

UNITED STATES PATENT OFFICE.

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PROCESS OF MAKING CAMPHENE.

No. 876,137.

Specification of Letters Patent.

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To all whom it may concern:

Be it known that we, AUGUSTUS BISCHLER, doctor of philosophy and chemist, a subject of the Emperor of Russia, and resident of Basel, Switzerland, and ANTON BASELLI, doctor of philosophy and chemist, a subject of the Emperor of Austria-Hungary, and resident of Basel, Switzerland, have invented a new and useful Process for the Manufacture of Camphene, of which the following is a full, clear, and exact specification.

The present invention relates to the manufacture of camphene used for the manufacture of camphor. One of the oldest methods for obtaining camphene free from chlorin consists in heating pinene hydrochlorid with a large excess of powdered sodium stearate or benzoate for 40 hours at 200° C. The chief objections to this process are the large excess of soap and the prolonged heating.

The process described in the British specification No. 26618 of 1901, namely heating pinene hydrochlorid with bases in aqueous solution as for instance soda lye or potash lye, in presence of alkali salts of higher fatty acids as solvents, for 20 hours at 210–220° C. in an autoclave, is said to be more economical.

The alkali salts of higher fatty acids do not melt easily when they are anhydrous. On the other hand numerous salts of higher fatty acids are known, which melt easily even when anhydrous. By higher fatty acids we mean palmitic, stearic and oleic acids, and as an example of the easily melted salts just referred to, we would refer to salts of either of these acids with heavy metals.

According to the present invention pinene hydrochlorid is heated with an easily fusible anhydrous metal salt of a higher fatty acid for some hours at about 200° C. It is thus converted into camphene without using an autoclave and in a considerably shorter time than is possible according to either of the aforesaid processes.

As suitable easily fusible salts of higher fatty acids, may be named the copper salts, manganese salts, lead salts and mercury salts.

In order that the operation may be conducted in a vessel without pressure, the vessel is provided with a column which serves as a reflux condenser and is so large that the temperature within the mass in which the

reaction is proceeding can rise to 200° C. A part of the camphene may distil during the process, but the bulk of it is distilled in steam when the reaction is at an end.

Example I: 75 parts of litharge are dissolved with aid of heat in 200 parts of stearic acid and the heating is continued until the salt is anhydrous. Into this lead stearate 100 parts of pinene hydrochlorid are introduced and the solution is heated to 195–200° C. for 4 hours in a vessel having a column as a reflux condenser. Lead stearo-chlorid separates at first and gradually reacts with the pinene hydrochlorid with formation of lead chlorid. The mass is allowed to cool to about 140° C. and the camphene is distilled in steam. The stearic acid is regenerated and is used again in the process. The reaction is analogous when lead oleate is used, but in this case lead oleo-chlorid does not separate, but only lead chlorid. Lead palmitate behaves similarly. It is not necessary, however, to use the said acids in the pure state; a mixture of acids such as is obtained by saponifying oils or fats may be used.

Example II: A mixture of oleic and stearic acids, which may also contain palmitic acid, is converted into copper salts in the known manner by means of the calculated proportion of freshly precipitated copper carbonate or cupric oxids. 300 parts of the dried copper salts are heated for some 5 hours at 195–200° C. with 100 parts of pinene hydrochlorid. From time to time a sample of the oil condensed in the reflux condenser is removed and tested to see if it is free from chlorin. The camphene is distilled in steam and the fatty acids recovered. When the fatty acid salt is not so easily melted as those mentioned in the previous examples, a substance which will aid the liquefaction, such as diethylanilin, may be added.

Example III: Manganese oleate is made by adding manganese sulfate to an oleic acid soap. 240 parts of this oleate are heated with 100 parts of pinene hydrochlorid and 100 parts of diethylanilin at 195–200° C. for 8 hours. When the reaction is complete the mixture is distilled in steam and the diethylanilin separated from the camphene in the distillate by addition of acid.

What we claim is:

1. The described process for the manufacture of camphene consisting of heating piene

hydrochlorid with an easily fusible, anhydrous metal salt of a higher fatty acid, and distilling the mixture of the reaction in steam in order to separate the camphene.

5 2. The described process for the manufacture of camphene consisting of heating pinene hydrochlorid with an easily fusible anhydrous metal salt of a higher fatty acid for some hours at about 200° C. and distilling
10 the mixture of the reaction in steam in order to separate the camphene.

3. The described process for the manufacture of camphene consisting of heating pinene hydrochlorid with an easily fusible
15 anhydrous metal salt of a higher fatty acid for some hours at about 200° C. in a vessel provided with a column serving as a reflux condenser and distilling the mixture of the reaction in steam in order to separate the
20 camphene.

4. The described process for the manufacture of camphene consisting of heating pinene hydrochlorid with an easily fusible, anhydrous metal salt of a higher fatty acid in presence of diethylanilin at about 200°
2 C. distilling the mixture of the reaction in steam, in order to separate from it the camphene and the diethylanilin and finally adding an acid to the distillate in order to separate the camphene from the diethylanilin.
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In witness whereof we have hereunto signed our names this 1st day of September, 1906, in the presence of two subscribing witnesses.

AUGUSTUS BISCHLER.
ANTON BASELLI.

Witnesses:

GEO. GIFFORD.
AMAND RITTER.