

PATENT SPECIFICATION

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(54) TRACE ACID REMOVAL FROM LIQUID HYDROCARBONS

(71) We, UOP INC, a corporation organized under the laws of the State of Delaware United States of America, of Ten UOP Plaza, Algonquin & Mt. Prospect Roads, Des Plaines, Illinois, United States of America, do hereby declare the invention, for which we pray that a Patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following Statement:-

This invention relates to the removal of trace acids such as H₂S and naphthenic acids from liquid hydrocarbons.

Many hydrocarbons contain sulfur in the form of mercaptans (thiols). Mercaptans are almost invariably present in LPG, cracked gasolines, straight run gasolines, natural gasolines, and in heavier hydrocarbon distillates including e.g., kerosene and fuel oil.

These mercaptan components are objectionable mainly because of their strong odor, but also, in some cases, due to their objectionable chemical reaction with other hydrocarbons or fuel system components.

There have been many attempts to provide processes which would remove or convert mercaptans. Some of the earliest processes included treatment of the hydrocarbon fraction with caustic, clays, and hydrotreating. A significant improvement in the treating of hydrocarbon fractions was made when the UOP Merox Process was announced to the industry in 1959. The *Oil and Gas Journal*, in the October 26, 1959 edition, contains a discussion of the Merox Process, and also of some prior art processes.

That process uses a catalyst which is soluble in caustic, or alternatively held on a support, to oxidize mercaptans to disulfides in the presence of oxygen and caustic.

In U.S. Patent 3,108,081, there is disclosed a catalyst comprising for the oxidation of mercaptans. This patent teaches that a particularly preferred phthalocyanine is the sulfonated derivative, with the monosulfonate being especially preferred.

In commercial operation, a number of catalyst poisons or other deleterious materials are present in the hydrocarbon feed to the processing units provided for mercaptan removal or conversion. Trace amounts of acidic components such as naphthenic acids and H₂S are frequently encountered.

H₂S is often naturally occurring but may also be present as a by-product of some earlier steps in processing wherein sulfur compounds, in the presence of hydrogen and high temperature, decompose to form H₂S. When the hydrocarbon feed stream being treated is either a naphtha or a kerosene, most of the H₂S is removed by distillation; however, such removal is not always complete and further treatment of the hydrocarbon stream is required.

Naphthenic acids, and other carboxylic acids, are commonly found in crude oil. During distillation naphthenic acids are co-distilled with the hydrocarbons of similar boiling ranges concentrating in the various distillate streams. Naphthenic acids possess characteristics which are conducive to solubility in both hydrocarbon and aqueous media and are often referred to as surfactants because of their activity at surfaces, such as the interface between a liquid hydrocarbon and water. When neutralized by alkalis, naphthenic acids form alkali naphthenates which are chemically similar to soaps. As such, they tend to emulsify hydrocarbon and aqueous phases, interfering with efficient separation of oil and water phases. Because of these properties, they must be removed from finished products where aqueous emulsions cannot be tolerated and from the feeds to chemical treating processes where they interfere with efficient processing.

Accordingly, the treating arts have developed a number of ways of handling these problems. One way is to simply provide a large vessel, termed a pre-wash, partially filled with dilute aqueous caustic, disperse the hydrocarbon containing trace acidic components into the aqueous caustic, and pass the hydrocarbon stream up through the vessel. Typically the entering hydrocarbon stream will enter the pre-wash vessel through a series of nozzles to insure that there is intimate contact of hydrocarbon with dilute caustic. Sometimes contact is obtained by circulating the caustic inventory with a pump to mix the caustic with entering hydrocarbon in the piping. The strength and quantity of the caustic solution used are generally adjusted so that very little of the weakly acidic mercaptans in the feed are absorbed by the caustic. Only the more acidic naphthenic acids, H_2S and other trace acidic compounds are removed by the caustic pretreatment. When very low acid contents in the product are required, the pre-wash vessel may be followed by a sand filter coalescer which will remove entrained droplets of aqueous salts from the hydrocarbon stream being treated. However, a sand filter requires frequent attention to maintain its coalescing efficiency and sand is subject to attack by aqueous basic solutions.

Unfortunately, such an operation does not always provide a satisfactory solution to the problem of removing acids. Use of a large pre-wash vessel adds to the capital expense of the plant and may not provide efficient utilization of the caustic solution. In the case of naphthenic acid removal, very dilute caustic must be employed for most efficient acid removal. Use of a batch pre-wash system also means that the efficiency of naphthenic acid removal is cyclical. The efficiency is greatest when the caustic is fresh, and lowest just before the weak caustic is discarded. Because of the batch nature of the process, and because of the surfactant nature of naphthenate soaps, a certain amount of unneutralized caustic is always discarded with the spent caustic.

