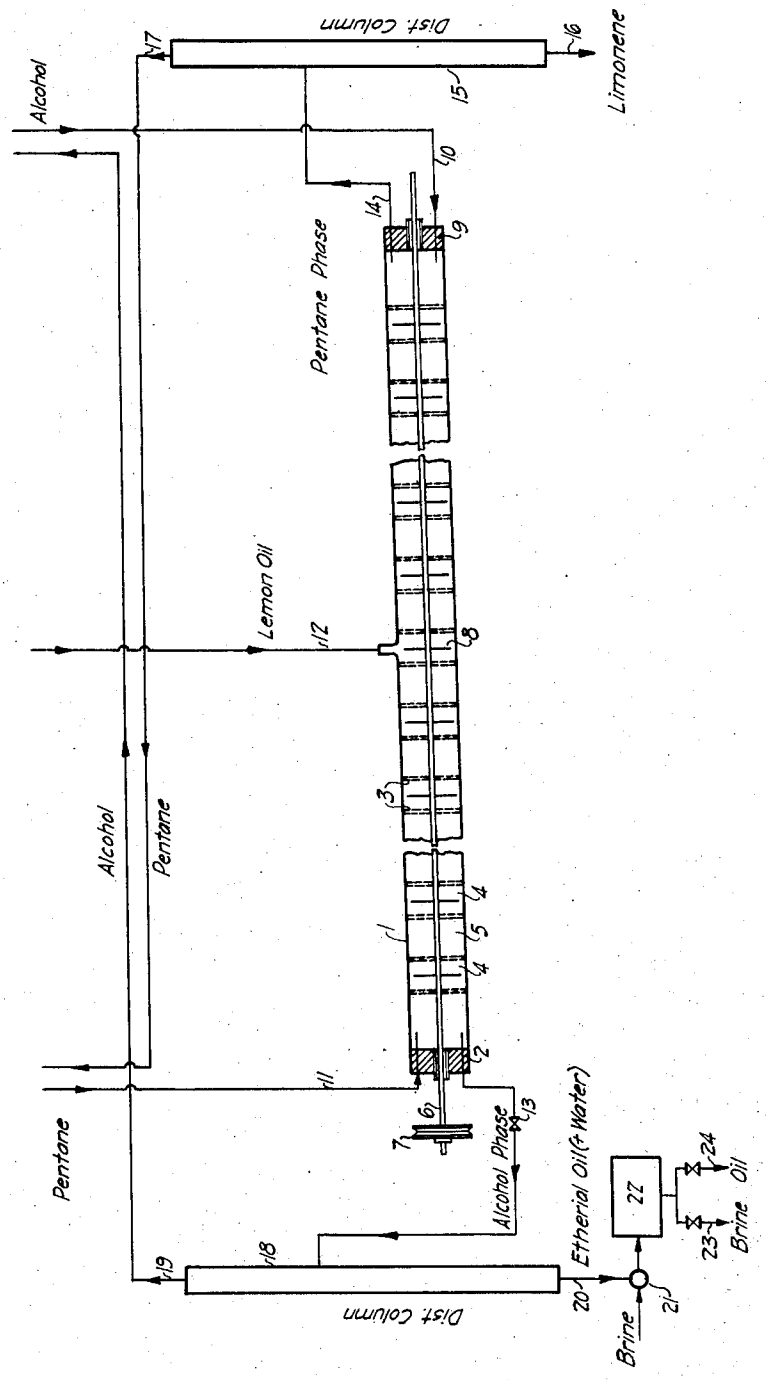
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PROCESS FOR EXTRACTING ETHEREAL OILS

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PROCESS FOR EXTRACTING ETHEREAL OILS

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This invention relates to a process for extracting, concentrating and purifying ethereal (essential) oils with the aid of solvents.

It is known to extract natural ethereal oils, such as lemon oil, with aqueous alcohol for the purpose of obtaining a concentrate of the essential oil which is largely free from terpenes. Such a process may yield essential oils of a high degree of purity, i. e. oils consisting almost entirely of the desired compounds, such as citral, geraniol, linalool and the like, but the yield of these compounds in the extract is low, and these operations are uneconomical and complicated.

