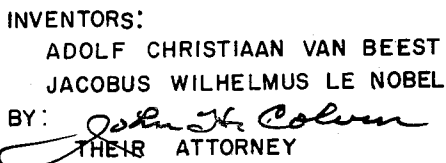


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ADOLF CHRISTIAAN VAN BEEST  
JACOBUS WILHELMUS LE NOBEL

BY: John H. Colver  
THEIR ATTORNEY

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2,980,606

## HYDROCARBON REFINING TO REDUCE SULFUR, NITROGEN, AND NAPHTHENIC ACID CONTENT

Adolf C. van Beest and Jacobus W. Le Nobel, Amsterdam, Netherlands, assignors to Shell Oil Company, a corporation of Delaware

Filed Aug. 12, 1957, Ser. No. 677,434

Claims priority, application Netherlands Aug. 14, 1956

4 Claims. (Cl. 208—254)

The present invention relates to the treatment of petroleum hydrocarbons and more particularly pertains to an improved method for the refining of hydrocarbon materials to reduce their naphthenic acid content.

Various crude oils, as for example, certain Venezuela, Trinidad, California, and Borneo crude petroleum contain minor amounts of naphthenic acids. In the processing of these crudes or their distillates, it is conventional practice to wash the crude oil or petroleum fraction with an aqueous alkali solution in order to separate the naphthenic acids in the form of water-soluble soaps from the hydrocarbons. Since the naphthenic acids and their salts are valuable industrial materials, the dissolved naphthenates are then usually acidified to permit their recovery from the alkali wash water. The naphthenic acids and their salts are used, among other purposes, as components in paint formulations, detergents, and for making various fungicidal compositions.

The foregoing alkali washing of the crude oil or petroleum fraction does not extract all of the naphthenic materials from the oil and trace amounts of the naphthenates remain behind, dissolved in the oil where they may and do frequently cause difficulties. For instance, when the oil comes into contact with water, as is likely to occur during transport, the trace naphthenates together with the water cause a very persistent turbidity in the oil, so-called permanent haze. It is also known that small amounts of the soap present in diesel fuel oils may result in injector and filter plugging. In addition, simple alkali washing of the petroleum fraction may be attended by serious emulsion troubles which are traceable to the entrainment of the alkali and of the naphthenate soaps in the oil being treated. Such emulsions are, of course, undesirable and will frequently necessitate further refining to assure their removal.

Methods have been suggested for preventing the emulsification and for reducing naphthenate soap entrainment in the treated petroleum fractions. It is known, for instance, that the foregoing difficulties may be appreciably lessened by treating the petroleum oil or fraction with an alkali solution containing not only say free alkali metal hydroxide but also the reaction products of that material with weak organic acids. These weak organic acids may be, among others, phenol, alkyl phenols, thiophenols, alkyl thiophenols, fatty acids such as isobutyric or naphthenic acids having lower average molecular weights than the naphthenic acids present in the oil being treated. The alkali metal hydroxide solution containing the above reaction product may be readily prepared by first treating a hydrocarbon oil which has a lower boiling range than the oil to be processed with an alkali metal hydroxide solution. The latter solution extracts phenols, thiophenols, low molecular weight naphthenic acids, etc. from the lower boiling hydrocarbon oil, thus providing an alkali solution especially adapted to the treatment of the heavier hydrocarbon oil. The foregoing reaction products of the alkali and weak organic acids are sometimes described as solutizers for the naphthenates. If conven-

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ient, the reaction products of the alkali metal hydroxide and the organic acid may be prepared separately and then added to the alkali metal hydroxide solution.

However, even with the use of a solutizer in the caustic solution used for neutralizing and extracting the naphthenic acids, the caustic treated petroleum fraction will still frequently contain trace amounts of naphthenates which cause haziness. Moreover, oils treated with caustic solutions containing a solutizer possess an offensive odor.

