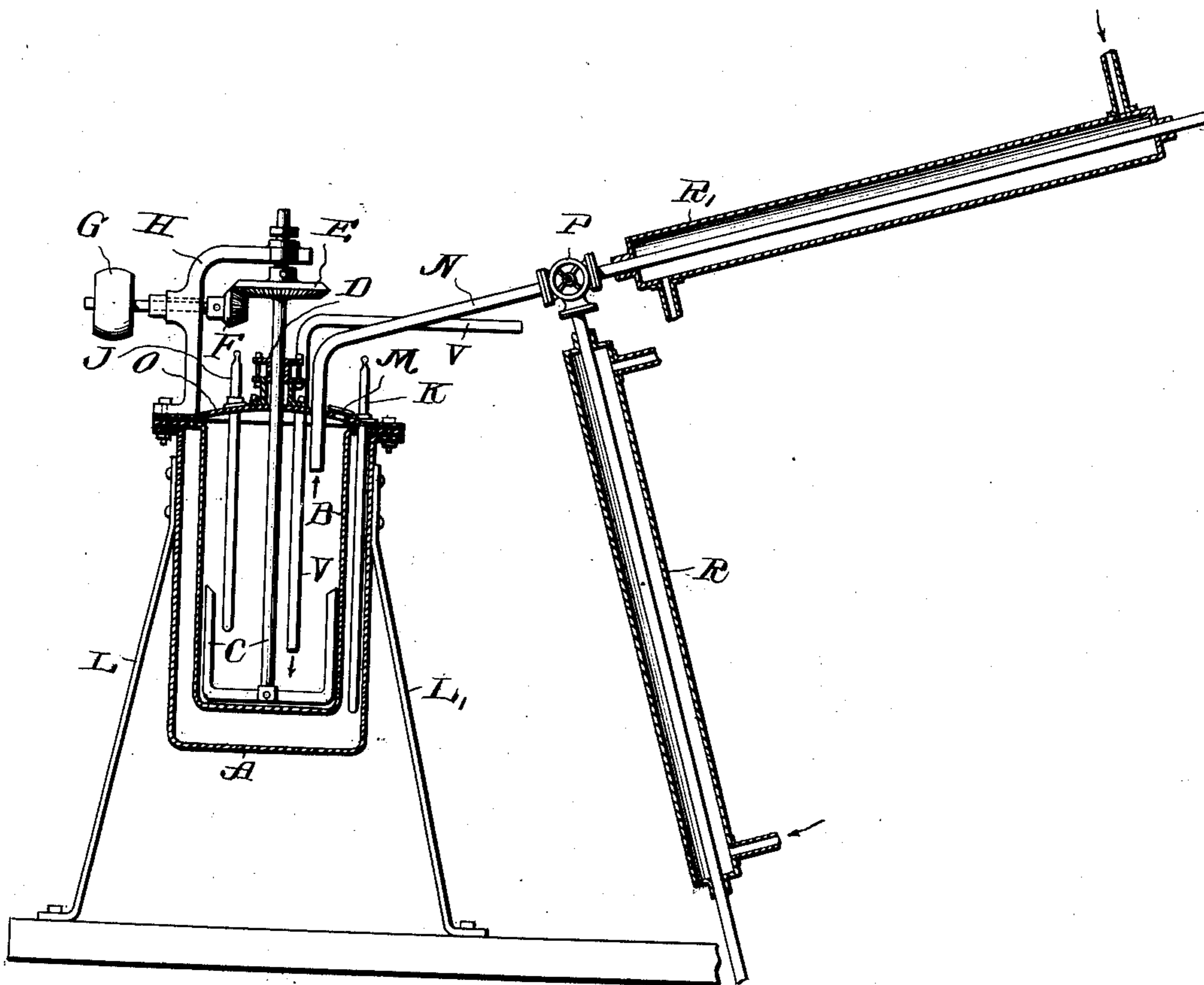


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PROCESS FOR THE PREPARATION OF BORNEOL ESTERS FROM TURPENTINE.
APPLICATION FILED JUNE 1, 1908.

901,293.

Patented Oct. 13, 1908.



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UNITED STATES PATENT OFFICE.

JOSEF HERTKORN, OF BERLIN, GERMANY.

PROCESS FOR THE PREPARATION OF BORNEOL ESTERS FROM TURPENTINE.

No. 901,293.

Specification of Letters Patent.

Patented Oct. 13, 1908.

Application filed June 1, 1908. Serial No. 435,889.

To all whom it may concern:

Be it known that I, JOSEF HERTKORN, doctor of philosophy, chemist, and resident of Berlin, Germany, (whose post-office address is Paulstrasse 8,) have invented a new and useful Improved Process for the Preparation of Borneol and Isoborneol Esters from Oil of Turpentine, of which the following is a specification.

