This invention relates to the manufacture of camphor-forming terpenes, and more particularly to a process of preparing borneol, iso-borneol, and camphene.

The principal object of this invention is to provide a practical and efficient process of preparing camphor-forming terpenes such as borneol, iso-borneol, and camphene.

An important object of this invention is to provide a practical and efficient process of the character described wherein a pinene acid addition product is converted into camphor-forming terpenes with a minimum production of camphor oils and decompositions products which are substantially unsuitable for use in the manufacture of camphor.

Heretofore, it has been suggested to treat an acid addition product of pinene, such as pinene hydrochloride, at an elevated temperature with caustic alkali as a hydrolyzing agent to produce borneol and the like. However, this suggested procedure has been attended with several practical disadvantages notable among which has been the excessive formation of camphor oils. We have discovered that this disadvantageous formation of camphor oils can be substantially reduced or eliminated by employing the alkali in a weekly ionized solution and preferably by employing the alkali in conjunction with an ionization retarder. By thus modifying the process the yields of the desired products are materially increased and the formation of undesirable compounds materially decreased or eliminated.

Our process consists broadly in reacting a pinene acid addition product at an elevated temperature with a base-forming metal hydroxide in a weakly ionized solution. In the practice of our process we prefer to employ pinene hydrochloride but in place thereof we may satisfactorily employ any other so-called "pinene salt", such as the reaction product of pinene with a nonoxidizing organic acid such as oxalic, salicylic, trichloracetic or like acid, and it is to be understood that such products are included in the term "pinene acid addition product".

As a hydrolyzing agent we may satisfactorily employ a hydroxide of any alkali or alkaline earth metal, such as sodium, calcium, barium, magnesium or like hydroxide, and it is to be understood that such compounds are included in the term "base-forming metal hydroxide". Moreover, as stated above, we prefer to use such compounds in conjunction with an ionization retarder and as such retarder we prefer to employ a water soluble salt of the metal present in the hydroxide used, and preferably a halide, such as the chloride or bromide, of such metal.

In the preferred practice of our process we treat in a closed container at an elevated temperature and with agitation a pinene acid addition product, preferably pinene hydrochloride, with a hydrolyzing agent, preferably sodium hydroxide, in an aqueous solution in the presence of an ionization retarder, preferably sodium chloride, for a sufficient period of time to hydrolyze the pinene acid addition product into camphor-forming terpenes, which consist primarily of iso-borneol with lesser amounts of borneol and camphene. In such preferred practice of our process the water used for dissolving the hydrolyzing agent and the ionization retarder is preferably employed in the proportions of approximately from 10 to 20 parts by weight or measure to 1 part of the pinene acid addition product. The metal hydroxide used is preferably in a slight excess of the theoretical amount required to combine with and remove the acid radical of the pinene acid addition product. As will be apparent the ionization retarder may be used in varying amounts depending upon the degree of retarding action desired. However, we have found that it is desirable to employ the retarder in such amount as to substantially saturate the water used, although a greater or lesser amount may be employed.

The following specific example of the practice of our process may be considered as illustrative of the invention. A suitable amount of pinene hydrochloride is introduced into any suitable container such as an autoclave which is preferably steam...
jacketed or otherwise provided with means for heating the same and which is also provided with suitable agitating means. To each part by weight or measure of the pinene hydrochloride is added from 10 to 20 parts, and preferably 15 parts, of water. To this mixture is then added sodium hydroxide in slight excess of the theoretical amount required to combine with the acid radical of the pinene hydrochloride. This is approximately 30 per cent. by weight of the pinene hydrochloride. Sodium chloride is then added in an amount to substantially saturate the water present. While either or both of the sodium hydroxide and sodium chloride may be added to the water after it has been introduced into the container as suggested above, we prefer to add these materials to the water before it is mixed with the pinene hydrochloride and mix the resulting solution with the pinene hydrochloride. The container is then closed and subjected to a temperature of from 225 to 300°F., preferably 275°F., for a period of from 8 to 12 hours. A pressure of from 30 to 50 pounds per square inch is developed during this treatment. As stated above, the material in the container is preferably agitated throughout the period of heating.

Upon the completion of the reaction which takes place during the heat treatment the terpene products which are formed are separated in any suitable manner from the aqueous solution in the container and are used as desired. The final product consists primarily of iso-borneol, and camphene, and a lesser amount of borneol, and we have found that this mixture is particularly adapted for use in the preparation of synthetic camphor.

As heretofore stated any acid addition product of pinene may be used in the practice of my process but we prefer to employ pinene hydrochloride because of its relative cheapness. Moreover, in place of a single hydroxide and a single ionization retarder we may employ mixtures of hydroxides and mixtures of retarders.

While we have described in detail the preferred practice of our invention it is to be understood that the details of procedure, the ingredients and proportions of ingredients employed, and the arrangement of steps may be widely varied without departing from the spirit of the invention or the scope of the subjoined claims.

We claim:

1. The herein described process which comprises mixing with a pinene acid addition product an aqueous solution of an alkali-forming metal hydroxide and a soluble salt of the metal present in said hydroxide, and heating said mixture with agitation in a closed container at a temperature favorable to the reaction of said addition product with said hydroxide, said hydroxide being present in a slight excess of the theoretical amount required to combine with the acid radical present in said addition product, the water present being in the proportion of from approximately 10 to 20 parts to 1 part of said addition product, and said salt being present in an amount sufficient to approximately saturate the water present.

2. The herein described process which comprises mixing pinene hydrochloride with an aqueous solution of sodium hydroxide and sodium chloride, heating said mixture with agitation for from approximately 8 to 12 hours in a closed container at a temperature of from 225 to 300°F., said sodium hydroxide being present in a slight excess of the theoretical amount required to combine with the acid radical present in said pinene hydrochloride, the water present being in the proportions of from approximately 10 to 20 parts to one part of said pinene chloride, and said sodium chloride being present in an amount sufficient to approximately saturate the water present.

In testimony whereof we affix our signatures.

HARRY P. BASSETT.
RICHARD C. MORRISON.
CERTIFICATE OF CORRECTION.

Patent No. 1,766,369. Granted June 24, 1930, to

HARRY P. BASSETT ET AL.

It is hereby certified that the above numbered patent was erroneously issued to "Charles A. Bianchi, of Nutley, New Jersey, and Meigs, Bassett & Slaughter, Inc., of Philadelphia, Pennsylvania, a Corporation of Pennsylvania", whereas said patent should have been issued to "Charles A. Bianchi, of Nutley, New Jersey", said "Bianchi" being assignee by mesne assignment of the entire interest in said invention, as shown by the records of assignments in this office; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 5th day of August, A. D. 1930.

(Seal)

Wm. A. Kinnan,
Acting Commissioner of Patents.