The trace naphthenic soaps present in the treated oil may be acidified with sulfuric acid, thus placing the naphthenates in their acid form which will obviate the problem of turbidity. However, the acid treated oil may be corrosive to metals, especially copper and zinc. If, in order to avoid corrosion difficulties, less than a stoichiometric amount of sulfuric acid is employed to wash the caustic treated oil, the problem of haze remains to the extent that the naphthenates are present. Therefore, from a practical standpoint, an excess of sulfuric acid should be employed.

It is an object of this invention to provide an improved method of treating a hydrocarbon oil which contains naphthenic acids to obtain a treated hydrocarbon free of naphthenic soaps and essentially free of naphthenic acids. This and still other objects of the present invention will become apparent from the following description of the invention, made in conjunction with the accompanying drawing in which the sole figure shows diagrammatically a preferred system for performing the process of the invention.

It has now been discovered that naphthenic acid-containing petroleum hydrocarbons can be caustic extracted, acidified, neutralized and water-washed to provide a product which is free of naphthenic acid soaps in amounts that cause product haziness in the presence of water. In a preferred embodiment of the process, the hydrocarbon is first washed with an aqueous alkali solution thereby converting the naphthenic acids present in the hydrocarbon material to their water-soluble soap form. The wash mixture is separated to obtain a washed hydrocarbon phase which will unavoidably contain a small amount of the naphthenic acid soaps (naphthenates) and an aqueous wash phase containing the vast share of the naphthenic soaps. The alkali washed hydrocarbon is then treated with sulfuric acid to acidify the naphthenates therein to their acid form. Subsequently, the sulfuric acid treated hydrocarbon is washed with an aqueous basic solution, preferably of a salt of a weak acid and a strong base, having a pH of less than 8.5 to neutralize any sulfuric acid remaining in the oil, without significantly saponifying the naphthenic acids present, thus leaving the naphthenic material in a form which will not cause haziness when the product is subsequently contaminated with water.

The product of the improved process is odorless, clear and possesses a light color and will generally have an acid number less than 0.1. The acid number is determined by the number of milligrams of potassium hydroxide required per gram of the hydrocarbon oil to neutralize the acids present. The product is substantially free from nitrogen bases and contains few mercaptans, shows no sludge formation and exhibits no discoloration on aging. The product of the present invention is not corrosive towards copper and zinc and will not develop turbidity when contacted with water.

The initial alkali or caustic treatment of the oil may be with or without a solutizer of the type already described. While sodium hydroxide is generally used, aqueous solutions of various other alkalis may be employed, for instance, other alkali metal hydroxides such as potassium hydroxide are satisfactory. The concentration of the

free alkali in the wash water may vary within quite wide limits but will generally be between approximately 10% and 40% by weight of caustic alkali based on combined weights of water and the alkali. In the instance where a solutizer is employed, the amount of the non-hydrolyzable reaction product of the alkali and organic acid materials should exceed 5% by weight and preferably the amount of solutizer used is in excess of 15% of the total caustic alkali solution. The upper limit of the concentration will be set by the solubility of the solutizer in the particular alkali solution utilized but in general not over 90% saturation is preferred.

The caustic treated hydrocarbon fraction may be processed with an undiluted sulfuric acid but preferably the acid treatment is had with a water diluted sulfuric acid containing from 60 to 90% acid by weight, based on water plus sulfuric acid. A typically suitable acid wash may be had with 80% sulfuric acid, where 500 parts of the hydrocarbon is treated with 125 parts of the diluted sulfuric acid. The proportions of acid to oil may vary quite widely but generally with an 80% sulfuric acid solution, 75 to 200 parts of sulfuric per 500 parts of the oil is adequate. On an undiluted sulfuric acid basis, sulfuric acid in an amount of 1 part to 3 parts of oil may be necessary but generally an amount of say 1 part of sulfuric acid to 5 parts of the oil is sufficient. In a petroleum fraction containing a relatively small proportion of naphthenic acid soaps, it may be adequate to employ 1 part of sulfuric acid to treat 8 parts of the oil. Whatever the proportion of acid to oil that may be employed, the object is to acidify the naphthenic soaps present in the alkali treated oil to their acid form.

