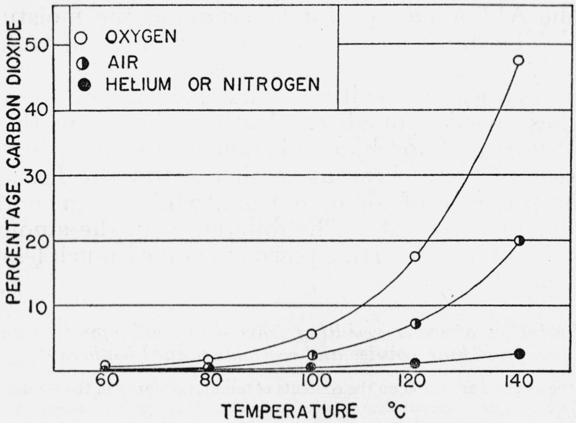

FIGURE 7.—*Effect of temperature upon the evolution of carbon dioxide from vegetable-tanned leathers heated in the presence of either oxygen, air, or one of the inert gases, helium or nitrogen.*

The experimental points represent averaged results from chestnut-, sumac-, cutch-, and quebracho-tanned leathers. Percentages are based on the weight of tannin substance in the conditioned leathers.

TABLE 1.—*Evolution of carbon dioxide from hide powder and vegetable-tanned leathers*

[Results for the leathers are based on the contents of tannin substance in the conditioned leather]

Leather	Gaseous atmosphere	Temperature— 60° C	80° C	100° C	120° C	140° C
		% CO_2	% CO_2	% CO_2	% CO_2	% CO_2
Chestnut	Oxygen	1.02	3.15	8.31	22.68	54.72
	Air	.47	1.52	4.26	11.28	27.61
	Helium	.26	.52	1.14	2.48	5.16
Sumac	Oxygen	.75	1.81	4.92	16.93	48.90
	Air	.20	.51	1.89	6.81	19.33
	Helium	.16	.20	.28	.75	2.95
Cutch	Oxygen	.60	1.43	4.94	16.26	45.66
	Air	.23	.54	1.94	6.20	18.17
	Helium	.09	.11	.23	.51	1.29
Quebracho	Oxygen	.43	1.19	4.17	14.50	41.20
	Air	.03	.30	1.25	4.55	14.74
	Nitrogen	.05	.08	.14	.41	1.06
Hide powder	Oxygen	.04	.10	.26	.95	4.05
	Air	.01	.02	.08	.32	1.21
	Nitrogen	0	0	0	.04	.18

(b) RATES OF EVOLUTION OF WATER

No attempt was made in this work to distinguish definitely between adsorbed water, water resulting from dehydration reactions, or water resulting from oxidation reactions. For purposes of comparison, all water evolved by heating at 60° C for 1 week may be considered as adsorbed water. For chestnut leather this value for adsorbed water at 60° C was 0.7 percent less than that obtained at 100° C by a method similar to the ALCA method for determining the moisture contents of leathers. The difference between the amounts of water given off at 60° C and that given off at a higher temperature was then considered as either water resulting from oxidation or dehydration reactions. These results for all the leathers, based on the content of tannin substance and for hide substance, are given in table 2. It may be observed that chestnut leather emits the least amount of water in the presence of air or oxygen, while, in general, cutch and quebracho evolve the most. The differences in the amounts emitted are, however, not large. Hide powder evolves much less water than any of the leathers.

