

Journal of the Society of Chemical Industry.

No. 23, Vol. XXXIII.

DECEMBER 15, 1914.

No. 23, Vol. XXXIII.

Official Notice.

DUTY-FREE ALCOHOL.

In view of the interest now associated with the conditions of supply of duty-free alcohol, the following statement has been prepared.

Duty-free alcohol in the form of methylated spirit is readily obtainable.

Mineralised methylated spirit.—To protect the immense revenue raised from potable spirit and to prevent misuse it is generally necessary to render duty-free alcohol non-potable. For common use this is effected by the addition of wood spirit (i.e., crude methyl alcohol) and a trace of light petroleum, so that the mixture contains 10% of wood spirit and three-eighths of 1% of petroleum spirit. These small additions, whilst sufficient to deter most people from drinking the spirit, do not interfere with its use for a very large number of commercial purposes. Such spirit, which is known as mineralised methylated spirit, may be purchased throughout the country without formality in quantities not exceeding four gallons at a time from any retailer of methylated spirit, and permission to receive it in larger quantities is readily granted on application to the Commissioners of Customs and Excise when ordinary facilities for obtaining it are inadequate.

Industrial methylated spirit.—For manufacturers and large users of alcohol generally, however, and in those cases where a purer spirit is necessary, further provision is made by what is known as "Industrial Alcohol." This alcohol is denatured by the addition of half the quantity of crude methyl alcohol or wood spirit which is used in the mineralised methylated spirit, and no petroleum spirit is used; i.e., this spirit contains 5% of wood spirit without other addition. Permission to receive this spirit must, however, be obtained and the use to which it is put be specifically authorised by the Board of Customs and Excise. Applications for such authorisation should in the first instance be made through the Surveyor of Customs and Excise for the district in which the spirit is to be employed. It should be noted that during 1913 the price of British industrial methylated spirit was lower than the price of alcohol in Germany.

Finally, in those cases where denaturing with wood spirit is proved to the satisfaction of the Commissioners of Customs and Excise to render the spirit unsuitable or detrimental for use in any art or manufacture, the Commissioners have power to grant the use of duty-free spirit under other conditions as explained in the following memorandum. Applications referring to this spirit should also be addressed to the Commissioners through the local Surveyor of Customs and Excise.

Pure spirit.—The following is the procedure to be observed in connection with the use in manufactures of pure spirit on which duty has not been paid (Sec. 8 of the Finance Act, 1902).

1. Any person desiring to use spirits without payment of duty in any manufacture carried on by him must make application in writing to the Commissioners of Customs and Excise for authority to receive and use such spirits, and must prove to the satisfaction of the Commissioners that the use of methylated spirits would be unsuitable or detrimental.

2. The applicant must give full particulars of the situation of the premises upon which and the purpose for which the spirits are to be used, together with a description of the process of manufacture. He must also state the means by which it is proposed to make the spirits unpotable before and during use, and the quantity likely to be required in the course of a year.

3. Any person authorised to receive spirits on which duty has not been paid must, if so required by the Commissioners of Customs and Excise, provide upon his

premises a warehouse, structurally secure to their satisfaction, and all such spirits received must be deposited and retained therein until delivered on proper notice to, and in the presence of, the officer. He must also, if so required, provide a room approved by the Commissioners in which be fixed a vat or other vessel of sufficient size to admit of at least one hundred bulk gallons of spirit being rendered unpotable at one time, and must also provide satisfactory accommodation for the Officer of Customs and Excise in attendance at his premises. No charge is usually made for the services of this officer.

4. Security to the satisfaction of the Commissioners of Customs and Excise must be given for the due removal, safe custody, and proper use of the spirits, and the due observance of all regulations and conditions made by the Commissioners.

5. The substance or materials to be used for the purpose of rendering spirits unpotable and the mode in which the spirits are to be rendered unpotable must be approved by the Commissioners of Customs and Excise, and the person authorised to receive spirits upon which duty has not been paid must, if so required by the Commissioners, provide a store to be approved by them, and used solely for storing and keeping the substance or material so approved.

6. Spirits which have been rendered unpotable under these regulations shall not thereafter be purified in any manner or be recovered by distillation or any other means, except with the express sanction of the Commissioners of Customs and Excise.

