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METHOD FOR IMPROVING THE QUALITY OF NAPHTHENIC ACIDS

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5 Claims. (Cl. 260—514)

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This invention relates to a process of purifying naphthenic acids and particularly to a process of extracting said naphthenic acids in a pure condition from petroleum oils.

This is a continuation in part of an application for patent Serial No. 738,214, filed March 29, 1947, now abandoned. In that application, a method of purification of naphthenic acids is described wherein the acids are washed with an aqueous alkaline media prior to saponification with sodium hydroxide. This washing accomplishes the removal of undesirable free or active sulfur.

Naphthenic acids are found in naphthenic base crude oils particularly those obtained from Colombia, Venezuela, Rumania, Russia, etc. The naphthenic acids heretofore were separated by treating the crude petroleum oil or fractions thereof with aqueous solutions of caustic soda to form sodium naphthenates which are soluble in the aqueous solutions. The aqueous solutions were then separated from the petroleum oil and treated with acids as sulphuric, HCl etc. to form and separate naphthenic acids. If any sulfur was present in the crude petroleum oil as generally is the case, the naphthenic acids obtained by this process contained free and reactive sulfur. Naphthenic acids containing free and reactive sulfur are not suitable to be used for many purposes especially where the sulfur would react with other materials, for example as in the manufacture of the heavy metallic soaps of the type used as siccatives.

The object of this invention is to separate the naphthenic acids from the petroleum oil substantially pure and without any free, or reactive sulfur.

It has now been found that the quality of the naphthenic acids can be greatly improved by washing the petroleum fraction from which the acids are to be extracted with an aqueous media having a pH between 1 and 9.8. It is of course more economical to use fresh water close to the neutral pH but conveniently other aqueous media within this pH range may be used, i. e., sea water, sodium bicarbonate solution and dilute acid solutions. The naphthenic acids may be then extracted by conventional extraction means.

Such treatment removes hydrogen sulfide and other reactive sulfur compounds which are generally found dissolved in the naphthenic acids if the petroleum fraction is not washed before the naphthenic acids are removed from the petroleum oil. When hydrogen sulfide remains in the petroleum crude oil treated with sodium hydroxide, sodium sulfide is formed. The sodium sulfide upon acidification with sulfuric acid breaks down to elemental sulfur which remains dissolved in the naphthenic acids.

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The lower pH limit is determined by the acidity which would evolve hydrogen sulfide and elemental sulfur. The latter would then undesirably remain dissolved in the naphthenic acids. A pH lower than 1 should not be used.

The upper pH limit is the alkalinity above which naphthenic acids would be extracted with a consequent loss in yield. A pH higher than 9.8 should not be used.

This invention will be more fully understood by reference to the following examples.

In the two examples that follow the starting material was the same in each of the procedures indicated i. e., a gas oil boiling in the range of 400–700° C. The first procedure of each example served as a control in that there was no preliminary washing step as taught by this invention, but the subsequent treatment was the same for each procedure. The free or reactive sulfur figures are the amounts of free or reactive sulfur remaining after the treatment of each of the procedures indicated. The free or reactive sulfur removed in each example by the process of this invention can be seen by comparing the figure for the material, in Procedure I, which was not first washed according to the process of this invention, with samples processed as taught by this invention i. e., Procedures II and III. Free or reactive sulfur was determined by reaction with a heavy metal and the same reaction was used in each case.

EXAMPLE I

The efficacy of washing with an alkaline media is illustrated in this example.

Procedure I

A petroleum gas oil fraction was neutralized to .05 neutralization number with 4° Baumé caustic soda, the aqueous sodium naphthenate solution was separated and acidified. The resulting freed naphthenic acids were separated from the aqueous solution, and salt water washed free of inorganic acid and then paper filtered bright. The wash water and naphthenic acids while being washed were maintained at a temperature of about 82° C.

Procedure II

Hydrogen sulfide in a gas oil was extracted by washing with 1% by volume of sodium bicarbonate solution ($NaHCO_3$ solution equivalent to 1° Baumé NaOH), and at atmospheric tem-

perature, the solution drawn off and the gas oil was then washed with 10% by volume of hot salt water, 82° C. temperature, the salt water removed, and the standard extraction procedure carried out as in method 1.

