

A METHOD OF REFINING SOUR HYDROCARBON DISTILLATES

The present invention relates to a method of refining sour hydrocarbon distillates such as kerosene to reduce the amount of the sulfur-containing compounds.

Crude oils are exceedingly complex mixtures, consisting predominantly of hydrocarbons but also containing sulfur, nitrogen, oxygen, and metals as impurities. While it is desirable to recover the hydrocarbon constituents in their pure form, and to remove these impurities so as to minimize their deleterious effect on the product and refinery apparatus, realistically this has been difficult to accomplish as most of the impurities occur bound with carbon and hydrogen. Separation of impurities such as those listed above is generally a costly process.

Perhaps the most ubiquitous impurity encountered in petroleum processing is sulfur. The presence of sulfur in petroleum products and, indeed, in the crude feedstock itself generally increases the corrosive characteristics thereof, and forms harmful and noxious reaction products upon combustion. In particular, the presence of sulfur-containing compounds reduces the combustion characteristics of gasoline and may render fuel oil unusable in many places due to local regulation on the amount of sulfur allowed therein. Consequently, at nearly every stage of production various measures are taken either to reduce the amount of sulfur or to render the sulfur-containing compounds inoffensive.

Hydrogen-treating of petroleum fractions has been known as a method of sulfur-removal since the 1930's. However, it was not until the advent of catalytic reforming, which made inexpensive hydrogen-rich off-gas available, that hydrogen desulfurization became commercially viable. Presently, hydrogen desulfurization is routinely accomplished by mixing the feedstock with recycle and make-up hydrogen and heating the mixture to 204-454°C (400 - 850°F). It is then charged to a fixed catalytic bed reactor of cobalt molybdate on an alumina carrier at 446-10,443 kPa (50-1,500 psig).

Hydrogen treating is now used extensively to prepare reformer feedstock and, to some extent, for preparation of catalytic cracking feedstock. It may also be used to upgrade middle distillates, cracked fractions, lube oils, gasolines and waxes. Hydrodesulfurization, however, is a high energy-consuming process which also requires a supply of hydrogen.

In other attempts to remove and/or render innocuous corrosive sulfur-containing compounds, especially mercapto compounds, i.e. RSH, a method of treating petroleum fractions having a boiling point between about 93°C (200°F) and 371°C (700°F), has been devised. These fractions are "sweetened" by oxidizing the mercapto compounds to disulfides, e.g., RSSR. While this method may be used for the treatment of any hydrocarbon fraction, it has been found particularly useful for the treatment of hydrocarbon distillates heavier than gasoline, including kerosene, solvent, stove oil, range oil, burner oil, gas oil and fuel oil.

The various sweetening processes developed to date include treatment of the hydrocarbon distillate with a doctor solution (e.g. sodium plumbite) and sulfur, reacting the mercapto compounds with copper chloride and the Hypochlorite process.

Perhaps the most effective sweetening process involves reacting mercapto compounds contained in the distillate fraction (i.e. mercaptans, thiophenols, and salts thereof) with an oxidizing agent, such as air, and an alkaline reagent in contact with a phthalocyanine catalyst, such as cobalt phthalocyanine. Typically, a phthalocyanine-catalyzed sweetening process includes a fixed bed of a composite of a metallic phthalocyanine with an activated carbon material. In most cases, this catalyst is found to be very effective and extremely stable, especially in the oxidation of comparatively low molecular weight mercapto compounds and those of primary and secondary configurations. Some difficulty is, however, experienced when this catalyst is used for the treatment of sour distillates containing high molecular weight mercapto compounds at least in part due to the presence of aliphatic and naphthenic acids, and phenolic materials, in

these sour distillates. It appears that in the presence of an alkaline reagent, these acidic materials (or salts thereof) are attracted to the surface of the phthalocyanine catalyst where they constitute a barrier to the approach of mercaptide anions, which is believed to be an essential step in the chemistry of the over-all oxidation reaction. In addition, these materials interfere with the formation of the mercaptide anions - apparently, by collecting at the interface between the hydrocarbon phase and the alkaline phase in the conversion zone.

