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(19)



(54) IMPROVED PROCESS FOR SWEETENING SOUR  
HYDROCARBON DISTILLATES

(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:-

The invention relates to a method of sweetening a sour hydrocarbon distillate by oxidizing mercaptans in the distillate to disulfides by passing an oxidizing agent and the distillate over a fixed bed of a mercaptan oxidation catalyst in the presence of an alkaline medium.

Sweetening of sour hydrocarbons is well known in the petroleum refining arts. Processes abound relating to the treatment of petroleum distillates, such as sour gasoline, cracked gasoline, straight run gasoline, naphtha, jet fuel, kerosene or fuel oil.

The prime offender in many sour hydrocarbon distillates is mercaptan sulfur, RSH. Mercaptan sulfur can be successfully removed by hydrotreating, using a catalyst containing Co, Mo, etc., on a carrier such as alumina, at high temperatures under high hydrogen pressures. This hydrotreating will convert mercaptan sulfur to H<sub>2</sub>S which can be removed from normally liquid hydrocarbon fractions by distillation.

Hydrotreating is relatively expensive, and many petroleum products can contain relatively high sulfur levels, as long as the sulfur is not in the form of a mercaptan. The mercaptans are objectionable because of their strong odor, and because they are more corrosive. For many processes, it is sufficient if the mercaptans are converted to disulfides, RSSH, or RSSR.

A process for the fixed-bed sweetening of hydrocarbon distillates is shown in U.S. Patent 2,988,500. In that patent, a novel catalyst was used to oxidize mercaptans to disulfides, namely cobalt phthalocyanine sulfonate composited with a charcoal carrier. A mixture of sour kerosene, aqueous NaOH solution, and air were passed over the catalyst to convert mercaptan sulfur to disulfide and reduce the mercaptan sulfur content to a level low enough that the kerosene product recovered would be doctor-sweet. The treating reaction was effected in the presence of an alkaline reagent. The patent taught that any suitable alkaline reagent could be used, the preferred reagents being sodium hydroxide and potassium hydroxide. Other reagents considered possible were aqueous solutions of lithium hydroxide, rubidium hydroxide, and cesium hydroxide.

Another treating process was disclosed in U.S. Patent 2,744,854. In that patent, a similar sweetening process occurred, but the sweetening reaction was always accomplished in storage tanks, rather than in a reactor vessel. Thus, reaction times of several days would be necessary to complete the conversion of mercaptan sulfur to disulfides. There is extremely detailed and broad teaching in that patent as to the type of basic reagent which may be used to facilitate the sweetening reaction. Both organic and inorganic bases are taught, although, from the examples, use of phenylene diamine is apparently preferred. Optionally, a metal chelate may be added to speed up the sweetening which occurs in the storage tank. In the specific teachings on basic compounds which may be used in addition to sodium hydroxide or potassium hydroxide, the patent teaches over 50 different compounds and classes of compounds which serve as basic reagents.

Sweetening of hydrocarbon distillates by placing them in storage tanks is, in general, not the preferred way to convert mercaptans to disulfides. Refineries prefer to use a more

positive treating step to obtain a doctor-sweet product. The fixed-bed sweetening process has enjoyed worldwide commercial success. Despite the great acceptance of fixed-bed sweetening by refining industry, there are still a few areas in which attempts have been made to improve the process. Specifically, the practice of using aqueous sodium hydroxide solutions to provide the basic medium required for oxidizing mercaptans to disulfides has resulted in a caustic disposal problem. Eventually the caustic solution used in a fixed-bed unit becomes unsuitable for further use. Most common reason for discarding of caustic solutions is that various toxins or catalyst poisons, generated by the oxidation reaction, accumulate in the caustic. Thus, for a number of reasons the caustic commonly used in fixed-bed sweetening processes must be discarded. Although sodium hydroxide is a very inexpensive chemical to buy, it is becoming a relatively expensive chemical to throw away, because of concern about pollution.

Also of concern to refiners is the danger that some of the caustic solution will somehow find its way into the final product. For some uses, e.g. jet fuel, neither sodium hydroxide nor water may be tolerated in the product. Elaborate measures are taken to make sure that the kerosene product destined for use as jet fuel will not contain either water or NaOH. The solution commonly used is to water-wash the kerosene effluent from the fixed bed treating process to remove sodium hydroxide solution. The water-washed kerosene is then passed through a bed of salt, so that the salt will react with any water contained in the hydrocarbon, and form a brine which will remain behind. Finally, the kerosene is passed through a bed of clay or sand to remove the last traces of water or brine solution which may be in the product. Although effective, such elaborate measures add to the cost of treating and increase the capital expenditure required to build a plant for the treating of fuels where the presence of small amounts of aqueous sodium hydroxide solutions is objectionable.