Even with use of a conventional coalescer following the pre-wash vessel, e.g., sand filter or mesh blanket coalescer, the entrainment of acidic salts is still sometimes excessive. This is because the efficiency of coalescers is dependent on many factors. Reasonable efficiency can only be obtained within a relatively narrow velocity range and deterioration in efficiency with use in common as particulate buildup, sand attrition, channeling, and other factors cause deterioration in performance. The inability of the conventional coalescers to maintain high efficiencies without frequent maintenance has led to the use of electrical coalescers. These devices are similar to the well known desalters used on crude petroleum to remove entrained water containing dissolved salts. With the use of an electrical coalescer, it is possible to remove enough of the entrained caustic containing the naphthenic acid salts from a pre-washed hydrocarbon to satisfy the requirements of downstream processing units and, where applicable, such specifications as water separation from jet fuel for example. Unfortunately, the electric coalescers are proprietary items and add greatly to the expense of pretreatment equipment. They also require careful attention increasing the utilities cost and operator expense.

Another problem experienced by the prior art pre-wash processes is disposal of large quantities of spent reagent. As previously mentioned, efficient operation of the batch type pre-wash vessel precludes total exhaustion of the alkali solution. There is always a significant amount of unneutralized caustic remaining in the relatively large liquid reserve of alkali solution in the pre-wash vessel. Thus, when the efficiency of acid removal by the alkaline solution is no longer satisfactory, a high percentage of unneutralized alkali is unavoidably discarded. This is a problem, not only because of inefficient use of reagents, but because the free alkali represents a disposal problem.

Another disadvantage of a batch pre-wash is that the naphthenic acids present in the spent caustic phase are difficult to recover. If an attempt is made to recover these acids it is first necessary to reacidify the spent caustic and then separate acids from admixed oil. Because of the dilute nature of the streams used in a pre-wash upstream of a mercaptan conversion process, the recovery of naphthenic acids is usually considered not worthwhile. Thus, a source of potentially valuable raw material is lost. Naphthenic acids can be used as paint driers, wood preservatives, and to some extent in extreme pressure lubricants. The naphthenic acids have also been used as solvents for vulcanized rubber, various resins and gums, for aniline dyes, as clarifying agents for mineral oil, as insecticides, and as additives to wood oil to permit drying without cracking.

Accordingly, refiners continue to search for a process which would provide for efficient acid removal, be economical to operate, and provide near stoichiometric utilization of the alkali solution. There is also a need for a process which would be continuous to avoid the necessity of frequent draining and handling of large volumes of alkali solution.

According to the present invention there is provided a method of removing acid from a liquid hydrocarbon comprising: (a) mixing an aqueous base with the hydrocarbon to form a dispersion; (b) then charging the two-phase dispersion from step (a), still containing water and hydrocarbon, into a coalescing bed of a solid, alkali-resistant, hydrophilic medium; (c)

separating in the coalescing bed a hydrocarbon phase and a separate aqueous phase; and (d) recovering from the coalescing bed as a product of the process a hydrocarbon phase containing a reduced acid content.

In a preferred embodiment the present invention provides a continuous method for removing a naphthenic acid component from a kerosene stream comprising: (a) continuously passing to mixing means the kerosene stream and 100 to 200% of the amount of 1 to 3 wt.% aqueous sodium hydroxide solution required by the stoichiometry to neutralize the naphthenic acid component in the kerosene stream and effecting mixing of the kerosene stream and the sodium hydroxide solution in the mixing means to form a two-phase dispersion; (b) passing the dispersion from step (a), still containing kerosene and water, downflow through a fixed bed of a solid, alkali-resistant, hydrophilic coalescing medium at a LHSV of 0.5 to 20, and coalescing in said bed a spent aqueous caustic phase and a separate kerosene phase; (c) withdrawing the kerosene phase containing 0 to 10% of its original naphthenic acid content from a lower portion of the fixed bed as a product of the process; and (d) withdrawing the spent aqueous caustic phase from the bottom of the fixed bed.

When the acids to be removed are naphthenic acids, which are neutralized by the aqueous base, the resulting naphthenic acid salts tend to be absorbed on the coalescing medium. They may be recovered from this medium by stopping the flow of hydrocarbon and aqueous phase and either treating the bed with high temperature steam to volatilize the salts or treating the bed with an acid medium to acidify the salts and then displacing the resulting acids with a desorbent such as steam at 200-400°C.

