Yorkshire Section.

Meeting held at Queen's Hotel, Leeds, on Monday,
November 30th, 1914.

MR. F. W. RICHARDSON IN THE CHAIR.

THE OXIDATION OF OILS AND OF FATTY ACIDS.

BY J. HYLAND AND L. L. LLOYD.

Owing to the production of partially hydrogenated oils, having chemical and physical values practically identical with those of olive oil, which are being placed on the market as a substitute for olive oil for use in the worsted trade, etc., an attempt has been made to discover some test by means of which these oils could be valued. Some hydrogenated oils have been placed on the market that have an iodine value practically the same as that of olive oil, but which, unlike olive oil, gradually become tacky when exposed in thin films to moist air, such as oiled tops, etc.

From the communication by Hird and one of us, on the action of sulphur dioxide upon oils (see this J., 1912, 317), it appeared possible to obtain a quantitative production of sulphuric acid by the action of sulphur dioxide and oxygen upon oils for a definite time at constant temperature. We have been able to obtain a constant yield of sulphuric acid from certain oils when diluted with several inert solvents. With many oils, however, particularly those that readily char with sulphuric acid, a constant production of sulphuric acid could not be obtained. With genuine pure oils fairly characteristic colour reactions may be observed during the action of sulphur dioxide and oxygen upon them. The colour reactions of the commercial oils vary so much, probably due to other oils having been in the same vessels for transport, etc., that it is of little value tabulating these results.

The yield of sulphuric acid by the action of sulphur dioxide and oxygen upon oils is greatly increased in the presence of a drier, the increase varying with the amount and nature of the drier. The order of activity, calculated from the production of sulphuric acid, of the metals which have been tested when dissolved as resins in the oils, is as follows:—Copper, cobalt, manganese, nickel, chromium, and iron. Lead did not assist the formation of sulphuric acid.

It has also been observed that the addition of small amounts of oxidisable oils to the "non-drying oils" greatly increases the rate at which these oils absorb oxygen, thicken, and become tacky. Similarly the addition of oxidisable oils to the "non-drying oils" affects the amount of sulphuric acid formed by action of sulphur dioxide and oxygen. In each of these cases the oxidisable oils apparently act as oxygen carriers or catalytic agents.

Ingle (this J., 1913, 639—641) has shown that with drying oils the amount of oxygen absorbed in dry air is in the ratio $2I=2O$ or $I_2=O_2$, but if the air be moist the peroxides thus formed are decomposed with production of volatile compounds—aldehydes and acids; also that the free acids of linseed and other oils only absorb half the amount of that absorbed by their glycerides. The same remarks also apply to their ethyl esters, these only absorbing one atom of oxygen for every two atoms of iodine absorbed. Ingle also showed that the maximum absorption of oxygen by the oils took place in dry air; moisture tends to lower it, and after maximum absorption, loss begins to take place.

We have made similar experiments with the so-called "non-drying oils" that are used in the textile trade for combing, spinning, etc., using both dry and moist air, to find whether they were oxidised to any great extent, and also to see whether the absorption of oxygen at any given temperature is quantitative. From a practical point of view more importance has been attached to the action of moist air, as better representing the conditions under which these oils are used.

Pure oleic acid was prepared from olive oil by means of the lead and barium soaps. Some of this acid, after having dissolved in it 5% of manganese resinate, was exposed in a very thin layer to the ordinary atmosphere. The acid increased in weight very slowly, the maximum being reached in three months. The iodine value was taken before exposure and after the maximum gain in weight. The results are given in the table. The acid although still liquid was very viscous. Attempts were then made to increase the rate of oxidation, using the apparatus illustrated. It

consists of a wide glass tube, A, surrounded by a water jacket, B. The water jacket is connected by glass tubing to the copper tube, C, for heating purposes and is also fitted with a water trap, T. The boats containing the oil, etc., were supported on a strip of plate glass inside the tube, A. A thermometer was also placed in the bottom of this tube. When the water is rapidly boiling in the copper tube, the temperature in the tube, A, remains extremely constant at 97°—98° C.

