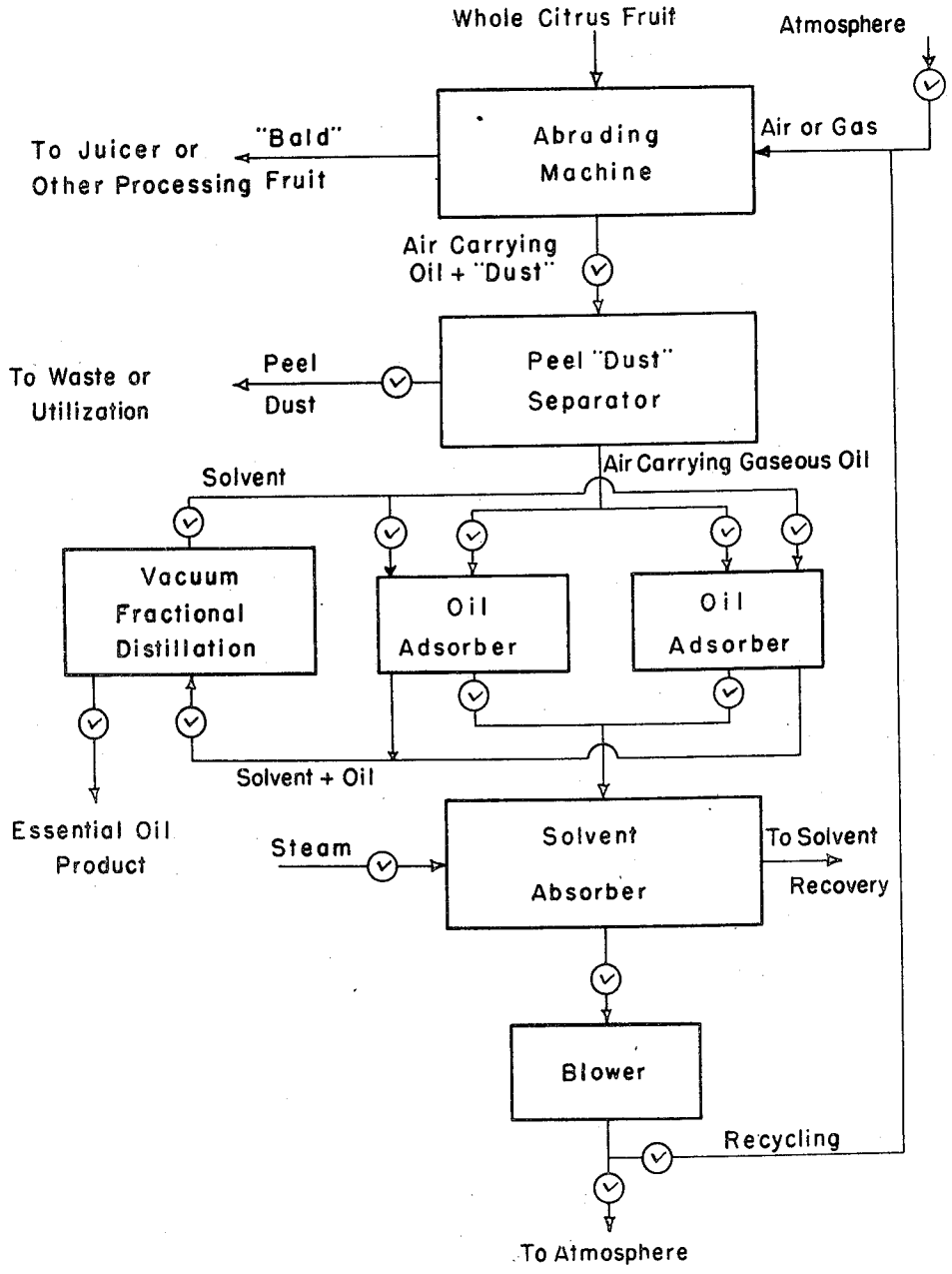
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RECOVERY OF CITRUS OIL

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RECOVERY OF CITRUS OIL

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8 Claims. (Cl. 99—105)

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This invention relates to the extraction or recovery of essential oil from the pulp and skin material of citrus fruits with which it is associated and more particularly deals with a process of obtaining citrus oils from the skins of various citrus fruits such as limes, lemons, oranges and grapefruit.

An object of my invention is to provide a method whereby an unusually high percentage of the oil approaching 100% recovery is obtained from these citrus fruit skins.

Another object of my invention is to produce an essential oil of very high quality, having for some purposes more valuable characteristics than that of the oil now produced.

A particular object of my invention is to produce a large percentage of high quality oil entirely free from citrus juice and peel liquids and solids, and at the same time produce a citrus juice which is entirely free from essential oil.

