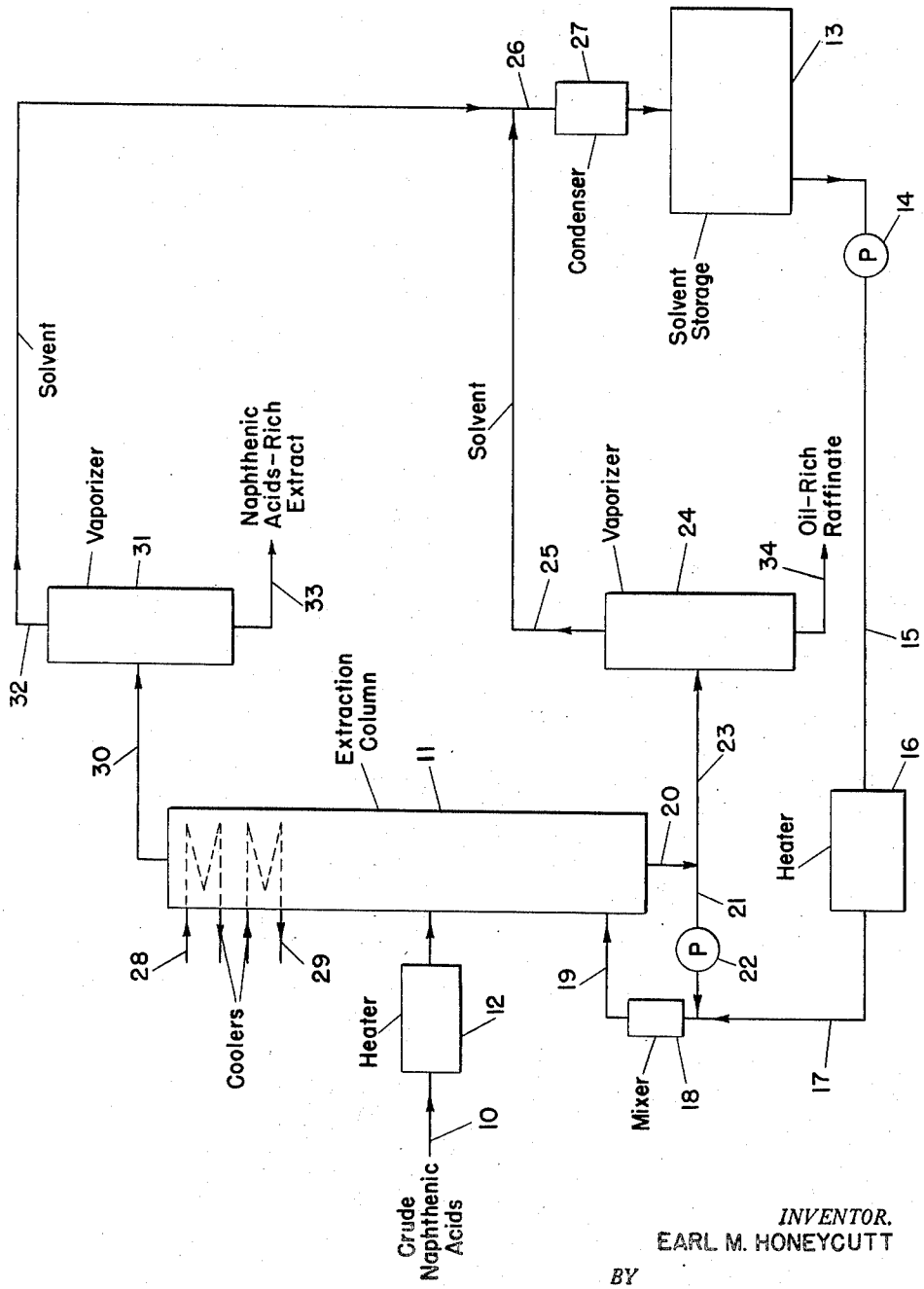
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SOLVENT EXTRACTION OF NAPHTHENIC ACIDS

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INVENTOR.
EARL M. HONEYCUTT

BY
Bisser and Hardway

ATTORNEYS

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SOLVENT EXTRACTION OF NAPHTHENIC ACIDS

Earl M. Honeycutt, Claymont, Del., assignor to Sun Oil Company, Philadelphia, Pa., a corporation of New Jersey

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This invention relates to the purification of naphthenic acids and more particularly is directed to a method for solvent extracting crude naphthenic acids to separate the acids from the contained hydrocarbon oil.