In order to eliminate or at least reduce the problem of catalyst deactivation, pretreatment procedures have been developed by which the deactivating materials can be removed from distillate fraction prior to contacting it with the phthalocyanine catalyst. In U.S. Patent No. 3,445,380 a method for pretreating sour distillate fraction is described which includes contacting the sour distillate fraction with finely divided alkali metal hydroxide, e.g., sodium and potassium hydroxide, and washing the contacted distillate with a detergent-containing aqueous solution. The resulting effluent is then subjected to a washing step in order to remove salts of the acidic material.

As a result of this two-step sweetening process, a serious problem arises in the continual production of a caustic waste stream containing phenolic compounds, thiophenols, naphthenic acids, and any residual mercaptans that form soluble and easily removable sodium mercaptide. These compounds are quite harmful to organic tissue and cannot be added to a petroleum processing refinery effluent which eventually is introduced into waterways, rivers, subterranean water formations and, in many places, the oceans and surrounding seas. In order to deal with the caustic effluent expensive processes must be employed to render it innocuous. An object of the present invention is therefore to overcome or alleviate this problem.

Accordingly, the present invention resides in a method for refining a hydrocarbon distillate fraction containing sulfur-containing compounds comprising:

washing the distillate fraction with a first aqueous alkaline solution;

treating the washed distillate fraction with a phthalocyanine catalyst in the presence of oxygen and a second aqueous alkaline solution;

incinerating the spent first aqueous alkaline solution in the presence of oxygen and a sulfur-containing fuel to convert the alkaline material to the corresponding sulfate.

By means of this invention, the stream of potentially hazardous spent caustic is rendered innocuous by conversion of the harmful ingredients to harmless alkaline metal sulfate. Additionally, a means of disposing of undesirable sulfur-containing effluents and/or fractions is provided. Furthermore, using the method of this invention it is possible to neutralize naphthenic acid salts which would be difficult to incinerate because of the high temperature required.

The accompanying drawing is a schematic illustration of a refining method according to one example of the invention.

Referring to the drawing, a distillate fraction which contains mercapto compounds is introduced to a caustic pretreatment unit designated generally as prewash vessel 10 into which a sufficient amount of fresh caustic is fed to effect washing of the fraction to remove phenolic compounds, thiophenols, naphthenic acids and any residual mercaptans that form soluble and easily removable sodium mercaptide. Preferred is washing with a solution containing from 3% to 5% by weight of sodium hydroxide. In a specific embodiment of the invention where the distillate fraction is kerosene which generally has an initial boiling point of between 149°C (300°F) and 232°C (450°F) and a final boiling point of between 246°C (475°F) and 288°C (550°F), pretreatment by caustic washing uses a 3-5% aqueous sodium hydroxide solution to remove the unwanted ingredients.

In general, the method used for contacting the alkali with the distillate is not of critical importance. In one method, the sour distillate and the finely divided alkali metal hydroxide are placed in the vessel 10 provided with a suitable agitation mechanism and the

treating step is carried out in a batch-type operation. In another method, the finely divided alkali is passed to the top of a treating column, simply represented by vessel 10, and counter-currently contacted with an ascending stream of the sour distillate. In yet another method, the finely divided alkali metal hydroxide can be suspended or entrained in a portion of the distillate to be treated or in a suitable organic liquid that is readily separable from the treated distillate, and the resultant slurry contacted with the distillate to be treated in a suitable contacting zone. It is also possible to employ multiple solid alkali treating steps.

After washing, the hydrocarbon layer is sent to the second refining step of the process, which involves oxidation of the mercapto compounds by contacting the prewashed fraction with a phthalocyanine catalyst in reactor chamber 20.

Any suitable phthalocyanine catalyst may be used in this sweetening step and preferably comprises a metal phthalocyanine. Particularly preferred metal phthalocyanines include cobalt phthalocyanine and vanadium phthalocyanine. Other suitable metal phthalocyanines include iron phthalocyanine, copper phthalocyanine, nickel phthalocyanine and chromium phthalocyanine. These metal phthalocyanines, in general, are not readily soluble in aqueous solvents, and, therefore, for use in an aqueous alkaline solution or for ease of compositing with a solid carrier, a derivative of the phthalocyanine is preferred. A particularly preferred derivative is the sulfonated derivative. Thus, an especially preferred phthalocyanine catalyst is cobalt phthalocyanine sulfonate. Such a catalyst comprises cobalt phthalocyanine disulfonate and also contains cobalt phthalocyanine monosulfonate. Another preferred catalyst comprises vanadium phthalocyanine sulfonate. These compounds may be obtained from any source or prepared in any suitable manner as, for example, by reacting cobalt vanadium phthalocyanine with 25-50% fuming sulfuric acid. While the sulfonic acid derivative is preferred, it is understood that other suitable polar derivatives may be employed. Other derivatives include the carboxylated derivative which may be