A weighed quantity of oil, about one gram, was exposed for oxidation on purified quartz contained in broad platinum boats, the boats containing about 10 grms. of finely powdered quartz which had been purified by repeated extraction with hydrochloric acid, washed, and dried. A piece of thick platinum wire was also weighed with the boat, this being used for stirring the mixture. Air was drawn slowly through the tube, A, by means of an aspirator, about 1.5 litres passing per hour. When dry air was used, it was first passed through a wash bottle containing sulphuric acid and then through two calcium chloride tubes. A calcium chloride tube was also placed between the exit of the tube and the aspirator to prevent diffusion of moisture into the tube. When moist air was used it was drawn through a wash bottle containing water and then through a tube containing cotton wool. The weighed boats and contents, etc., were exposed to oxygenation and were taken out at intervals, dried in a desiccator and weighed. When the maximum had been reached or just as loss began to take place, the contents of the boats were extracted with ether, the ether driven off, and the iodine value taken.

The treatment was at first carried out at 97°—98° C., but it was soon observed that the products of oxidation were far too unstable at that temperature, and that loss in weight began to take place long before a theoretical increase had been reached.

Other temperatures were then tried, and 50° C. was found to be the highest temperature at which

constant results could be obtained, the oxidation at this temperature being far quicker than at the ordinary temperature. This temperature was consequently used for the experimental work.

the oxidation products of these bodies than those of the free acids. It will be observed from the table that the oils are nothing like saturated when the maximum gain in weight is obtained, the

TABLE I.

Oil and additions.	Conditions of experiment.	Maximum gain in weight. %	Time.	Calculated iodine equivalent of gain.		Iodine values by determination.		Actual decrease in iodine value.
				O=I ₂	O ₂ =I ₂	Before.	After.	
Oleic acid + 5% manganese resinate..	Ordinary air, cold	5.8	3 months	92.0	46.0	90.8	51.6	39.2
Oleic acid + 5% manganese resinate .	Dry air, 50° C.	4.3	90 hrs.	68.2	34.1	90.8	36.6	54.2
Oleic acid + 5% manganese resinate .	Moist air, 50° C.	4.1	30 hrs.	65.0	32.5	90.8	52.7	38.1
Oleic acid alone	do.	4.9	250 hrs.	77.7	38.8	90.0	40.4	49.6
Ethyl oleate alone	do.	4.5	270 hrs.	71.4	35.7	75.0	40.2	35.4
Ethyl oleate + 5% manganese resinate	do.	4.4	45 hrs.	69.8	34.9	70.5	38.1	38.4
Olive oil alone	do.	5.8	114 hrs.	92.0	46.0	87.0	46.5	41.4
Olive oil + 5% manganese resinate...	do.	5.6	47 hrs.	89.2	44.6	88.0	40.2	48.7

The numbers in columns 5 and 7, and also the numbers in columns 6 and 9, should agree for each separate experiment.

From the above table it will be observed that the increase in weight corresponds in almost every case to $O=I_2$. With oleic acid, however, a theoretical increase in weight is not obtained, which is doubtless due to the fact that the oxidation products are so unstable at this temperature that they decompose and volatilise some time before complete oxidation has taken place, and it is this decomposition which no doubt accounts for the slight irregularity in the results for the oleic acid. The volatility of oleic acid and of ethyl oleate was tested at 100° C. in a current of carbon dioxide; in 15 hours about 0.5% was lost in either case, but at 50° C. no loss was obtained.

The effect of moisture is apparent from the difference in the iodine values of oleic acid and resinate in dry air and the same mixture in moist air. In dry air the reduction in iodine value is 54.2, in moist only 38.1, whereas the difference in the increase in weight would only account for a difference in the iodine value of 3.1, the actual difference being 16.1. The greater reduction in iodine value in dry air than in moist, with approximately the same increase in weight, is probably due to polymerisation taking place more readily in dry than in moist air or to the formation, by addition of water, of dihydroxy compounds, etc. But with the esters, ethyl oleate or olive oil, figures much nearer the theoretical value have been obtained, showing the greater stability of

actual decrease in iodine value being approximately only half the original iodine value, so that the ratio between the increase in weight and the reduction in iodine value is really $O_2=I_2$, and not $O=I_2$. It is highly probable that condensation or polymerisation takes place, the double bonds being thus shielded from oxidation, or that the oxidation products combine with some of the unoxidised compound during resinification.

The experiments in dry air tend to show that complete oxidation is possible, but the present communication only deals with the absorption of oxygen until a maximum gain in weight is obtained; further oxidation is no doubt possible, but is accompanied by loss in weight.