A further object of my invention is to produce essential oil of unusually good keeping quality due to the absence of foreign matter, and also citrus juice of unusually good keeping quality.

Although my process is also applicable to other citrus fruits, as mentioned above, I particularly use my process in the production of essential oil from the skins of limes, especially the variety known as Persian limes, also called Bearss and Tahiti.

Basically, oil of lime has been produced in the past by either one of two rather crude processes. These have been to either crush the entire fruit under high pressure rollers so as to produce a mixture of lime juice and oil of lime which must be steam distilled to remove the oil, thus producing a distilled oil of lime of poor quality. The second method has been to carefully press out the lime juice without disturbing the oil of lime in the skin and then separately pressing the lime skins so as to form a cold press oil of lime. This cold pressed oil is of considerably higher quality and brings a higher price than the steam-distilled oil. It is principally used in the perfumery industry. However, cold pressed oil of good quality is difficult and expensive to make, largely due to the careful handling of the skins that is necessary and the low yields usually obtained.

The low yield of good quality oil of lime is probably due to the fact that the bulk of the oil of lime remains in the pulp material of the skin. Another factor in reducing the quality and yield of the oil of lime which has not been previously recognized is that the limes which are used for making oil of lime are usually the culls from the

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packing plants. These culls have already been processed through the packing plant and in the packing plant processing they have been coated with a thin coat of wax, and sometimes a mold preventive such as borax, so as to preserve them and improve their appearance. This wax on the skin undoubtedly contributes to the poor yield and poor quality of oil of lime usually obtained. When the usual process of squeezing, producing a mixture of juice, pulp and wax is used, the presence of the wax makes it very difficult to separate the essential oil from the mixture.

For a description of the prior art methods, see the series of articles by Dr. Ernest Gunther, entitled "The production of oil of lime" appearing in the "The American Perfumer and Essential Oil Review," issued November and December of 1942, January, February, March and April 1943, particularly the section near the end of the series of articles entitled "Florida's lime industry."

In general, my process involves recovering the essential oil from the skins of the whole fruit, without disturbing the juice tissues so that the fruit juice may be later recovered without contamination by the essential oil of the skin.

The process involves, broadly, the following steps: Removing most of the skin of the fruit with an abrasive means such as a rotating wire brush or sand paper, or abrasive wheel, taking up the essential oil, pulp and vapor in the air stream in such a manner that the oils are substantially all vaporized; separating the peel particles or dust from the air stream by natural settling or screening; absorbing the vapor of the essential oil on an absorbent such as activated carbon or silica gel, etc.; removing the essential oil from the carbon by some means such as solvent extraction, followed by fractional distillation of the solvent solution or similar means.

As a result of this procedure, the essential oils are almost instantaneously separated from the waxes and pulp material of the skin which normally holds them tightly. In addition, the fruit comes out of the process practically devoid of skin, herein called a bald fruit, so that it can be squeezed to produce a fruit juice containing practically no essential oil.

The rapid separation of the essential oil from the peel liquids and internal juice liquids, before any appreciable chemical interaction between them can take place, is important in obtaining a high quality essential oil and a juice of good keeping quality.

Some essential oil, particularly the more desirable distilled fractions of the same, is neces-

sary in the juice to give it taste quality, but too much will impair its keeping quality. Hence a juice with no oil is desirable so that only the desirable fractions of oil can be added in accurate known amounts. This is particularly important in the case of lime juice which is very often canned or bottled and kept for long periods of time before use.

Thus, in my process, the oil cells of the skin of the fruit are ruptured in such a way that the essential oil is brought into an air or gas stream that is unsaturated with respect to the lime oil. As a result, the oil almost instantly flashes into the vapor phase by virtue of its very finely dispersed state. In order to accomplish this result the skin of the fruit is subjected to rapid abrading blows by some medium which causes relatively instantaneous rupture of the oil bearing cells and structure, this mechanical action being carried out in a gas stream, preferably an air stream, but nitrogen, carbon dioxide or other gases may be used to minimize the effect of oxygen on the oil, which is unsaturated with respect to the essential oil. The gas stream containing the vaporized essential oil, with the abraded peel solids, is passed through some separator means such as a sharp change in direction of the stream which settles out most of the solid material and then through a screen where any remaining solid material is removed.

The gas stream then passes through an absorber such as a bed of absorbent carbon, or bubbled through a solvent so as to remove the essential oil. The essential oil can be removed from the absorbent carbon by solvent extraction or by steam distillation. The solvent extraction method is preferred since it avoids the use of high temperatures which lower the quality of the essential oil. The oil is recovered from the solvent.