According to the present invention it was found that the losses in such extractions can be considerably reduced in a simple manner by subjecting the initial oil to the extracting action of two solvents or mixtures of solvents, flowed preferably in countercurrent, which are not completely miscible with each other under the conditions of the process and in the presence of the oil being extracted. The first of these solvents or solvent mixtures is a polar substance and preferentially dissolves the desired constituent of the oil having the higher polar moment, e. g., the terpene alcohol, aldehyde, ester, phenoloid body, or the aromatic aldehyde or ketone; the second of these solvents or solvent mixtures consists entirely or predominantly of non-polar substances, such as hydrocarbons.

As the first solvent we may employ any polar liquid which is a preferential solvent for the constituent of the higher polar moment. Examples of such solvents are: liquid ammonia, liquid sulfur dioxide and organic compounds containing one or more of the following radicals: ≡COH (including primary, secondary and tertiary alcohols), =CO, =C(OH).O.C≡, —NO_2, —CN, ≡CX (wherein X represents halogen), —NH_2, =NH, ≡N, and —COOR, wherein R is an aliphatic or aromatic radical.

The preferred class of solvents consists of the lower molecular weight oxygen-containing aliphatic compounds, particularly the lower alcohols, such as methanol and ethanol, ketones, such as acetone and methyl ethyl ketone, esters, such as methyl formate, methyl acetate and ethyl formate, and lower molecular nitro-compounds, such as nitromethane. These may often be diluted with an ether, such as diethyl ether. Of these solvents methanol and ethanol are the preferred embodiments.

Halogenated, and particularly chlorinated derivatives of the above compounds are also suitable. Other examples of solvents are: methyl cyanide, chlormethyl alcohol, diethanol amine, dimethyl amine, isopropyl alcohol, and cyclic compounds, such as aniline, chloraniline, cresol, nitrobenzene and phenyl acetate. Suitable solvents are only those which can easily be removed and do not give a disagreeable odour to the products of the extraction.

The treatment may also be effected in the presence of water, or a highly polar water-soluble organic substance. This presents some advantages if the miscibility of the two solvents used is too great at the temperature selected. The addition of water reduces the miscibility of the first and second solvents, and raises the critical miscibility temperature. The quantity of water must, of course, be of a small amount to preclude an undesirably large reduction in the solvent power of the resulting aqueous first solvent for the desirable constituents of the essential oil. The water may be introduced into the process at any point, but it was found most practical to add it to the first solvent prior to its introduction into the extraction apparatus.

The second solvent consists entirely or for the greater part of non-polar liquids, such as liquid or liquefied hydrocarbons having boiling points which are different from the constituents which are present in the initial essential oil being extracted. While it is in certain cases possible to employ a high-boiling hydrocarbon liquid, we prefer to employ a relatively low-boiling hydrocarbon, such as one containing not over twelve carbon atoms. Moreover, since many of the hydrocarbons contained in natural ethereal oils boil not far above 150° C., it is in most cases advantageous to employ a hydrocarbon solvent boiling below 150° C. Lower molecular weight hydrocarbons which are particularly suitable are those containing more than two and less than seven carbon atoms. Specific examples of suitable low molecular weight hydrocarbons are: propane, butane, pentane, light gasoline, naphtha and the like; but unsaturated hydrocarbons, such as pentene, aromatics, such as benzene and its homologues, and naphthenes, such as cyclopentane and cyclohexane, may also be used. Examples of high molecular weight hydrocarbons are paraffinum liquidum or a well-refined lubricating oil. Use may further be made of mixtures of hydrocarbons, as also of non-hydrocarbon liquids which in the presence of the ethereal to be separated are not completely miscible with one of the aforesaid polar solvents to be applied. Examples are liquid CO_2, CF_2Cl_2, CS_2, whilst other

polar-substituted hydrocarbons which are non-polar are likewise suitable.

The temperature and pressure conditions under which the process is carried out, and the relative concentrations of the solvents and the initial oil are chosen in such a manner that two liquid phases are formed. One or more (and, in most cases, all) of the components of the initial are distributed over the two liquid phases in different ratios. For example, when extracting lemon oil (obtained by pressure from the fresh peel of the *Citrus medica*) the process may be carried out so that the phase rich in the second solvent (e. g., the hydrocarbon phase) chiefly contains the terpenes, while the phase rich in the first solvent contains the desired ethereal oil, such as citral, geraniol, linalool, etc.