prepared, for example, by the action of trichloroacetic acid on the metal phthalocyanine or by the action of phosgene and aluminum chloride. In the latter reaction the acid chloride is formed and may be converted to the desired carboxylated derivative by conventional hydrolysis.

The phthalocyanine catalyst may be utilized either as a suspension or in solution in a suitable alkaline solution or as a fixed bed in a conversion zone. When used as a solution, the catalyst is preferably used in amounts below 1% by weight of the alkaline solution. Excellent results have been obtained using 5 ppm to 1000 ppm based on the weight of the alkaline solution.

In a preferred embodiment the catalyst is employed as a fixed bed in the conversion zone and, accordingly, the catalyst is prepared as a composite with a solid support. Any suitable support may be employed and preferably comprises activated charcoal, coke or other suitable forms of carbon. In some cases, the support may comprise silica, alumina, magnesia, etc., or mixtures thereof. The solid catalyst is prepared in any suitable manner. In one method, preformed particles of the solid support are soaked in a solution containing the phthalocyanine catalyst, after which excess solution is drained off and the catalyst is used as such, or is subjected to a drying treatment such as mild heating, blowing with air, hydrogen, nitrogen, etc., or successive treatments using two or more of these treatments prior to use in the oxidation. In other methods of preparing the solid composite, a solution of the phthalocyanine catalyst may be sprayed or poured over the particles of the solid support, or such particles may be dipped, suspended, immersed or otherwise contacted with the catalyst solution. The concentration of phthalocyanine catalyst in the composite may range from 0.05% to 10% by weight or more of the composite, with a preferred value of .01% to 1.0%.

Oxidation of the mercapto compounds is effected in the presence of an alkaline solution. A preferred alkaline reagent comprises sodium hydroxide or potassium hydroxide. Other suitable alkaline solutions include lithium hydroxide, rubidium hydroxide, and

cesium hydroxide, although in general, these hydroxides are more expensive and therefore are not preferred for commercial use. Preferred alkaline solutions are 1% to 50%, by weight concentration of sodium hydroxide or potassium hydroxide preferably in water, or any other suitable solvent. Particularly preferred are alkaline solutions containing from 15% to 35% by weight of sodium hydroxide.

Oxygen is particularly preferred as the oxidizing agent although air and other oxygen containing gases may be advantageously used. Oxygen is preferably utilized in at least the stoichiometric amount necessary to oxidize the mercapto compounds.

Oxidation of the mercapto compounds in the treated hydrocarbon distillate is effected in any suitable manner. In general, the oxidation is effected at temperatures of ambient (38°C) to 93°C (200°F), when operating at atmospheric pressure, or when desired, a higher temperature which may exceed 204°C (400°F) when operating at superatmospheric pressure. Preferably, oxidation is effected at a pressure of 446 to 1136 kPa (50 psig to 150 psig since this ensures that sufficient oxygen is dissolved in the hydrocarbon distillate being treated.

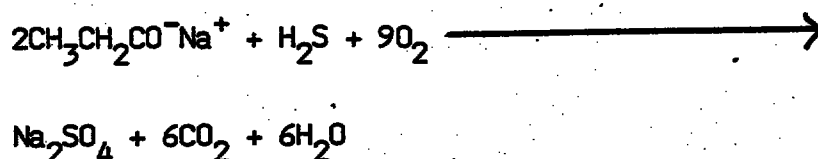
The time of contact between the reactants with the catalyst in the conversion zone can generally be adjusted to produce the desired level of mercapto compound oxidation and may vary widely depending on the nature and concentration of mercapto compounds, the viscosity and temperature of the distillate, the accumulated life of the catalyst, and the like. In general, this is not a critical parameter and may range from minutes to greater than one hour with a preferred range of 5 to 30 minutes.