Procedure III

A gas oil was washed with 20% hot salt water of a pH of about 8 in 2 applications (2×10%), 82° C. temperature, and then the standard extraction procedure was carried out as in method 1.

RESULTS

Procedure No.	Naphthenic Acids		
	I	II	III
Neutralization No.	234.2	225.9	236.8
Unsaponifiable Matter, per cent	4.7	7.4	4.8
Free or Reactive Sulfur mg./100 cc.	80	1.3	1.3
Percentage Free or Reactive Sulfur based on I, per cent	100	1.6	1.6

EXAMPLE II

The efficacy of washing with an acid to approximately neutral media is illustrated in this example.

Procedure I

The petroleum fraction, gas oil, was neutralized to 0.05 neutralization number with 4° Baumé caustic soda. The sodium naphthenates were drawn off and acidified. The resulting naphthenic acids were water washed free of inorganic acids and then paper filtered bright. This batch served as a control.

Procedure II

The petroleum fraction, gas oil, was washed free of hydrogen sulphide with fresh water. The petroleum fraction was then neutralized to 0.05 neutralization number with 4° Baumé caustic soda, the sodium naphthenates drawn off and acidified. The resultant naphthenic acids were water washed free of inorganic acids and then paper filtered bright.

Procedure III

The petroleum fraction, gas oil, was washed free of hydrogen sulphide with slightly acidic water, 1 pH. The naphthenic acids were then extracted from the petroleum fraction as in Procedure II.

RESULTS

Procedure No.	Naphthenic Acids		
	I	II	III
Neutralization No.	224	224	224
Unsaponifiable Matter	9.3	9.2	9.2
Free or Reactive Sulphur mg./100 cc. in Finished Naphthenic Acid	55	2.5	2.5
Percentage Free or Reactive Sulfur based on I, per cent	100	4.5	4.5

Free sulfur and reactive sulfur compounds in naphthenic acids can therefore be considerably reduced by water washing the petroleum oil at a temperature between about 45° to 100° C. with a preferred range of 80–85° C. prior to the extraction of the naphthenic acids. The temperature of the washing helps prevent emulsification and promotes more rapid separation of the wash water. Conveniently the volume of water used may be from about ¼ to an equal volume of the oil being treated. If additional purification is desired multi-stage washing may be employed.

It will be understood that this invention is not limited to the specific examples which have offered merely as illustration and that modification may be made within the scope of the claims without departing from the spirit of the invention.

What is claimed is:

1. The process for separating naphthenic acids free of reactive sulfur which comprises washing an untreated petroleum gas oil distillate fraction containing naphthenic acids with an aqueous media that has a pH about that of sea water and no greater than 9.8, contacting the washed petroleum oil with an aqueous solution of an alkali metal hydroxide, separating the aqueous solution from the petroleum oil, acidifying the separated aqueous solution, separating naphthenic acids from the acidified aqueous solution, and washing the separated naphthenic acids with water.

2. The process of separating naphthenic acids free of reactive sulfur which comprises washing an untreated petroleum gas oil distillate fraction containing naphthenic acids with sodium bicarbonate solution having a pH about that of sea water and no greater than 9.8, contacting the washed petroleum oil with a sodium hydroxide solution, separating the sodium hydroxide water solution containing naphthenates from the petroleum oil, acidifying said separated water solution containing naphthenates, separating naphthenic acids from the acidified water solution, and washing the separated naphthenic acids with water.

3. The process of separating naphthenic acids free of reactive sulfur from an untreated petroleum gas oil distillate fraction which comprises washing a pertoleum oil with sea water, contacting the washed petroleum oil with a sodium hydroxide water solution, separating the sodium hydroxide water solution from the petroleum oil, acidifying the separated water solution with sulfuric acid, separating naphthenic acids from the acidified water solution and washing the separated naphthenic acids with water.

4. The process as in claim 1 in which the aqueous media is water.

5. Process as in claim 4 in which the petroleum oil is washed at a temperature in the range of 45 to 100° C.

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