In the refining of crude oils containing naphthenic acids, the acids are often recovered by various techniques in the form of a crude product containing a relatively large amount of hydrocarbon oil. The oil content of such products may, for instance, range from 25% to 75%. It is generally desirable to subject the crude product to further treatment for the purpose of reducing the oil content and improving the market value.

The treatment of crude naphthenic acids by means of selective solvents capable of preferentially dissolving the naphthenic acids, and without first converting the acids into their corresponding salts by means of an alkali, is known. In order to achieve the desired degree of separation by this type of solvent extraction procedure, it is usually necessary to carry out the extraction in countercurrent fashion and to utilize reflux in the operation. Simple batch extraction or countercurrent extraction without reflux generally will not effect sufficient purification.

A process for countercurrently extracting crude naphthenic acids, utilizing reflux to achieve the desired degree of separation, has been described and claimed in McCorquodale Patent No. 2,391,729. In such process the crude naphthenic acids are fed into a countercurrent extraction zone, such as a packed column, at an intermediate level. The portion of the column below the feed introduction constitutes a raffinate-enriching section while the portion above constitutes an extract-enriching section. Solvent is fed into the raffinate-enriching end at the bottom and flows upwardly through the column countercurrent to the feed. An oil-rich raffinate phase is withdrawn from the bottom and a portion of it is admixed with the incoming solvent and returned to the column as reflux for the raffinate-enriching operation. The saturated solvent phase, which is withdrawn from the top, is sent through a vaporizer to remove part of the solvent and yield a naphthenic acids-rich extract which is essentially saturated with solvent. A portion of this extract is then returned to the top of the column as reflux for the extract-enriching operation. Solvent is vaporized from the remaining extract, as well as from that part of the raffinate phase not returned as reflux, to obtain the finished products and recover solvent for re-use.

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For successfully practicing the foregoing process the solvent employed should have the following characteristics: first, it should have preferential solvency for the napthenic acids; and secondly, it should not be completely miscible with naphthenic acids of the purity desired. The solvents which possess these characteristics are ones which are composed mainly of water-miscible polar organic liquids. Specific solvents heretofore proposed for use in the process have been mixtures of such polar organic compounds with minor amounts of water sufficient to render the mixture incompletely miscible with the naphthenic acids, such as the following: (1) methanol containing at least 12% water by volume; (2) a mixture composed of 73.5% methanol, 22.7% anhydrous formic acid and 3.8% water by volume; and (3) acetic acid containing at least 5.7% water by volume.

Practice of the process of Patent No. 2,391,729 when employing these multicomponent solvents is rendered difficult by reason of the fact that changes in the composition of the solvent tend to occur during its partial vaporization from the solvent phase due to the different boiling points of the components. Accordingly, in order to reflux extract material in which the residual solvent has the desired composition, it generally will not suffice merely to vaporize part of the solvent from the solvent phase. Usually it is necessary first to remove all of the solvent from the extract so that the solvent composition will remain uniform and then re-mix part of the recovered solvent with the extract which is to be refluxed. This results in added expense in conducting the operation.

The present invention provides an improved process for countercurrently extracting crude napthenic acids whereby the refluxing for the extract-enriching operation is accomplished in simplified manner. The improvement depends upon the fact, as I have discovered, that the solubility of naphthenic acids in solvents of the foregoing kind varies considerably with temperature. Accordingly, the refluxing can be effected internally of the extraction zone by cooling the solvent phase as it passes through the extract-enriching section, thus eliminating any necessity for returning reflux from outside the column.

According to the invention the crude naphthenic acid feed and the solvent are introduced into the extraction zone in heated condition so that countercurrent treatment in the raffinate-enriching section is done at elevated temperature. The solvent phase flowing through the extract-enriching section is then cooled before it

reaches the outlet to cause a portion of the contained extract to precipitate. The precipitated extract flows countercurrent to the solvent phase as reflux for the extract-enriching operation.

The accompanying single sheet of drawings constitutes a simplified schematic flowsheet illustrating the invention. Crude naphthenic acids enter the system through line **10** and are fed into countercurrent extraction column **11** at an intermediate level. The portion of column below the point of feed introduction constitutes the raffinate-enriching section while the upper part of the column constitutes the extract-enriching section. An elevated temperature should be maintained within the raffinate-enriching section. For this purpose the feed may be passed through heater **12** prior to entering the column in order to raise its temperature to substantially that at which the raffinate-enriching operation is to be conducted.

Solvent for countercurrently extracting the feed is withdrawn from storage tank **13** by means of pump **14** and is sent through line **15** to heater **16**. In the latter the solvent is heated sufficiently to maintain the temperature desired within the raffinate-enriching section. The heated solvent passes through line **17** and mixer **18** and then is introduced through line **19** into the column near its bottom. Preferably the solvent enters the column somewhat above the bottom to provide a zone below the point of introduction for accumulating the raffinate phase and maintaining an interface between it and the solvent.