My invention relates to a process for producing borneol and isoborneol esters from oil of turpentine.

It is well known that borneols and their esters can be produced from oil of turpentine in various ways, as, for instance, by treatment with boric acid or with benzoic acid, but a serious objection exists to all these known processes on account of the small yield of borneol, which is far less than the theoretical yield.

I have found that the temperature suitable for esterification when treating oil of turpentine with anhydrous acids or their anhydrides does not lie between 130 and 132° C. as has hitherto been assumed, for after digestion for days at this temperature, only very small quantities of the borneol ester are obtained, and therefore only very small quantities of camphor can be produced. In this reaction the pinene of the oil of turpentine is probably first converted into camphene, and this by a secondary action into the borneol esters.

If the esterifying acid, boric acid for example, be mixed with anhydrous oil of turpentine and heated for days at a temperature of from 130 to 132° C., the same poor yield of borneol esters is obtained. If, however, metaboric acids, and particularly pyroboric acids be employed, that is to say boric acid anhydrides, and if at least enough of these acids is added to combine in equivalent proportions to form camphene tri-borate, and the temperature is raised to from 165 to 176° C., there is obtained in a far shorter time a considerably greater yield, namely from 5 to 10% of borneol esters. 10 to 13 per cent. of such an acid is necessary.

As is well known, solid camphene when heated at high temperatures from 130 to 180° C., forms borneol and isoborneol esters in an almost theoretical yield, there being practically no by-products, but this action only takes place at quite a high temperature. It is also well known that camphene can be formed in small quantities from oil of tur-

pentine by the action of anhydrous acids or similar hydrolytically acting substances, such as concentrated sulfuric acid, acetic acid, and the like.

The chemical reaction in the above mentioned formation of borneol esters from pinene is therefore quite different from what has hitherto been universally assumed, because the secondary formation of borneol esters presupposes an intermediate formation of camphene, and this in turn presupposes a primary rearrangement of the pinene molecule in the direction of camphene. Pinene molecules can be rearranged either in the direction of camphene or in the direction of limonene, or these two substances can be formed concurrently according to the kind of acid, the method of working, or the hydrolytically acting additions.

Limonene is not adapted for the direct formation of borneol and is consequently a troublesome by-product. The yield of borneol esters is therefore dependent wholly upon the quantity of the camphene formed.

It is well known that pinene when heated with free acids to from 120 to 130° C. is almost entirely changed into limonene, and that therefore only very little camphene is produced. The quantity of limonene is the greater the stronger the acid, the longer the heating is kept up, and the higher the temperature. At the temperature mentioned above, the small quantity of camphene formed is only very incompletely converted into borneol esters, since a temperature of from 160 to 180° C. is necessary for this purpose. In the ordinary process, the formation of camphene is practically entirely precluded at this high temperature because the formation of limonene increases rapidly at anything above 132° C. The chemical reaction considered, generally presents two main phases:—

1. The formation of camphene at about from 120 to 140° centigrade and

2. The formation of the borneol ester from camphene at from 160 to 180° centigrade.

I have discovered by further experiments that the formation of limonene can be partially or entirely stopped, resulting in an increased production of camphene, by the use of protective substances, such as anhydrous alcohols, phenols, or their derivatives and materials acting like alcohols and phenols, such as glycerin. The neutral or acid esters

are especially valuable for the purpose of yielding such protective substances. In fact, any esters which will break down at from 120 to 140° C. (the camphene forming temperature) or at a higher temperature, into acid esters or into free acids without splitting off water, are particularly adapted for this purpose. Such decomposable esters yield acid radicals which become readily combined with the camphene as it forms, protecting the pinene at from 120 to 140° C. during the first stage and favorably affecting the direction of the reaction. The protective materials, which are at the same time set free and can be distilled off, mix with the water formed by the principal reaction and the subsidiary reactions and immediately carry such water off innocuously.

Preferably the esterification acids and the hydrolytically acting added substances must be partially or wholly already combined with the protective substances before they are added to the oil of turpentine, so that the pinene does not come in direct contact in the first stage of the operation with the free acid, as this would aid the formation of limonene in a high degree. The protective substances act simultaneously as acid-binding, acid-diluting, acid-distributing, and acid-dissolving agents, when the esterification acid or the ester produced is soluble with difficulty or insoluble in oil of turpentine. Examples of such esterification acids are the meta- and pyroboric acids, phosphoric acid, arsenic acid, oxalic acid, lactic acid, cumaric acid, cresotinic acid, salicylic acid, benzoic acid, tartaric and citric acids, succinic acid, oxynaphthoic acid, phthalic acid, gallic acid or other mono- or polybasic weak organic or inorganic acids or oxyacids or their derivatives.

