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PATENT SPECIFICATION

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COMPLETE SPECIFICATION.

Process for Isolating Alcohols or Phenols from Mixtures.

We, the firm ANTON DEPPE SOHNE, a German firm, of Hamburg-Billbrook, Germany, and FRANZ OTTO ZEITSCHEL, of 45, Marienthalerstrasse, Hamburg, Germany, a German citizen, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

Pure alcohols or phenols can be converted into boric acid esters by allowing them to react with the mixed anhydride of boric acid and acetic acid $B(OCOCH_3)_3$. The tri-borates produced can then be readily obtained pure after distillation or crystallisation.

It has now been found that this reaction which takes place smoothly can not only be used in connection with pure alcohols but that with the assistance of this reaction it is possible almost quantitively to isolate alcohols of all kinds; primary, secondary or tertiary or also phenols from mixtures without injuring the by-products contained therein. The method of operation is the same in all cases. After having ascertained by acetylising the quantity of alcohols present in a mixture to be examined, a suitable quantity of the double anhydride is prepared and added to the above mixture. With the development of a slight heat decomposition takes place and it is only necessary at ordinary or preferably at reduced pressure to distil off the acetic acid formed, and the more readily volatile by-products from the tri-borates which are more difficult to volatilise. If the borates are solid they can be further purified before splitting up by recrystallisation from a suitable solvent. The esters obtained are decomposed by the addition of water or watery alkalies and the alcoholic dissociation products are rectified or recrystallised for purification.

The new method is more particularly applicable with advantage to the field of chemistry of terpenes and the essential oils but it may also be of use for other industries.

In a quite analogous manner as with the boric acid acetic acid anhydride the reaction can also be carried out with the corresponding double anhydrides of arsenious acid, $As(OCO\ CH_3)_3$, of antimonious acid $Sb\ (OCO\ CH_3)_3$ or phosphorous acid, $P\ (OCO\ CH_3)_3$. The acetic acid anhydride may be replaced by any other organic acid anhydride. In practice however there are preferably used those which are more easily available and inexpensive such as propionic acid anhydried, butyric acid anhydride, valeric acid anhydride, benzoic acid anhydride, and phthalic acid anhydride.

The reaction can also be carried out by using boric acid, arsenious acid, antimonious acid or phosphorous acid, or their anhydrides, alone, instead of using the double anhydrides with organic acid anhydrides.

It is the object of the present invention to isolate alcohols or phenols contained in a mixture of any character by converting them into the esters, which are difficult to volatilise, of boric acid, arsenious acid, antimonious acid or phosphorous acid.

According to the present invention one of the above acids or their anhydrides, or the double anhydride of one of these acids with the anhydride of an organic acid, is caused to act on the mixture containing the alcohols or phenols. When an ester, difficult to volatilise, has been obtained by one method or the other, the constituents of the mixture, which are of a non-alcoholic nature, can be removed by distillation, whilst the

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alcohols and phenols, which are combined with the acids used, remain in the distillation apparatus as a residue which is difficult to volatilise. By the decomposition of the resultant esters by means of dilute alkalies into their components, alcohols (phenols) and acids, the alcohols, freed from admixtures of non-alcoholic nature, are obtained in a pure form or may be further purified if necessary.

For the purpose of separating the alcohols into various classes (primary, secondary and tertiary) the operations above referred to are carried out in stages in that the boric acid or other acids, or their anhydrides, or their double anhydrides with organic acid anhydrides are used in suitable quantities.

EXAMPLES.

I. SAPONIFIED JAPANESE PEPPERMINT OIL.

702 gr. with 54.2% total alcohols were treated with a solution of 45 gr. $B(OH)_3$ in 225 gr. acetic acid anhydride. During the vacuum distillation, there passed over, besides the acetic acid, 353 gr. indifferent oil, whilst on cooling 347 gr. solidifiable borates remained as a residue in the flask. After neutralisation 332 gr. of an alcohol were obtained therefrom by steam distillation, which soon solidified in the cooler and from the constants: $d_{15} = 0.903$, $\alpha_{100} = -35.60°$ was found to be almost pure menthol.

A second treatment of the indifferent oil only gave 14.3 gr. alcoholic constituents.