Raffinate phase, saturated with solvent settles to the bottom of column **11** and is continuously withdrawn through line **20**. A portion of it then passes through line **21** and pump **22** into line **17**, where it meets the heated solvent stream and is admixed therewith by means of mixer **18**, thence returning to the column. The portion of raffinate phase recycled in this manner constitutes reflux for the raffinate-enriching operation. The amount thus returned should be sufficient to accomplish the desired enrichment of the raffinate or in other words to reduce the naphthenic acids content to the desired value.

The remainder of raffinate phase not utilized as reflux passes through line **23** into vaporizer **24** for recovery of the solvent. From the vaporizer the distilled solvent issues overhead through line **25** and passes through line **26** to condenser **27**, from which it then returns to storage tank **13**. Oil-rich raffinate is removed from the bottom of the vaporizer by means of line **34**.

The solvent phase which flows upwardly beyond the point of feed introduction in column **11** is cooled before it reaches the top in order to produce reflux for the extract-enriching operation by precipitation of part of the contained extract. For this purpose a cooling coil **28** may be provided within the column near the top for removing heat by means of water or other suitable cooling fluid. Alternatively a plurality of coolers spaced apart within the extract-enriching section may be provided in order that heat may be removed at several different levels. In this manner a more or less even temperature gradient between the point of feed introduction and the top of the column may be maintained, if desired. In the drawings two banks of cooling coils, **28** and **29**, are shown for purposes of illustration but it is to be understood that any desired number of coolers may be employed. Also, in place of having cooling coils within the column, the cooling may be done by withdrawing liquid from the side of the column at one or more levels, passing it through suitable coolers and then introducing the cooled material back to the column.

The reduction in temperature of the solvent phase resulting from the cooling causes part of the contained extract to precipitate and flow back down the column countercurrent to the upcoming solvent. Sufficient cooling should be done so that the amount of precipitated extract will provide the necessary reflux for achieving the desired purification of the naphthenic acids.

The solvent phase leaving the top of column **11** passes through line **30** to vaporizer **31** wherein solvent is distilled from the extract. The vaporized solvent flows overhead through line **32** and then via line **26** into condenser **27**, from which it returns to storage tank **13** for re-use. Purified naphthenic acids are withdrawn through line **33** at the bottom of vaporizer **31** as a product of the process.

Solvents which may be used in the above described process are of the kind previously discussed, namely, those composed of at least a major amount of water-miscible polar organic liquid and which have selectivity for the naphthenic acids but incomplete miscibility with acids of the purity desired. The most suitable solvents usually are mixtures comprising a major amount of such polar liquid with a minor amount of water sufficient to cause the incomplete miscibility with naphthenic acids.

In employing this type of solvent I have found that the solvent phase before it leaves the extraction column should be cooled to at least 25° F. below the temperature in the raffinate-enriching section and preferably to a temperature at least 35° F. lower. Further, the raffinate-enriching operation should be conducted at an elevated temperature substantially above room temperature and preferably at a temperature above 150° F. If the temperature in the lower part of the column is maintained within the range 150–200° F., the desired differential temperature may readily be secured by using cooling water at normal temperature. Still higher temperatures may be employed if desired, provided sufficient pressure is maintained to prevent boiling within the column, but usually no advantage will be gained by exceeding a temperature of 200° F. Recommended temperature ranges are 150–200° F. for the raffinate-enriching section and 115–160° F. at the top of the column, with the temperature differential being at least 35° F. As an illustrative preferred embodiment, temperatures of about 175° F. in the raffinate-enriching section and about 135° F. at the top of the column may be used.

Among the various water-miscible polar organic liquids, methanol is one of the best with respect to selectivity between the naphthenic acids and hydrocarbon oil. However, methanol alone is not suitable for use in the process due to its complete miscibility with naphthenic acids. The addition of minor amounts of water to the methanol produces a solvent having both good selectivity and incomplete miscibility with the naphthenic acids but reduces the solvency of the methanol. On the other hand, higher molecular weight alcohols, such as isopropyl or normal propyl, containing minor amounts of water have higher solvency but are poorer with respect to selectivity between the naphthenic acids and oil.