Moist air appears to prevent the complete oxidation of glycerides, the oxidation products having approximately half the original iodine value, whereas with fatty acids moisture actually aids oxidation.

From the knowledge obtained in the above experiments it seemed desirable to compare the liability to firing of oils of different iodine values. The iodine values of a number of oils were determined and these oils were then tested by the Mackey Cloth-Oil Tester; 14 grms. of oil were distributed on the usual amount of cotton wool and allowed to remain in the tester until a dangerous temperature had been reached or until the temperature remained practically constant. The oily "wool" was removed, extracted with

TABLE II.

Oil.	Maximum temperature.	Time.	Iodine value before.	Iodine value after.	Decrease.	Effect on cotton wool.	Remarks.
Cottonseed oil	217° C.	1 h. 25 m.	111.0	75.1	35.9	Charred	Test stopped to prevent firing, etc.
Malaga olive oil	210	4 h. 38 m.	87.9	52.0	35.9	Charred	do.
Sperm oil	102	5 h.	75.0	65.1	10.5	No effect	Temperature was rising extremely slowly.
50% oleine (dark) contd. 41% free fatty acids	106	3½ h.	88.0	67.1	21.5	do.	This was a maximum temperature and remained constant for a considerable time.
Unsataponifiable matter from the 50% oleine	97.2	3 h.	92.0	70.2	10.7	do.	do.
Fatty acids from the 50% oleine...	98.5	5 h.	80.0	67.0	13.0	do.	Still rising, but extremely slowly.
70% oleine contd. 61% free fatty acids	98.5	3 h.	71.8	65.4	6.4	do.	Constant at this temperature for a considerable time.
Unsataponifiable matter from the 70% oleine	96	3 h.	62.1	60.3	1.8	do.	do.
Fatty acids from 70% oleine	99.5	5 h.	77.8	72.1	5.7	do.	Still rising, but extremely slowly.
Oleic acid	200	1 h. 45 m.	90.0	62.5	27.5	Charred	Stopped to prevent firing.
Ethyl oleate	213	5½ h.	75.0	41.8	33.8	Charred	do.

ether, and the iodine values of the extracted oils determined. In those tests where a dangerous temperature was reached the inlet and exit tubes were tightly corked and the vessel cooled as quickly as possible. The results are given in the Table II.

It will be observed that with all of the oils where any considerable degree of heat was produced, it was accompanied by a considerable decrease in the iodine value, while in practically every case the extracted oil was much thicker and darker.

It is well known that an olive oil containing free fatty acids is much more dangerous than one which is neutral. The time for oleic acid to attain a dangerous temperature in the Mackey Tester is short compared with ethyl oleate or Malaga olive oil. Comparing the iodine values of these substances it does not appear that the liability to fire is governed entirely by the unsaturated nature of the oil but also by the constitution of the substances.

The experiments with distilled oleines, with the fatty acids, and with the unsaponifiable matter separated from these oleines, indicate that the iodine value is of little value as a guide to liability to firing. Although firing is due primarily to oxidation, this alone is not the only cause; if it were, then the 50% oleine which gave a decrease in iodine value of 21.5% should have shown a considerable rise in temperature. It is evident that firing is due to some reaction other than oxidation.

Although a high acid content in olive oil aids firing, it appears not so much the mere acidity, as the constitution of the fatty acids, which governs their behaviour. Also it is not simply the oxidisability of the fatty acids, since the 50% oleine oxidises almost as much as the oleic acid and is yet so much safer. It therefore appears probable that the decomposition of the oxidation products plays an important part.

The experiments with ethyl oleate show it to be far safer than the free acid. The previous experiments (those in the tube) show that it oxidises almost as rapidly as the acid; but with the ester an almost theoretical increase in weight is obtained, whereas with the acid decomposition occurs some time before the theoretical increase in weight is reached. This shows that the oxidation products of ethyl oleate are much more stable than those of oleic acid, and this fact, coupled with the results obtained in the Mackey Tester, upholds the view that the production of heat is due to the decomposition of the oxidation products, and that the more dangerous oils are those whose oxidation products are more easily decomposed or polymerised.

Oleic acid is oxidised more readily in moist air than in dry, as is shown in the first table. This no doubt accounts for the fact that moisture increases the tendency of the oils to fire, when on the fibre, and especially those rich in oleic acid.