According to my invention, the protective substances or their readily decomposable esters prevent the formation of limonene either wholly or partially and thereby aid, to a high degree, the formation of camphene and of borneol esters. The introduction, even in small proportions and at wide intervals of time, of the esterification acid diluted with a protective substance into the oil of turpentine, which preferably has been previously diluted with a protective substance, causes a materially better yield (20 to 25%) of borneol ester.

My experiments have shown that the greatest yield that is about 70% of borneol esters is obtained by the use, as readily decomposable esters heretofore referred to, of weak polyvalent inorganic or organic acids, which are capable of easily forming acid esters and which at high temperatures again split up, partially or wholly and without profound decomposition, into protective substances and acids. As such decomposable esters, preferably only those substances are used

which do not on decomposition yield water, and which in addition are easily soluble in water or in alkaline solutions, the protective substance of which is easily volatile, and the terpene esters of which are easily decomposed by water or alkaline solutions for the easy separation and recovery thereof from the borneol and the by-products.

The esters of the protective substances may be formed separately and added to the oil of turpentine or to the mixture of oil of turpentine and acid. As an alternative method, the protective substances or their esters may be led as gases into the oil of turpentine, or into the mixture of oil of turpentine and acid at a temperature below the boiling point of the oil of turpentine or of the acid used.

In the accompanying drawing which shows in cross section an apparatus for carrying out my invention, A represents an oil bath supported on legs L and L₁ and provided with a thermometer K. Mounted within the oil bath is the digesting vessel B having a rim at its upper end extending over the top of the oil bath A. A cover O extends over the top of the digester vessel and the oil bath and is bolted thereto, washers being used if desired to make tight joints. The cover O is provided with a stuffing box D through which projects a stirrer C provided with any desired form of stirring blades. The cover is also provided with a man hole opening M, a thermometer J, and a tube V for introducing vaporized alcohol into the vessel B.

N represents a discharge tube for the vaporized materials and it delivers into either one or the other of the two Liebig condensers R and R₁, a three-way cock P being provided, so that the volatilized materials may be directed either into the condenser R or the condenser R₁, as desired. The condenser R₁ is used as a reflux cooler, while the condenser R is directed downwardly for the discharge of the materials condensed therein.

Mounted on the top of the cover O is a bent bracket H, and through a bearing in the upper horizontal portion of this bracket the shaft of the stirrer passes, which shaft is provided with a bevel gear wheel E which meshes with a similar wheel F on a horizontal shaft mounted in the vertical part of the bracket H, and which shaft is provided with a driving pulley G. The oil bath may be heated by a gas lamp or in any desired way, and instead of the oil bath a closed steam boiler might be employed.

Example 1. Into the vessel B are fed 150 kilos of anhydrous rectified oil of turpentine, rich in pinene, together with from 50 to 100 kilos of absolute alcohol or methyl alcohol, and from 20 to 30 kilos of finely powdered boric acid anhydrid. The cock P is turned so as to connect the pipe N with the pipe in

the interior of the reflux condenser R_1 , the stirring apparatus is set in motion and the oil bath A heated. This heating and stirring, with the reflux cooling arrangement, is continued for about 12 hours at about from 70 to 100° C., until the alcohol has become esterified with the acid. The cock P is then turned to connect the pipe N with the condenser R, and the uncombined alcohol and the water produced in the previous boiling are then distilled off at from 70 to 90° C. The cock P is then turned to connect the apparatus with the reflux condenser R_1 , and the mixture in the vessel B is boiled under a slowly increasing heat until the temperature reaches about 115° C., this operation taking about an hour. The cock P is then turned to connect the pipe N with the condenser R and then the temperature in the vessel B is raised progressively and slowly from 115° up to about 135° C., this operation consuming about twelve hours, during which time the water produced by the various reactions is distilled off together with any alcohol in the vessel B and with the volatile and neutral alkyl borate, and when this distillation is complete the boiling point of the material in the vessel B rises. The neutral alkyl borate is thus decomposed, first, into the acid ester and alcohol in the presence of the unchanged neutral borate; and at a later phase, partially into free acid and free alcohol. The material in the vessel B is then heated for about twelve hours, the temperature being slowly raised from 135° C. to about 160° C., whereby the last portions of the volatile alkyl ester and the alcohol which has been set free are slowly distilled off. The acid borate first converts the pinene into camphene by rearrangement, and the camphene becomes converted by the acid of the ester, or the boric acid which has been set free, into the borneol ester, which can be recognized by the increasing viscosity of the liquid. When the mass has become viscous, it is heated for about six hours at from 160 to 176° C., whereupon the last portions, including about 3 kilograms of alkyl ester with terpenes and alkylenes and traces of water distil off. There remains in the vessel a mixture of the boric acid ester of borneol and isoborneol in the form of a reddish brown, transparent and solid jelly, which liquefies again between 100 and 150° C. and is easily broken up in the air, or with water, into the hydrates of borneol and boric acid. Above 180° C., the raw borneol borates which usually still contain free boric acid, decompose into water and viscous jellies, which yield practically no camphor on oxidation. It is of the highest importance, therefore, that the temperature should not be allowed to rise as high as 180° C.