After separating the oil phase and the acid phase, the oil which will no longer possess an offensive odor is preferably passed through a coalescer to agglomerate and separate acid particles that may remain distributed in the oil. The coalesced acid particles are then removed.

The acid treated hydrocarbon which contains traces of sulfuric acid along with the naphthenic acids is then subjected to treatment with an aqueous basic solution having a pH of less than 8.5 and preferably in the range of 7.5-8.2. The aqueous basic solution is preferably prepared with a salt of a weak acid and a strong base, for example, sodium acetate or sodium bicarbonate at a concentration of the salt in the basic solution of generally between 1-5% by weight. The solution is normally used in a quantity of 10-50 parts by volume per 100 parts by volume of the oil being treated and may be recycled to contact further quantities of the oil. The sulfuric acid solution of the preceding step may likewise be recirculated. By using basic solutions of the specified pH only the small amount of the mineral acid present in the oil is neutralized, leaving the naphthenic acids formed by sulfuric acid treatment unsaponified, with the result that the product from the aqueous basic solution treatment does not exhibit a permanent haze when contacted with water. It may be desirable to incorporate a small quantity of alcohol, for example, ethanol in the weak basic wash water.

The product from the basic wash procedure may, if desired, be further washed with water and then dried in a salt filter. The acid number of the resulting oil will normally be less than 0.1 and frequently less than 0.05 and the mercaptan sulfur content is generally less than 0.002% by weight.

The process may be advantageously applied to the treatment of hydrocarbons boiling between 200 and 400° C., particularly gas oils. It also may be used for the acid neutralization of kerosene, domestic fuel oil and lubricating oil. The temperature of the various stages of the process is generally between 20-80° C. The mixing of the hydrocarbon with the various treating liquids may be carried out in conventional mixing devices such as propeller mixers or centrifugal mixers.

## EXAMPLE

500 parts by volume of a heavy Venezuelan gas oil is supplied per hour through a line 10 to a pump 11. The gas oil had an initial boiling point of 202° C. and at 250° C., 7½% by volume of the oil distilled, at 300° C., the amount volatilized was 33% by volume and at 371.1° C., the distillate portion constituted 83½% of the original volume. 15 parts by volume of a prepared caustic solution containing a solutizer is supplied via a line 12 to a pump 14. The two pumps discharge into a common line 15 which opens in turn into a propeller mixer 16.

The solutizer containing caustic solution is prepared by treating a catalytically cracked gasoline with an aqueous sodium hydroxide solution, containing 20% by weight of sodium hydroxide, based on the water and alkali. The product of the alkali treatment contains 12% by weight of free sodium hydroxide and approximately 22% by volume of sodium salts of weak organic acids.

The gas oil caustic mixture carried by the line 15 is commingled with 125 parts by volume of a recycling caustic solution circulating in line 17. The caustic treated gas oil is then admitted to the propeller mixer 16 where the entering stream is violently agitated to assure an adequate mixing of the caustic solutions with the gas oil. The sodium hydroxide neutralizes substantially all of the organic acids including the naphthenic acids, forming water-soluble naphthenates. The agitated stream leaves the mixer propeller through a line 18 which opens into a settler 19 and here the mixture separates into an alkali extract aqueous layer and an overlying extracted hydrocarbon layer which retains a small amount of the naphthenic soaps. But by far the vast proportion of the naphthenic soaps is dissolved in the lower aqueous wash water phase. At the far end of the settler, remote from the point of entry of line 18, a line 17 is provided for removing the separated alkali wash water from a quiescent zone, from where it is recycled through a pump 18 disposed in the line 17 to the aforementioned propeller mixer 16. A quantity of the recycling caustic solution equal in amount to the caustic solution introduced through the make up line 12 is drawn off from the recycle line 17 through a line 19. The caustic treated gas oil which may still contain an appreciable amount of caustic solution dispersed throughout it, leaves the settler 19 via a line 21 which leads to coalescer 22 and from there to a settling tank 24 placed preferably immediately below the coalescer, in which tank a further quantity of the caustic solution is separated from the gas oil and passed to the recycle line 17 via a line 25.

