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quâ naphthalene, a previous deposit of naphthalene might be moved so as to block a pipe. If, as Mr. Hehner had said, there was a deposit of naphthalene in an old pipe, it might be moved so as to choke up a local service. If anyone present could say whether Mr. Leather had had a perfectly clean main to experiment on in a new district with washed coal gas, that would be a help towards understanding the paper from their point of view, and could be claimed by Mr. Allen in support of his theory.

Mr. H. Leicester Greville said that the tendency of naphthalene to accumulate in bends and angles of pipes was probably due to friction, though moisture probably had influence on the formation of deposits. The statement in the paper, that gas normally left the works free from naphthalene vapour, would require corroboration, considering that the presence of naphthalene in quantity was so evident at all points of the manufacture. That naphthalene—a substance always regarded as essentially a product of high temperature—could be absolutely produced in the gas at the ordinary temperature of the air, would also require a large amount of confirmation. If naphthalene could possibly be permanently retained in the gas instead of being deposited, it would be a great boon to gas companies on the ground of its great value as an illuminant.

Mr. R. W. Allen, in reply, said he had treated the matter purely from the scientific standpoint. For the statements he had made about the deposits in the mains he had the authority of Prof. F. D. Brown, Chairman of Directors of the local company, and also of the Chief Engineer. The work extended over a year, and that to a very great extent eliminated any variations that otherwise might have been supposed to exist in the amounts of naphthalene in the gas as it issued from the mains. Reference had been made to Mr. Leather. In a paper on "Naphthalene Deposits" read by him before the Gas Institute (see Journal of Gas Lighting, **73**, 1734) he had stated that gas which contained at the most only 14 grains of naphthalene per 100 cb. ft.—an amount insufficient, as he (Mr. Allen) had shown, to saturate the gas at a very much lower temperature than it was likely to be subjected to in the mains—yet deposited naphthalene. In reply to Mr. Watson Smith he might say that he made no effort to prevent the benzene being removed along with the naphthalene, but experimented afterwards with gas from which the naphthalene was carefully removed and the benzene reintroduced in a quantity insufficient to saturate it at the temperature of the bath. Mr. Hehner had asked why he did not convert the frozen-out naphthalene into picrate of naphthalene. It was because the benzene would also have been converted into solid picrate, whereas by first converting the mixture into nitrobenzene and nitronaphthalene and oxidising this with chromic acid, the nitronaphthalene formed nitrophthalic acid, which separated out on cooling, whereas the nitrobenzene did not give a similar compound. Mr. Hehner had also remarked that he (Mr. Allen) had worked with much too small a volume of gas to ensure accuracy. It was true that the volume of gas was comparatively small, but he had the utmost confidence that his weighings were correct in every instance to, say, a tenth of a milligramme, and the total errors were probably under 1 per cent. The weight carried over by the volume of gas he worked with was 0·0056 grm. at the lowest temperature employed, 8·0° C.—a perfectly appreciable quantity, capable of being weighed accurately, especially when account was taken of the great care he took to prevent the U-tubes of naphthalene absorbing moisture. The large number of experiments made at each temperature also tended to reduce errors to a minimum. He also stated that he never had had a doubt but that the weight of naphthalene required to saturate hydrogen, coal gas, carbon dioxide, air, &c., was exactly the same. This is not the point; the doubt—one held by many men of note—was whether all these gases would saturate themselves completely with naphthalene with equal rapidity, and what the speed of complete saturation was. In reply to Mr. Helps' question he regretted to say he could not throw any light on the point, as he was not a practical man. But it seemed to him that the statement made by Mr. Helps, that a hot summer's day increased the deposition of naphthalene, rather supported his own view. A hot day was just the time when the benzene would not condense out, and the conditions then might be those necessary for the formation of the naphthalene in the gas. Other references had been made to the way in which abrupt bends seemed to facilitate the formation of naphthalene. On the hypothesis that the gas and pipes were mutually electrified by the friction of the gas passing along, it was conceivable that the naphthalene molecules, being the heaviest ones present in the gas, might be attracted by the oppositely charged iron of the pipes, and held fast at the bends, where a sort of back eddy might be produced in the gas. He had endeavoured to test this by highly electrifying the gas as it passed along a tube presenting many obstacles to its passage, but could obtain no result, although both high alternating currents and large static charges were employed to electrify the gas.