II. CITRONELLA OIL CEYLON.

380 gr. with 57.6% total geraniol contents were treated with a solution of 15 gr. $B(OH)_3$ in 75 gr. acetic acid anhydride. By the vacuum distillation 120 gr. of borate were obtained as a residue in the flask which by steam distillation after neutralisation produced 107 gr. total alcohols ($d_{15} = 0.904$, $\alpha_{100} = -2.50°$), which reacted with pulverised $CaCl_2$ and was mainly found to be geraniol.

III. SHIU OIL.

385 gr. (with $d_{15} = 0.878$ and $\alpha_{100} = -11.00°$) of which the main portion consists of linalool, was treated with 50 gr. $B(OH)_3$ and 250 gr. acetic acid anhydride. By vacuum distillation there remained 278 gr. borate, which when neutralised with a soda solution and distilled with steam produced 270 gr. of almost pure linalool ($d_{15} = 0.870$, $\alpha_{100} = -15.00°$). The indifferent oil 78 gr. showed however $d_{15} = 0.906$, $\alpha_{100} = +8.50°$.

IV.

For examining the accuracy of the method 200 gr. of benzyl acetate (with 94% ester and 6% benzyl alcohol respectively) were subjected to the reaction of this method and were treated with 3 gr. $B(OH)_3$ + 15 gr. acetic acid anhydride. By vacuum distillation there remained a residue of 10 gr. which split up with a soda solution produced 10 gr. benzyl alcohol. The ester contents of the non-reacting parts had increased to 100%. The course of the method was therefore quantitative.

The amounts of boric acid used in Examples I to IV are calculated according to the following equations:

$$a)\ \underset{62.2:}{B(OH)_3} + 3\,\underset{306}{(CH_3CO)_2O} = 3\,CH_3.COOH + B(OCO\,CH_3)_3$$

$$b)\ B(OCO\,CH_3)_3 + 3\,C_{10}H_{19}.OH = \underset{\text{Menthol}:468.}{3\,CH_3.COOH} + B(OC_{10}H_{19})_3$$

The ratio numbers for the conversion of menthol are therefore: 62.2 : 306 : 468.

In the Example I (peppermint oil): 702 gr. have been found to be 54.2% total menthol = 380.48 gr. on the basis of acetylisation. For the conversion 50.5 gr. $B(OH)_3$ were therefore necessary theoretically. 45 gr., less than the theoretical amount, were therefore used as in peppermint oil esters and other alcohols and phenols are present besides menthol so that there were deviations from what would be expected theoretically.

The differences in connection with citronella oil (Example II) are more considerable as in the presence of citronella oil there is found a too great content of geraniol when acetylising (see Gildemeister (1913) II page 239).

The calculation of boric acid was therefore made in a similar manner in connection with Example III and IV.

It was further found that the formation of esters difficult to volatilse can also be obtained if the boric acid or its anhydride (or arsenious acid, antimonious acid, phosphorous acid or their anhydrides), are allowed as such to act on the mixture in the presence of heat. The reaction takes place according to the following formulæ:

$B(OH)_3 + 3\ HO.R = 3\ H_2O + B(OR)_3$ or

$B_2O_3 + 6\ HO.R = 3\ H_2O + 2B(OR)_3$.

where R indicates an alcohol or a phenol residue, and where B can be replaced by As, Sb or P.

It is only necessary to take care that the water produced during the reaction is removed by distillation or otherwise. The quantity of the distilled water gives a direct indication as to the procedure of the reaction. To the same extent as the water separation takes place the boric acid or the analogue which is used (As_2O_3, Sb_2O_3, P_2O_3) is gradually dissolved in the oil mixture.

The method of operation can be explained by the following examples:

V.

624 gr. of a comphor oil fraction with $d_{15}=0.974$, $\alpha_{100}=+1.60°$ and a total alcohol content of 50.3%, consisting of terpineol and borneol, were heated with 60 gr. $B(OH)_3$ in the flask to about 80 to 100°. The water is very soon separated and is condensed in the cooler in the form of drops. Under a slight vacuum it distils off with a small quantity of oil and can be measured in the receiver (32 gr.). After about two hours the separation of the water ceases and the boric acid has passed into solution. With a good vacuum the indifferent oil is now completely distilled off and the borates remaining as a residue in the flask are decomposed by means of a soda solution and the alcohols are evaporated. There are obtained:

Alcohols: 295 gr. with $d_{15}=0.941$, $\alpha_{100}=-0.00°$.