Other problems which have been encountered in the fixed bed sweetening process are the occasional plugging of the catalyst bed due to formation of soaps. A number of hydrocarbon distillates contain naphthenic acids, and the naphthenic acids react with aqueous sodium hydroxide to form a soap which forms a gel with the hydrocarbon which in turn plugs the charcoal bed. It has been necessary to put in caustic prewashes to remove these naphthenic acids from feeds containing them, so that the feed to the fixed bed sweetening unit will be substantially free of naphthenic acids. The typical naphthenic acid prewash is a large vessel filled with a dilute solution of sodium hydroxide. While such a vessel is efficient, and relatively inexpensive, it still adds to the cost of operating a fixed bed treating process.

Because of these difficulties encountered with some feedstocks, and some product specifications, we have tried to find some way to eliminate these problems entirely, rather than to add on an extra step upstream or downstream of existing fixed bed treating units. Our investigations have shown that most of the problems are caused either by something in the feed reacting with the aqueous sodium hydroxide solution used as a basic medium, or by remnants of the basic medium appearing in the product. We have now discovered a highly satisfactory replacement for the sodium hydroxide solutions currently used as alkaline medium in fixed-bed sweetening processes, viz. the tetra-alkyl guanidines.

According to the present invention there is provided a process for treating a sour hydrocarbon distillate containing mercaptans by passing the distillate and an oxidizing agent over a fixed bed of a mercaptan oxidation catalyst, preferably a phythalocyanine catalyst composited with a carbon carrier, in the presence of an alkaline medium, characterised by the use of a tetra-alkyl guanidine as alkaline reagent to provide the alkaline medium.

In addition to eliminating some of the problems caused by the prior art sodium hydroxide solutions, we have found that there is an unexpected benefit obtained by using a tetra-alkyl guanidine as a basic medium, namely an unexpected and surprising increase in apparent catalytic activity of the fixed-bed sweetening unit. The use of tetra-alkyl guanidines permits significantly improved mercaptan conversion to be effected in a fixed-bed sweetening process. Use of tetra-alkyl guanidines is also beneficial in that the guanidines remain in the hydrocarbon phase and pass into storage tanks used for the hydrocarbons. The guanidines act to suppress color degradation in storage, and may also act as a corrosion inhibitor. Further, the guanidines do not change the color of the hydrocarbon product, in contrast to some of the phenylene diamines which impart a red color to the product.

An excellent method of carrying out the fixed-bed sweetening of sour hydrocarbon distillate is disclosed in U.S. Patent 2,988,500, previously mentioned. All things taught in this patent can be used to good effect in practicing the present invention, with the substitution of a tetra-alkyl guanidine for the alkaline reagent of that patent.

The tetra-alkyl guanidine is preferably tetramethyl guanidine. Instead of four methyl groups, four ethyl, propyl, butyl, etc., groups may be used, or guanidines containing alkyl groups of varying chain lengths can also be used. Tetramethyl guanidine is preferred

because it is readily available and inexpensive. Another advantage of the tetramethyl guanidine is that it can react with light and heavy naphthenic acids, phenols, etc., without forming soap-like salts. The reaction product of the guanidine and the naphthenic acids is soluble in hydrocarbon medium, so that it does not plug the catalyst bed. This is in contrast to the reaction product of naphthenic acids with sodium hydroxide in aqueous solution, which forms soaps and gels which completely plug and render ineffective a catalyst bed. Also, emulsion problems are eliminated because the sodium salts are eliminated. Emulsions cause water to be carried into storage tanks, causing an excess of water in the tank. These soaps can also carry sodium and water into the finished product which are not desirable.

Because of the vast number and variety of crude stocks which are being treated, it may be desirable to use heavier alkyl guanidines to treat very heavy charge stocks. In general, the longer the alkyl groups the more soluble will be the guanidine in the hydrocarbon. Our experiments have shown, however, that even the lightest of the tetra-alkyl guanidines can do a very effective sweetening job at such low concentrations that it is completely soluble in the hydrocarbon oil, e.g. kerosene, treated.

The concentration of the tetra-alkyl guanidine should be sufficient to provide the basic medium necessary for these catalytic sweetening reactions to occur. A suitable concentration range is from 1 to 500 wt.ppm, based on the weight of sour hydrocarbon distillate. The tetra-alkyl guanidine is preferably added continuously to the hydrocarbon to be treated or, alternatively, it may be placed in an aqueous or alcoholic solution which is periodically pumped over a fixed bed of catalyst to wet the surface thereof, with basic solution.

