



Fig. 1. $\ln(100-c)$ as a function of time.

removed. In theory it is possible to calculate the specific activities of the sulphur liberated in the two stages of the desulphonation, but to do so on the basis of the present incomplete data would be premature.

Experimental. Active BaS (from Oak Ridge) was diluted with inactive sulphide and the sulphide ions were precipitated as CdS. Hydrogen sulphide, liberated by treatment with conc. orthophosphoric acid, was combusted to sulphur dioxide which was absorbed in 2 N sodium hydroxide. The active sulphite solution was acidified to pH 1.5 with inactive sulphur dioxide and then used for the sulphonation of the Kullgren acid⁴. (Temperature 135°, time 6 hours.) The product was isolated in the usual manner⁴. Sulphur was determined by the method of Salvesen and Hogan⁵.

For desulphonation, the active barium lignin sulphonate (0.8 g) was dissolved in water and the solution was heated to 100°. Sodium hydroxide solution (0.2 mol), preheated to 100°, was then added (final volume 80 ml, nitrogen atmosphere). The reaction was stopped by the addition of conc. hydrochloric acid. The sulphur dioxide was expelled by a current of nitrogen and absorbed in a Grote-Krekeler apparatus containing dilute hydrogen peroxide solution. The sulphuric acid formed was determined by precipitation with barium

chloride, and the barium sulphate precipitate prepared for the measurement of the S^{35} activity by centrifugation in tubes with removable bottoms, using a refined procedure developed by G. Aniansson and A. Edhborg (cf. Larson *et al.*⁶).

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Studies on the Chemistry of Oil Tanning. I. Formation of Peroxide Groups in the Oils

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The very old method of tanning, oil tanning, is, in this country, carried out in the following way. After the skins, mostly from sheep or deer, have been split, the flesh layers are impregnated with oil which is squeezed into the skins with heavy beaters in a stamping mill. This milling is repeated about ten times. Between every treatment the skins are exposed to the sun for about one hour and then packed close together until the next milling, new oil being sometimes added. Between the last millings the skins are hung in heated rooms where the tanning process proceeds rapidly with the liberation of heat and the skins assuming a yellowish colour. When heat ceases to be evolved the tanning process has finished.

The oils used in the tanning are highly unsaturated, usually marine oils, such as

cod liver and seal oils, preferably having an iodine number about 120–160 and an acid number about 20–40. Fahrion¹ suggested that the reactive groups involved in the tanning process are peroxide groups formed by the action of atmospheric oxygen on the unsaturated constituents of the oils. This theory has been questioned by other authors (for a discussion, see Gnamm²), but seems to be generally accepted today. Probably because reliable methods for the determination of peroxides are of fairly recent origin, it seems that the oil tanning process has never been studied by following it by means of peroxide determinations. As a contribution to the chemistry of oil tanning, this paper reports the results of a series of such studies.

The material used was a batch of sheep skins tanned by "Dansk Chromlaederfabrik", Copenhagen, by the method outlined above, samples being taken out after each milling. The oil was extracted from each skin sample by shaking with xylene for an hour and then centrifuging for 5 minutes. The acid numbers, iodine numbers, and peroxide values of the resulting solutions were then determined. The values were calculated on the basis of the dry substance in the xylene solution. The acid number was determined by titration with 0.1 *N* KOH, the iodine number by the method of Rosenmund & Kuhnhenh³, and the peroxide value by the method⁴ described by the present authors. The results are summarized in Table 1.

It will be seen that the values are somewhat erratic. This is due partly to the fact that the heterogeneity of the material makes the sampling difficult, and especially to the addition of fresh oil carried out between the millings.

The results show, however, that the acid number decreases sharply initially, from 34 for the oil before the tanning to 20 after the first milling. Probably the oil is partly neutralized by residual alkali from the limeyard. After the 7th milling

Table 1.

Days after 1st milling	Number of millings	Acid number	Iodine number	Peroxide value
0	0 (fresh oil)	34.0	134.0	22
0	1	20.0	115.5	135
3	2	21.8	126.7	182
5	3	18.5	110.0	251
6	4	20.5	105.3	646
8	5	22.2	91.1	72
9	6	21.6	103.8	314
10	7	28.7	103.1	2 340
12	8	32.9	94.5	2 150
14	9	36.3	63.2	900
29	9	34.8	71.9	568

when the tanning process proceeds rapidly, the acid number increases.

It was to be expected that the iodine number of the oil would decrease as the processes related to peroxidation of unsaturated compounds normally lead to saturation of the compounds. In this study, the iodine number was found to decrease slowly at first, then more rapidly as the peroxide formation became more vigorous.

The peroxide values, finally, increase steadily during the course of the first few days, then quite violently after the 7th or 8th milling when the tanning process, as judged by the heat formation, is at its maximum, and then decrease slowly as the process ceases. These observations indicate very definitely that peroxide formation plays a decisive role in the chemical processes underlying oil tanning.

A preliminary study of this problem was carried out jointly by J. Glavind and a student of his, N. Klenow. This preliminary work was published by Klenow⁵, on his own initiative, in connection with certain other investigations.

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Studies on the Chemistry of Oil Tanning. II. On the Chemical Nature of the Bonds between Peroxidized Fats and Collagen

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As mentioned in the preceeding paper, the most generally accepted theory of the chemistry of oil tanning was advanced by Fahrion¹, who suggested that peroxide groups in the fats are the reactive groups which combine with the collagen of the skin. In our experiments we were able to confirm Fahrion's views. As to the nature of the bonds between the peroxidized fats and collagen, Fahrion thinks that peroxides react with collagen ($R'NH_2$) in a manner which can be summarized as follows:

On this theory oil tanned leather should be a derivative of hydroxylamine. This seems *a priori* very improbable, and, as has been pointed out by Gnamm², has never been proved. Furthermore, it is a well-known fact that the tanning process takes place only at an acid pH. For instance, L. Klenow³ followed the pH during oil tanning and found that it decreased from 12 to 3.5 and that the tanning did not start until the pH had decreased to 5.5. In the preceeding paper we reported on a similar observation: that it was not until the acid number began to increase rapidly, *i.e.*, the alkali in the skin had been neutralized, that vigorous peroxidation and the tanning process itself commenced. These facts make it appear highly improbable that the peroxide groups of the fats do react at all with the amino-groups of the collagen since, on the acid side of the isoelectric point of collagen (about pH 4.8) only a very small proportion of free amino-groups should be found.

Estimation of the amount of fixed fatty acids. Samples of skin and leather were extracted with petrol ether and ethyl ether to remove free fat. The ash contents of the dried samples were determined by incineration and the nitrogen contents by the Kjeldahl method. The skin contained 3.3 % ash and 17.27 % N, corresponding to 17.80 % N on the basis of the organic matter. The leather contained 3.3 % ash

