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PROCESS FOR THE RECOVERY OF
ESSENTIAL OILS

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This invention relates to a process for the recovery of essential oils, such as orange oil, lemon oil, lime oil or other oils from citrus fruit.

It is common practice at present to recover orange oil from orange peel by cold pressing the orange rind and pulp to separate a portion of the oil contained therein and recover the remainder of the oil present in the pressed residue by steam distillation. The oil recovered from the pulp by steam distillation is considered inferior to the cold pressed oil because of the inclusion of undesirable constituents due to their volatility with the steam. Consequently, the oil which is recovered by steam distillation is of inferior quality to the cold pressed oil and, therefore has a somewhat lower commercial value. The yield of cold pressed oil from orange peel, however, is rather low, in fact on the basis of the whole fruit, from 0.1 to 0.3% is about the highest yield of oil which can be recovered by cold pressing. Therefore, the remainder of the oil which may amount to 0.45 to 0.7% is recovered by steam distilling the cold pressed rind or pulp.

By our process we have discovered a method by which we are able to recover a major portion of the oil present in the citrus pulp or peel and at the same time retain in the recovered oil the desirable quality characteristics of cold pressed oil. The oil recovered by our process is completely soluble in 95% ethyl alcohol, which permits its incorporation in alcoholic flavoring extracts without the necessity of filtration for the preparation of clear solutions. While it is possible to treat unpulped orange peel by our process it is preferable that the citrus peel be pulped or ground by any suitable method into a fine slurry in the presence or absence of water. This slurry or ground citrus peel is then extracted with a suitable solvent which has a high solvent power for the oil and a minimum solvent power for the undesirable constituents of the peel or pulp. The solvent solution of the citrus oil is then separated from the pulp or slurry and subjected to distillation for the removal of solvent from the oil.

More specifically, the process consists in pulping the citrus peel or grinding in the presence of water to form a slurry containing the highest possible content of essential oil, which upon concentration by rejecting the juice and oil free portions of the fruit may actually reach 1 to 5% of essential oil. This pulp or slurry is then contacted with an appropriate solvent, such as liquid normal butane at a temperature of about 70° F. to 80° F. We have found it preferable to extract

the essential oil at temperatures substantially above 32° F. in order to avoid freezing of oil cells which would reduce the yield of oil. The solvent and citrus pulp or slurry is then thoroughly agitated for a period of time sufficiently long to completely extract the essential oil. The mixture is then permitted to settle, the heavier pulp precipitating to the bottom of the container. After removal of a major portion of the water and pulp by any suitable means, the butane or other hydrocarbon solution is then separated from the remainder of the insoluble material by ordinary decantation or by filtration or by a combination of decantation and filtration, or, if desired, the butane solution may also be separated from the butane insoluble materials by centrifuging the mass. The butane phase recovered by the foregoing extraction contains the major portion of the essential oil in solution as well as some undesirable resins. In order to remove these undesirable resins from the butane solution of essential oil, this solution is cooled sufficiently to cause the resins present to precipitate. The chilled butane solution is filtered, centrifuged or settled for the separation of the precipitated resinous material, after which the substantially resin-free butane solution of essential oil is distilled for the removal of the butane from the oil. By the foregoing process we are able to recover as high as approximately 90% of the essential oil present in the citrus fruit.

It is, therefore, an object of the present invention to recover citrus oil from citrus fruit or products by means of a solvent and to purify the recovered oil by separating wax or resinous constituents therefrom.

It is a further object of the present invention to remove wax or resinous material from citrus oil by dissolving the citrus oil in an appropriate solvent such as liquid butane, cooling the solvent solution of oil to a temperature sufficiently low to precipitate the wax or resinous material, removing the precipitated resinous or waxy material by centrifuging, settling or filtering and then recovering the dewaxed or deresinated oil from the solution by removing the solvent present by distillation.

It is a further object of the present invention to recover citrus oil from citrus fruit by preparing a pulp or slurry of citrus fruit and contacting the pulp with an appropriate solvent, such as liquid normal butane, to dissolve the oil, separating the normal butane solution of citrus oil from the pulp, chilling the solution to precipitate the resinous material present in the solution,

separating the precipitated resinous material from the butane solution of oil and by recovering the oil from the solution by removing the butane from the distillation.

5 The following is a specific example of the method for carrying out our invention:

Orange pulp and rind is ground or macerated in the presence of water to form a slurry containing approximately 2½% orange oil. This slurry is then mixed with liquid normal butane at a temperature of about 70° to 80° F. in the proportion of 2.75 parts by volume of liquid normal butane to one part by volume of the orange slurry. The mixture of orange slurry and normal butane is then agitated at a temperature of 70° to 80° F. for a period of about thirty minutes, after which the mass is permitted to settle for a period up to about twelve hours. A large portion of the water and solid pulp is then withdrawn from the extraction vessel. The butane solution of the orange oil remaining in the extraction vessel is then cooled to a temperature of about 32° F. for the precipitation of the resinous materials in the solution. The chilled solution is then filtered through paper or other suitable medium and thereby freed from the precipitated resinous material, after which it is heated to about 125° F. for the removal of the major portion of the normal butane and finally to a maximum of 212° F. for not over fifteen minutes to remove any heavy ends of the hydrocarbon extractant from the orange oil. The oil recovered by the foregoing method is equal in quality to cold pressed orange oil and a yield of 86% of the total orange oil present in the slurry is obtained.