TABLE 2.—*Evolution of water resulting from dehydration and oxidation reactions from hide powder and vegetable-tanned leathers* [1]

[Results for the leathers are based on the contents of tannin substance in the conditioned leather]

Leather	Gaseous atmosphere	Temperature— 80° C	100° C	120° C	140° C
		% H_2O	% H_2O	% H_2O	% H_2O
Chestnut	Oxygen	2.62	6.03	14.02	31.02
	Air	2.27	4.93	10.32	21.28
	Helium	2.45	3.59	5.57	9.27
Sumac	Oxygen	2.28	5.31	13.94	33.90
	Air	2.09	3.82	8.90	20.39
	Helium	1.38	2.09	4.72	8.03
Cutch	Oxygen	1.97	6.17	16.20	37.34
	Air	1.77	4.29	10.06	21.97
	Helium	1.03	1.80	3.37	6.57
Quebracho	Oxygen	2.30	6.29	15.28	32.17
	Air	1.14	3.12	8.02	17.94
	Nitrogen	.92	1.46	2.84	5.85
Hide powder	Oxygen	.38	.80	2.05	5.85
	Air	0	.24	.92	2.76
	Nitrogen	0	.13	.28	.99

[1] These results represent the differences between that evolved at the indicated temperature and that evolved at 60° C.

The amounts of water given off in oxygen or air and the amounts in helium or nitrogen with increase in temperature are compared in figure 8, where the average results for all the leathers are plotted. These results, showing the amounts emitted at different temperatures, are similar to those obtained with regard to change in rate of evolution of carbon dioxide with increase in temperature and to the relative effects of oxygen, air and helium. The amounts of water evolved in the presence of helium indicate that only a part of the water obtained in the presence of oxygen and air can result from oxidation reactions. If the amounts obtained in helium are subtracted from those obtained in oxygen and air, then the ratio of the formation of water of oxidation in oxygen to that in air is approximately 2 to 1 at the higher temperatures. These results obtained with each leather are shown in table 3.

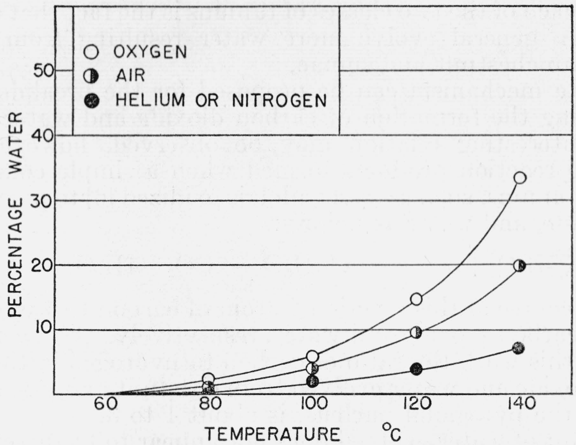

FIGURE 8.—*Effect of temperature upon the evolution of water from vegetable-tanned leathers heated in the presence of either oxygen, air, or one of the inert gases, helium or nitrogen.*

The experimental points represent averaged results from chestnut-, cutch-, sumac-, and quebracho-tanned leathers. Percentages are based on the weight of tannin substance in the conditioned leathers.

TABLE 3.—*Water resulting from oxidation reactions, evolved from vegetable-tanned leathers* [1]

[Results are based on the contents of tannin substance in the conditioned leather]

Leather	Gaseous atmosphere	Temperature			
		80° C	100° C	120° C	140° C
		% H_2O	% H_2O	% H_2O	% H_2O
Chestnut	Oxygen	0.17	2.44	8.45	21.75
	Air	−.18	1.34	4.75	12.01
Sumac	Oxygen	.90	3.22	9.22	25.87
	Air	.71	1.73	4.18	12.36
Cutch	Oxygen	.94	4.37	12.83	30.87
	Air	.74	2.49	6.69	15.40
Quebracho	Oxygen	1.38	4.83	12.44	26.32
	Air	.22	1.66	5.18	12.09

[1] These results represent the differences between that evolved in the presence of either air or oxygen and that evolved in the presence of helium or nitrogen at the same temperatures.