By comparison of the results obtained with oleic acid from olive oil and with oleic acid obtained from distilled oleine, it appears that the constitution of the oil or acid is of most importance from a firing aspect, and that the change in the properties is due to change of constitution probably brought about during distillation. It appears that with regard to stability not only unsaturation but also the position of double bonds and the influence of steric groups must be considered.

Further work is being carried out upon the oxidation of oleic acid.

DISCUSSION

The CHAIRMAN stated that the Bradford Wool-combers' Association had tried the use of arachis

oil on "tops" and at first with apparent success, only to discover later that the tops became very sticky. The trial referred to was a small laboratory experiment only, and the result amply proved that arachis oil was a drying oil and was quite unsuitable to replace olive oil as a lubricant for tops. As a result of this laboratory test, arachis oil was never tried on a larger scale.

Prof. H. R. PROCTER quoted several papers published from his laboratory on this subject. One of them (this J., 1898, 1021), on the relation of the constitution of oils to refractive index and specific gravity, showed that both were raised by the presence of double bonds, and also by oxidation, but that the refractive constant, whether calculated by Gladstone and Dale's formula or by that of Lorenz and Lorentz, was lowered by oxidation. The former formula gave a value near 0.5 for all oils, but it was the apparently small differences from this figure which were significant. In their experiments on oxidation (this J., 1905, 1287) the oils were blown in test tubes instead of being exposed in thin films. While such experiments had a technical importance, the only way to obtain precise information was by further study of the chemical constitution of the different oils.

Mr. W. McD. MACKAY agreed with Dr. Lloyd that the iodine value did not give a reliable criterion as to whether or not an oil was safe from the insurance point of view. One point to be borne in mind when considering the indications given by such an instrument as the Cloth-Oil Tester was that one was dealing not with an oil alone but with the oil in very intimate contact with cotton wool, and there was little doubt that the action between the oil and the cotton had something to do with the result. Thus, if wool were used instead of cotton wool, the action was slower, and it might be useful to make some experiments of the same nature as those of Dr. Lloyd, spreading the oil on an inert substance such as, say, glass wool.

Mr. T. FAIRLEY considered that the very different results obtained by the authors when using dry air, from those obtained when moist air was used, were due to the presence of moisture, which gave scope for bacteria to start the heating process. In every case where a cargo of wool from Australia had been shipped in a wet condition, a case of spontaneous combustion had arisen. The raw wool contained about 33% of fatty matter. The same applied to cotton shipped in a wet state. He had made experiments with both cotton wool and wool, and as might be expected there were great differences. Raw wool was also different from scoured wool. Scoured wool was used when an insurance company wished to know what might happen in a factory. The last investigation which he had carried out was in connection with rape oil. In the Leicester district rape oil was used extensively, and he found that pure oil was perfectly safe, in fact, almost as safe as olive oil.

Prof. J. W. COUS thought that the investigation of the connection between rise in temperatures and chemical changes carried out on oxygen absorbing substances of established composition could not fail to be of service, not only as regards those substances, but also as forming a basis for the understanding of more complicated phenomena of the same order, such as the spontaneous combustion of coal. Dr. Lloyd had expressed the opinion that the evolution of heat was often due, not to the primary oxidation, but to after-decomposition of the compounds so formed, and experimental evidence in support of that view would be interesting to consider. Mr. Winmill and his collaborators had decided that, so far as coal was concerned, it was advisable to

commence an experiment at a low temperature if a deduction was to be drawn as to the liability of the coal to spontaneous combustion. Were the same considerations not applicable in this case?

Mr. RUSBY stated that there had been several cases of serious fires in the district caused by the spontaneous combustion of oiled wool. It would be very helpful if in such cases the insurance companies would have the oil used tested and the results published. In his opinion the presence of moisture was a chief predisposing cause. In regard to the objection to the presence of fatty acids in olive oil used in Bradford, it was not that the acids in themselves were objectionable, but that their action on the copper and iron in the combing machines formed minute quantities of salts which catalytically caused gumming of the oiled tops. He deprecated the use of resins by the authors as not imitating anything actually used by woollen or worsted manufacturers.

