

adopt any process which, if it gave the same results, would add a fraction of a penny to the cost of production, even if the leathers produced by this means were slightly better. Thanks to Procter's work and to the work of other of their members, they had advanced very considerably in their knowledge of the chemistry both of the raw materials and of the process of leather manufacture during the last eighteen years. They now understood more fully the action of the acids and alkalis upon hides. They understood how to accelerate the penetration of the tan through the hide substance—so much so that really good leather could be turned out in the tanyard in fourteen days—therefore, the advantage of speed claimed by those who advocated the use of electricity was not now so important a matter as it was eighteen years ago. The authors, while they had not dealt with the subject from a practical standpoint, had certainly given some theoretical points for consideration, and he was thinking how those theories which they had propounded might be carried out on a practical scale. If they would come to the Leathersellers' Technical College he would provide 20 or 40 hides, or as many as they wanted, and they could fit up their apparatus, and if they got any more weight than he could get, or if they could produce leather more quickly than he could, or better leather, and, last but not least, cheaper, they would have him for a convert at once. He would be prepared to take corresponding hides to them, using the same liquors but using drums or paddles, as the case might be. All that took place in the process of leather manufacture was not yet understood, but much information had been gained by the work of Procter and others in connection with colloidal chemistry, and the researches which had been carried out dealing with the effect of swelling and tanning of hides by means of acids and various salts in the liquors. He did not desire to convey the impression that he looked upon the use of electricity in connection with tanning to be hopeless, but he had tried it with weak currents, alternating and direct, and had tried it all ways, but he had now given it up. Another point, and one on which he bowed to the authors of the paper, was that he was not sure whether his process would conserve the tanning acid as much as they claimed to do. They did not give figures, but they pointed out that there was not the same decomposition of tannic acid by their process as by the ordinary processes, but he had been taught to believe that the decomposition of tannic acid, or rather the hydrolysis of tannin, produced beneficial acids, and the fermentation of the glucoses produced acids. Unless the early liquors were kept acid enough, that is to say, if one did not have a proper fermentation going on in the tanyard which could produce sufficient lactic, acetic and propionic acids, they would not get sufficient swelling. If the leather was not sufficiently swelled in the early processes of tanning they would neither get sufficient weight into the leather, nor would the leather be thick and solid, as it must be to possess good wearing qualities; and unless these acids were present there would not be the deposition of semi-soluble substances inside the hide. It had been claimed as an advantage that the electrical process kept the liquors sterile. He would be rather sorry for the tanner whose liquors were sterile, because, unless he had misunderstood the authors, he was afraid that if the liquors were kept sterile and there was no acidity present, the leather would be flat, tinny and brittle, and practically would not produce a commercial product.

Dr. E. RIDEAL, in reply, said it had been mentioned that the decomposition at the electrode varied, and it seemed to have been gathered from the paper that the rate of movement in the liquid itself varied with the nature of the electrodes used. That was not what they had intended to convey. What they had intended to say was, that, supposing they had a soluble anode, the decomposition was less than if they had an insoluble anode, because, instead of oxygen being liberated and attacking the tanning substance, the electrode itself went into solution and the tannic acid was left unchanged. The actual actions in the body of the electrolyte itself, the velocity of the tanning, and the rate of diffusion was not influenced very much by the electrodes. With reference to an iron chloride indicator, certainly iron travelled a certain rate with the current, but there was always sufficient iron to give a colouration; and the natural diffusion was also a check on

it, because the same error ran through the whole of the results, which were strictly comparable.

With reference to the unsuccessful nature of the past experiments on practical electric tanning on a large scale, he thought a great deal could be attributed to the high conductivity of the bath itself. When they worked on a large scale they got little traces or possibly even large amounts of salts of lime, etc., which got in from the previous treatment undergone by the hides before they were ready for the tan bath; that affected the conductivity and thus permitted a great deal of current to go through which was not aiding the tanning, which in fact acted rather detrimentally to the tannic acid; for the greater current caused greater action at the electrodes themselves, which action decomposed the tannic acid and involved a great waste of tannic acid. If, however, the bath had to be acid, carbon electrodes should be used instead of copper ones. They did not intend to suggest that the liquor was kept sterile by means of electric current itself, but they suggested it should be kept sterile by adding some suitable steriliser, provided that the right quantity of acid which was demanded was kept there. Apparently in practice the baths might get very powerfully acid and the liquor become inefficient, or they might cease to be sufficiently acid. There ought to be some degree of acidity which is the correct acidity for hide treatment. Procter was not quite certain which was the correct acidity, but that should be experimentally arrived at.

