II—There will occur an accumulation of volatilized potash in the back end of the kilns, the kiln housings and the gas coolers which in time may clog up the system.

III—Under normal precipitator conditions the circulating dust will increase in potash up to a certain limit, the increase being governed by the amount deposited and the efficiency of the precipitators and following the laws of a converging geometric progression.

IV—In spite of fairly ideal precipitator conditions there will occur a loss of potash through the stacks, a loss steadily increasing up to a certain limit and also governed by the amount deposited and the efficiency of the precipitators and following the laws of a converging geometric progression.

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TOLUOL FROM SPRUCE TURPENTINE

By A. S. WHEELER

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The heavy demand for trinitrotoluol is taxing the resources of the country in toluol, and any new source for the latter requires careful investigation in the hope of increasing the supply. It has been suggested that spruce turpentine, a waste product of the sulfite process of making sprucewood paper pulp, might serve as an important source of toluol. Spruce turpentine is remarkable in that it consists largely of one aromatic hydrocarbon, cymol (cymene). It has been attracting interest in several quarters in recent years. The French chemists Boedtke and Halse¹ subjected the crude turpentine and also pure cymol to the Friedel-Crafts reaction with benzol and obtained high yields of toluol and cumol. On account of the importance of the reaction I have attempted to repeat their best experiment in order to confirm their findings and offer in this paper a preliminary report, giving the results of the first two experiments.

Boedtke and Halse reported on four experiments as follows: (1) 150 g. crude 90 per cent cymol (spruce turpentine itself), 1 kg. benzol and 30 g. aluminium chloride boiled 6 hrs. on the water bath. Products: 52 g. toluol, 75 g. cumol. (2) 100 g. cymol, pure, 1 kg. benzol and 20 g. aluminium chloride boiled 6 hrs. Products: 41 g. toluol, 85 g. cumol. (3) 100 g. cymol, pure, 1 kg. benzol and 10 g. aluminium chloride boiled 8 hrs. Products: 31 g. toluol, 67 g. cumol. (4) 90 g. cymol, pure, 900 g. benzol and 4.5 g. aluminium chloride boiled 10 hrs. Products: 44 g. toluol (80 per cent), 68 g. cumol (85 per cent yield). (The figure, 80 per cent, is an error. A recalculation shows that this ought to be 71 per cent, the theoretical yield being 61.8 g.) A Vigreux column was used in the distillations but no statement is made as to the number of fractionations and no figures are given for the boiling points of the fractions. Further, it is not known what the authors mean by pure cymol. A number of boiling points have been given for this compound but Schorger² seems to have prepared a pure product. This

was due to the observation that concentrated sulfuric acid removes impurities which have defied a variety of active agents. As late as 1916, Bogert and Tuttle¹ worked with an impure cymol.

In the two preliminary experiments reported below the purification of the cymol was not carried to the extreme limit. The Champion Fiber Company, of Canton, North Carolina, is generously furnishing the spruce turpentine for this investigation. The first experiment was carried through by the author. The second, or parallel, experiment was carried through from the beginning to the end by Mr. E. P. Wood, a senior student in chemistry and I wish to thank him here for his careful work.

The spruce turpentine was purified by first subjecting it to distillation in superheated steam, the vapor being carried through hot 10 per cent caustic soda and then condensed in the usual way. The crude turpentine was pale red, but the condensed oil was brilliant and water-white. The caustic soda assumed a reddish color. Seventy per cent of the oil passed over into the receiver but a newer shipment is giving a larger yield as high as 87 per cent. If caustic soda is not used the distillate is lemon-yellow in color. The oil was separated from the water and shaken several times with 0.5 per cent potassium permanganate, then 20 times with one-sixth its volume of concentrated sulfuric acid. The first addition of sulfuric acid assumed a very dark color, later washings a red color and finally a pale yellow color. Schorger states that pure cymol gives no color with this acid. The oil was then shaken with water several times, dried with calcium chloride and finally boiled with metallic sodium. It was distilled with a Glinsky still head and the main portion, boiling at 177–177.5°, was employed in the reaction. The benzol was a sample of Baker's C. P. It was dried over calcium chloride and boiled with metallic sodium. The aluminium chloride was freshly prepared by passing dry hydrochloric acid gas over hot aluminium filings.

EXPERIMENT I

90 g. cymol, 900 g. benzol and 4.5 g. aluminium chloride were boiled together on a water bath for 10 hrs. The solution became dark red. The fractionations of the product were carried out with a 3-section Young still head, with results as follows:

Fraction No.	Temperature Interval	Volume Cc.	Fraction No.	Temperature Interval	Volume Cc.
1.....	79–80°	380	7.....	113–141°	15
2.....	80–81°	242	8.....	141–151°	11
3.....	81–83°	184	9.....	151–154°	47
4.....	83–95°	167	10.....	155–200°	6
5.....	95–110°	18	11.....	200°+	3 (a)
6.....	110–131°	27		(a) Fluorescent.	

The second distillation was begun with Fraction No. 4 and gave the following results:

Fraction No.	Temperature Interval	Volume Cc.	Fraction No.	Temperature Interval	Volume Cc.
1.....	80–83°	80	8.....	115–120°	6
2.....	83–95°	50	9.....	120–131°	6
3.....	95–100°	3	10.....	131–151°	19
4.....	100–105°	2	11.....	151–154°	43
5.....	105–109°	4	12.....	154–156°	4
6.....	109–113°	15	13.....	156–170°	4
7.....	113–115°	11	14.....	170°+	2

Accumulations occur at the vicinity of the boiling points of toluol, 110°, and cumol, 153°.

¹ Bull. soc. chim., [4] 19 (1916), 444.