The Chairman remarked that the subject was one of the highest importance to coal gas makers, and it only remained for him as Chairman, in tendering to Mr. Allen the thanks of the meeting, to endorse the suggestion which had been made by Prof. Clowes, that the author should continue his investigations and endeavour to obtain some experimental proof of the revolutionary view of the genesis of naphthalene in coal gas which had been submitted to them that evening.

THE IODINE VALUE OF OILS.

BY ARTHUR MARSHALL, F.C.S., A.I.C.

Although there is an extensive literature on the subject of the determination of the iodine value of oils, yet the exact nature of the reactions taking place in the various methods that have been proposed is still somewhat obscure. A great advance in the practical carrying out of the determination has been made by Wijs (Berichte, 1898, **31**, 750), who has proposed to employ a solution of iodine monochloride in acetic acid in the place of Hübl's solution of iodine and mercury bichloride in alcohol. Wijs's solution possesses the two great advantages that it is rapid in its action, and that it alters very little in titre. Lewkowitsch has shown that it gives the same iodine values as Hübl's solution, if the latter be properly applied (Analyst, 1899, 257).

In opposition to Ephraim (Zeit. angew. Chem. 1895, 254), and his own previous opinion (Zeit. anal. Chem. 1898, 277), Wijs considers that with Hübl's solution, iodine monochloride is not added on to the unsaturated acid radicles directly, but that the iodine chloride formed reacts with water, producing hypoiodous acid—

$$ICl + H_2O = HIO + HCl \qquad (1),$$

and that this is added on to the oleic acid or other unsaturated substance—

$$C_{17}H_{33}CO_2H + HIO = HOIC_{17}H_{33}CO_2H \qquad (2).$$

That this addition product then reacts with the hydrogen chloride formed according to the previous equation (1).

$$HOIC_{17}H_{33}CO_2H + HCl = ClIC_{17}H_{33}CO_2H + H_2O \qquad (3).$$

In support of this view Wijs states that, if hydrogen chloride be added to Hübl's solution, it retards its action. Hydrogen chloride, he says, would increase the amount of iodine chloride in the solution, but would, to some extent, prevent the formation of hypoiodous acid, as shown in equation (1). It is true that it has this effect, for, if iodine and mercuric chloride be dissolved in alcohol in suitable proportions, and if then hydrochloric acid be added, the brown colour of iodine disappears and only the yellow colour of iodine chloride remains. It is, however, practically impossible to predict what effect the hydrogen chloride would have upon the reaction between iodine chloride and oleic acid, &c. Wijs then proceeds to show that freshly prepared hypoiodous acid is absorbed to the full extent by arachis oil practically instantaneously. He, however, omits to show that hypoiodous acid is present in Hübl's solution in any quantity. As it is an extremely unstable substance, there is probably never more than a very small quantity present. As soon as it is formed it must be converted into iodic acid. In order to prove that hypoiodous acid does not necessarily take any part in the action, it is only requisite to show that the

addition takes place equally well, where there cannot possibly be any present. I prepared a solution of iodine monochloride in dry carbon tetrachloride. The solution was kept over fused calcium chloride to prevent the presence of any trace of moisture. The iodine values of some samples of oil were then determined by means of this solution, and also by means of a solution of iodine chloride in glacial acetic acid.

Time.	Oil.	Iodine Value.	
		ICl in CH_3COOH.	ICl in CCl_4.
Mins.			
10	Rape	103·0	103·8
10	,,	102·6	103·0
10	,,	102·6	103·2
10	,,	102·2	104·2
½	,,	..	102·8
30	,,	..	104·8
10	Linseed	178·0	178·0
10	,,	178·5	178·9
1	,,	..	178·0

It is evident from these figures that iodine chloride acts in exactly the same way in the absence of water as it does in the presence of it. If anything, it acts more energetically, for Wijs found that the action on linseed oil of a solution in acetic acid containing 5 per cent. water took about seven minutes, whereas, with carbon tetrachloride, it is apparently completed in one minute. I doubt, however, whether the addition ceases immediately potassium iodine solution is added. From the colour of the carbon tetrachloride beneath the aqueous layer, it is evident that it contains no free iodine, but a considerable quantity of iodine chloride, which no doubt acts further upon the oil whilst the titration is proceeding.