THE JOINT ACTIONS OF CATALYTIC AGENTS.

DEHYDRATION OF ETHYL ALCOHOL AND ETHYL ETHER.

BY GENERAL W. IPATIEW.

In a communication by Sprent (this J., 1913, 32, 171—173) on a technical process for the preparation of ethane is described a method of hydrogenisation of ethylene by hydrogen and reduced nickel under pressure and at a high temperature. The ethylene employed was obtained by passing the vapours of ethyl alcohol over alumina as catalyst.

In this communication no reference was made to the fact that the use of alumina was first made by myself (Ber., 1903, 36, 2016) in a series of experiments in which it was shown that by means of this agent at temperatures of 350°—360° C. theoretically quantitative yields of ethylenic hydrocarbons could be obtained from the respective aliphatic as well as cyclic alcohols (Ber., 1904, 37, 2990). Shortly afterwards I showed that the alumina required special preparation, otherwise it was not active. For efficient action it must be precipitated and then gently ignited—only so much that it will still dissolve readily in hydrochloric acid or caustic soda.

I showed that in the presence of alumina ether was first formed, from the alcohol, which then split up into water and ethylene, and this first phase of the catalytic action was a reversible one:—



At the same time I showed that methyl ether could be prepared by heating methyl alcohol and alumina in my high pressure apparatus. Although these results were published in German in the *Berichte*, publications have appeared from Senderens and Mailhe several years later, since 1908, in which they state that alumina is the most convenient catalytic agent and that this alumina must be heated to redness, and that this ignited oxide converts alcohols into ethers or ethylenic hydrocarbons, depending on the temperature to be subsequently employed.

As Senderens and Mailhe do not refer to my work in their publications, although attention (Ber. 1910, 43, 3383) was drawn in the *Berlin Berichte* to this lapse, Sprent naturally, but in error, ascribes the priority of employment

of alumina to them. In addition Sprent does not mention my experiments on hydrogenisation of ethylene under the influence of catalysts and high temperature and pressure, which also appeared in the *Berichte* (Ber., 1909, 42, 2089; this J., 1909, 745).

At present I am continuing work on the simultaneous or joint action of catalytic agents on the hydrogenisation and dehydration of organic compounds: the results so far show that by the simultaneous action of catalysts the temperature necessary, can be reduced and the process proceeds more energetically. For instance when a mixture of nickel oxide and alumina is employed for hydrogenisation the reaction takes place at 200° C. instead of 300° C., and the reduction in the case of ketones (for example) proceeds to the completely saturated hydrocarbons. Camphor is also completely converted at 200° into $C_{11}H_{18}$, isocamphane.

Experiments on the decomposition of alcohols under ordinary pressure in contact with a mixture of alumina and cupric oxide have shown that the temperature at which dehydration takes place is 25°–30° lower than when alumina is the sole agent.

Further work is being continued in this direction.

Yorkshire Section.

Meeting held at the Queen's Hotel, Leeds, on Monday, April 14, 1913.

MR. GEORGE WARD IN THE CHAIR.

PRELIMINARY NOTES ON THE OXIDATION OF OILS.

BY DR. HARRY INGLE.

Many methods have been devised for determining the increase of weight when oils are exposed to air; Kissling (this J., 1894, 117; 1895, 479) has examined this at ordinary temperature and at 100°–105° C. Livache (this J., 1886, 494) spread the oil upon finely divided lead and determined its increase in weight. Bishop (1904) used fine silica, dissolving the oil first in petroleum spirit as a means of offering a large surface for oxidation. The results from all these trials agreed but little with oxygen absorption calculated from the iodine value.

Lippert (Chem. Rev., 1899, 65) modified Livache's experiments and showed that in the case of linseed oil on copper powder an increase in weight of from 13.4 to 19.25 per cent. was obtained.

