

ON THE DETERMINATION OF THE IODINE VALUE.

BY DR. J. J. A. WILS.

(Read at the Meeting, December 6, 1899.)

I READ with great pleasure the paper by Dr. Lewkowitsch on this subject recorded in the ANALYST, p. 257, and am desirous of making the following observations on the subject-matter of it:

I. *Iodine Values found for Allyl Alcohol.*—I fully agree with Dr. Lewkowitsch that allyl alcohol is not a substance specially suitable for deciding the respective values of the different methods for determining iodine values. The rapidity with

which the addition process takes place in allyl alcohol being less than that of the oil which has the smallest rapidity (linseed-oil), allyl alcohol demands a greater additive force on the part of the liquid than is necessary in its ordinary application.

From some experiments published in my first paper (*Zeits. f. Anal. Chem.*, 1898, 277), Dr. Lewkowitsch calculates for allyl alcohol the iodine value 392. These experiments are, however, unsuitable for this purpose. The whole series was made merely with a view to determining the splitting off of acid from the ICl-addition product, and in order to have this splitting-off process as uncomplicated as possible, and not affected by the formation of acid which always takes place when a Hübl solution is allowed to stand for any length of time, the duration of the reaction was kept very short (quarter to half-an-hour). The iodine values calculated from these experiments are therefore much too low, particularly for substances such as allyl alcohol, linseed oil, or cholesterol, which possess a small rapidity of addition.

Dr. Lewkowitsch obtained with ICl-acetic acid liquid for a sample of allyl alcohol iodine values of 419-420, and with the Hübl method 421-422, whereas I found with the same sample with ICl-acetic acid liquid 429, and for another sample by Hübl's method 425. The difference between the results obtained with the same method depends, as is evident from a letter I received from Dr. Lewkowitsch, upon a different method of working, *i.e.*, having a different excess of iodine present. I always used an excess of about 75 per cent. of the quantity originally added, whereas Dr. Lewkowitsch writes that he also in every case employed an excess of 75 per cent., and in most cases considerably more, approximating to 100 per cent. It is evident that this can only have been 75 to 100 per cent. of the quantity of halogen absorbed, *i.e.*, only 43 to 50 per cent. of the quantity originally added. It is, therefore, not at all a matter of surprise that Dr. Lewkowitsch obtained lower iodine values than mine.

II. *Effect of Time on the ICl-acetic Acid Liquid.*—Dr. Lewkowitsch finds that a solution of iodine chloride in 95 per cent. acetic acid is much more liable to alteration (decrease) than a solution in an acid of 99 per cent. When the acid is pure and especially free from oxidizable matters, there is, theoretically, no possibility of any decrease. Dr. Lewkowitsch found that a solution in 95 per cent. acid, after sixty-four hours, had decreased 4 per cent. of its value; whereas I had stated (*Berichte d. deutsch. Chem. Ges.*, xxxi., 750) the decrease to be 0.3 per cent. in ninety-six hours. I can find no other explanation for this difference than the assumption that Dr. Lewkowitsch's 95 per cent. acid was not so pure as mine.

III. In the third place, Dr. Lewkowitsch writes that the iodine determinations made with Hübl solution lead to correct results provided that the Hübl method is applied in a proper manner, and further on he says that the solution should not be allowed to act longer than six or seven hours on the fat under examination. I must add here that this limitation to seven hours only bears reference to those cases in which, in the first place, fresh (*e.g.*, sixteen-hours-old) iodine solution is used; and, secondly, where an excess of about 75 per cent. of the added iodine is employed. When treating oils of a high iodine value (*e.g.*, linseed oil) with a Hübl solution that is not fairly fresh, say about five days old, twenty-four hours are required.

It is clear that what I call a proper application of the Hübl method is but little

different from the usual one carried out in the case of oils with a low iodine value ; whereas in the case of oils with a high iodine value the difference is greater.

I was therefore convinced that the iodine value of linseed-oil especially required a revision, and I made one (*Revue ii. d. Fett- und Oelindustrie*, 1899, 29). This paper not having appeared in the ANALYST in abstract form, I give a short account of it.

I determined the iodine values of eighty-six samples of guaranteed pure linseed-oil, all from seeds of known origin ; sixty-nine were pressed from unmixed seeds, and seventeen from mixed. The results were as follows :

Iodine Values.			
Dutch linseed oils	...	From 191.5 to 201.8	
North Russian (Baltic) oils	...	192.1 ,, 200.0	(only one had a value 188.5)
South Russian oils	...	176.3 ,, 186.3	
Indian oils	...	182.2 ,, 187.5	
La Plata oils	...	174.7 ,, 182.7	
North American oils	...	177.8 ,, 188.5	

The more rapidly-drying varieties (Dutch and North Russian), which are only used for paints and varnishes, have higher iodine values than those used solely for soap-making. I also determined the specific gravity at 15° C. of twenty-four of these samples, and found the following relation between this constant and the iodine value :

Iodine Values.				Specific Gravity.
One sample	...	Higher than 200	...	0.9352
Mean of four samples	...	Between 195.0 and 200.1	...	0.9339
„ „ „	...	190.0 ,, 195.1	...	0.9329
„ „ „	...	185.0 ,, 190.1	...	0.9322
„ six „	...	180.0 ,, 185.1	...	0.9317
„ five „	...	Lower than 180.1	...	0.9310

DISCUSSION.