The liquid hydrocarbon streams which may be treated in the process of the present invention are those containing any trace amount of acid. For example, naphthenic acids are usually found in stream with ASTM D 86 end points in excess of 150°C. H₂S can be found in most refinery intermediate product streams. Carboxylic acids are often present in catalytically cracked stocks. The method of the present invention can be applied with great success to all of these stocks.

Many kerosene charge stocks which must be treated for mercaptan conversion frequently contain high naphthenic acid contents. Naphthenic acid content is generally indicated by acid number, with typical units being milligrams of KOH required to neutralize one gram of sample. The product specification for most jet fuels sets the maximum acid number at 0.010 mg KOH/g. Charge stocks are being encountered today which have acid numbers in excess of 0.100 mg KOH/g. The existing batch type pre-wash units followed by a coalescer cannot efficiently remove naphthenic acids in a range above about 0.025 mg KOH/g. The presence of such large amounts of naphthenic acids in the feed to a mercaptan conversion unit, if not removed, would result in operating difficulties with the treating unit and loss of product. The acid number of a kerosene or other hydrocarbon can be determined by any of several methods of test such as ASTM-D-3242, ASTM-D-3339, ASTM-D-974, ASTM-D-664, etc.

The aqueous base suggested for use may be any inorganic base soluble in aqueous (or alcoholic) solvent. Both NaOH and KOH are suitable, with NaOH being preferred because of its availability and low cost. A relatively dilute aqueous base is required to effect solubility of the naphthenic acid in the aqueous phase. Solubility of the alkali naphthenates in the aqueous phase decreases as the concentration of alkali in the aqueous phase increases. Solubilities of other acid salts also limit the concentration of base in the solution that may be practically used at normal temperatures.

Regardless of the type or concentration of the base used, the present invention permits operation with only a slight excess of base to allow for variation in acid concentration of the feed stock.

The feed stream and the aqueous alkaline phase are contacted in a simple mixing device to form a two-phase dispersion before entering the coalescing bed.

The solid, alkali-resistant, hydrophilic medium for the coalescing bed may for example be activated charcoal, coal, lignite, shale, slag or calcined coke. Examples of suitable charcoals include those derived from ground wood pulp, lignite coal, anthracite coal, bituminous coal, peat, petroleum black, and similar charcoals. Especially preferred is ground and graded anthracite coal. The use of these materials is to be contrasted with the use of sand, which is not hydrophilic.

The contact of the dispersion of hydrocarbon and aqueous base with the coalescing bed may occur in any suitable manner. The coalescing medium may be maintained as a fixed or moving bed. Batch contacting may also be employed. The stream may pass over the coalescing medium in upflow, downflow or radial flow.

The amount of coalescing medium provided must be adjusted to conform to the properties of the feed and to the desired properties of the product. It may be desirable to provide parallel coalescing beds so that one bed can be used while another is being regenerated. Series flow to promote maximum removal of acids can also be used. Use of

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multiple beds in series flow with a parallel train is also possible.

The amount of coalescing medium required for optimum results may be specified as a function of liquid flow rate. Preferably, enough coalescing medium should be provided so that the liquid hourly space velocity will be in the range of 0.5 to 20. Similarly, the preferred geometry of the fixed bed of coalescing medium is such that the superficial liquid velocity through the bed provides the highest efficiency and lowest cost.

For best results, the particle size distribution of the coalescing medium should be in a range of 0.1 millimeters to 6 millimeters with particle sizes in a range of 0.6 to 2 mm exhibiting excellent properties.

The conditions of temperature and pressure at which aqueous base contacts the feed, and in which the resulting dispersion contacts the coalescing medium are not critical. In general ambient temperatures which are above the freeze point of the aqueous phase or the pour point of the oil phase can be used. The typical sundown temperatures of refinery hydrocarbon product streams are 10 to 60°C, and the present invention works well within these temperature ranges. The lower limit on temperature is usually set by the temperature at which the viscosity of the fluid becomes so great that good contacting of aqueous phase and fresh feed is precluded, and subsequent separation of aqueous phase from organic phase is hindered. The upper limit of temperature is usually set by the degree of dehydration that can be tolerated in the system and allowable water content of the treated hydrocarbon stream. Operation at temperatures of 25 to 60°C gives satisfactory results with many feed streams. The normal materials are fluid at these temperatures, and contact and separation of aqueous and hydrocarbon phases is facilitated. Operation at much higher temperature is possible, and may be desirable in the case of very heavy or viscous oils which must be treated. Higher temperatures promote contacting and rate of reaction but adequate acid removal, for example, can usually be obtained without the expense of heating the stream to high temperature. The pressure under which the acid removal process of the present invention operates should be sufficient to maintain liquid phase operation as both the contact and separation of organic and aqueous phases occur entirely in liquid phase. Pressure is not believed to be a significant variable. Accordingly, the pressure will generally be the least amount of pressure required to get the fluids through the processing units.