² J. Am. Chem. Soc., 39 (1917), 2671.

¹ J. Am. Chem. Soc., 38 (1916), 1352.

A sample of No. 6, 109–113°, was easily and smoothly converted into trinitrotoluol (TNT), according to the method recommended by Hoffmann.¹ The crude product, washed with hot water, melted at 76–78°. After one recrystallization from a mixture of alcohol (9 parts) and benzol (1 part), pale yellow needles, melting sharply at 80–80.5°, were obtained in excellent yield.

EXPERIMENT II

88.5 g. cymol, 88.5 g. benzol and 4.5 g. aluminium chloride were boiled together on a water bath for 10 hrs. A 3-section Young still head was used in the first fractionation and a 5-section Young still head in the second.

Fraction No.	Temperature Interval	Volume Cc.	Fraction No.	Temperature Interval	Volume Cc.
1.....	79–81°	501	7.....	141–151°	11
2.....	81–83°	299	8.....	151–154°	37
3.....	83–95°	151	9.....	154–170°	15
4.....	95–110°	21	10.....	170–180°	3
5.....	110–131°	16	11.....	180–200°	2
6.....	131–141°	16	12.....	200°+	3

For the second distillation, Fraction No. 2 was started with.

Fraction No.	Temperature Interval	Volume Cc.	Fraction No.	Temperature Interval	Volume Cc.
1.....	80–81°	249	7.....	115–120°	4
2.....	81–83°	126	8.....	120–131°	7
3.....	83–95°	62	9.....	131–141°	4
4.....	95–108°	6	10.....	141–149°	7
5.....	108–112°	22	11.....	149–154°	52
6.....	112–115°	8	12.....	154°+	4

The accumulations again show toluol and cumol. The amounts are less in both experiments than those claimed by Boedtker and Halse. They gave no statement as to the purity of their products so that question is in doubt. On our part some necessary step may still be lacking for maximum yields. The investigation is being actively pursued. Boedtker and Halse introduced in each of their experiments two variants so that it cannot be said which variant changed the results. It will be noted that 17 molecules of benzol were used for one molecule of cymol. It is hoped to materially reduce this proportion. The mechanism of the reaction will be studied in order to determine whether the cymol furnishes the methyl or the tolyl group for the toluol. It is noted that the published work on the nitration of cymol and of cumol is of an unsatisfactory character and these reactions are being reexamined.

CONCLUSIONS

Spruce turpentine yields toluol when subjected to the combined action of benzol and aluminium chloride.

The other product, cumol, is not a waste product since it may be oxidized directly to benzoic acid. This will save a like amount of toluol now used to make benzoic acid.

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ARSENIC IN SULFURED FOOD PRODUCTS

By W. D. COLLINS

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INTRODUCTION

It has been recognized for a long time that appreciable quantities of arsenic might be taken up by food

products through treatment with sulfur dioxide fumes obtained by burning sulfur which contained arsenic.

The most notable case of contamination of food products with arsenic was the well-known instance of poisoning at Manchester, England, caused by arsenic in beer. The investigation that followed showed that the arsenic in the beer came from the use of glucose or brewers' sugar which was made from starch by the use of sulfuric acid which contained large amounts of arsenic. Analyses of some of the samples of sulfuric acid showed as much as 2 per cent of arsenic as As_2O_3 . Samples of the glucose contained from 0.01 up to nearly 0.1 per cent of arsenic. Samples of the beer in question contained up to 1.0 or 1.5 grains of arsenic per gallon of beer, and some even as high as 3 grains per gallon. The average medicinal dose of arsenic mentioned in the *U. S. Pharmacopoeia* is 2 mg. or one-thirtieth of a grain. In the report of the English Commission which investigated these cases of arsenical poisoning, it was recommended that liquid food materials should be considered adulterated if they contained as much as 0.01 of a grain of arsenic per gallon, and that solid food materials should be considered deleterious if they contained as much as 0.01 grain of arsenic per pound. The results of the investigation showed that it was entirely possible to keep the arsenic below these limits in all the materials used in the production of the beer and in the other food materials which were investigated at that time, provided care was taken to keep the materials free from arsenic.

In connection with an investigation of the subject of arsenic in wines, Dr. H. D. Gibbs,¹ in 1905, suggested arsenical sulfur as one of the possible sources of arsenic. Several samples of the Japanese sulfur which he examined showed amounts of arsenic up to several hundred parts per million. Dr. W. W. Stockberger,² in a bulletin published in 1908, suggested that sulfur was probably the cause of the presence of appreciable amounts of arsenic in certain samples of sulfured hops. It appears to be recognized by the dealers in sulfur that it is desirable to use for bleaching hops and dried fruits sulfur which is free from arsenic. It is probable that certain users of sulfur have made some effort to obtain sulfur which contained no arsenic.

In 1914, as a result of objections made to some shipments of hops from the United States to foreign ports on account of the fact that the hops were said to contain more arsenic than was permissible, the Department of Agriculture investigated again the question of the source of arsenic in dried hops. Dr. Stockberger, of the Bureau of Plant Industry, visited the hop-growing districts and collected samples of unsulfured hops, sulfured hops and samples of the sulfur used. He also collected samples of sulfur used on the hops in the shipments which were rejected on account of excessive arsenic. Two samples of sulfur from this lot showed 329 and 356 parts of arsenic per million. The writer made a study of various methods for the determination of small quantities of arsenic in such

¹ *J. Am. Chem. Soc.*, **27** (1905), 1484–96.

² *U. S. Dept. of Agr., Bureau of Plant Industry, Bull.* **121** (1908), 41–46.

¹ Bureau of Mines, *Technical Paper* **146** (1916).