It is also possible, by regulating the temperature, and/or the water concentration in the first solvent, to vary the solvent power and thereby to change the character of the separation between the various components of the initial oil. For example, one of the polar components may be removed with the terpenes, and only the more polar components removed in the phase rich in the first solvent.

It is not necessary that the two solvents or solvent mixtures be entirely insoluble in each other, nor that they be only sparingly miscible; it is sufficient that they are not completely miscible with each other in the presence of the oil being extracted.

When the liquid phases in the process have been contacted with each other, e. g., when they have been passed preferably countercurrently to each other, they are withdrawn at spaced points in the extraction zone. The solvents may then be separated from the dissolved constituents in any suitable manner, e. g. by distillation, rectification, freezing out, salting out, washing (e. g., with water), chemical action, etc., or with a combination of these methods.

The boiling points or the boiling ranges of the two solvents or solvent mixtures are preferably chosen to be below those of the constituents of the oil to be treated. When recovering the solvents and producing the valuable extracts the oxygen-containing products need then not be distilled off, which is an advantage, since most ethereal oils are easily destroyed by heat and their value usually diminishes as a result of distillation.

When a higher boiling polar material is employed as the first solvent, it is often possible to remove it by washing the withdrawn liquid phase with a highly polar material, like water, in which the ethereal oils are only slightly soluble.

The hydrocarbons contained in the second solvent may, however, have higher boiling points than the ethereal oil. In most cases this does not present any difficulty, since the components dissolved in the hydrocarbon extracting agents may be distilled off without any trouble and/or are less valuable than the odorous substance which are preferentially dissolved in the first solvent. This distillation may be conducted under vacuum or at atmospheric pressure.

The temperature of the extraction depends upon the nature of the ethereal oil and the solvents employed. In general, however, it will take place at normal or not very high temperatures, e. g., below 100° C. Reduced temperatures are also possible.

The temperature need not be uniform throughout the extraction zone, since a temperature gradient may be employed in a part or in the whole of the apparatus. As a result of this temperature gradient the highest temperature may occur at the middle of the zone, or near the point of introduction of the initial oil (which may be near the middle, or nearer to one end); alternatively, the temperature may be highest at one or at both ends of the extraction zone. By regulating the temperature at various points the miscibility of the two liquid phases in contact at the different points in the apparatus may be varied within wide limits.

As the extracting apparatus any of the known types of apparatus for effecting the countercurrent contact of liquids may be employed, e. g., one or more horizontal or vertical columns, or one or more mixers and liquid phase separators. As separators settling vessels or centrifuges may be employed.

The initial oil may be introduced into the center of the extraction apparatus, or at any other point intermediate between the ends of the extraction zone, asymmetrically with respect thereto. It is, moreover, possible to introduce the initial oil at one of the ends of the apparatus.

Before being introduced into the apparatus, the initial oil may be dissolved or dispersed in one of the two solvents, and introduced at one end of the apparatus; it is, however, preferable to introduce the resulting solution of the initial oil in the solvent at an intermediate point of the system, and to introduce only a small part of the total solvent at this point, introducing the greater portion of the solvent at the end of the apparatus, or at several points in the apparatus. In order to check the formation of non-readily separable emulsions of one of the two phases in the other, substances reducing the stability of the emulsion may be added to the initial oil or to one of the solvents, or introduced separately into the apparatus. For example, in the extraction of lemon oil with 90% aqueous methanol and pentane it was found that the addition of 0.1% of citric or tartaric acid is helpful in preventing the formation of these obnoxious emulsions.