The function of the caustic injection is twofold. Not only does the caustic neutralize the acid in the feed, it also wets the surface of the bed of coalescing media. Thus, the process of the present invention works efficiently because acids and caustic react not only in the mixing devices upstream of the coalescing bed, but also in the coalescing bed. It is because of this extensive and efficient contact of caustic and acid that the present invention works so efficiently.

There is still an aqueous phase dispersed in the hydrocarbon stream after reaction of acid and alkali is complete; this aqueous phase must be removed. This is another function of the coalescing bed. The dispersed aqueous phase is gradually coalesced into larger droplets by the bed finally forming large drops which separate and gravitate to the bottom of the coalescing vessel for removal. Preferably a level controller automatically drains the aqueous phase from the coalescing vessel as it accumulates. The advantage of the automatic level control is that it makes the process truly continuous requiring little or no operator attention.

The charcoal bed is preferably supported by a flat screen which will hold up the charcoal but allow the spent aqueous base to pass therethrough for removal from the bed. Especially preferred are the well known Johnson screens available from the Johnson Division of UOP Inc. These screens consist of wedge shape rods welded onto a support. They are very strong and generally non-clogging, and provide a relatively large open area for fluid flow. The hydrocarbon stream may be added to and removed from the charcoal bed via circular screens of the same type of construction.

The accompanying drawing shows a simplified, schematic flow diagram of one embodiment of the present invention wherein a dilute alkali solution is continuously injected into an acid bearing feed and the mixture passed through a coalescing bed.

Referring to the drawing, in the first step of the process an acid bearing feed stream in line 10 is contacted with a dilute aqueous base from storage tanks (not shown) charged by metering pump 1 taking suction via line 21 and discharging via line 22. Caustic is charged to mixing device 2. The mixture (dispersion) of feed and base is charged via line 11 to the coalescing vessel 3. Coalescing vessel 3 consists of coalescing bed 4, inlet distributor 8, collector pipe 5, and drain screen 6.

Treated hydrocarbon, substantially free of acids, is removed from the coalescing bed via collector pipe 5 and product line 12, then charged to other processing units or storage (not shown).

The aqueous phase coalesced by the coalescing bed trickles down through the coalescing bed exiting via drain screen 6, into drain pot 7. Sight glass and level control means (not shown) provide for the continuous withdrawal of spent aqueous phase via line 23.

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EXAMPLE I

A miniature pilot plant was used to test this invention. The feed was a kerosene with an extremely high acid number of 0.084 mg KOH/g. The coalescing bed consisted of 50 cc of charcoal made by the Norit Co. The charcoal was designated as 10/30 mesh, and 90% of it had a particle diameter between 0.6 and 2.0 mm. The charcoal was disposed as a fixed bed in a small pressure vessel. The internal diameter of the vessel was 25 mm and the height of the bed was 100 mm. The charcoal was supported at the bottom by a plug of glass wool. The alkali solution added to neutralize the naphthenic acids was a dilute aqueous solution of NaOH. The caustic strength was 1.5 wt. %. The base was added by slowly closing a hypodermic syringe. Such a method of adding caustic was necessary because the plant was small and because the present invention makes very efficient use of caustic. An ultrasonic mixer was used to mix the kerosene with the NaOH upstream of the coalescing bed.

The feed was tested for acid number. The hydrocarbon product, after passage through the bed of activated charcoal, was analyzed for both sodium content and acid number. The feed, after mixing with caustic, but before coalescing, was measured to confirm the calculated addition of NaOH. Both acid titration and atomic absorption spectroscopy analyses of the mixture were used to determine alkali content.

Tests were run at 2.0 and a 4.0 LHSV, i.e., a charge rate of 100 cc/hr and 200 cc/hr, respectively.

The experimental results are reported in the following Table 1.

