PREPARATION OF ETHYL BROMIDE FROM PHENOBARBITAL PRODUCTION WASTE LIQUID

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Bromine and its compounds are used in the synthesis of a whole series of medicinal preparations. In connection with the short supply of bromine, attempts have been made repeatedly to extract it from the waste waters from production of phenobarbital, hexamidine, or synthomycin. Methods of regenerating bromine which are described in the literature are associated with preparation of sodium bromide, hydrobromic acid, or free bromine [1-3].

In the preparation of phenobarbital, ethyl bromide is used as the ethylating agent in the stage of preparing ethyl ethylphenylcyanoacetate. After the ethylation process is over, waste liquors in a volume of 1.1 m^3 per metric ton of finished product are formed; these contain 30-40% sodium bromide and are contaminated with reaction products, solvents, and resins. The specific gravity of these liquors is 1.38 -1.40 g/cm^3; and the bichromate oxidation demand is 60-70 g of O_2 per liter. It is possible to prepare a technical sodium bromide from this waste liquor by refining and evaporating the solution; however, the product is not a starting material for phenobarbital synthesis.

Various bromides (sodium bromide, potassium bromide, iron bromides etc.) serve as raw materials for the preparation of ethyl bromide in industry [4]. We have effected a synthesis of ethyl bromide directly from the waste waters which contain the sodium bromide. According to our proposed method, the aqueous sodium bromide solution is added to a mixture of sulfuric acid and ethyl alcohol, and the ethyl bromide formed is distilled off.

$$2NaBr + 2C_2H_5OH + H_2SO_4 \rightarrow 2C_2H_5Br + Na_2SO_4 + 2H_2O.$$

The yield of product is 85-90%, based on sodium bromide.

EXPERIMENTAL

To 68 ml of sulfuric acid (93.5-96.6%) with cooling is added 48 ml of ethyl alcohol, and then 100 ml of waste water containing 51.5 g of sodium bromide. The mixture is heated in an oil bath, and ethyl bromide is distilled at once along with water and alcohol into a receiver which is cooled in ice and water. Distillation starts at 36° and is finished at a vapor temperature of 110-115° or pot temperature of 135-140°. The lower layer of ethyl bromide in the distillate is separated, and 48-50 g of product is obtained; as a rule this conforms to the requirements of All-Union State Standard 2658-56. In case it does not meet these requirements, the ethyl bromide is subjected to an additional purification, for which it is shaken with 2 ml of sulfuric acid and distilled on a water bath.

The consumption of sulfuric acid is 2.6 kg, that of alcohol 0.9 kg, per kg of ethyl bromide.

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Determination of the sodium bromide in the waste water was conducted by oxidizing a sample with nitric acid, with subsequent airblowing and absorption of the bromine formed by a sodium sulfite solution. The bromides in the absorption solution were determined by the Volhard procedure [5-6].

On the basis of the work done, one can obtain the following products and wastes per metric ton of phenobarbital: 1) 0.54-0.55 metric ton of ethyl bromide; 2) 0.8 m^3 of aqueous distillate containing up to 15% ethanol and traces of ethyl bromide; the distillate can be used for diluting the reaction mixture in the ethylation stage; 3) 0.4 m^3 of acid waste liquors, which are discarded after neutralization, since it is not economical to regenerate the sulfuric acid.

Thus, an ethyl bromide which can be returned to the ethylation stage has been prepared from the waste waters from phenobarbital production. The amount of waste liquors thereupon is reduced threefold; and the content of organic contaminants, as expressed in bichromate oxygen demand, is reduced from 60-70 to 16-17 g of O_2/liter.

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