The oil may be treated repeatedly by the so-called batch method with the mixture of extracting solvents, but the process is more conveniently and efficiently carried out continuously. The extraction may further be carried out as a single or as a multiple process, in the latter case preferably by applying the countercurrent principle. However, the application of the crosscurrent principle is also possible (cf. the diagram in Figure 8 on page 307 of the "Nederlandsch Tijdschrift voor Natuurkunde", Vol. II, 1935). When applying this principle it is, for instance, possible to extract repeatedly with fresh quantities of the polar solvent liquids containing constituents of the oil dissolved in the other solvent used. The reverse is also possible, viz. washing a solution in the polar solvent repeatedly with fresh quantities of the non-polar solvent. A combination of these methods may also be applied. Thus a solution of certain constituents of the oil in the first solvent may be repeatedly extracted with fresh quantities of the other solvent; the extracts obtained, after having been mixed, may then be repeatedly extracted with fresh quantities of the first solvent used. The extracted portions dissolved in the first solvent obtained in the latter treatment and contingently after having been mixed with fresh oil being identical with the solution of certain constituents in the first solvent, may again be repeatedly extracted with

fresh quantities of the second solvent, and so on.

One form of apparatus which is suitable for the present process is described by Cornish, Archibald, Murphy and Evans and illustrated in Figures 4 to 7 inclusive, pages 401 to 404 of the Journal of Industrial and Engineering Chemistry, vol. 26, No. 4 (1934).

Example

The process may be carried out in the apparatus illustrated in the accompanying drawing, in which 1 is a tubular shell, which may be placed horizontally or slightly inclined. In the present example the shell was about 2 metres long and 4 cm. in diameter, and placed at a very slight inclination, the end 2 being lower. Perforated transverse partitions 3, made of wire gauze, divided the tube into 21 mixing spaces 4 and 22 settling spaces 5, the former being about 1.5 cm. in length and the latter about 7.0 cm. Any number of such spaces may, of course, be provided. A central shaft 6, provided with a driving pulley 7 and stirring two pins 8 in each mixing space and journalled in the end blocks 2 and 9 agitated the liquids in the mixing spaces. In the four mixing spaces nearer the end 2 double pins were provided, since more intense mixing was possible at this end without forming pertinaceous emulsions.

The tube was filled with 90% aqueous methanol, introduced through the conduit 10, and pentane, introduced through the conduit 11, in the ratio of about 2 to 3, and the stirrers started. Pentane was introduced at the middle through a conduit 12 and the drain valve 13 for the alcohol phase was regulated. The temperature of operation was 20° C. When the interfaces were constant and the apparatus was in equilibrium, lemon oil having a citral content of about 4% by weight, containing an amount of other oxygen-containing ethereal substances of about 4.5% by weight and consisting for the rest of terpenes and sesquiterpenes was introduced through the conduit 12 instead of pentane, and feed rates then being 24 cm^3, of 90% methanol, 8 cm^3. of pentane and 8 cm^3. of lemon oil per minute. The alcohol phase was continuously drawn off through the valve 13, and the pentane phase was drawn off through the outlet 14, these phases being separately treated to remove the solvents from the dissolved constituents.

The pentane phase was distilled under atmospheric pressure in the column 15, the dissolved constituents being withdrawn at 16 and the pentane at 17. The alcohol phase was distilled under reduced pressure in the column 18 at a temperature below 55° C. to prevent the deterioration of the extract until about 80% of the alcohol had been vaporized and removed through the conduit 19. The distillation residue was then withdrawn at 20, agitated in the mixer 21 with five parts by volume of brine, and allowed to stratify in the phase separator 22, the oxygen compounds separating out as an oily top layer, which was separated from the brine by decantation, brine and ethereal oil being withdrawn at 23 and 24 respectively. Losses were reduced by further extracting the brine layer with pentane.

The ethereal oil recovered from the alcohol phase contained 40% by weight of citral and consisted, for the rest, chiefly of the other oxygenated substances of the lemon oil, while the product withdrawn at 16 contained most of the terpenes and sesquiterpenes. The yield of terpeneless oil was 8% by weight of the lemon oil extracted, as compared to a yield of 5% which is obtained by extraction with methanol alone.

It is, of course, possible to use other solvents besides methanol and pentane, as explained above. Thus, a light gasoline fraction boiling, for example, between 40 and 60° C. may be substituted for pentane in the above example.

It is also possible to extract the oil so as to produce more than two fractions. This may be effected by subjecting one or both of the products of the above process to a second extraction, which may be similar to the one described above.