The colour of the carbon tetrachloride solution gives considerable information of what is proceeding in it, for, if it contain free iodine, it becomes brilliant purple, whereas iodine chloride colours it a pale brownish yellow. When substitution takes place, iodine is at once set free in accordance with the equations—

$$RH + ICl = RCl + HI; \text{ and}$$
$$HI + ICl = HCl + 2I.$$

If, therefore, a considerable amount of substitution take place, it will become apparent to the eye. There is, however, a more delicate test for substitution, viz., the acidity of the solution. This can be very conveniently estimated iodometrically. After the iodine has been titrated with thiosulphate in the usual way, potassium iodate is added to the solution. When this is done every equivalent of acid present liberates an equivalent of iodine—

$$6HCl + KIO_3 + 5KI = 6KCl + 3H_2O + 6I \quad (1.)$$

The iodine is then titrated with thiosulphate. This was carried out with the oils above, but in no case did potassium iodate bring back the colour when proper precautions had been taken to exclude moisture.

A mere trace of water in the carbon tetrachloride solution rapidly produces the change—

$$3ICl + 3H_2O = HIO_3 + 3HCl + 2HI \quad (2.)$$

The hydriodic acid then reacts with more iodine chloride liberating iodine, as becomes evident to the eye—

$$2HI + 2ICl = 2HCl + 2I \quad (3.)$$

The solution at the same time becomes cloudy in consequence of the separation of iodic acid, which is insoluble in carbon tetrachloride. If the solution be dried over calcium chloride, it becomes clear once more.

From the above equations it will be seen that for every molecule of iodic acid formed there are also six equivalents of acid, which, it might be supposed, should be sufficient to convert the iodic acid into iodine again in accordance with equation (1). This action is, however, only complete when there is present a considerable excess of both iodide and iodate.

Wijs has stated that with Hübl's reagent the oil, after absorbing iodine and chlorine, splits off a certain amount of hydrogen chloride (Zeit. anal. Chem. 1898, 277), thus :—

$$CO_2HC_{17}H_{33}ICl = CO_2HC_{17}H_{32}I + HCl.$$

and the experiments he cites makes this appear very probable.

From what I have said above, it is evident that this does not take place in the carbon tetrachloride solution.

Hübl, in his original paper (Dingler's polyt. Journ. 1884, 281), mentions that with his reagent he obtained a product having the composition $C_{18}H_{31}O_2ICl$. Further evidence that iodine and chlorine are added on in these simple atomic proportions is given by the colour of the carbon tetrachloride solution, which remains unchanged during the addition. If, however, the mixture be allowed to remain sufficiently long for substitution to take place, the purple colour can be seen to develop.

I think that the above experiments make it clear that the so-called "iodine absorption" consists simply in the addition of iodine chloride directly to the double linking of the unsaturated acid, and that no other reaction takes place to any appreciable extent.

That the absorption is complete in the case of the ordinary unsaturated fatty acids is proved by the following facts :—

(1) That iodine absorptions demanded by theory have been obtained in the case of oleic, isoleic, brassidic, and isoerucic acid.

(2) That the same values are obtained with Hübl's solution, with Wijs's solution, with a solution of iodine chloride in alcohol (Ephraim, Zeit. angew. Chem. 1895, 254), and with iodine chloride in carbon tetrachloride.

(3) That in the case of Wijs's solution the iodine value obtained is unaffected by the excess of the reagent employed (Lewkowitsch, Analyst, 1900, 34).