Dr. LLOYD, in reply, said that there fractive index was governed by the iodine value, and since two sources of oleic acids having approximately the same iodine value had been found to absorb oxygen at such different rates and had different properties, they did not include those readings. The oxidation of oils at the ordinary temperature took place so slowly that, although the iodine value was decreased, a rise in temperature was not observed. Most cases of spontaneous combustion in mills, etc., were probably due to initial oxidation being caused by steam leakages, radiators, or some other source of heat aided by the moisture in the wool, waste, etc. It seemed most probable that the evolution of heat was due to a number of reactions taking place at the same time, such as the absorption of oxygen, and the action of moisture upon the oxidised compounds, this being accompanied by polymerisation and also decomposition of the resulting bodies. The time required for pure oleic acid to be oxidised in air at 50° C., until maximum gain in weight was obtained, was so long that the experiments were carried out with addition of manganese resinate, the assumption being that the rate of oxidation of other acids would be in a similar ratio to that of oleic acid and oleic acid *plus* resinate. Some (distillation) oleines were much safer than oleic acid, and he thought the constitution accounted for the differences. The unsaponifiable matter increased the value of the oil as regards safety. Oleines were generally bought containing not less than 50% saponifiable; in some cases the saponifiable matter was increased by addition of cottonseed oil, which was one of the worst that could be employed. No doubt that was the cause of several cases of firing.

Communication.

GERMAN CHEMICAL INDUSTRY THIRTY YEARS AGO.

BY THE RIGHT HON. SIR HENRY ROSCOE, F.R.S.

The following short report, written by myself for the Royal Commission on Technical Instruction, of which I was a member, was printed in 1882. This shows that even in those early years the Germans had seized upon the methods which have made their chemical industries so successful; and that money cannot secure success unless it is accompanied by perfect scientific method, and above all by the recognition of the importance of original investigation.

ON THE INFLUENCE OF TECHNICAL EDUCATION ON CERTAIN BRANCHES OF CHEMICAL INDUSTRY.

We have here collected our notes on certain special industries, viz., 1. chemical colours; 2. beet-sugar; and 3. the alkali trade, upon which the influence of technical education is plainly observable.

I.—*Influence of Technical Training on the Chemical Colour Industry of Germany and Switzerland.*

Among the coal-tar colour works visited by the Commissioners, were those erected on the banks of the Rhine at Basle by Messrs. Bindschedler and Busch. These works, though far less extensive than those of Messrs. Meister, Lucius, und Brüning, at Höchst, or of the Baden Aniline and Soda Works at Ludwigshafen, are carried on in a no less scientific spirit, and the general method of working adopted in all these establishments is identical.

The first principle which guides the commercial heads of all the Continental colour works, is the absolute necessity of having highly trained scientific chemists, not only at the head of the works, but at the head of every department of the works where a special manufacture is being carried on. In this respect this method of working stands in absolute contrast to that too often adopted in chemical works in this country, where the control of the processes is left in the hands of men whose only rule is that of the thumb, and whose only knowledge is that bequeathed to them by their fathers.

On entering the works of Messrs. Bindschedler and Busch one is struck, in the first place, with the adaptation of means to ends, with the substantially-built, well-lighted, well-ventilated workshops, and, above all, with the all-pervading cleanliness and neatness. But it is not of these things that we now desire to speak, but rather of the method by which their business is conducted. In the first place, then, the scientific director (Dr. Bindschedler) is a thoroughly educated chemist, cognisant of, and able to make use of the discoveries emanating from the various scientific laboratories of the world. Under him are three scientific chemists, to each of whom is entrusted one of the three main departments into which the works are divided. Each of these head chemists, who have in this instance enjoyed a thorough training in the Zürich Polytechnic, has several assistant chemists placed under him, and all these are gentlemen who have had a theoretical education in either a German University or in a Polytechnic School. An important part of the system has now to be noticed, viz., that directly under these scientific assistants come the common workmen, who have, of course, no knowledge whatever of scientific principles, and who are, in fact, simple machines, acting under the will of a superior intelligence. The many and great advantages of this arrangement are patent to all; and the fact of having men of education and refinement in positions of this kind, renders the foreign manufacturer who adopts this system less liable to annoyance and loss (from sources which we need not more nearly specify) than his English competitor, who works on a different plan.

So much for the *personnel* of the works. Now for the mode in which they carry on their work. To begin at the beginning, we find no less than ten well-equipped, airy, experimental laboratories in these works, perfectly distinct from the workshops where the manufacturing processes are carried on. In these ten laboratories, the chief departmental chemists and their assistants work out their investigations respecting the production of new colouring matters, or the more economic manufacture of old ones. To assist them in their work, a complete scientific library is at hand containing all the newest researches, for those, as