The use of *absolute alcohol* is covered by the above regulations as to "Pure spirit."

Attention is also directed to the Report of the Departmental Committee on Industrial Alcohol (see this Journal, 1905, pp. 397—420), and also to the Minutes of Evidence taken before that Committee (No. Cd. 2477, price 2s. 4d.).

Birmingham Section.

Meeting held at Birmingham University, on Thursday, November 5th, 1914.

MR. H. T. PINNOCK IN THE CHAIR.

THE ESTIMATION OF MOISTURE IN ZINC ASHES.

BY ERNEST A. LEWIS.

The ferrocyanide assay of zinc is largely used in technical work and is accurate when carried out under standard conditions, but sometimes differences of 2% or more are obtained by assayers working on the same sample which has been passed through a 30 mesh sieve. The samples are prepared by grinding the ashes whilst hot, in which case the metallic zinc easily rubs up to a fine powder. The oxidation being negligible, this method is largely used by English smelters, and is to be preferred to the method of separating the fines and metallics by pounding and stating the percentage of each on the packets.

If the samples whilst hot are placed in bottles and sealed with sealing wax all over the top to exclude all moisture, there is seldom any serious discrepancy between assayers. It is evident that the errors must be due to the absorption of moisture which is not driven off by heating to 100° C., as is the practice of many assayers. In order to see to what extent zinc ashes of various types would absorb moisture, the following experiments were made. The material, which had been passed through a

30 sieve, was heated with continual stirring in an iron ladle for some minutes, as hot as possible without melting the zinc, put into corked bottles and allowed to cool in a desiccator. These conditions of heating are the same as many smelters use to estimate moisture. The samples were weighed out between watch glasses and then allowed to remain in the open air protected from dust for some days and re-weighed from time to time. A galvanizer's ashes containing about 3% chlorine gained 4.15% by weight in 24 hours, 4.66% in 48 hours, and 4.82% in 72 hours. A sample of re-melted ashes free from chlorine gained .57% in weight after 24 hours, 0.72% in 48 hours, and 0.76% in 72 hours. Some of the previous samples were left for some days in an artificially damp atmosphere; the material, which became caked together, was ground up in a porcelain mortar and transferred to a stoppered bottle. About 10 grms. was weighed out between watch glasses and put into a steam oven, and later to a hot air oven, remaining in each oven until the weights were practically constant. A sample of ashes containing about 75% Zn lost 1.87% after 4 hours in a steam oven, and a further 4.14% after 4 hours at 200° C., a total of 6.01%. The loss to the seller from being dried at 100° C. instead of 200° C. is thus equal to about 2.9% zinc.

Loss in weight per 100 parts. In another case, after 4 hours in the steam oven, the loss in weight was 0.88%, and after a further 4 hours at 200° C., 0.62%; total loss 1.5%. The loss in this case is equal to 0.4 unit of zinc.

The experiments were repeated with two other kinds of remelted ashes, free from chlorine. One sample gained 0.53% on exposure to air for 24 hours; and 0.75% for 192 hours; when heated in the steam oven the loss amounted to 0.57%, whilst a further 0.31% loss occurred at 200° C. Another sample gained 0.30% during 24 hours exposure, and 0.52% in 192 hours; the loss in the steam oven in 4 hours was 0.25% and at 200° C. in 5 hours 0.32%. A sample of zinc oxide containing about 0.2% Cl gained 0.80% in weight on exposure to air for 24 hours and 0.84% after 72 hours; on heating for 4 hours in the steam oven the loss was 0.43%, and after a further 4 hours at 200° C., 0.46%, or a total of 0.89%.

Prolonging the heating much over 4 hours at 200° C. led to an increase in weight, due no doubt to oxidation of the metallic zinc.

These experiments show that it is not possible to remove all water from zinc ashes by heating to 100° C., especially when chlorides are present. Drying the sample at 200° C. for four hours practically removes all the moisture in all kinds of zinc ashes.

DISCUSSION.

The CHAIRMAN said the subject was of importance and might be given a much wider application, for there were difficulties in making such estimations in organic substances.

Mr. ALCOCK pointed out that difficulty was experienced in determining the amount of moisture in many substances, particularly in volatile oil and drugs. It must not be assumed that loss was always moisture; it might also be compensated by oxidation.