Table 1

Hours	LHSV	Product: Acid No.	Na(ppm)	Moles Added	NaOH/Mole Titration	Acid in Feed: AAS
0-8	2	0.001	0.25			
8-17	2	0.010		1.11	0.46	
17-38	2	0.011				
38-73	4	0.029	1.5	1.77	1.29	0.27
73-80	4	0.009	0.34	1.26	0.60	0.10
80-100	4	0.004	0.45	1.28	1.29	0.10
100-124	4	0.023	2.2	1.14	0.60	0.34
124-152	4	0.005	3.6	1.14	0.58	0.77
152-179	4	0.018	8.1	1.14	0.40	0.74
179-197	4	0.036	19	1.14	0.48	1.03
197-221	4	0.006	3.6	1.14	0.34	0.53
221-248	4	0.004	7.1	-	-	0.80
248-273½	4	0.003	6.1	-	-	0.74

EXAMPLE II

Another test was made of this invention in a commercially sized unit. The charge stocks used were kerosenes derived from Louisiana and from Illinois. The unit used an existing refinery vessel as a coalescing bed. No attempt was made to design the vessel beforehand, rather an attempt was made to use the equipment existing at the plant to try out this invention on a slightly larger scale.

No mixing device was readily available to permit intimate contacting of the kerosene feed with the alkaline medium. As a substitute, a valve was pinched partially shut upstream of the coalescer.

The alkaline medium used was caustic available in the refinery, which had a concentration of 4-6° Baume. This concentration was higher than desired but was the only strength obtainable for the experiment. Calculations indicated that approximately 11.4 liters per hour of caustic injection was necessary to neutralize the kerosene derived from the Louisiana crude, while 5.7 liters per hour caustic was required for neutralization of acids contained in the kerosene derived from the Illinois basin material. The coalescing medium used was Calgon SGL charcoal, 8 × 30 mesh. Caustic injection, using the Louisiana crude, was begun at a rate of 37.8 liters per hour, or considerably in excess of that required by stoichiometry to neutralize acids, primarily naphthenic acids. This caustic injection rate reduced the initial acid number of the kerosene from 0.10 mg KOH/g to 0.0096 mg KOH/g. The resulting drained caustic was only about 50% spent. Caustic injection was further decreased to about 28.8 liters per hour, but this resulted in inadequate acid removal. The kerosene product by analysis contained an unacceptably high naphthenic acid content, 0.032 mg KOH/100 ml. This analysis might be questioned due to difficulty in obtaining a representative sample. The drained caustic was 60% spent, however. The amount of caustic which remained entrained in the product kerosene ranged from 0.042 to 0.067 ppm NaOH.

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This lower caustic entrainment was expected, because from our experience it is easier to separate caustic from hydrocarbons in a commercially sized unit than in a pilot plant.

EXAMPLE III

Further tests were then run in the pilot plant facility described in Example I. These tests were run with charcoal obtained from the Darco Company which had a nominal size of 10-30 mesh (90% of the particles had a diameter between 0.6 and 2.0 milliliters). The charge stock used was identical to that used in Example I. In Example III the target amount of the caustic injected was 1.2 times that theoretically required to neutralize naphthenic acids. The caustic material used was slightly more concentrated than that used in the first experiment, namely 5° Baume NaOH (equivalent to 3.2 wt. % NaOH). The reactor temperature was 78°F, the reactor pressure was 80 psig.

The test results are reported in Table 2.

Table 2

Hours	LHSV	Product Acid No. Na(ppm)	*PPM NaOH Added Addition Titration
0-12	4	0.005	73 78
12-23	4	0.017	73 16
23-37	4	0.010	73 22
37-45	4	0.007	(Temporary Haziness in Product)
45-53	4	0.005	73 32
53-64	4	0.016	(Jelly Appearing in Separator)
64-73	4	0.009	75 20
73-80	4	0.006	75 19
80-89	4	0.005	— —
89-99	4	0.005	75 45
99-108	4	0.003	75 64
108-118	4	0.005	75 11
118-126	4	0.008	— —
126-137	4	0.023	73 15
137-150	4	0.010	73 13
150-159	4	0.007	73 19
159-166	4	0.005	71 68
166-189	4	0.006	71 11
189-196	10	0.012	69 78
196-204	10	0.011	68 39

*NOTE: 62 ppm NaOH required by stoichiometry

A gel like substance appeared in the separator after 64 hours of operation and continued to be produced for the remainder of the experiment. A temporary plug developed at 99 hours into the experiment. From time to time some temporary haziness would appear in the product but this would usually go away after several hours. The hazy product at the end of the run, however, required a standing period of up to 7 days to clear. It is believed that the higher concentration of NaOH caused the production of the gel-like substance indicating the need to adjust the caustic concentration carefully.

EXAMPLE IV

The same test apparatus and charge stock was used as in Examples I and III. In this example the coalescing material used was ground anthracite coal. The nominal particle size of the coal was 0.84 to 2.0 mm, also designated as 10 × 20 mesh.