The catalyst used can be any catalyst which will speed up the rate of mercaptan oxidation in the presence of an alkaline reagent enough to permit sweetening of a sour hydrocarbon distillate over a fixed bed of the catalyst. Some metal chelates possess sufficient activity to permit their use in such a process. Preferred among the metal chelates are the phthalocyanines. Especially preferred are the monosulfonated derivatives of cobalt phthalocyanine. The sulfonation of the cobalt phthalocyanine makes the material soluble enough in various solvents to permit the impregnation of a fixed bed of charcoal with the catalyst. The monosulfonate derivative is preferred because the more highly sulfonated derivatives are more soluble in the hydrocarbon means to be treated, permitting the leaching away of catalyst from the bed. Recent work done with polyphthalocyanine catalysts, and mixtures of different metal phthalocyanines, indicates that these catalysts too may be acceptable for use in the present invention, although forming no part thereof.

The catalyst material may be formed into a fixed bed in any convenient manner e.g. by being composited with charcoal. It may be composited with any suitable form of charcoal by conventional means. An excellent way of preparing the catalyst is to dissolve, e.g., cobalt phthalocyanine monosulfonate in methanol and pass the methanol-catalyst solution repeatedly over a bed of activated charcoal. The precise type of catalyst used, its method of preparation and its incorporation onto a bed of charcoal support are not crucial for the present invention.

#### *Examples*

To evaluate the effectiveness of the tetra-alkyl guanidines proposed by the present invention, a number of experiments were run. A kerosene which was very difficult to sweeten was used as the reference feed stock. The kerosene contained 180 wt ppm mercaptan sulfur.

The test that was used is not meant to be indicative of commercial operation, rather it was meant to be a simplified procedure which would quickly separate good alkaline reagents from bad ones. The test procedure was to put 2 grams of catalyst, wetted with 5 ml of the alkaline reagent being tested, plus 100 ml of feedstock in a 300 ml flask which was then capped. The flasks were then placed in an automated shaking device. Temperature was not measured, but all tests were conducted at ambient temperature in a room maintained at about 25°C, so changes in temperature are not believed to be significant. The contents of the flasks were sampled at uniform intervals and the mercaptan sulfur content of the hydrocarbon was determined.

To ensure the validity of the test, a number of blanks were run, i.e., operation with charcoal which contained no metal phthalocyanine catalyst on it, and operation with conventional alkaline reagent (sodium hydroxide solution). The same charcoal material was used throughout the test, a vegetable derived charcoal sold by the Nuchar Co. The catalyst was prepared by impregnating the charcoal with a cobalt phthalocyanine monosulfonate. The catalyst was prepared by dissolving 0.15 grams of cobalt phthalocyanine sulfonate in 100 cc of methanol. The cobalt phthalocyanine was difficult to dissolve, so to insure that all of it went into solution, the dissolution proceeded stepwise, i.e. one-fourth of the alcohol was mixed with the phthalocyanine, then decanted, then the next one-fourth portion was

added to the cobalt phthalocyanine remaining in the bottom of the flask with grinding of the cobalt compound. This was repeated a third and a fourth time to make sure that all of the active material was dissolved in the alcohol. The alcohol was then placed in a container with 15 grams (100 cc) of charcoal, stirred slightly, and allowed to stand overnight. The alcohol was then drained from the material, and the charcoal dried under a water pump. The filtrate had only a faint blue color, but did not contain any significant amount of cobalt, so the catalyst contained a 1 wt. % of the cobalt phthalocyanine sulfonate. This catalyst was divided into several 2 gram portions for use in carrying out the activity tests. The bases used, and the results of the test are reported in the following table.

TABLE 1: INORGANIC BASES

TEST	1	2	3	4	5	6
Wt. % Catalyst	-0-	1.0	1.0	1.0	1.0	1.0
Ml Base	-0-	-0-	20	20	20	20
Base Description	-	-	*Aqueous NaOH	**Alcoholic NaOH	***Aqueous NH <sub>4</sub> OH	****Alcoholic NH <sub>4</sub> OH
Shaking Time (Minutes)				wt - ppm RSH		
0	180	180	180	180	180	180
5	167	158	44	5	-	-
15	164	152	16	2	78	44
30	164	146	11	1	53	38
60	164	137	7	1	30	33
90	-	-	3	-	26	22
120	-	-	3	-	25	-
*	1 N NaOH in H <sub>2</sub> O					
**	1 N NaOCH <sub>3</sub> Solution Made Up Reacting Na Metal With Methyl Alcohol					
***	1 N NH <sub>4</sub> OH in H <sub>2</sub> O					
****	1 N NH <sub>4</sub> OH Solution Made Up Using Reagent Grade Aqueous NH <sub>4</sub> OH and Methyl Alcohol					

