Patented Sept. 15, 1942

2,296,039

UNITED STATES PATENT OFFICE

2,296,039

REFINING NAPHTHENIC ACIDS

Edwin C. Knowles and Frederic C. McCoy, Beacon, N. Y., assignors, by mesne assignments, to The Texas Company, New York, N. Y., a corporation of Delaware

No Drawing. Application January 29, 1941, Serial No. 376,476

7 Claims. (Cl. 260—514)

This invention relates to naphthenic acids, and more particularly to a new process for refining naphthenic acids and separating the naphthenic acids into fractions of different properties.

A known method of recovering naphthenic acids involves the treatment of petroleum fractions or solvent extracts with aqueous solutions of an alkaline material, such as caustic soda, and then acidifying the resulting solution of water-soluble naphthenates to form free naphthenic acids, which are water-insoluble and may be removed by skimming or by similar methods. The resulting crude naphthenic acids retain substantial amounts of undesirable substances such as color-imparting bodies and carbonaceous matter, as well as non-saponifiable materials which may be objectionable. Somewhat purer products may be obtained by extraction of the aqueous solution of water-soluble naphthenates with a solvent such as naphtha or propane in the presence of metallic salts, such as sodium chloride, to prevent the formation of stable emulsions, and then acidifying the naphthenate solution. The present invention relates to the treatment of the crude naphthenic acids obtained by these methods or any other method.

It has been found that crude naphthenic acids may be improved by dissolving the crude naphthenic acids in a liquefied normally gaseous hydrocarbon, such as propane, the proportions being about one volume of crude naphthenic acids to several volumes of propane, and preferably about 10 volumes of propane. It has previously been suggested to dissolve crude naphthenic acids in cold propane, and to remove undesirable substances by chilling. Our invention lies in the discovery that, from these solutions of naphthenic acids, fractions may be obtained of different physical properties by further treatment. We have found that as the temperature of the propane solution is raised, there is a tendency for the separation of a fraction containing the higher molecular weight naphthenic acids from the solution. The separated naphthenic acids have materially different physical properties from the naphthenic acids retained in solution. For example, in one test the separated naphthenic acids were dark, brittle, and resinous, while the naphthenic acids retained in solution were viscous, red oils.

The following example is given in order to illustrate the application of our invention. About 1000 grams of crude naphthenic acids are diluted with 250 cc. of pentane and then propane is added to bring the total volume of the mixture up to about 13,000 cc. The propane may be added at room temperature, and the mixture is agitated during the addition of propane. Sufficient pressure is applied to the mixture to maintain the propane in a liquefied state throughout the process. The temperature is then raised gradually with continued agitation until a temperature of about 165° F. is reached. Further agitation for 10–15 minutes at about 165° F. is desirable, and then the precipitated substances are allowed to settle for 20–30 minutes while still maintaining the temperature at about 165° F. When settling is complete the clear propane solution is drawn off.

In the above procedure, a small volume of pentane is used since it has a higher solvent power for the crude naphthenic acids, and after the crude acids are thinned with a small volume of pentane, propane is more readily incorporated in the mixture. However, propane alone may be used as the solvent.

After drawing off the propane solution, the precipitate may be washed with suitable proportions of propane, while maintaining the temperature sufficiently high to prevent re-solution of the precipitated substances. Typical results are summarized in the following table.

	Propane-insoluble fraction	Propane-soluble fraction
Yield, per cent	30	70
Saponification number	90	108
Unsaponifiable, per cent	45.8	28.7
Neutralization number of extracted acids	133	158
Average molecular weight (determined by freezing point method in cyclohexane)	794	432
Viscosity, Say. Univ. at 210° F	Solid	206

Both the acids and the unsaponifiable matter in the propane-insoluble fraction were dark, brittle, and resinous solids. Both the acids and unsaponifiable matter in the propane-soluble fraction were viscous, red liquids.

There is a marked difference in the characteristics of the propane-soluble naphthenic acids and the propane-insoluble naphthenic acids. The better color and the liquid state of the propane-soluble naphthenic acids particularly adapt this fraction for commercial sale. The difference of 362 in molecular weights of the acids in the two fractions shows that a marked separation according to molecular weights may be effected by the propane treatment.