A slightly more dilute caustic was used in this experiment, namely 3° Baume NaOH (equivalent to 1.8 wt. % NaOH). The experiment was conducted at a 4.0 LHSV, and continued until supplies of feed stock were exhausted. The experimental results are reported on Table 3.

Table 3

	Hours	LHSV	Product Acid No.	Na(ppm)	PPM NaOH Addition	Titration	
5	0-11	4	0.046	-	68	-	5
	11-23	4	0.014	3.9	68	12	
	23-35	4	0.008	-	-	8	
	35-48	4	0.007	1.9	67	31	
10	48-70	4	0.005	0.63	67	60	10
	70-89	4	0.006	0.50	67	23	
	89-97	4	0.005	-	67	28	
	97-120	4	0.004	0.92	67	31	
	120-144	4	0.006	0.66	67	40	
15	144-168	4	0.006	1.05	67	36	15
	168-175	4	0.006	-	67	35	

This experiment was generally more successful in lowering the naphthenic acid content of the product, as indicated by the acid number thereof. This experiment was also very satisfactory in that the sodium content of the product was significantly lower than that indicated in earlier examples, although the sodium content of the product of Examples I and III is satisfactory.

Most of the improvement in Example IV is due to the lowered NaOH concentrations but there is perhaps a synergistic effect due to the use of anthracite as coalescing medium.

The coalescing bed of the present invention when used for removal of naphthenic acids may eventually become saturated with naphthenic acid salts. To permit reactivation of the bed, and also to permit recovery of the naphthenic acid salts for use as a valuable by-product, a number of regeneration procedures can be used.

It is believed that a reasonable regeneration can be performed by merely removing the bed from the flow stream and passing hot steam over the bed. To provide a more complete regeneration of the bed, and to permit recovery of the naphthenic acid salts in the form of the acid rather than the salt, it would be also possible to re-acidify the salts in situ. This may be accomplished by isolating the coalescing bed from the hydrocarbon and aqueous streams, circulating an aqueous, acidic solution over the bed, and desorbing the naphthenic acids from the charcoal. If a sufficient quantity of acidic water is used, much of the naphthenic acids will be displaced in the acidification step. The desorption of naphthenic acids may be promoted by passage of hot steam over the reactor. The naphthenic acids are volatile with steam and this procedure should provide for almost complete regeneration of the coalescing bed. If the charcoal bed is not readily regenerable with these mild techniques it may be necessary to go to higher temperature steam treatment, or treatment with various well-known hydrocarbon solvents such as benzene, acetone and methanol mixtures to assist in removal of naphthenic acids and acid salts from the coalescing bed.

One of the interesting features of this invention is that while doing an excellent job of removing acids in the kerosene product or for feed to a mercaptan conversion unit, it also produces as much as a 1000 fold increase in the concentration of naphthenic acids, permitting the possible recovery of naphthenic acids where they are a desired by-product, and simplifying the disposal of these compounds where there is no market for them. Most of the naphthenic acids will be recovered in the aqueous phase once an equilibrium amount has accumulated on the coalescing bed.

The present invention may also be used to remove H₂S from hydrocarbon streams. A hydrocarbon stream containing, e.g., 0.01 wt. % H₂S may be contacted with an aqueous 6 wt. % NaOH stream and passed downward concurrently through a coalescing bed. The coalescing bed preferably comprises a charcoal having a nominal granulation range of 0.6 to 2.0 millimeters available under the trade name of Calgon. Utilizing 30 percent excess base, the hydrocarbon product from the coalescer should contain less than 0.0005 wt. % H₂S.

The efficiency of removal of certain acids is limited by equilibrium considerations at the operating conditions desired. Partial removal of very weak acids, e.g., mercaptans and phenols, is also possible subject to equilibrium considerations, adjustment of base concentration, and dependent on the specific acidic component being removed.

It is preferred to use more concentrated base for removal of H₂S than for removal of naphthenic acids. This is because salts of H₂S are more soluble than salts of naphthenic acids. NaOH concentrations of 2 to 10 wt. % will give good results.

As applied to removal of naphthenic acids, the data indicate that the process of the present invention is very effective in reducing the acid number of a kerosene severely contaminated with naphthenic acid. In general, the naphthenic acid content could be

reduced to acceptable levels for further processing or sale.

it can be seen that in its preferred forms the method of the present invention allows for nearly stoichiometric utilization of the caustic. There is also more effective acid neutralization because of the larger effective surface area of basic medium, not only in the mixing means, and piping, but also in the coalescing bed. There is greater flexibility and efficiency permitting operation with hydrocarbon flow rates much less than normal. There is negligible entrainment of aqueous solution with hydrocarbon because of the ability of the coalescing bed to coalesce aqueous droplets into a separate phase that will separate by gravity, from the hydrocarbon. There is also afforded a reduction in cost of pretreatment facilities.