Besides the two final products, however, there may also be obtained intermediary products, for example, by removing a portion of the extraction mixture at one or more points in the extraction apparatus between the ends, stripping the desired phase of the solvents and, if desired, returning the remainder of the withdrawn material at the same or at another point.

The present process may be applied to the treatment of all types of natural ethereal oils. For example, orange peel oil may be extracted to remove citral and other oxygenated substances from limonene. Lavender oil, containing esters, linalool, geraniol and sesquiterpenes, may be concentrated by removing the hydrocarbon; or it may be separated into several fractions by repeated extractions.

Other essential oils which may be extracted are: rose oil, rosemary oil, onion oil, lime oil, jasmine oil, anise oil, acacia oil, calamus oil, etc., but the invention is not limited to any specific example disclosed herein. In many extractions the separation is not between polar and non-polar constituents, but between polar constituents having different polar moments. In the preferred application of the invention, however, terpenes and sesquiterpenes are removed from essential oils, to isolate the odorous constituents.

We claim as our invention:

1. A process for separating ethereal oil containing constituents of different dipole moments into fractions containing concentrates of different constituents by means of solvents, comprising the steps of subjecting said oil to the extracting action of a liquid polar preferential solvent for a non-hydrocarbon ethereal constituent of said oil having a relatively high dipole moment, and a non-polar solvent in the liquid state, said solvents being at least partially immisicible under the extracting conditions in the presence of said oil, said extracting conditions being such as to cause the formation of a liquid phase rich in said polar solvent having dissolved therein a concentrate of said non-hydrocarbon constituent, and a liquid phase rich in said non-polar solvent having dissolved therein a concentrate of a constituent of said oil having a lower dipole moment than said first non-hydrocarbon component, and separating the said liquid phases from one another.

2. The process according to claim 1, in which the liquid polar solvent comprises an organic compound containing a radical of the group consisting of ≡COH, =CO, —COOR, =C(OH).O.C≡, —NO_2, —CN, ≡CX (wherein X represents halogen), —NH_2, =NH, ≡N.

3. The process according to claim 1, in which the polar solvent and the non-polar solvent flow countercurrently to each other through a countercurrent extraction system.

4. A process for separating ethereal oil containing constituents of different dipole moments

into fractions containing concentrates of different constituents by means of solvents, comprising the steps of subjecting said oil to the extracting action of a liquid polar preferential solvent for a non-hydrocarbon ethereal constituent of said oil having a relatively high dipole moment, said polar solvent having a boiling point below said non-hydrocarbon constituent, and a hydrocarbon solvent in the liquid state, said solvents being at least partially immiscible under the extracting conditions in the presence of said oil, said extracting conditions being such as to cause the formation of a liquid phase rich in said polar solvent having dissolved therein a concentrate of said non-hydrocarbon constituent, and a liquid phase rich in said hydrocarbon solvent having dissolved therein a concentrate of a constituent of said oil having a lower dipole moment than said first non-hydrocarbon component, and separating the said liquid phases from one another.

5. The process according to claim 4, in which at least two constituents of the ethereal oil, dissolved in one of the solvents, are at least once contacted with fresh quantities of the other solvent to form two liquid phases each of which contains a different one of said constituents in a more concentrated form.

6. The process according to claim 4, in which the solvents are counterflowed through a countercurrent extraction system and the initial ethereal oil is introduced into an intermediate stage of said system.

7. A process for separating ethereal oil containing constituents of different dipole moments into fractions containing concentrates of different constituents by means of solvents, comprising the steps of subjecting said oil to the extraction action of a liquid polar preferential solvent for a non-hydrocarbon ethereal constituent of said oil having a relatively high dipole moment, and comprising a low molecular weight oxygenated aliphatic compound, and an aliphatic low boiling non-polar solvent in the liquid state, said solvents being at least partially immiscible under the extracting conditions in the presence of said oil, by introducing said solvents at spaced points in a countercurrent extraction zone, counterflowing said solvents within said zone, and introducing the ethereal oil into said extraction zone, under conditions causing the formation of a liquid phase rich in said polar solvent having dissolved therein a concentrate of said non-hydrocarbon constituent, and a liquid phase rich in said non-polar solvent having dissolved therein a concentrate of a constituent of said oil having a lower dipole moment than said first non-hydrocarbon component, and separating the said liquid phases from one another.