I have now found that mixtures composed of a major amount of methanol and minor amounts of

a propyl alcohol and water constitute particularly useful solvents for conducting the process. The addition of propyl alcohol in amounts not exceeding about 40% permits a reduction in the proportion of methanol required and causes the solvency to increase without adversely affecting the selectivity to any substantial extent. As the propyl alcohol, either isopropyl or n-propyl alcohol may be used, although isopropyl is preferred. Not only is the solvent power improved but also the heat requirements for recovering the solvent are decreased by virtue of the lower heat of vaporization of propyl alcohol as compared to methanol. Suitable concentrations of propyl alcohol and water for solvent mixtures of this type are, respectively, 10–40% and 10–25% by weight of the mixture, the remainder being methanol which is present in major amount. The solvent mixture most recommended for use in the process is one having a composition approximately as follows: about 67% methanol, 23% isopropanol and 10% water.

I claim:

1. In the purification of naphthenic acids by solvent extraction in a countercurrent extraction zone comprising an extract-enriching section at one end and a raffinate-enriching section at the other, the method which comprises feeding crude naphthenic acids, containing hydrocarbon oil, in heated condition to said zone intermediate said sections, feeding into the raffinate-enriching end a heated solvent selective for naphthenic acids but having incomplete miscibility therewith and composed mainly of a water-miscible polar organic liquid, flowing the solvent through said raffinate-enriching section countercurrent to the feed and thence through said extract-enriching section, withdrawing from the raffinate-enriching section end a raffinate phase rich in hydrocarbon oil, cooling the solvent phase flowing in said extract-enriching section to precipitate a portion of the contained extract, said precipitated extract flowing countercurrent to the solvent as reflux for the extract-enriching operation, and withdrawing solvent phase from the extract-enriching section end of said zone.

2. In the purification of naphthenic acids by solvent extraction in a countercurrent extraction zone comprising an extract-enriching section at one end and a raffinate-enriching section at the other, the method which comprises feeding crude naphthenic acids, containing hydrocarbon oil, in heated condition to said zone intermediate said sections, feeding into the raffinate-enriching end a heated solvent selective for naphthenic acids and composed of a major amount of a water-miscible polar organic liquid and a minor amount of water at least sufficient to render the solvent incompletely miscible with the naphthenic acids, flowing the solvent through said raffinate-enriching section countercurrent to the feed and thence through said extract-enriching section, withdrawing from the raffinate-enriching section end a raffinate phase rich in hydrocarbon oil, cooling the solvent phase flowing in said extract-enriching section to a temperature at least 25° F. lower than the temperature in said raffinate-enriching section to precipitate a portion of the contained extract, said precipitated extract flowing countercurrent to the solvent as reflux for the extract-enriching operation, and withdrawing saturated solvent phase from the extract-enriching section end of said zone.

3. Method according to claim 2 wherein the solvent is composed of a major amount of methanol and minor amounts of a propyl alcohol and water.

4. Method according to claim 3 wherein the propyl alcohol is isopropyl alcohol.

5. Method according to claim 2 wherein the solvent is composed of a major amount of methanol, 10–40% isopropanol and 10–25% water by weight.

6. Method according to claim 2 wherein the temperature in said raffinate-enriching section is within the range 150–200° F. and the temperature of the solvent phase after said cooling is within the range 115–160° F.

7. In the purification of naphthenic acids by solvent extraction in a countercurrent extraction zone comprising an extract-enriching section at one end and a raffinate-enriching section at the other, the method which comprises feeding crude naphthenic acids containing hydrocarbon oil to said zone intermediate said sections at a temperature of 150–200° F., feeding into the raffinate-enriching end at a temperature of 150–200° F. a solvent selective for naphthenic acids and composed of a major amount of a water-miscible polar organic liquid and a minor amount of water at least sufficient to render the solvent incompletely miscible with the naphthenic acids, flowing the solvent through said raffinate-enriching section countercurrent to the feed and thence through said extract-enriching section, withdrawing from the raffinate-enriching section end a raffinate phase rich in hydrocarbon oil, cooling the solvent phase flowing in said extract-enriching section to a temperature within the range of 115–160° F. and at least 35° F. below the temperature in said raffinate-enriching section to precipitate a portion of the contained extract, said precipitated extract flowing countercurrent to the solvent as reflux for the extract enriching operation, and withdrawing solvent phase from the extract-enriching section end of said zone.

8. Method according to claim 7 wherein the solvent is composed of a major amount of methanol, 10–40% isopropanol and 10–25% water by weight.

9. Method according to claim 7 wherein the solvent is composed of about 67% methanol, 23% isopropanol and 10% water by weight, the temperature in the raffinate-enriching zone is about 175° F. and the solvent phase is cooled to a temperature of about 135° F. before leaving the extract-enriching section end.

EARL M. HONEYCUTT.

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The following references are of record in the file of this patent:

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