Dr. LEWKOWITSCH said that although Dr. Wijs and himself were more or less in agreement on this subject, there were one or two points raised in the paper which seemed to require correcting or amplifying. He was very glad that after all Dr. Wijs agreed with him in thinking that allyl alcohol was not a suitable substance to decide the question at issue. It had, in fact, been introduced by a third party, and it was this that had led him (the speaker) to calculate, from one of Dr. Wijs' former papers, the number 392. He quite accepted the author's remarks on this point. Dr. Wijs thought that he could explain the divergence in the iodine numbers of the same sample of allyl alcohol examined by both (viz. : Wijs, 426 ; Lewkowitsch, 420), by the fact that different excesses of the reagent had been used. There was, indeed, some misunderstanding as to the excess to be employed. Dr. Wijs considered that if from 100 parts of iodine added 25 were absorbed, an excess of 75 per cent. was used, whereas he (the speaker) should call that an excess of 300 per cent. However, he had started a number of experiments for the purpose of settling this point. The following figures showed that the variations between different observations were sometimes greater than those due to differences of excess, and it would seem that it did not really much matter whether one worked with an excess—in Wijs' sense—of

75 per cent. or 43 per cent. (or, as he would call it, 300 per cent. and 100 per cent. respectively):

Substance.	Iodine Value.	Excess of Iodine	
		in W.'s sense. Per cent.	in L.'s sense. Per cent.
Allyl alcohol	413.2	73.7	281.2
" "	416.0	52.8	89.3
" "	416.0	52.8	89.3
Linseed oil	179.8	77.6	347
" "	180.9	76.0	315
" "	179.3	57.2	133
" "	178.6	52.5	110
Candle-nut oil	163.4	73.6	278
" "	163.4	72.99	270.3
" "	162.1	53.4	115.0
" "	159.1	49.5	97.9
" "	163.9	77.5	308.9
" "	163.9	77.5	308.9
" "	162.1	51.6	106.8
" "	162.1	51.6	106.8
Oleic acid	82.9	76.1	319.9
" "	83.25	73.9	283.2
" "	82.81	52.7	115.5
" "	82.82	50.0	100.4

As a rule, the excess he used was not calculated beforehand, but left more or less to chance, and varied generally between, say, 100 per cent. and 150 per cent. (in his own sense). But even making the largest possible allowance, the difference of about 1 per cent. in the value of allyl alcohol did not explain the difference of Dr. Wijs' own figures for allyl alcohol. He thought, therefore, that the matter might fairly be allowed to drop there, accepting the conclusion that it did not really matter whether the excess was 300 per cent. or half of that, because, according to the law of mass action, secondary reactions were bound to occur with the possible formation of substitution products, thus probably introducing greater errors than those due to differences in the excess. The temperature variations had only a very slight influence, as Dr. Wijs himself had shown. The explanation Dr. Wijs had given for the somewhat rapid decomposition of the speaker's solution, prepared with 95 per cent. acetic acid—viz., that the acid had been impure—did not hold good, it having been prepared from pure glacial acetic acid, it was the same sample from which the 100 per cent. glacial acid solutions were made later on. With regard to the figures given by Dr. Wijs for the various linseed oils, these numbers were very valuable as far as they went, but they ought not to be taken as indicating the order in which the oils derived from the various countries ranked in quality (or purity). He himself had examined some Indian linseed oils, the iodine value of which came up to 193, tested by the old Hübl process, allowing the solution to act from four to six hours. The specific gravity table showed the regularity one would expect, as the higher the iodine value, *i.e.*, the larger the quantity of linolic and linolenic acid present, the higher the specific gravity must be, since the specific gravities of linolic and linolenic acids were higher than

that of oleic acid. But it would not be permissible to allow the rule shown by the table to pass into literature as a general one.

Mr. A. MARSHALL said that, in his experience, solution made even with perfectly pure acetic acid, although it lost very little strength during the first few days, showed on keeping for some months a considerable decrease in strength, and became much darker, probably owing to chlorination of the acetic acid and reconversion of the iodine chloride into iodine.

Dr. LEWKOWITSCH said that in Dr. Wijs' process long hours of standing were not permissible at all. The author, in his fourth paper, had proved pretty accurately the occurrence of side reactions after a certain time, which affected the result in a reverse direction. This was well known to every observer, for if after titration of the iodine the solution were allowed to stand it became blue again. One of the chief points in Wijs' work was in showing that the importance which had been attached to a standard time for exposure was well founded, and that it was necessary to adhere strictly to a certain period, sufficiently long to insure the reaction coming to an end. He (Dr. Lewkowitsch) had been able to show that Hübl's method gave identical results with that of Wijs', but in the case of the latter the solution would keep for at least half a year, so that a blank determination was not absolutely necessary, and actually less time was required for a test than for a determination of the saponification value. It was so easy in preparing the Wijs' solution to hit exactly the point when the titer was doubled that there seemed to be no necessity for having an excess of either chlorine or iodine. He considered that a point had been reached when the discussions on, and the endless modifications of, the Hübl process might with advantage cease.