In the treatment of certain crude naphthenic

acids, it is advantageous to treat the crude acids at ordinary temperatures with propane or other liquefied normally gaseous hydrocarbons, and separate a phase which is insoluble at ordinary temperatures or at low temperatures. If the crude naphthenic acids contain carbonaceous substances, color-imparting substances, odor-imparting substances and the like, these substances are largely insoluble in propane or form a separate phase containing propane, and therefore may be separated from the propane solution of naphthenic acids. In some cases, it may be necessary to chill the mixture to low temperatures of the order of −20° F. or below, in order to bring about effective separation.

While the invention has been illustrated by showing the effect of propane on the separation of naphthenic acids into fractions of different properties, it is to be understood that other liquefied normally gaseous hydrocarbons may be used. In general, hydrocarbons having 5 or less carbon atoms per molecule, such as ethane, propane and butane, or mixtures thereof, are of utility, and hydrocarbons such as pentane are of utility as a preliminary solvent for the crude naphthenic acids or as components of mixtures containing higher proportions of the lower molecular weight hydrocarbons.

Obviously, many modifications and variations of the invention, as hereinbefore disclosed, may be made without departing from the spirit and scope thereof, and therefore only such limitations should be imposed as are indicated in the appended claims.

We claim:

1. The method of treating crude naphthenic acids which comprises dissolving said crude naphthenic acids in a solvent comprising at least one liquid hydrocarbon of the class consisting of liquid propane and other liquified normally gaseous hydrocarbons, heating the resulting solution to a temperature at which said solvent has a precipitating action substantially equivalent to that of liquid propane at about 165° F., to effect two-phase separation of said solution into two fractions, each of said fractions containing naphthenic acids and one of said fractions containing naphthenic acids of higher molecular weight than the naphthenic acids in the other fraction, and recovering the two fractions thus separated.

2. The method of treating crude naphthenic acids which comprise dissolving the crude naphthenic acids in a liquefied normally gaseous hydrocarbon solvent comprising principally propane and raising the temperature to about 165° F. to effect the separation of a fraction containing naphthenic acids of higher molecular weights than those retained in solution.

3. The method of treating crude naphthenic acids which comprises treating said crude naphthenic acids with a solvent comprising at least one liquid hydrocarbon of the class consisting of liquid propane and other liquified normally gaseous hydrocarbons, separating any substances which are insoluble at low temperatures, heating the resulting solution to a temperature at which said solvent has a precipitating action substantially equivalent to that of liquid propane at about 165° F., to effect two-phase separation of said solution into two fractions, each of said fractions containing naphthenic acids and one of said fractions containing naphthenic acids of higher molecular weight than the naphthenic acids in the other fraction, and recovering the two fractions thus separated.

4. The method of treating crude naphthenic acids which comprises treating the crude naphthenic acids with a liquefied normally gaseous hydrocarbon solvent comprising principally propane, separating any substances which are insoluble at low temperatures, and raising the temperature to about 165° F. to effect the separation of a fraction containing naphthenic acids of higher molecular weight than those retained in solution.

5. The method of separating naphthenic acids according to molecular weight which comprises dissolving the naphthenic acids at ordinary temperatures in a liquefied normally gaseous hydrocarbon solvent comprising principally propane, raising the temperature to about 165° F., maintaining the mixture at about 165° F. for a time sufficient for the separation of a portion of the naphthenic acids from solution, said portion comprising naphthenic acids of higher molecular weight than those retained in solution, allowing the separated naphthenic acids to settle, and removing the upper layer containing dissolved naphthenic acids.

6. The method of separating naphthenic acids according to molecular weight which comprises dissolving one volume of the naphthenic acids in several volumes of propane, raising the temperature to about 165° F. to effect the separation of naphthenic acids of higher molecular weights than those retained in solution, and removing the solution of naphthenic acids from the separated naphthenic acids.

7. The method of treating crude naphthenic acids which comprises dissolving said crude naphthenic acids in a relatively small volume of a preliminary hydrocarbon solvent, adding a relatively greater volume of a second solvent comprising at least one liquid hydrocarbon of lower molecular weight than said preliminary hydrocarbon solvent and chosen from the class consisting of liquid propane and other liquified normally gaseous hydrocarbons, heating the resulting solution, while applying sufficient pressure to maintain said second solvent liquified, to a temperature at which said second solvent has a precipitating action substantially equivalent to that of liquid propane at about 165° F., to effect two-phase separation of said solution into two fractions, each of said fractions containing naphthenic acids and one of said fractions containing naphthenic acids of higher molecular weight than the napthenic acids in the other fraction, and recovering the two fractions thus separated.

EDWIN C. KNOWLES.
FREDERIC C. McCOY.