The solvent is preferably ethyl alcohol but carbon tetrachloride, ethylene dichloride, chloroform, isopropyl alcohol, a nitro-paraffin or some other organic solvent having a low boiling point may be used. Although technically, methanol or wood alcohol could be used, it is probably undesirable, due to its poisonous nature.

In another variation of my invention, the alcohol or other solvent solution can be used or sold as such without recovering the oil separately, or the solution may be partially distilled so as to form a solution of any concentration desired.

The oil cells in the skin of the green, fresh fruit are normally flush with the surface of the skin. The oil cells may, however, in advanced states of drying, project considerably above the surface due to loss of liquid from the surrounding skin area at a greater rate than from the oil cell.

The oil cell wall on the surface of the peel is only from two to five thousandths of an inch thick and is comparatively weak. I have, therefore, found that by in effect having a piston thrust into each cell of approximately the same diameter as the cell, oil can be forcibly ejected from the cell without disturbing the surrounding area appreciably; oil cells ruptured under such conditions tend to send out a very minute stream of liquid oil which forms barely visible droplets. Due to their small size and large area per unit volume, these droplets evaporate almost instantly.

This piston ejection process is very closely approximated in practice by buffing the fruit with a rapidly rotating wire or other type of filament

brush the bristles of which are approximately the same diameter as the cells and preferably about three quarters of the diameter of the cells. These cells are approximately twenty-thousandths of an inch in diameter. If the bristles of the brush are of the proper flexibility they will tend to ride along the surface of the skin except where they encounter the weaker oil cell walls. The bristles breaking through into the oil cells displace the oil as would a loose fitting piston. Some scooping or scraping action naturally occurs at the same time. Although the process could be stopped at this point I have found it preferable to continue the abrading action of the wire brush so as to wear away the greater part of the skin of the fruit which contains the oil cells. This is preferably done in such a way as to break the peel matter up into minute particles of the order of ten to fifteen mesh or less. Such particles tend to float off into the gas or air stream and opportunity is given for whatever oil is present in these peel solids, sometimes called peel dust, to evaporate into the air or gas stream.

The air stream is then led through a suitable separator such as of the dust separation or centrifugal type and the gas stream is then ready for the recovery of the oil. A reasonable excess of air or other gas that is used must be present since due to the low vapor pressure of the essential oil, the air would be quickly saturated with respect to the oil unless an excess were present.

As mentioned above, the vapor stream containing the essential oil could be simply bubbled through a solvent, in a suitable scrubbing tower, to recover the essential oil. However, this is not the preferred procedure since the amount of solvent required and the size of the scrubbing tower would be uneconomically large. The preferred method, therefore, is to absorb the essential oil in a bed of absorbent activated carbon. The essential oil is thus concentrated on the carbon from which it may be more economically recovered by solvent extraction such as with alcohol. The essential oil is then easily recovered from the alcohol or other solvent by fractional distillation at low temperature and pressure.

It has been found in practice that by using my method practically one hundred percent recovery of the essential oil in the fruit is obtained. This is shown by the fact that the abraded peel and the peel dust were found on examination to contain only traces of essential oil. Also, no essential oil is found in the juice which is recovered from the abraded fruit.

The accompanying drawing shows a flow diagram which illustrates one method of carrying out my invention.

In it citrus fruit culls or juicing grade fruit from a packing plant are passed through an abrading machine containing wire brushes or other similar means. The skinned or bald fruit is then directed to juicers such as the rotary type for making a juice free from essential oils. The peel solids and vaporized oil are carried by an air or gas stream through a separator where the peel solids are removed. The air stream containing vaporized oil is then passed through a bed of absorbent carbon and then through a solvent recovery bed of absorbent carbon. The solvent recovery or economizer bed may be omitted, if desired. Preferably, the blower to move the gas stream, is placed as shown after the last solvent economizer absorber. This maintains a slight vacuum on the system so as to avoid possible loss

of oil. Other arrangements of the blower could obviously be used.

Finally, the gas stream is either vented to the atmosphere or recycled, if desired. The essential oil is removed from the absorbers by a solvent such as alcohol preferably passing in same direction as the gases. A spare absorbent carbon bed to provide continuous operation is shown.

While one bed is being used to absorb oil, the other bed can be washed with solvent to remove the essential oil, thus obtaining flexible and continuous operation.

The oil is recovered by vacuum fracional distillation at low temperature and simultaneously the solvent is recovered for re-use in the process.

The solvent recovery or economizer bed is used to prevent excessive loss of solvent when the gas stream carries the solvent out of the wet absorbent carbon beds. The solvent is recovered from the economizer by steam distillation.