Max Weger (Chem. Rev., 1898, 213, 236) carefully examined the oxygen absorption of oils by the "plate method," in which weighed quantities of oils were spread on thin glass to nearly equal thickness and the increase of weight noted. For linseed oil the increase was 18 per cent. (calculated from iodine value 11.4). For Chinese wood oil the increase was 14–16 per cent. (calculated from iodine value 10.1). For hemp oil the increase was 13.5 per cent. (calculated from iodine value 9.9).

To ascertain the relationship of the iodine value to the increase of weight of exposed oils, the papers of Weger (Chem. Rev.) and Ingle (this J., 1902–1904) should be consulted.

It has been shown that the gain in weight of an oil on exposure to air differs according to the humidity of the atmosphere (Lippert, *Z. angew. Chem.*, 1905, ii 3). The author has examined cottonseed and linseed oils, the free acids and ethyl esters, with a view to determining the exact relationships between the iodine value and the oxygen absorption; the examination was carried out in ordinary moist

air first and then in dried air. First of all samples of the free acids of a Baltic oil of iodine value 198 were prepared and the ether driven off by distillation, coal gas being finally driven through the flask. These acids showed an iodine value of 202.5. An ordinary (probably Plate) oil of iodine value 181.0 was then saponified and the acids removed by ether, which was distilled off as before; their iodine value was 182.5. The acids were converted into their ethyl esters by alcohol and dry hydrogen chloride. Pieces of filter paper were soaked in a 1 per cent. solution of manganese resinate in benzol and dried in a desiccator over calcium chloride. Drops of the acids or their ethyl salts were then distributed over the paper as evenly as possible, exposed to air, dried in the desiccator, and weighed at intervals.

Increase in weight of the free acids and ethyl esters of linseed oils.

	Baltic acid.	Ordinary acids.	Ethyl Esters of ordinary oil.
Iodine value (Wijs) of original oil	198	181	181
Iodine value of sample	202.5	182.5	153
Theoretical oxygen absorption from iodine value:			
$O = \frac{1}{2}$	12.75	11.5	9.8
$O_2 = \frac{1}{2}$	25.5	23.0	19.6
Found:			
22½ hours	12.7	12.7	10.4
26 "	13.0	12.9	
42½ "	—	—	9.8

Weger and Mulder obtained for the liquid acids of linseed oil 15.6 to 17.9 (calculated value of the liquid acids is 15.7; $O = 2 I$). The acids used above contained both liquid and solid acids (compare Bauer and Hazura and Ingle; this J., 1902, 594) and so their oxygen absorption is proportionately lower.

The next experiments were intended to show the actual change in the composition of linseed oil acids on exposure to air. Fahrion has shown that oxidised unsaturated acids are insoluble in low boiling petroleum ether. I have repeatedly tried the method with blown oils, and am convinced of its usefulness. Some of the acids from the ordinary oil were spread upon glass and exposed for 20 months under cover. Even then they remained rather tacky. They were then removed from the glass and extracted with petroleum spirit, ether, and alcohol. The following table gives the results:—

Petroleum spirit soluble	3.26	{ Iodine value 41.5 Acid value 158 Colour: Yellow
Petroleum insoluble but ether-soluble	80.41	{ Iodine value 47.0 Acid value 151 Saponification value 328 Amber brown
Petroleum and ordinary ether-insoluble but alcohol soluble	17.42	{ Iodine value 22 Acid value 95 Saponification value 133.4
	100.79	

It is difficult to explain the above results, for the solid fatty saturated acids of the oil amount to some 10 per cent. (Bauer and Hazura and others).

In order to study the action of dry air upon the oils, the following experiments were carried out—Strips of filter paper 4 in. × 18 in. were dipped into a 1 per cent. solution of precipitated manganese resinate dissolved in benzol and hung up to dry. One of them was then dried in a wide drawn-out tube closed with a tight-fitting rubber stopper through which a tube passed, and a current of dried air drawn through; when constant weight of the tube and filter paper was obtained, the paper was spotted with the oil (weighed) as equally as possible. The tube was