The gas oil is removed from the top layer of the settler tank through line 26 to a second propeller mixer 28. The alkali treated hydrocarbon flowing in the transfer line 26 has added to it, 125 parts by volume per hour of a recycled sulfuric acid phase supplied by a recycle line 29. Sulfuric acid makes up approximately 80% by weight, based on water plus sulfuric acid, of the recycling phase. The hydrocarbon and sulfuric acid phase are passed in a stream to the mixer 28 where they are thoroughly stirred together, acidifying the naphthenates remaining in the hydrocarbon to oil-soluble naphthenic soaps. From the propeller mixer 28 the mixture of oil and acid phase is passed through a line 30 to a settler 32 where the two phases are separated from each other. The acid phase which forms the lower layer is continuously removed from a quiescent zone of the settler and recycled through the aforementioned line 29 and a pump 33 disposed therein to the transfer line 16 where it joins the alkali treated hydrocarbon stream from the earlier processing. One part by volume of fresh sulfuric acid of 98% by weight is added to the recycling sulfuric phase per hour through a sulfuric acid make up line 34 which is provided with a pump 35. A quantity of the spent acid phase is withdrawn via a line 36 from the recycle line 29 to maintain the proper circulating volume. The

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gas oil which may contain a significant amount of the dispersed sulfuric acid phase is led from the top layer of the settler 32 via a line 38 to a second coalescer 39, and then to a settling tank 40 disposed immediately below the coalescer, in which tank a further quantity of the acid phase is separated from the gas oil and returned through a line 42 to the recycle line 29.

The now acid treated and alkali treated hydrocarbon is transferred from the settling tank 40 through a line 44 to a third propeller mixer 46. 125 parts per volume per hour of an aqueous sodium bicarbonate solution containing about 20 grams of sodium bicarbonate per liter is added to the transfer line 44 through a line 45. The bicarbonate solution and acid treated hydrocarbon are passed into the propeller mixer 46 where they are thoroughly agitated, thereby effectively contacting the hydrocarbon with the sodium bicarbonate solution. The pH of the bicarbonate solution is about 7.8. From the propeller mixer the mixture of oil and aqueous phase are continuously led through a line 48 to a settler 49 where the mixture separates into a hydrocarbon and aqueous phase. The aqueous basic solution neutralizes the small amount of sulfuric acid contained in the hydrocarbon without significantly saponifying the naphthenic acids, thereby retaining the naphthenic acids in a form that does not create a permanent haze when the oil is subsequently contacted with water. Naphthenic acids per se are not a contributory factor to the formation of the haze. The separated aqueous phase is removed from the bottom of the settler 49 through the aforementioned recycle line 45 which has placed within it a pump 50. Fresh aqueous sodium bicarbonate solution (5% by weight sodium bicarbonate) is added to the stream of the recycle line 45 in an amount of 4 parts per volume per hour. A small amount of the spent solution is removed via a line 52 to maintain the circulating volume. The added fresh sodium bicarbonate solution enters the recycle line 45 through a make up line 54 under the pressure of a pump 55.

The separated gas oil layer leaves the settler 49 through a line 57 to a coalescer 58 and from there passes to a settling tank 59 disposed immediately below the coalescer. In the latter tank, a further quantity of the aqueous sodium bicarbonate solution is separated from the oil and returned through a line 60 to the previously mentioned recycle line 45.

The gas oil from the top layer of the settling tank 59 moves through a transfer line 62 to a fourth propeller mixer 63. Water is added in a quantity of 50 parts by volume per hour to the sodium bicarbonate treated hydrocarbon stream at a point preceding the mixer through a line 65 under the pressure of a pump 66. The hydrocarbon and wash water stream is thoroughly mixed and agitated in the mixer 63 and from there the mixture is transferred via a line 68 to a settler 70 where the water is separated from the gas oil and withdrawn from the bottom of the tank through a line 71. The washed gas oil leaves the settler through a line 72 and is passed to a salt filter 73. From the latter unit the substantially dehydrated petroleum product is drawn off in the quantity of 485 parts by volume per hour through a conduit 75. A salt solution is removed from the filter 73 via a line 76.