As an example of carrying out the process of my invention, the following was carried out:

EXAMPLE

The skin was buffed from fresh edible cull Persion limes that were rejected from a packing plant after washing and waxing. A 4" wire wheel, having wires with a diameter of .0118" and rotating at a speed of 1800 revolutions per minute was used to abrade the skins of the Persian limes. One charcoal bed was used, having a total weight of 186.4 gr., and dimensions of 3¼" diameter by 3¼" deep. A good commercial grade absorbent activated charcoal was used.

Results are shown in the following table:

Table

Theor. Gms. increase bed wt. (cumulative)	Pounds of Fruit Buffed (cumulative)	Grams of increase in weight carbon (cumulative)
2.5	2	5
5.2	4	27.5
7.7	6	30.8
10.7	8	37.8
13.0	10	34.
16.1	12	35.3
19.0	14	36.2
21.7	16	36.8
24.3	18	37.5
27.2	20	36.
30.0	22	37.5
32.7	24	38.2

On testing it was found possible to obtain only traces of oil from the abraded fruit and peel dust. This shows that practically 100% of the essential oil in the lime skins was vaporized, most of which was retained on the carbon which when extracted with alcohol yielded a very fine quality essential oil. This was evidenced by the fact that the oil was clear and its solution in alcohol was water-white and of very fine odor, practically indistinguishable from the odor of the fresh fruit.

It is understood throughout the accompanying specification and claims that the terms "absorb" and "adsorb" are used interchangeably since it is not definitely known how the essential oil is taken up by the charcoal or other absorbent. It is probable in the case of charcoal that the essential oil is held on the surface whereas in the case of silica gel or solvent absorbents the essential oil is actually absorbed in the body of the absorbent.

The exact conditions and apparatus may be varied with oranges, limes, lemons, tangerines, etc., depending on value of oil and its constituents,

and properties, but without departing from the spirit or scope of my invention which is to be limited only by the following claims.

I claim:

1. The process of producing a high quality essential oil that comprises abrading the skin of whole citrus fruit so as to cause the essential oil to vaporize into a gas stream which is unsaturated with respect to said oil before any appreciable chemical interaction with the peel liquids or internal juice liquids can take place, the gas stream being then freed of entrained solids and liquids and the oil recovered by suitable means.

2. A process of obtaining high quality essential oil from the skins of citrus fruits that comprises removing the skin of the citrus fruit by an abrasive means in the presence of a gas stream which is unsaturated with respect to the essential oil, the gas stream being sufficient to remove and vaporize the essential oil, separating the peel solids from the gas stream containing the vaporized essential oil, passing the air stream through an absorber so as to remove the essential oil, and recovering the essential oil from the absorber.

3. The process of treating citrus fruits so as to obtain high quality essential oil and high quality citrus juice that comprises removing the skin by abrasive means in an air current such as to substantially vaporize all of the essential oil, separating the peel solids from the air current, removing the essential oil from the air current by means of activated carbon and recovering the oil free citrus juice by squeezing the skinned fruit and later adding a small controlled amount of essential oil to the juice so as to give it taste quality without impairing its keeping quality.

4. The process of treating citrus fruit which has had wax or mold preventive material applied to its surface, so as to recover a high quality essential oil from the skin and also an oil free citrus juice from the body of the fruit which comprises removing the skin by an abrasive means in the presence of an air current which is unsaturated with respect to the essential oil, passing the air current containing the vaporized essential oil and skin pulp solids through a separator to separate the said solids, then removing the essential oil from the air stream by an absorbent and recovering the essential oil by solvent extraction.

5. The process of recovering high quality essential oil from citrus fruit that comprises removing the skin of the citrus fruit by an abrasive means in the presence of a current of air that carries off the peel solids and vaporizes substantially all of the oil, separating the peel solids, absorbing the essential oil in an activated carbon absorber and recovering the essential oil by solvent extraction.

6. The process of recovering high quality lime oil from limes that comprises removing the skin of the limes by an abrasive means in the presence of a current of air that carries off the pulp solids and substantially vaporizes all of the lime oil, separating the pulp solids, absorbing the lime oil in a charcoal absorber and recovering the essential oil by solvent extraction.

7. The process of treating citrus fruit that has been previously treated with a preservative that comprises removing the skin by abrasive means in the presence of an air current which substantially removes the peel solids and vaporizes the essential oil from the skin, separating the peel solids, absorbing the essential oil on charcoal, recovering the essential oil from the charcoal by extraction with alcohol and recovering the alcohol for re-use in the process by vacuum distilla-

tion at low temperature so as to produce a high quality essential oil.

8. The process of producing a high quality citrus juice that comprises removing the skin of the citrus fruit by an abrasive means in the presence of air current that carries away substantially all of the ground skin pulp and solids and essential oil, and then squeezing the citrus juice from the skinned fruit and later adding a small controlled amount of essential oil to the juice so as to give it taste quality without impairing its keeping quality.

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