PROCESS FOR SWEETENING SOUR HYDROCARBON DISTILLATES WITH METAL PHTHALOCYANINE CATALYST IN THE PRESENCE OF ALKALI AND AIR

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This invention relates to the treatment of hydrocarbon distillates and more particularly to a novel method of sweetening sour hydrocarbon distillates.

The novel process of the present invention is particularly applicable to the treatment of petroleum distillates and particularly sour gasoline, including cracked gasoline, straight run gasoline, natural gas oil, or mixtures thereof, naphtha, jet fuel, kerosene, aromatic solvent, stove oil, range oil, fuel oil, etc. Other hydrocarbon distillates include lubricating oil, as well as normally gaseous fractions. In still another embodiment the novel features of the present invention may be utilized for purifying other organic fractions containing certain acidic impurities. These organic compounds include alcohols, ketones, aldehydes, etc.

In one embodiment the present invention relates to a process for sweetening a sour hydrocarbon distillate which comprises reacting said distillate with an oxidizing agent in the presence of a phthalocyanine catalyst.

In a specific embodiment the present invention relates to the process for sweetening sour gasoline which comprises oxidizing mercaptans contained in said gasoline in the presence of a caustic solution and cobalt phthalocyanine disulfonate.

While the present invention may be utilized to effect sweetening of a sour distillate having a comparatively high mercaptan content, in general it is preferred to remove a major portion of the mercaptans from the distillate. For example, removal of mercaptans from gasoline is preferred rather than conversion of the mercaptans to disulfides and subsequent retention of the disulfides in the gasoline. Sulfur compounds have an unfavorable effect on tetraethyl lead susceptibility. However, conventional treating methods remove from about 50 to about 95% of the mercaptans but leave a product still containing a minor concentration of mercaptans and accordingly a product which is still sour. In a preferred embodiment of the present invention, the final sweetening is effected by oxidizing the mercaptans in the presence of an alkaline reagent and a phthalocyanine catalyst.

Any suitable phthalocyanine catalyst meeting the requirements of high activity and stability during use may be employed in the present invention. Particularly preferred metal phthalocyanines comprise cobalt phthalocyanine and vanadium phthalocyanine. The metal phthalocyanine in general is not readily soluble in aqueous solutions and, therefore, for improved operation is preferably utilized as a derivative thereof. A particularly preferred derivative is the sulfonated derivative. Thus, a preferred phthalocyanine catalyst comprises cobalt phthalocyanine disulfonate. Another preferred catalyst comprises vanadium phthalocyanine disulfonate. These compounds may be obtained from any suitable source or may be prepared in any suitable manner as, for example, by reacting cobalt or vanadium phthalocyanine with 20% fuming sulfuric acid. While the sulfonic acid derivatives are preferred, it is understood that other suitable derivatives may be employed. Other derivatives include particularly the carboxylated derivative which may be prepared, for example, by the action of trichloroacetic acid on the metal phthalocyanine or by the action of phosphene and aluminum chloride. In the latter reaction the acid chloride is formed and may be converted to the desired carboxylated derivative by conventional hydrolysis.

As herebefore set forth, sweetening is effected in the presence of an alkaline reagent. Any suitable alkaline reagent may be employed. A preferred reagent comprises an aqueous solution of an alkaline metal hydroxide, such as sodium hydroxide solution, potassium hydroxide solution, etc., or these reagents containing a solubilizer or solubilizer including, for example, alcohol such as methanol, ethanol, etc., phenols, cresols, etc., tannin, iso-butyrate, etc. A particularly preferred alkaline solution is an aqueous solution of from about 5 to about 50% by weight concentration of sodium hydroxide, and, when employed, a preferred solubilizer is methanol which may be used in a concentration of from about 5 to about 200 volume percent of the caustic or other alkaline solution.

The phthalocyanine catalyst is both very active and highly stable. Because of its high activity, the catalyst is used in exceedingly small concentrations. These may range from 5 to 500 and preferably from 10 to 100 parts per million by weight of the alkaline solution, although lower or higher concentrations may be used in some cases. The use of higher concentrations are unnecessary in most cases but may be used if desired, and thus may range up to 25% or more by weight of the alkaline solution. Because of its high stability, the catalyst is used for exceedingly long periods of time. After a long period of use, the alkaline solution may become saturated with acidic compounds which may adversely affect its further use, and the caustic solution either may be discarded or in some cases may be regenerated by conventional means. As hereinbefore set forth, sweetening of the sour hydrocarbon distillate is effected by oxidation of mercaptans.

Accordingly, an oxidizing agent is present in the reaction. Air is preferred, although oxygen or other oxygen-containing gases may be utilized. In some cases the sour petroleum distillate may contain entrained oxygen or air in sufficient concentration to accomplish the desired sweetening, but generally it is preferred to introduce air into the reaction. The amount of air must be sufficient to effect oxidation of mercaptans, although an excess thereof generally is not objectionable.