8. The process according to claim 7, in which the initial oil is dissolved in a portion of the oxygenated low molecular weight compound, and the resulting solution is introduced into the extraction zone at a point intermediate between said two points.

9. A process for concentrating non-hydrocarbon ethereal constituents of ethereal oil containing non-hydrocarbon ethereal constituents and hydrocarbon constituents, by means of a liquid polar solvent, which is a preferential solvent for the non-hydrocarbon constituents of said oil and has a boiling point below said constituents, and a non-polar solvent in the liquid state, said solvents being not completely miscible under the extracting conditions in the presence of said oil, which comprises subjecting the ethereal oil to the extractive action of said solvents introduced at different points of an extraction system containing two zones, in the first of which hydrocarbon constituents of the ethereal oil are separated from the non-hydrocarbon constituents with the aid of the non-polar solvent whereafter the purified non-hydrocarbon constituents leave the first zone, and in the second of which non-hydrocarbon constituents of the ethereal oil are separated from the hydrocarbon constituents with the aid of the polar solvent whereafter the purified hydrocarbon constituents of the oil leave said second zone.

10. A process according to claim 9, in which the ethereal oil is introduced between the two zones mentioned.

11. The process according to claim 9, in which the liquid polar solvent consists predominantly of a low molecular weight oxygenated aliphatic compound.

12. The process according to claim 1, in which the initial oil is lemon oil, and the liquid polar preferential solvent is an alcohol having less than three carbon atoms.

13. A process for separating natural ethereal oil into two portions having different properties, comprising the steps of counterflowing a first liquid selective solvent for the relatively more polar constituent of said oil and a second liquid solvent consisting predominantly of hydrocarbons, said solvents, when mixed, being capable of forming two liquid phases, bringing said ethereal oil into contact with said counterflowing solvents, to form a liquid phase rich in said first solvent having dissolved therein a concentrate of the relatively more polar constituent of said oil, and a liquid phase rich in said second liquid solvent having dissolved therein a concentrate of less polar constituents of said oil, and separating the resulting liquid phases.

14. A process for removing hydrocarbons from lemon oil, which comprises the steps of contacting said oil with an alcohol having less than three carbon atoms and with a hydrocarbon solvent boiling below 150° C., under conditions causing the formation of two liquid phases, one of said phases being rich in said alcohol and containing dissolved therein a concentrate of the ethereal non-hydrocarbon constituents of said lemon oil, and the other of said phases being rich in said hydrocarbon solvent and containing dissolved therein a concentrate of the hydrocarbons of said lemon oil, and separating said phases.

15. The process according to claim 14, in which the alcohol is aqueous methanol of about 90% concentration, and the hydrocarbon contains not less than three and not more than six carbon atoms.

16. A process for treating an ethereal oil comprising an aldehyde and terpene hydrocarbons to remove the hydrocarbons therefrom, which comprises the steps of subjecting said oil to the extractive action of two solvents which, under the conditions of the process and in the presence of said oil, are capable of forming two liquid phases, one of said solvents comprising a polar liquid which is a preferential solvent for said aldehyde, and the other solvent comprising a hydrocarbon, to form a liquid phase rich in said polar liquid having dissolved therein a concentrate of said aldehyde, and a liquid phase rich in the hydrocarbon of the said other solvent having dissolved therein a concentrate of the terpene hydrocarbons, and separating said liquid phases.

17. A process for separating natural ethereal

oil containing constituents of different dipole moments into two portions having different properties, comprising the steps of subjecting said oil to the extractive action of two solvents which, under the conditions of the process and in the presence of said oil, are capable of forming two liquid phases, the first of said solvents comprising an organic compound containing a radical of the group consisting of ≡COH, =CO, —COOR, =C(OH).O.C≡, —NO_2, —CN, ≡CX (wherein X represents halogen), and —NH_2, =NH, ≡N, and the second solvent comprising a hydrocarbon, to form a liquid phase rich in said first solvent having dissolved therein a concentrate of the constituent of said oil having a relatively higher dipole moment, and a liquid phase rich in said second solvent having dissolved therein a concentrate of the constituent of said oil having a relatively lower dipole moment, and separating said liquid phases.

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