Mr. W. CLIFFORD asked Mr. Lewis if he had any experience of drying the oxide, on the large scale. Was the moisture more easily driven off when chloride was absent than when present? It was not easy to get the moisture in the crude (galvanizer's) oxide below 50% by mere drainage and evaporation, especially if it contained a small amount of chloride. Was there a colloidal form of oxide which retained the moisture more tenaciously?

Mr. O'SHAUGHNESSY pointed out that in the estimation of moisture, or what was called moisture, one was always faced with the difficulty referred to by Mr. Alcock; but in many cases (in which such estimations were required not for scientific work, but for practical and control work, the difficulty might be overcome by the adoption of an arbitrary method, viz., drying at a fixed temperature under known conditions. After practical experience it was possible to interpret the values obtained very accurately.

Mr. LEWIS said that to most smelters the word "moisture" meant everything volatile. The moisture was

determined in order to get the dry weight of the whole bulk, and such residues were sold on the zinc content of the dry material. Some assayers adhered to the old method of drying at 100° C., and while a specially made steam oven might give that temperature, the average steam oven did not. He had had no experience of drying oxide in bulk. The moisture in the oxide was not as a rule much more than 1%, but he did not know how the makers got the amount down.

THE ESTIMATION OF NAPHTHALENE IN SPENT OXIDE.

BY WILLIAM C. DAVIS, B.Sc. (LOND.), F.I.C.

The ordinary spent oxide from gas works contains very little if any naphthalene; the sample, however, which is the subject of this examination had been used in the Williams process for the extraction of cyanogen from the gas and contained a considerable quantity of naphthalene. It must, therefore, be assumed that the Williams process has in this case purified the gas, not only from cyanogen, but also from naphthalene.

The naphthalene is usually determined by means of picric acid as described by Colman and Smith (this J., 1900, 19, 128), Kuster (Ber., 1894, 1101) and Dickenson Gair (this J., 1905, 1279; 1907, 1263). These methods deal with the estimation of the naphthalene in coal gas, but Dickenson Gair gives a method for the estimation in spent oxide by dissolving out the naphthalene with alcohol and precipitating the clear solution with picric acid; no details are given.

A method for the estimation of naphthalene in tar is described in Lunge's Technical Methods of Chemical Analysis, vol. ii. p. 803; this method, which is proposed by White and Ball (J. Gas Lighting, 1904, 88, 262), consists in weighing about 1 gm. of tar into a 50 c.c. Erlenmeyer flask provided with an air inlet and connected to a U tube. The first two-thirds of this tube is filled with quicklime and the remaining space with glass wool and phosphorus pentoxide. The entire apparatus is heated in an air-bath at 70°–80°. The outlet of the U tube is connected outside the air bath with a weighed second U tube immersed in ice-water. A current of air is drawn through the apparatus at a velocity of 2 litres per hour, which causes the naphthalene to volatilise and deposit in the cooled U tube. The operation is continued until the second U tube no longer shows an increase in weight.

For separation of the naphthalene from spent oxide the method of White and Ball modified as described below and also distillation with steam have been employed, and this latter method has proved more satisfactory.

Separation of the naphthalene by a current of warm air.—When working with this method great difficulty was experienced in completely volatilising the naphthalene. Ten grms. of the spent oxide were weighed into a bottle fitted with inlet and outlet tubes, so that a current of air could be drawn through it. The air current was passed for two hours over the sample of spent oxide, then through 10% citric acid solution to retain any ammonia, and then through three wash bottles containing measured quantities of a saturated picric acid solution of known strength in which any volatilised naphthalene is collected. The bottle containing the sample and also that containing citric acid were kept at 100° in an air bath. The contents of the wash bottles containing picric acid were then mixed together in a tightly stoppered bottle, heated in the water bath until all the naphthalene picrate was dissolved, and then cooled, with occasional shaking. The solution was made up to known volume, the naphthalene picrate separated by filtration and the picric acid in the filtrate estimated by titration with *N*/10 sodium hydroxide, using lacmoid as indicator.

When a current of dry air was used to volatilise the naphthalene the quantity found after two hours' treatment was 1.35%, and with moist air 1.9%. In both cases an examination of the spent oxide after treatment showed visible crystals of naphthalene.

Separation of the naphthalene by steam distillation.—The naphthalene, as was expected, was very easily