The chilling step for the separation of the resinous material is subject to some variation since certain of the oils extracted contain more of the resinous or waxy material than others. In general a temperature of about 32° F. is satisfactory to remove sufficient of these resinous materials, however, we do not wish to limit ourselves to this specific temperature since we have satisfactorily employed temperatures as low as 0° F. for precipitation of the resinous or waxy material from the solvent solution of oil. In carrying out the resin separating step it is important to note that it is desirable to leave from 2 to 5% of the resin or wax in the oil since oil containing lower concentrations than these tend to resemble artificial oil and has a somewhat poorer flavor.

We have described liquid normal butane as being the preferred solvent since it has a high solvent power for the essential oils and a minimum solvent power for the undesirable constituents, its vapor pressure is sufficiently low at 70° to 80° F. that it does not necessitate the use of especially heavy equipment, it is available commercially in a sufficiently high state of purity to prevent contamination of the essential oil, and the boiling point is sufficiently low to permit complete removal from the essential oil without heating to temperatures high enough to impair the quality of the oil. However, we do not wish to limit ourselves to this solvent since many other solvents may be employed, as for example, isobutane, liquid ethane, liquid propane, the liquid pentanes, a suitable fraction from casinghead or primary gasoline and mixtures thereof. Furthermore, we may also employ other solvents, as for example, ketones such as acetone and methyl acetone, and ethers such as ethyl and isopropyl ether or mixtures of those solvents. Preferably the solvents which we employ should have a lower boiling point than that of the citrus oil in order

to permit good fractional distillation between the oil and solvent. Furthermore the solvents should be free from malodorous or maltasting constituents which impart to the oil a bad taste or odor.

It is also preferable that the solvent employed should not be water soluble to any appreciable extent. In some instances the solvent may be treated for removal of constituents present which unfavorably influence the quality of the oil. For example, low boiling hydrocarbon solvents may be pretreated with caustic soda for the removal of hydrogen sulphide or mercaptans both of which impart a highly undesirable odor to citrus oil. Furthermore, we have described a process in which 2.75 volumes of solvent and one volume of citrus are mixed together for the recovery of the oil, but we do not wish to limit ourselves to these proportions since in many cases it may be desirable to alter this ratio. In some instances it may require three or four volumes of the liquid butane to one volume of the citrus pulp or slurry and in other instances it may be desirable to use equal or even smaller volumes of solvent than of pulp or slurry.

We have described a process in which we have employed an extraction temperature of about that of atmospheric, namely 70° F. to 80° F. However, we do not wish to limit ourselves to this temperature since in some instances it may be desirable to employ temperatures which are greatly in excess of atmospheric, for example, the orange slurry may be charged into a pressure bomb together with the liquid normal butane and this mixture may be heated to a temperature of about 150° F. to 200° F. together with agitation in order to insure complete solution of the oil in the solvent. After complete solution, the mixture may then be cooled and after removal of the water and the resinous materials present in the solution by cooling and separating, as described above, the orange oil may then be recovered by simply removing the normal butane present.

Another modification of the process consists in leaching the slurry at a temperature at which the resinous material will not go into solution. This temperature will be about 32° F. to 35° F. At this temperature the slurry is a solid mass due to the crystallization of the water present. When operating according to this cold leaching method the chilled slurry at a temperature of 32° F. to 35° F. is intimately mixed with chilled normal butane at about the same temperature. After thorough agitation the chilled mixture containing the dissolved orange oil is then separated from the insoluble pulp and after filtration to remove any solid material which may be present the solvent is removed from the oil by distillation.

It is to be understood that these disclosures are presented as illustrative of the generic invention and not as limiting, inasmuch as other modifications will be obvious to those skilled in the art.

We claim:

1. A process for the purification of citrus oil containing resinous impurities which comprises grinding citrus peel in the presence of water and thereby forming a slurry, commingling said slurry with a liquefied normally gaseous hydrocarbon solvent under sufficient pressure to maintain said solvent in a liquid state, settling the mixture of slurry and solvent under pressure and thereby forming a solvent layer containing the citrus oil and a slurry layer, separating said layers, cooling the solvent layer to precipitate resinous material, removing the precipitated resinous mate-

rial from the solvent layer and removing the solvent from the de-resinated oil.

2. A process according to claim 1 in which the solvent is liquid butane.

5 3. A process according to claim 1 in which the solvent layer is cooled to a temperature between 0° F. and 32° F. for precipitation of the resinous material.

10 4. A process for the purification of citrus oil containing resinous impurities which comprises grinding citrus peel with water and thereby forming a slurry, commingling said slurry with cooled

liquefied normally gaseous hydrocarbon solvent under sufficient pressure to maintain said solvent in a liquid state, settling the mixture under pressure and thereby forming a liquid solvent layer containing the citrus oil and a slurry layer, separating said layers, and removing the solvent from the layer containing the citrus oil. 5

5. A process according to claim 4 in which the leaching temperature is between 0° F. and 32° F. 10

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