IV. GENERAL DISCUSSION

A relationship appears to exist between the type of tanning material and amounts of carbon dioxide and water evolved. Chestnut and sumac tannins are generally classified with the pyrogallol group of tannins, while quebracho and cutch are classified with the catechol tannins. The former give off more carbon dioxide in the presence of air and oxygen than the latter, which is in accordance with Jany's findings [1] that the amount of oxidation taking place depends in part upon the number of hydroxyl groups in the tannin molecule. Chestnut and sumac leathers heated in the presence of helium also give off more water and more carbon dioxide than the cutch and quebracho leathers heated under similar conditions. This is an indication that these tannins are of such a nature as to permit considerable direct break-down. Another point of similarity among the members of each of the two classes of tannins is the fact that quebracho and cutch in general evolve more water resulting from oxidation reactions than chestnut and sumac.

No definite mechanism can be proposed for the breakdown of the tannins during the formation of carbon dioxide and water by oxidation. An interesting relation may be observed, however, from a study of the reaction products formed when a simple compound related to the tannins, such as pyrogallol, is oxidized [6] to purpurogallin, carbon dioxide, and water as follows:

$$4C_6H_6O_3+3O_2 \longrightarrow 2C_{11}H_8O_5+2CO_2+4H_2O.$$

Thus in the course of this reaction 1 atom of carbon to 4 hydrogen are oxidized to carbon dioxide and water, respectively. From the results obtained in this work the ratio of carbon to hydrogen in the amounts of carbon dioxide and water evolved from chestnut and sumac tannins, which have the pyrogallol nucleus, is about 1 to 3.

The amount of water evolved does not appear to be directly related to the stabilities of the leathers; for example, chestnut leather is least stable with regard to the amounts of carbon dioxide evolved

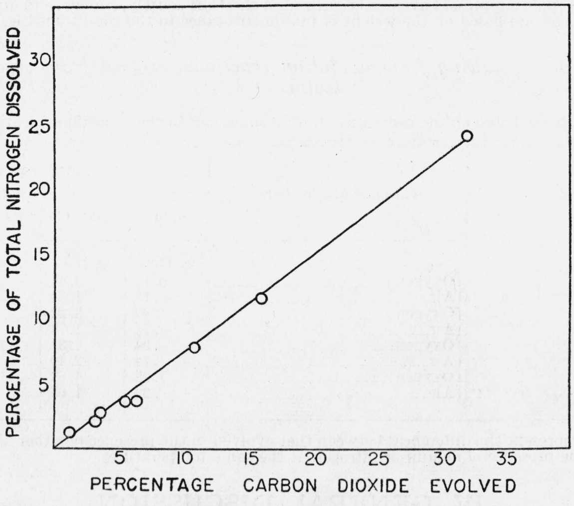

FIGURE 9.—*Correlation of the amounts of carbon dioxide evolved from vegetable-tanned leathers with the percentages of the total nitrogenous materials extractable by a 0.1 N solution of sodium carbonate.*

Percentages are based on the weight of the conditioned leather.

and to the amounts of nitrogenous materials extractable, but it gives off less water than any of the other leathers, while quebracho leather is most stable in these respects but gives off more water than chestnut leather. An explanation for this fact is apparent from a study of some of the reaction products probably formed in the course of the oxidation of a tannin. In the first stages of these oxidations quinones are formed. The formation of quinones by oxidation of polyphenols results in the elimination of water. Since quinones have strong tanning properties, the tanning effect of a polyphenol might actually be enhanced by oxidations in which water is formed.

The present work and the results from previous work indicate that the amounts of carbon dioxide evolved are related to the comparative stabilities of the leathers under various conditions. In a previous paper [5] the increase in the percentages of the total nitrogenous materials extractable from leathers with increase in the temperature of aging in the presence of either oxygen, air, or helium is shown. The curves in figure 4 of that paper are similar to those shown in figure 7 of the present paper, where the increases in the amounts of carbon dioxide evolved with temperature of heating are given. The results in these two figures were combined by plotting the percentages of the total nitrogenous materials extractable at one temperature, against the carbon dioxide evolved at the same temperature. This is shown in figure 9. A linear correlation is obtained between the carbon dioxide evolved and the percentages of the total nitrogenous materials extractable. It therefore appears that the chemical breakdown in the tannins is directly related to the chemical deterioration that takes place in the hide substance.

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