In a preferred embodiment, the catalyst is disposed as a fixed bed in a conversion zone and the sour hydrocarbon distillate, oxygen, and the alkaline solution are passed, at the desired temperature and pressure into contact with the catalyst in either upward, downward, or radial flow. The reaction mixture from the contacting zone is passed into a separating zone, where excess air is directed away from the sweetening step for use in an integrated disposal system. After separation, the distillate, e.g., kerosene, is

sent to a drying stage (not depicted herein) and the alkaline/catalyst is mixed with air and sent to an oxidizer where make-up oxidation catalyst and alkaline solution are introduced.

Simultaneously with the progress of the distillate fraction, the aqueous alkaline solution from the pretreatment wash which cannot be recycled is directed away from the continuous distillate refining and is sent to an incinerator 30. This portion of used alkaline contains salts of phenolic compounds, naphthenic compounds, and residual mercaptans and consequently cannot be disposed of by introduction into a natural waterway. The incinerator 30 which operates on the principle that an alkaline compound is capable of reacting with a sulfur-containing fuel in the presence of oxygen to form a harmless sulfate. The fuel used to support the combustion reaction may be hydrogen sulfide gas which may be derived from hydrodesulfurization processes. Pure H_2S is not required but rather various H_2S containing refinery streams can be used. This form of the process is especially attractive since the combustion of gas is easier than the combustion of a liquid sulfur-containing fuel, such as fuel oil.

The essential features of the combustion process are shown in the equation below in which sodium propionate and H_2S are used as examples of spent caustic and sulfur-containing fuel respectively:



Other sulfur-containing fuels such as sulfur-containing fuel oil may also be used, alone or to augment H_2S gas with similar results. This option becomes particularly attractive when the crude stock is exceptionally high in sulfur content thereby requiring extensive hydrodesulfurization to obtain a fuel oil which is marketable in those parts of the country that require the use of a relatively sulfur-free fuel oil for industrial and domestic heating.

Hydrodesulfurization, however, is an energy intensive process that requires a constant supply of hydrogen. Instead of processing the fuel oil fraction to the extent required to eliminate nearly all the sulfur-containing compounds found therein, cost analysis may show that a savings could be realized by burning the high-sulfur-content fuel oil in the process described above to render the caustic effluents harmless.

As seen from the equation, a final reaction component necessary for the conversion of waste caustic to the innocuous sulfate is oxygen. Conveniently, this reaction component is provided by the excess air used in the oxidation reaction of the "sweetening" step. In this way, the refining process described above is an entirely integrated system providing a means of disposing of its own caustic waste product utilizing reaction components generated and/or derived from the refining steps.



CLAIMS:

1. A method for refining a hydrocarbon distillate fraction containing sulfur-containing compounds comprising:
 washing the distillate fraction with a first aqueous alkaline solution;
 treating the washed distillate fraction with a phthalocyanine catalyst in the presence of oxygen and a second aqueous alkaline solution;
 incinerating the spent first aqueous alkaline solution in the presence of oxygen and a sulfur-containing fuel to convert the alkaline material to the corresponding sulfate.
2. The process of Claim 1 wherein the distillate fraction is kerosene.
3. The process of Claim 1 or 2 wherein one or both of the first and second aqueous alkaline solution is a sodium hydroxide solution.
4. The process of Claim 3 wherein the sodium hydroxide is present in the solution in an amount of from 3% to 5% by weight.
5. The process of any preceding claim wherein the phthalocyanine catalyst is cobalt phthalocyanine sodium sulfonate.
6. The process of Claim 5 wherein the sodium hydroxide is present in the second aqueous alkaline solution in an amount of from 15% to 35% by weight.
7. The process of any preceding claim wherein the sulfur-containing fuel comprises hydrogen sulfide gas.
8. The process of Claim 7 wherein the hydrogen sulfide comprises a component of a refinery off-gas.



22

-11-

9. The process of Claim 7 wherein the sulfur-containing fuel comprises sulfur-containing fuel oil.

10. The process of any preceding Claim wherein the oxygen required for incineration comprises excess air derived from the treating step of the distillate fraction.