Indifferent oil: $\frac{310 \text{ gr.}}{605 \text{ gr.}}$ with $d_{15}=1.002$, $\alpha_{100}=+10.50°$.

In Example V more boric acid was used than is theoretically required as the tertiary alcohols, for example terpineol cannot be esterilised quantitatively. With the camphor oil used the values obtained by esterilisation would have been too small and for this reason an excess of boric acid was used. The examples are only adapted to explain the procedure of the reaction and therefore these have not been strictly limited to the theoretical figures.

It was further found that when carrying out the treatment in stages according to the borate method an approximate separation of alcohols of different classes could be effected. This possibility is based upon the fact that the reaction capacity of the primary alcohols is greater and quicker than that of the secondary alcohols, that of the secondary is greater than that of the tertiary alcohols, so that by suitably dosing the boric acid or other acids as may be desired it is possible to obtain from a mixture either the primary or primary and secondary, or if the primary are not present, the secondary.

VI.

From a mixture of 60 gr. geraniol and 140 gr. terpineol, which at the start will not in any way react with calcium chloride, 72 gr. of alcohols are obtained by treatment of 10 gr. boric acid in the manner described, distillation of the indifferent part and decomposition of the remaining borates, which smoothly react with calcium chloride and prove to be a geraniol of high percentage. In the distillate the terpineol has been correspondingly enriched.

VII.

From a mixture of 60 gr. borneol and 140 gr. terpineol it is possible in quite a similar manner by means of 10 gr. boric acid to isolate about 75 gr. borates difficult to volatilise, which already become solid in the cooler by steam distillation and are mainly found to be borneol.

VIII.

From a mixture of 30 gr. geraniol, 30 gr. borneol and 140 gr. terpineol it is possible in a quite similar manner to separate by means of the borate method 120 gr. of almost pure terpineol from 70 gr. geranyl-bornyl-borates which it is difficult to volatilise.

As the conversions with the other acids above referred to are more difficult than when using boric acid, the reaction, for example with arsenious acid anhydride (As_2O_3) is carried out at a somewhat higher temperature, Example IX. 200 gr. of a liquid raw Japanese peppermint oil ($d_{15}=0.898$, $\alpha_{100}=-29.70°$, and 44.5% total menthol) were heated with 19.8 gr. As_2O_3 to 150° as long as there was a separation of water. The further treatment was carried out in the usual manner and produced at room temperature alcohols: 70 gr., $d_{15}=0.907$, $\alpha_{100}=-35.60°$.

Indifferent oils: 128 gr., $d_{15}=0.8935$, $\alpha_{100}=-26.10°$.

In the specification the wave length for the specific rotary powers are based on sodium light = D.

It will be understood that instead of the artificial mixtures here referred to oils occurring in nature or technical oils can be used.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. A method of isolating alcohols or phenols from mixtures consisting in treating the mixtures with quantities of boric-acid-acetic acid-anhydride corresponding with the alcohols or phenols contained therein, distilling off the volatile admixtures, decomposing the remaining borates by a solution of alkalies in water, and further purifying or, in so far as they are solid, previously recrystallising them.

2. A process according to Claim 1 with the distinguishing feature that instead of boric-acid acetic-acid anhydride there are used the anhydrides of arsenious acid or of antimonious acid or phosphorus acid with acetic anhydride.

3. A process according to Claim 1 with the distinguishing feature that instead of boric acid acetic-acid anhydride there is used the anhydride of boric acid with the anhydride of another organic acid.

4. A process according to Claims 1 to 3 with the distinguishing feature that instead of the double anhydrides, boric acid, arsenious acid, antimonious acid or phosphorus acid or their anhydrides are caused to act alone upon the raw material.

5. A process according to Claims 1 to 4 consisting therein that for the purpose of obtaining an approximate separation of alcohols of different classes boric acid, arsenious acid, antimonious acid or phosphorous acid or their anhydrides or their double anhydrides with organic acid anhydrides are used in corresponding quantity.

6. Methods of isolating alcohols or phenols from mixtures, substantially as described.

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