

UNITED STATES PATENT OFFICE.

OLIVIER LOUIS ANDRÉ DUBOSC, OF ROUEN, FRANCE, ASSIGNOR TO STÉ. J. BASLER & CIE.,
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PREPARATION OF CAMPHENE.

937,928.

Specification of Letters Patent.

Patented Oct. 26, 1909.

No Drawing.

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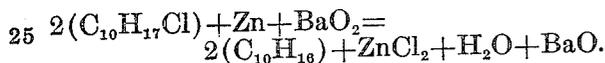
To all whom it may concern:

Be it known that I, OLIVIER LOUIS ANDRÉ DUBOSC, a citizen of the Republic of France, residing at Rouen, Seine Inférieure, France, have invented certain new and useful Improvements in the Preparation of Camphene, of which the following is a specification.

This invention provides a method of preparing camphene from hydrochlorid of pinene with the aid of metals and peroxids, the camphene thus obtained being oxidized to form camphor.

The transformation of hydrochlorid of pinene into camphene has been realized by me more simply than by previous methods proposed.

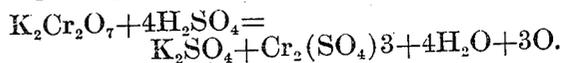
The method which is the object of this application consists in the action at the same time upon the melted hydrochlorid of a metal susceptible of forming with the hydrochlorid, a chlorid, and a peroxid susceptible of forming water with the hydrogen. The reaction in figures is as follows:—



For two molecular proportions of hydrochlorid of pinene, it is necessary to use one proportion of metal and one of peroxid. Thus for two molecular proportions or 344 parts by weight of solid hydrochlorid of pinene, there are used 65 parts by weight of metallic zinc, 169 parts by weight of the peroxid of barium; or 56 parts by weight of iron and 87 parts of peroxid of manganese. The metals which have given the best results are powdered zinc, the finely pulverized turnings of cast iron, copper and fine lead dust. The best operating peroxids are the peroxid of barium and the dioxid of manganese.

The camphene obtained is oxidized and transformed into camphor preferably by means of the "chromic sulfuric liquor" of Berthelot (published in *La Chimie Organique of Behal*, Vol. II, page 540), to which 1/1000 of vanadium chlorid is added. The liquor in question is a saturated solution of an alkaline (sodic or potassic) bichromate, to which is added a quantity of sulfuric acid such that the base of the bichromate is first combined to the state of sulfate, and so that the remaining sulfuric acid is in such pro-

portion as to be able to form with the chromic acid set free in the formation of the sulfate, protoxid of chromium, thus generating oxygen, thus,—



The conditions of heat and pressure are the following: The reactions can occur as described only when the hydrochlorid of pinene is in a state of fusion, or between 125 and 130 degrees centigrade. No pressure is necessary, the reaction taking place at normal atmospheric pressure. A reflux or circulating apparatus of any type may be used. The hydrochlorid of pinene is first mixed with the indicated quantities of pure metal in the form of a powder, and of the peroxid. If we use zinc powder and dioxid of manganese, the mixture is easily effected. If turnings of cast iron are used, they must be finely pulverized. With iron one can heat the mass without special care up to the point of fusion of the hydrochlorid. With zinc or aluminum the heating must be very cautious, the reaction being very strong and quick; so much so that practically iron is preferable. The operation continues for 24 to 36 hours. The end of the operation is indicated by applying to nitrate of silver the liquid part of the mass. If there remains any hydrochlorid of pinene not transformed, there is formation of a cloudy precipitate of silver. The camphene is separated from the chlorid of zinc or iron and from the sediment of barium or of manganese by distillation in a current of vapor.

The oxidation of the camphene takes place at a temperature of 105 degrees centigrade in a circulating apparatus, at ordinary pressures, but in a great quantity of water. Unless a great quantity of water is used, there is risk of explosion. The water should be at least twenty times the weight of the camphene. In order to avoid superoxidations it is well to add the chromic liquor in successive small parts. The end of the operation may be recognized by the fact that all the bichromate is transformed into sulfate. The coloration of the liquor changes from red to dark green, and this permits an empiric determination of the operation. The

camphor formed is carried off by a current of vapor in order to separate it from the sulfate of chrome.

What I claim is:—

The process which consists in transforming hydrochlorid of pinene into camphene through the cooperating action of a metal and a peroxid on the melted hydrochlorid.

In witness whereof I have hereunto signed my name this 27th day of March 1906, in the presence of two subscribing witnesses.

OLIVIER LOUIS ANDRÉ DUBOSC.

Witnesses:

HANSON C. COXE,
GABRIEL BELLARD.