McIlhiney in a recent paper having endeavoured to resuscitate the "bromine value" (Journ. Amer. Chem. Soc. 1899, 1084), I thought that it was of interest to determine the bromine value of the same sample of linseed oil, with which the above experiments were made. I made a solution of bromine in carbon tetrachloride of about N/5 strength (McIlhiney recommends N/3 strength) and proceeded in the usual way. Calculating the result as iodine, I obtained the following results :—In 10 mins., 140·2 per cent. of iodine ; in 20 mins., 141·3 per cent. of iodine. The mean of the results with iodine chloride was 178·3. It is therefore evident that under these conditions the absorption is far from complete. There was no evidence of substitution. McIlhiney also obtained values lower than those given by Hübl's method. He states that substitution takes place, and that the addition is instantaneous.

I also tried the effect of iodine bromine. Iodine and bromine were dissolved in carbon tetrachloride and the operations carried out as usual. In ten minutes I obtained an iodine absorption of 167·0, *i.e.* 11·3 below the true value. It is evident from these experiments, that iodine chloride must not be replaced by either bromine or bromine iodide.

Both Wijs and Lewkowitsch have made statements as to the effect of time on the iodine chloride-acetic acid solution. Wijs (Berichte, 1898, 752) stated that a solution in 95 per cent. acetic acid lost only 0·3 per cent. of its titre in the first 96 hours. Lewkowitsch with acid of the same strength found a decrease of 4 per cent. in 80 hours, but with 99 per cent. acetic acid he found the solution unaltered after two months.

I have not found the titre to keep as constant as is stated by Lewkowitsch, although it does not vary sufficiently rapidly to cause any inconvenience. Even when new the titre does not alter so rapidly as to prevent use at once, but after months it still continues to decrease slowly.

In order to investigate this point I further purified my acid by recrystallising twice, and pouring off part of the acid each time. I then placed 25 c.c. in a dry stoppered bottle with 25 c.c. of my solution of iodine chloride in

carbon tetrachloride. After 10 minutes potassium iodide was added, and the iodine was titrated in the usual way. It required only 90·6 c.c. of $\frac{N}{20}$ thiosulphate, whereas the iodine chloride used should have required 95·75 c.c. There was an absorption, therefore, equal to 5·38 per cent. of the original amount in 10 minutes. This experiment was repeated, allowing the action to proceed for 12 hours. There was then an absorption of 22·9 per cent. of the halogen present. In a similar experiment, in which a few drops of water were added, there was an absorption of 24·1 per cent. in 12 hours. In all these cases the bottles were kept in a dark cupboard during the action.

It is well known that chlorine acts upon acetic acid in the presence of iodine quite readily if the liquid be warmed, producing chloracetic acid. From the above experiments it is evident that the action takes place also in the cold, though slowly. This substitution must gradually weaken the solution under ordinary circumstances, though it is evident from Lewkowitsch's statement, that this does not always take place. In any case the action is too slow to seriously interfere with the value of the method.

The weakening of the solution must depend to a large extent upon the amount of chloracetic acid formed in the preparation of the reagent, and this may account for the differences observed by different observers.

In conclusion I wish to say that I do not propose to substitute carbon tetrachloride solution in the place of that proposed by Wijs for general use, but in some cases it will be found more useful. On the whole, acetic acid is more convenient to work with than carbon tetrachloride.

Discussion.

Dr. Lewkowitsch said that he did not think that the paper added much to their knowledge. The literature on the subject of iodine values was so startling in its proportions that he had himself stated in that room that he congratulated any chemist who did not add to it. It was true he had himself lately committed a few ideas on the subject to print, but his excuse was that Wijs' beautiful method had appeared meanwhile, and this method had, in his opinion, completely cleared the air. Stability of Wijs' solution was demonstrated for at least five months, and no one could complain if alterations should occur after that time.

Mr. P. Kay asked what was the best way of preparing Wijs' solution. The ordinary method of finding the strength by titration was inconvenient, and he would like to know if there were any physical sign to guide one as to when the combination with chlorine was complete.