The yield of borneol is increased if the last portions of the free boric acid are removed

from the mixture, and this can be done by boiling the mixture for several hours at from 170 to 176° C., and at the same time passing a current of absolute alcohol through said mixture.

The operation is materially shortened if instead of the alcohols and acids, the equivalent quantity of neutral or acid ester of these acids be used with or without the addition of some absolute alcohol or free acid, the latter forming with the neutral ester the desired acid ester.

Example 2. The heating of the substances mentioned in the foregoing example may be carried out in an autoclave or digester provided with stirring and distilling-off appliances. After the stirring apparatus has been started, the digester is heated at about 100° C. for about five hours at a pressure of from 5 to 7 atmospheres above that of the atmosphere, or even at a greater pressure. The pressure is then released, and the uncombined alcohol and water produced in the reaction are distilled off at 115° C. The heating is then continued at about 115° to 125° C. under a pressure of from 5 to 7 atmospheres, and from time to time a certain amount of liquid is blown off in the form of vapor, the heat being gradually raised until the temperature reaches about 135° C. This takes from 6 to 8 hours. The digester is now heated at about 135° to 145° C. for about seven hours at an internal pressure of from 5 to 7 atmospheres. The pressure is then released and the easily volatile products are distilled off, until the boiling point of the liquid rises to about 160° C. The further treatment is the same as in the first example.

Example 3. Into a digester such as is described in Example 2, are fed 150 kilos of dehydrated and rectified oil of turpentine, 50 kilos of absolute alcohol, from 10 to 13 kilos of boric acid anhydrid, and from 50 to 80 kilos of ethyl borate. Instead of the borate of ethyl the oxalate, lactate, silicate, salicylate, citrate, tartrate, gallate, naphthoate, cresotinate, acetate, benzoate, or phosphate of ethyl may be used. The digester is then heated to about 115° C. from 10 to 12 hours at an internal pressure of from 7 to 10 atmospheres above that of the atmosphere, the stirring apparatus being set in motion. The pressure is then reduced and the products are distilled off up to a temperature of 140° C. The digester is then again heated at a temperature of 140° to 160° C. from 5 to 6 hours at a pressure of from 5 to 7 atmospheres above the pressure of the atmosphere, during which time, at intervals, according to the nature and behavior of the particular ester, a small percentage of distillate is blown off for the purpose of removing the injuriously acting subsidiary product of the reaction and increasing the boiling point. The

digester is again heated slowly under a reflux condenser at ordinary pressure up to 176° C. as in Example 1.

Example 4. A charge of turpentine, absolute alcohol, and boric acid anhydrid as mentioned in Example 1, having been introduced into the digester, and the mixture heated to from 70 to 100° C., the vapor of from 100 to 150 kilos of absolute alcohol or methyl alcohol is introduced into the digester. The water produced by the reaction is distilled off with the uncombined alcohol continuously. The further treatment may be effected as in Example 1 or Example 2.

The alkyl ester distillates and alcohols obtained in the various examples may be used over again after being dehydrated. The use of the already formed neutral or acid esters in place of the ester components, and the carrying on of the operation under a pressure of from 5 to 10 atmospheres and the formation of the alkyl ester above the boiling point of its components, shortens the operation considerably, and yields a considerably larger output of borneol ester.

The raw borneol esters obtained as described above, are saponified by heating with water, or with a soda solution, or with dilute caustic soda in the usual way, the unevaporated reagents used and the other unevaporated products of the reactions and the acids passing into the aqueous or alkaline solution while the raw borneols are separated out and

removed. These borneols are then purified by the well known method of fractional steam distillation, or by progressively cooling down and fractionating out in supersaturated solutions.

I claim:—

1. The process of preparing borneol esters, which consists in heating a mixture of oil of turpentine with an alcohol and an acid anhydrid at from 120° to 140° C. for several hours, distilling off the uncombined alcohol and water formed by the reaction, then heating the mixture to from 170° to 180° C. and purifying the product, substantially as described.

2. The process of preparing borneol esters, which consists in mixing oil of turpentine with alcohol and boric acid anhydrid, heating the same until the alcohol has become esterified, distilling off the water and uncombined alcohol, slowly heating up to about 135° C., and allowing the volatile products to escape, finally heating the mass up to 176° C. and purifying the residual product containing borneol esters, substantially as described.

In testimony, that I claim the foregoing as my invention, I have signed my name in presence of two witnesses, this nineteenth day of May 1908.

JOSEF HERTKORN.

Witnesses:

HENRY HASPER,
WOLDEMAR HAUPT.