Sweetening of the petroleum distillate may be effected in any suitable manner and may be in batch or continuous process. In a batch process the sour hydrocarbon distillate is introduced into a reaction zone containing the phthalocyanine catalyst and alkaline reagent, and air is introduced therein or passed therethrough. Preferably the reaction zone is equipped with suitable stirrers or other mixing devices to obtain intimate mixing. In a continuous process the caustic solution containing phthalocyanine catalyst is passed countercurrently to an ascending stream of sour petroleum distillate in the presence of a continuous stream of air. In a mixed type process, the reaction zone contains the alkaline solution and phthalocyanine catalyst, and gasoline and air are continuously passed therethrough and removed, generally from the upper portion of the reaction zone.

In general the sweetening reaction is effected at ambient temperature. In some instances a temperature of at least 100° F. or more, depending upon the pressure utilized therein, is used. The reaction temperature may be employed and generally will be within the range of from about 100° to about 400° F. or more, depending upon the pressure utilized therein, but usually below that at which substantial vaporization occurs.

As hereinbefore set forth, final sweetening of the gasoline may be preceded by extraction of acidic components and particularly mercaptans from the gasoline in any
suitable manner. This pretreatment preferably comprises contacting of the gasoline with an alkaline solution, usually at ambient temperature and either in a batch or continuous process. In some cases elevated temperatures which may range up to about 200°F. may be employed. The alkaline reagents and, when employed, solubilizer or solutron heretofore set forth generally are utilized in the pretreatment. Following this treatment, the petroleum distillate will not be sweet and is subjected to final sweetening in the presence of air and the phthalocyanine catalyst.

The following examples are introduced to illustrate further the novelty and utility of the present invention but not with the intention of unduly limiting the same.

**Example I**

The gasoline used in this example is a cracked gasoline having a mercaptan sulfur content of 0.003% by weight. It is subjected to sweetening by being passed in contact with 20° Baume caustic solution containing 50 parts per million of cobalt phthalocyanine disulfonate based on the active NaOH content of the caustic solution. On the basis of treating 1,000 barrels per day of cracked gasoline in a continuous process, 10 barrels of caustic solution are used, and air is introduced at a rate of 10 cubic feet per hour into the sweetening zone. In order to effect intimate contact in the sweetening zone, the caustic solution containing the phthalocyanine catalyst is preferably introduced into the upper portion of the sweetening zone through a suitable spray arrangement. Similarly, the air is introduced into the lower portion of the sweetening zone through a suitable spray arrangement, and the sour gasoline is introduced at an intermediate point in the sweetening zone. Preferably the sweetening zone contains suitable contacting means such as side to side pans, bubble decks, bubble trays, etc. in order to effect intimate mixing therein. The sweetening is effected at ambient temperature and the treated gasoline withdrawn from the sweetening zone will be doctor sweet.

**Example II**

In this example sour kerosene containing 0.005% by weight of mercaptan sulfur is treated in a batch type process with a 28% potassium hydroxide aqueous solution containing 100 parts per million, based on the KOH content of the potassium hydroxide solution, of cobalt phthalocyanine disulfonate. The potassium hydroxide solution containing cobalt phthalocyanine disulfonate, sour kerosene and air are charged into the reaction zone and are intimately mixed by means of stirring blades. The sweetening is effected at ambient temperature.

After treatment for 2 hours in this manner, the kerosene is separated from the potassium hydroxide solution and cobalt phthalocyanine disulfonate. The kerosene so recovered is doctor sweet.

**Example III**

This example describes sweetening effected in the manner described in Example I except that 20% by volume, based on the caustic solution, of methanol is included in the reaction mixture. The gasoline treated in this manner will be doctor sweet in less than 3 hours of contacting in the manner described in Example I and utilizing the same constituents except for the addition of the methanol.

We claim as our invention:

1. The process for treating a sour hydrocarbon distillate which comprises reacting said distillate with an oxidizing agent in the presence of an alkaline reagent and a phthalocyanine catalyst selected from the group consisting of metal phthalocyanines and their sulfonated and carboxylated derivatives.

2. The process for treating a sour hydrocarbon distillate which comprises reacting mercaptans contained in said distillate with oxygen in the presence of an alkaline reagent and a phthalocyanine catalyst selected from the group consisting of metal phthalocyanines and their sulfonated and carboxylated derivatives.

3. The process for treating a sour hydrocarbon distillate which comprises reacting mercaptans contained in said distillate with oxygen in the presence of an alkaline reagent and cobalt phthalocyanine disulfonate.

4. The process for treating a sour hydrocarbon distillate which comprises reacting mercaptans contained in said distillate with air in the presence of an alkaline reagent and vanadium phthalocyanine disulfonate.

5. The process for sweetening sour gasoline which comprises reacting mercaptans contained in said gasoline with air in the presence of caustic solution and cobalt phthalocyanine disulfonate.

6. The process for sweetening sour gasoline which comprises reacting mercaptans contained in said gasoline with air in the presence of caustic solution and vanadium phthalocyanine disulfonate.

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