WHAT WE CLAIM IS:-

1. A method of removing acid from a liquid hydrocarbon which method comprises:
 - (a) mixing an aqueous base with the hydrocarbon to form a dispersion;
 - (b) then charging the two-phase dispersion from step (a), still containing hydrocarbon and water into a coalescing bed of a solid, alkali-resistant, hydrophilic medium;
 - (c) separating in the coalescing bed a hydrocarbon phase and a separate aqueous phase; and
 - (d) recovering from the coalescing bed as a product of the process a hydrocarbon phase containing a reduced acid content.
2. A method as claimed in claim 1 wherein the aqueous base is continuously added in an amount sufficient to neutralize from 100 to 200% of the acid present in the hydrocarbon.
3. A method as claimed in claim 1 or 2 wherein the coalescing medium is anthracite coal or a charcoal derived from ground wood pulp, lignite coal, anthracite coal, bituminous coal, peat or petroleum black.
4. A method as claimed in claim 1 or 2 wherein the coalescing medium is anthracite coal.
5. A method as claimed in any preceding claim wherein the particle size of the coalescing medium is from 0.1 to 6 mm.
6. A method as claimed in claim 5 wherein the particle size of the coalescing medium is from 0.6 to 2 mm.
7. A method as claimed in any preceding claim wherein the dispersion from step (a) contacts the coalescing bed while flowing down through it at a liquid hourly space velocity, based on liquid hydrocarbon flow, of 0.5 to 20 volumes per volume of coalescing medium.
8. A method as claimed in any preceding claim wherein the aqueous base is an aqueous solution of NaOH or of KOH.
9. A method as claimed in any of claims 1 to 7 wherein the aqueous base is an aqueous solution of NaOH or of KOH containing from 0.01 to 50 wt. % alkali.
10. A method as claimed in any preceding claim wherein the hydrocarbon feed is a kerosene containing naphthenic acid.
11. A method as claimed in any preceding claim wherein the acid comprises naphthenic acid and the aqueous base is NaOH having a concentration of 1 to 3 wt. %.
12. A method as claimed in any of claims 1 to 9 wherein the hydrocarbon feed is naphtha or kerosene and wherein the acid comprises H_2S .
13. A method as claimed in any of claims 1 to 9 and 12 wherein the acid comprises H_2S and the aqueous base is NaOH having a concentration of 2 to 10 wt. %.
14. A continuous method for removing a naphthenic acid component from a kerosene stream comprising:
 - (a) continuously passing to mixing means the kerosene stream and 100 to 120% of the amount of 1 to 3 wt. % aqueous sodium hydroxide solution required by stoichiometry to neutralize the naphthenic acid component in the kerosene stream and effecting mixing of the kerosene stream and the sodium hydroxide solution in the mixing means to form a two-phase dispersion.
 - (b) then passing the dispersion from step (a), still containing kerosene and water, downflow through a fixed bed of a solid, alkali-resistant, hydrophilic coalescing medium at a liquid hourly space velocity of 0.5 to 20, and coalescing in said bed a spent aqueous caustic phase and a separate kerosene phase;
 - (c) withdrawing the kerosene phase containing 0 to 10 % of its original naphthenic acid content from a lower portion of the fixed bed as a product of the process; and
 - (d) withdrawing the spent aqueous caustic phase from the bottom of the fixed bed.
15. A method as claimed in claim 10, 11 or 14 wherein naphthenic acid salts obtained by neutralization of naphthenic acids present in the hydrocarbon feed and absorbed onto the bed of coalescing medium are recovered by removing the bed from contact with the flowing hydrocarbon and aqueous dispersion and treating the bed with high temperature steam to volatilize the salts.
16. A method as claimed in claim 10, 11 or 14 wherein the naphthenic acid salts

reduced to acceptable levels for further processing or sale.

it can be seen that in its preferred forms the method of the present invention allows for nearly stoichiometric utilization of the caustic. There is also more effective acid neutralization because of the larger effective surface area of basic medium, not only in the mixing means, and piping, but also in the coalescing bed. There is greater flexibility and efficiency permitting operation with hydrocarbon flow rates much less than normal. There is negligible entrainment of aqueous solution with hydrocarbon because of the ability of the coalescing bed to coalesce aqueous droplets into a separate phase that will separate by gravity, from the hydrocarbon. There is also afforded a reduction in cost of pretreatment facilities.