Mr. A. Marshall, replying to the last speaker first, said that it was quite easy to stop the passage of the chlorine at the correct time without titrating. The solution of iodine in acetic acid was dark brown in colour, whereas the solution of iodine monochloride was light yellow. The chlorine should therefore be passed in until this change of colour took place. The final change took place at quite a sharp point. He could not agree with Dr. Lewkowitsch as to the want of necessity for this investigation. No doubt Wijs' method for the determination of the iodine value would be generally adopted by chemists. There would consequently be a tendency to adopt Wijs' theory as to the nature of the reactions taking place. He thought it was a matter of importance that the exact meaning of the term "iodine value" should be known with certainty.

As to the keeping properties of Wijs' solution, he thought it was remarkable that the solution prepared by Dr. Lewkowitsch should retain its strength so much better than those prepared by Wijs or himself. He suggested that perhaps Dr. Lewkowitsch's solution had been prepared on a hot day, and that consequently a great part of the acetic acid had been converted into chloracetic acid during the preparation of the solution.

Dr. Lewkowitsch remarked that, on the contrary, it was a very cold day.

Mr. Marshall, continuing, said that possibly chlorination of the acetic acid would not occur if the solution were quite free from water. In consequence of the hygroscopic character of glacial acetic acid, it could not be kept anhydrous unless access of damp air were prevented.

Dr. Lewkowitsch said that perhaps Mr. Kay would like to know that a still more convenient way of preparing the solution was to accurately weigh off quantities of iodine and iodine trichloride.

Mr. Marshall added that iodine monochloride itself could be prepared without difficulty in a sufficiently pure state, and might even be bought so. He had prepared with it the solution of carbon tetrachloride with which the above experiments were performed.

The Chairman said that he thought that the Committee were justified in extending a hearing to papers of this description, which contained carefully recorded statements of actual results obtained in painstaking work.

Manchester Section.

Meeting held on Friday, March 2nd, 1900.

DR. J. GROSSMANN IN THE CHAIR.

THE NATURE OF INDIA-RUBBER.

BY DR. CARL OTTO WEBER.

The great experimental difficulties encountered in the investigation of colloidal bodies are responsible for the slow development of the chemistry of these substances. Their physical constants are highly indeterminate; and instead of melting points, boiling points and solubility, they simply exhibit a gradual merging of one state into another. Thus the characterisation of the colloids and their derivatives, and their isolation and purification from reaction mixtures is generally a matter of the very greatest difficulty.

These difficulties are met with in a pronounced degree in the chemical investigation of india-rubber, which forms the most important raw material of a large and, though perhaps only in a mechanical sense, highly developed industry. Indeed, not even is the empirical formula of india-rubber established with certainty; the question as to whether it should be regarded as a practically uniform substance, a hydrocarbon, an oxygenated product, a mixture of isomeric or polymeric compounds still being open to discussion. It is thus not surprising that we should be entirely in the dark respecting the question of the cause and nature of the difference exhibited by the numerous varieties of india-rubber obtained from plants belonging to very different botanical families.

If unworked, crude rubber* be treated with chloroform or carbon bisulphide, partial solution gradually takes place; and it was very early observed that, by this treatment, the rubber was separated into two parts, the one being soluble, the other insoluble, and presenting a peculiar reticulated appearance under the microscope. Very divergent statements are to be found respecting the relative proportions in which these two constituents occur. In one case the amount of the insoluble body is given as varying from 30 to 70 per cent. (Ladenburg's Handwörterbuch, Bd. V., 479), but on the other hand Gladstone and Hibbert (Jour. Chem. Soc. Trans. 1888, 679) found in Para rubber 4 per cent. only. For this reason I have thought it desirable to re-examine this point.

Gladstone and Hibbert suggested that the insoluble "modification" of india-rubber was produced during the drying of the juice, because they observed that by heating the soluble part it was more or less changed, and less susceptible of subsequent solution. They found this heat effect to increase as the temperature was raised and also with the length of time during which the heat continued. For this reason I employed for my experiments, not washed and dried rubber, but the thin films into which the inner parts of a crude loaf of rubber can be split. These films contain a considerable proportion of water which was got rid of by often repeated treatment with acetone. During this operation the films, which were white at first, assumed

* All the following statements refer to Para rubber, unless some other variety is expressly stated.