- A dash indicates that the mercaptan content was not tested. The results reported under test 3, i.e., use of aqueous NaOH solution, may be considered the standard activity for a conventional fixed bed process. Surprisingly, the use of an alcoholic NaOH solution gives much better results than use of an aqueous NaOH solution; however, the use of an alcoholic sodium hydroxide forms no part of the present invention. Not all solutions showed an improvement in going from an aqueous to an alcoholic phase, as can be observed by comparing the results of aqueous  $\text{NH}_4\text{OH}$  to alcoholic  $\text{NH}_4\text{OH}$ . The alcoholic  $\text{NH}_4\text{OH}$  appeared to give slightly higher initial activity, but after a 60 minute period, the mercaptan content was 10 to 20% higher for the alcoholic solution than for the aqueous solution.
- A number of organic bases were tested. The results are presented in Table II.

TABLE II: ORGANIC BASES

TEST	3	7	8	9	10
Wt. % Catalyst	1.0	1.0	1.0	1.0	1.0
MI Base	20	20	20	20	20
Base Description	Aqueous NaOH	*Alcoholic Diethylamine	**Alcoholic Diethylene-Triamine	***Alcoholic Tetramethyl-Guanidine	****Alcoholic Arquad
Shaking Time (Minutes)			wt - ppm RSH		
0	180	180	180	180	180
5	44			8	5 (Hcbn Dark Green)
15	16	31	71	7	3 (Hcbn Dark Green)
30	11	27	53	5	3 (Hcbn Dark Green)
60	7	22	42	3	2 (Hcbn Medium Green)
90	3	19	36	3	2 (Hcbn Medium Green)
120	3				

\* 1 N Diethylamine Solution Made Up Using Pure Base And Methyl Alcohol  
 \*\* 1 N Diethylene Triamine Made Up Using Pure Base And Methyl Alcohol  
 \*\*\* 1 N Tetramethyl-Guanidine Solution Made Up Using Pure Base And Methyl-Alcohol  
 \*\*\*\* 1 N Armour ArquadT-50 (Trimethyl Tallow Ammonium Hydroxide) Made Up Using The Base And Methyl Alcohol.

The process of the present invention is illustrated in the example wherein the base was alcoholic tetra-methyl guanidine. The last test, alcoholic trimethyl tallow ammonium hydroxide, is an illustration of a basic medium which does work to convert mercaptan sulfur, but which is not acceptable for use in petroleum refining. The base used in that example imparted a deep green color to the kerosene tested, and resulted in the formation of an emulsion when the kerosene was given the doctor test. Either property alone, i.e., color formation or emulsion formation, would disqualify that particular base from use as a commercial petroleum additive.

Accordingly, it can be seen that the process of the present invention provides a way to treat even difficult to sweeten kerosenes without the use of an aqueous sodium hydroxide solution. Further, the basic reagent of the present invention provides a more effective sweetening process than aqueous NaOH solution or several organic bases suggested by the prior art.

WHAT WE CLAIM IS:-

1. A process for treating a sour hydrocarbon distillate containing mercaptans by passing the distillate and an oxidising agent over a fixed bed of a mercaptan oxidation catalyst in the presence of an alkaline medium, characterised by the use of a tetra-alkyl guanidine as alkaline reagent to provide the alkaline medium.

2. The process of claim 1 wherein the tetra-alkyl guanidine is tetra-methyl guanidine.

3. The process of claim 1 or 2 wherein the alkaline medium consists of an alcoholic solution of the tetra-alkyl guanidine.

4. The process of claim 3 wherein the alcohol is methyl alcohol.

5. The process of any of claims 1 to 4 wherein the guanidine compound is present in an amount equivalent to 1 to 500 wt. ppm, based upon the weight of sour hydrocarbon distillate.

6. The process of any of claims 1 to 5 wherein the mercaptan oxidation catalyst is a phthalocyanine catalyst composited with a carbon carrier.

7. The process of claim 6 wherein the phthalocyanine catalyst is a monosulfonated derivative of cobalt phthalocyanine.

8. The process of any of claims 1 to 7 wherein the sour hydrocarbon distillate is a sour kerosene.

9. A process for treating a sour hydrocarbon distillate as claimed in claim 1 and carried out substantially as hereinbefore described or exemplified.

10. Sweetened hydrocarbon distillates obtained by the process of any of claims 1 to 9.

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