WHAT WE CLAIM IS:-

1. A method of removing acid from a liquid hydrocarbon which method comprises:
 - (a) mixing an aqueous base with the hydrocarbon to form a dispersion;
 - (b) then charging the two-phase dispersion from step (a), still containing hydrocarbon and water into a coalescing bed of a solid, alkali-resistant, hydrophilic medium;
 - (c) separating in the coalescing bed a hydrocarbon phase and a separate aqueous phase; and
 - (d) recovering from the coalescing bed as a product of the process a hydrocarbon phase containing a reduced acid content.
2. A method as claimed in claim 1 wherein the aqueous base is continuously added in an amount sufficient to neutralize from 100 to 200% of the acid present in the hydrocarbon.
3. A method as claimed in claim 1 or 2 wherein the coalescing medium is anthracite coal or a charcoal derived from ground wood pulp, lignite coal, anthracite coal, bituminous coal, peat or petroleum black.
4. A method as claimed in claim 1 or 2 wherein the coalescing medium is anthracite coal.
5. A method as claimed in any preceding claim wherein the particle size of the coalescing medium is from 0.1 to 6 mm.
6. A method as claimed in claim 5 wherein the particle size of the coalescing medium is from 0.6 to 2 mm.
7. A method as claimed in any preceding claim wherein the dispersion from step (a) contacts the coalescing bed while flowing down through it at a liquid hourly space velocity, based on liquid hydrocarbon flow, of 0.5 to 20 volumes per volume of coalescing medium.
8. A method as claimed in any preceding claim wherein the aqueous base is an aqueous solution of NaOH or of KOH.
9. A method as claimed in any of claims 1 to 7 wherein the aqueous base is an aqueous solution of NaOH or of KOH containing from 0.01 to 50 wt. % alkali.
10. A method as claimed in any preceding claim wherein the hydrocarbon feed is a kerosene containing naphthenic acid.
11. A method as claimed in any preceding claim wherein the acid comprises naphthenic acid and the aqueous base is NaOH having a concentration of 1 to 3 wt. %.
12. A method as claimed in any of claims 1 to 9 wherein the hydrocarbon feed is naphtha or kerosene and wherein the acid comprises H_2S .
13. A method as claimed in any of claims 1 to 9 and 12 wherein the acid comprises H_2S and the aqueous base is NaOH having a concentration of 2 to 10 wt. %.
14. A continuous method for removing a naphthenic acid component from a kerosene stream comprising:
 - (a) continuously passing to mixing means the kerosene stream and 100 to 120% of the amount of 1 to 3 wt. % aqueous sodium hydroxide solution required by stoichiometry to neutralize the naphthenic acid component in the kerosene stream and effecting mixing of the kerosene stream and the sodium hydroxide solution in the mixing means to form a two-phase dispersion.
 - (b) then passing the dispersion from step (a), still containing kerosene and water, downflow through a fixed bed of a solid, alkali-resistant, hydrophilic coalescing medium at a liquid hourly space velocity of 0.5 to 20, and coalescing in said bed a spent aqueous caustic phase and a separate kerosene phase;
 - (c) withdrawing the kerosene phase containing 0 to 10 % of its original naphthenic acid content from a lower portion of the fixed bed as a product of the process; and
 - (d) withdrawing the spent aqueous caustic phase from the bottom of the fixed bed.
15. A method as claimed in claim 10, 11 or 14 wherein naphthenic acid salts obtained by neutralization of naphthenic acids present in the hydrocarbon feed and absorbed onto the bed of coalescing medium are recovered by removing the bed from contact with the flowing hydrocarbon and aqueous dispersion and treating the bed with high temperature steam to volatilize the salts.
16. A method as claimed in claim 10, 11 or 14 wherein the naphthenic acid salts



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obtained by neutralization of naphthenic acids present in the hydrocarbon feed and absorbed onto the bed of coalescing medium are recovered by removing the bed from contact with the hydrocarbon and aqueous dispersion, treating the bed with an acid medium, thereby acidifying the naphthenic acid salts, and subsequently displacing the resulting acids from the bed with a desorbent.

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17. A method as claimed in claim 16 wherein 200 to 400°C steam is used as the desorbent.

18. A method of removing acid from a liquid hydrocarbon as claimed in claim 1 carried out substantially as described in any one of the foregoing specific Examples.

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19. A liquid hydrocarbon whenever obtained as product of a method as claimed in any preceding claim.

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20. Naphthenic acids and naphthenic acid salts when recovered by a method as claimed in any of claims 15 to 17.

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