UNITED STATES PATENT OFFICE.

CURT PHILIPP, OF DRESDEN, GERMANY, ASSIGNOR TO CHEMISCHE FABRIK VON HEYDEN AKTIENGESELLSCHAFT, OF DRESDEN, GERMANY.

PROCESS OF PRODUCING ISOBORNYL ESTERS.

No. 919,762. Specification of Letters Patent. Patented April 27, 1909.

Application filed May 4, 1906. Serial No. 315,203.

To all whom it may concern:

Be it known that I, CURT PHILIPP, a subject of the King of Saxony, and resident of Dresden, in the Kingdom of Saxony, German Empire, have invented a new and useful Improvement in the Manufacture of Isobornyl Esters from Pinene Hydrochlorid or Pinene Hydrobromid, of which the following is a specification.

It is known that by heating a solution of pinene hydrochlorid in glacial acetic acid with silver acetate for several weeks in the water bath, a mixture of much camphene with a small quantity of isobornyl acetate (about 70 grams isobornylacetate from 400 grams of pinene hydrochlorid) is obtained (see *"Berichte der Deutschen Chemischen Gesellschaft"*, Vol. 32, page 2309). It is also known that, by addition of fatty acids to camphene, with or without condensing agents, isobornyl esters are formed (see *"Chemisches Centralblatt"*, 1902, I, page 1219).

By boiling a solution of pinene hydrochlorid in glacial acetic acid with lead acetate, camphene is obtained, while by heating these ingredients in an autoclave to 180° C. a mixture of bornyl- and isobornyl- acetate is obtained (see French Letters Patent 349896).

In working according to the improved method hereinafter described, the transformation of pinene hydrochlorid into isobornyl acetate can take place at water bath temperature without the use of an autoclave.

The improved method consists in heating pinene hydrochlorid with the fatty acid salts of heavy metals in an excess of fatty acids. A halogen salt of a heavy metal, for example chlorid of zinc, may also be added. Instead of the fatty acid salts of the heavy metals, the oxids or carbonates of those metals may be employed, these being intermediately transformed into the said salts by the excess of the fatty acids employed. If fatty acid salts of zinc, iron, or copper are employed, the addition of a halogen salt of a heavy metal is not necessary. But if the fatty acid salts of other heavy metals, *e. g.* oxid of lead, are employed, the addition of chlorid of zinc is necessary, as otherwise the reaction will take place in a different way. Probably chlorid of lead and the zinc salts of fatty acids are then formed intermediately (see example 7). The reaction takes place at water bath temperature and can be considerably hastened by heating to the boiling point under reflux.

Example 1: 172 parts of pinene hydrochlorid, 500 parts of formic acid of 98 to 100 per cent. strength, 45 parts of oxid of zinc, are heated together using a reflux condenser. Zinc formate insoluble in the excess of the formic acid, is formed and very quickly dissolved on boiling. The process is completed in a short time. The mass is poured into water, the oil floating on the surface is separated off, washed with water and with a solution of soda and distilled *in vacuo*. The distillate consists chiefly of isobornyl formate possessing the known properties.

Example 2: 172 parts of pinene hydrochlorid, 500 parts of glacial acetic acid, 45 parts of oxid of zinc, are digested for 20 hours on a boiling water bath and then worked up according to Example 1. Isobornyl acetate possessing the known properties is obtained.

Example 3: 172 parts of pinene hydrochlorid, 300 parts of glacial acetic acid, 45 parts of oxid of zinc, are boiled for 1 to 2 hours using a reflux condenser and then worked up according to Example 1. Isobornyl acetate is obtained in this case also.

Example 4: 172 parts of pinene hydrochlorid, 500 parts of isobutyric acid, 45 parts of oxid of zinc, are boiled for ½ to 1 hour using the reflux condenser and are worked up according to Example 1. Isobornyl-isobutyrate having the known properties is obtained.

Example 5: 172 parts of pinene hydrochlorid, 500 parts of glacial acetic acid, 60 parts of ferric oxid, are boiled for 20 hours, using the reflux condenser, and then worked up according to Example 1. A good yield of isobornyl acetate is obtained.

Example 6: 172 parts of pinene hydrochlorid, 500 parts of glacial acetic acid, 45 parts of oxid of copper, are boiled for 20 hours using the reflux condenser and are worked up according to Example 1. Isobornyl acetate is obtained.

Example 7: 172 parts of pinene hydrochlorid, 500 parts of glacial acetic acid, 165 parts of oxid of lead, 30 parts of chlorid of zinc, are boiled for 24 to 30 hours using the reflux condenser. The product of the reaction is precipitated with water, neutralized with soda and distilled with steam. The distilled oil is separated from the water and dis-

tilled *in vacuo*. Isobornyl acetate of the known properties is obtained.

Example 8: 172 parts of pinene hydrochlorid, 500 parts of glacial acetic acid, 216 parts of oxid of mercury, 30 parts of chlorid of zinc, are boiled for 20 hours using the reflux condenser and then worked up according to Example 7. Isobornyl acetate is obtained. Addition of chlorid of zinc is indispensable in this case also.

What I claim is:

Process for the direct manufacture of isobornyl esters consisting in heating pinene hydrochlorid with fatty acids and with fatty acid salts of heavy metals, substantially as described.

In testimony, that I claim the foregoing as my invention, I have signed my name in presence of two witnesses, this 23rd day of April, 1906.

CURT PHILIPP.

Witnesses:

PAUL E. SCHILLING,

PAUL ARRAS.