The data in Table I show the properties of the untreated feed, of the product, and of the hydrocarbon at various stages of processing. The data appearing in the far right hand column pertain to the treated product, following water washing and drying. The latter two steps of water washing and drying are desirably included in the practice of the process but are not necessary. It will be seen that the oil from the caustic solution treatment and prior to the acid treatment and sodium bicarbonate wash develops a permanent haze on contact with water. However, the completely processed product remains wholly clear to like handling. Moreover, as a result of

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the treatment, the content of the nitrogen bases is also very much reduced and there results a significant reduction in the mercaptan sulfur content. The acid number value appearing in the fourth column under the heading "After Acid Treatment" is principally attributable to the presence of mineral acid.

Table I

|    | Feed Venezuelan Gas Oil                                                                    | After Caustic Solution Treatment | After Acid Treatment | After Sodium Bicarbonate Treatment, Water Wash And Drying |
|----|--------------------------------------------------------------------------------------------|----------------------------------|----------------------|-----------------------------------------------------------|
| 10 |                                                                                            |                                  |                      |                                                           |
| 15 | Sulfur content..... 1.63%<br>Acid Number, mg KOH/g. 2.83                                   | 0.02-0.03                        | 0.1-0.2              | 0.04                                                      |
|    | Ash content, percent wt. 0.018                                                             |                                  | <0.001               | <0.001                                                    |
|    | Mercaptans, percent wt. S. 0.0021                                                          | 0.0020                           | 0.0004               | 0.0004                                                    |
| 20 | Nitrogen bases calculated as parts by wt. N <sub>2</sub> per million parts by wt. oil. 121 | 121                              | 5                    | 5                                                         |
|    | Union color..... 2 min.                                                                    |                                  |                      | 1 min.                                                    |
|    | Union color after 24 h. heating to 100° C. in the presence of iron. 7 min.                 |                                  |                      | 2 min.                                                    |
| 25 | Odor..... Good                                                                             | Offensive. Permanent haze.       |                      | Good. Completely clear.                                   |
|    | Appearance of the gas oil after shaking with water, followed by ½ hour centrifuging.       |                                  |                      |                                                           |

We claim as our invention:

1. In a process for refining a petroleum hydrocarbon mixture containing naphthenic acids, sulfur compounds and nitrogen bases wherein there is a mixing of the hydrocarbon with an aqueous alkali wash solution whereby the naphthenic acids are converted to water-soluble soap and wherein there is a separation of the mixture of hydrocarbon and wash solution to obtain a washed hydrocarbon phase containing a small amount of naphthenic soaps and an aqueous wash phase containing the remainder of said soaps, the improvement comprising treating the alkali-washed hydrocarbon with an excess of sulfuric acid to remove nitrogen bases and to acidify the naphthenic soaps contained therein and subsequently washing the acid treated hydrocarbon containing excess sulfuric acid with an aqueous basic solution of a salt of a weak acid and a strong base, said solution having a pH of less than 8.5, to neutralize substantially the sulfuric acid remaining therein from the acid treatment without significantly saponifying the naphthenic acids to the extent that they form a permanent haze when the oil is contacted with water.
2. A process in accordance with claim 1 wherein the aqueous basic solution contains sodium bicarbonate present in the amount of between about 1-5% by weight of the solution.
3. A process in accordance with claim 1 wherein the aqueous basic solution contains sodium acetate present in the solution in an amount between approximately 1-5% by weight.
4. A process in accordance with claim 1 wherein the aqueous basic solution contains a salt of a weak acid and a strong base present in an amount between about 1-5% by weight of the solution and wherein 10-50 parts by volume of said solution are employed to wash about 100 parts by volume of the hydrocarbon.

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