PRODUCTION OF GLYCEROL α-MONOCHLOROHYDRIN FROM EPICHLOROHYDRIN

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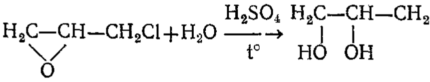
Glycerol α-monochlorohydrin is used in the L'vov chemical-pharmaceutical plant for the synthesis of diprophyllin and glyceryl p-chlorophenyl ether. It is prepared by the reaction of glycerol with technical hydrochloric acid at the boiling point of the reaction mixture, in cast-iron enameled apparatus, in the presence of acetic acid as a catalyst for the process [1].

Even after repeated, or even threefold distillation, the product obtained was deeply colored and had a sharp odor, and always contained an impurity of glycerol dichlorohydrins, which led to formation of turbid solutions when the product was dissolved in water.

The actual percentage of glycerol α-monochlorohydrin in the product fluctuated from 75 to 85%. The apparatus used for the reaction of glycerol with hydrochloric acid was often out of service. The production cycle lasted for up to 5 days. The low quality of the α-monochlorohydrin did not permit obtaining diprophyllin which corresponded to technical requirements with regulation yields. The diprophyllin synthesized was unsuitable for sealing in ampoules (the turbidity of 10% aqueous solutions exceeded GFIKh standard No. 4). The diprophyllin for sealing in ampoules was repeatedly recrystallized from ethyl alcohol, which led to large losses of alcohol and product. The p-chlorophenyl glyceryl ether (used for "tsinkundan" ointment) synthesized with the use of this α-monochlorohydrin was also obtained in low quality.

We have introduced in our plant an α-monochlorohydrin production technology which used the method of epichlorohydrin hydration [2]:



$$\underset{\diagdown\, O\, \diagup}{H_2C-CH}-CH_2Cl+H_2O \xrightarrow[t^\circ]{H_2SO_4} \underset{HO}{H_2C}-\underset{OH}{CH}-CH_2Cl$$

Into a cast-iron-enamel apparatus of 100-liter capacity, with an anchor stirrer, an oil jacket, and electrical heating was charged 30 liters of desalinated water from a measuring tank, and through a charging port was charged 0.1 kg of concentrated sulfuric acid (catalyst). With the stirrer operating, the water was preheated to 50-60°, and then, from the same measuring tank, over a 2-h period, 60 kg of technical epichlorohydrin (MRTU 6-01-3765) was added to the apparatus. After addition of the first portions of epichlorohydrin the reaction mixture heated spontaneously to boiling; therefore the remaining amount of epichlorohydrin was added carefully to avoid excessively vigorous boiling and possible boiling-over of the reaction mixture.

The part of the water and epichlorohydrin which had distilled out through a downward enameled steel condenser into receiver No. 1 while the mixture boiled was returned to the apparatus. The reaction mixture (at 98-102°) was stirred for 2 h more without heating (hold time). After this time the reaction mixture had cooled to 85°. With stirring, it was neutralized with 30% sodium hydroxide to pH 5.0-5.5 (universal indicator). After 10-min stirring, the pH was checked again. The water was stripped off at 700-750 mm into receiver No. 1, bringing the temperature to 80-85°. Then a VN-4 pump was attached, the mixture was heated, and the α-monochlorohydrin was distilled into receiver No. 2 at a residual pressure of 3 to 5 mm in the system, being collected over the range 96-106°. Over a 5 to 6 h period 55 to 56 kg of α-monochlorohydrin were distilled. The α-monochlorohydrin yield was 75%. The product slowly yellows; it contains 87-99% of the basic component, and does not contain dichlorohydrin impurities.

Introduction of the technology described permitted simplifying the apparatus scheme (compared to the old production technology), shortening the production cycle from 5 days to 1 day, and markedly raising the

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quality of α-monochlorohydrin and, moreover, the quality and yield of the diprophyllin and p-chlorophenyl glyceryl which were synthesized using the α-monochlorohydrin.

LITERATURE CITED

1. Synthesis of Organic Preparations [in Russian], Vol. 1, Moscow (1949), p. 278.
2. E. Fourneau, I. Ribas, and T. R. Marques, Bull. soc. chim. France, 38, 699 (1926).