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SWEETENING GASOLINE

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1

This invention relates to the oxidation of weakly acidic sulfur compounds of obnoxious nature which occur in hydrocarbon oils and more particularly to the conversion of these weakly acidic sulfur compounds, such as mercaptans, to innocuous non-acidic compounds and, further, to the regeneration of alkaline solutions which have been used to extract such mercaptans and related sulfur compounds from hydrocarbon liquids.

This application is a continuation-in-part of our United States Patent 2,529,670, issued November 14, 1950, entitled Sweetening Gasoline.

One practice in the refining of petroleum hydrocarbons includes the sweetening of hydrocarbon oils, such as gasoline and other distillates, by oxidizing the acidic sulfur compounds occurring therein, such as mercaptans, with alkali solutions containing small amounts of oxidation promoters. A class of promoters for this type of reaction includes, in general, polyhydroxy phenols having their hydroxy groups oriented so that they are oxidizable to quinone form.

The oxidation type process employed in this invention is to be distinguished from extraction type hydrocarbon sweetening systems in which the mercaptans contained in light hydrocarbons such as gasolines and naphthas are separated from the hydrocarbon liquid by contacting the mercaptan-containing hydrocarbon with an aqueous or alcoholic solution of an alkali metal hydroxide. Although the alkali metal hydroxide solution alone will function to effect this physical separation, its efficiency is enhanced by the addition thereto of certain organic compounds, termed "solutizers," which operate as mercaptan solubility promoters. Examples of these solutizers are potassium isobutyrate, alkali metal naphthanates and alkali metal alkyl phenolates. Thus in the extraction type process the mercaptans are removed by being selectively dissolved in the alkaline extractant whereas in the process of this invention which is an oxidation type process the mercaptans are catalytically oxidized to innocuous polysulfides, the presence of which does not affect the so called sweetness of the hydrocarbon fluid.

Though oxidation type processes for sweetening sour gasolines by oxidizing the obnoxious sulfur compounds in place are rather well known when this type of treatment is effected utilizing polyhydroxy aromatic compounds as oxidation catalysts which are capable of being oxidized to the quinone structure, there results an attendant operational difficulty in the practice thereof which lies in the formation of color bodies in the gasoline or the hydrocarbon liquid being sweetened. That is, though they are quite effec-

2

tive in oxidizing the sulfur compounds characteristic of hydrocarbon sourness, they also add an objectionable amount of color to the sweetened hydrocarbons. It seems that the material used as a catalyst either forms the color bodies or, at least, aids in the formation thereof and is slowly taken into solution in the hydrocarbon. Thus, catalyst is lost in proportion to the color deterioration of the product and although the hydrocarbon oil obtained can be sweet and satisfactory for technical use, it will often have sufficient undesirable color to require additional processing or washing to make it commercially valuable.

Accordingly, it is a fundamental object of this invention to provide a process for the alkaline catalytic sweetening of hydrocarbon liquids by aeration and oxidation which will result in the production of a sweet hydrocarbon showing little or no color deterioration.

It is a second object of this invention to provide an alkaline solution to be used in aeration sweetening of hydrocarbon liquids which employs an oxidation catalyst substantially none of which is lost in the hydrocarbon.

A further object of the invention is to provide a process for the preparation of doctor sweet hydrocarbons which avoids the formation of foreign color bodies.

Other objects and advantages of the invention will in part be obvious and in part appear hereinafter.

This invention, accordingly, comprises a process for the sweetening of hydrocarbons in which they are aerated while in contact with an alkali catalytic treating solution, the process involving agitating the two in a vessel or tower and, after thorough contact, permitting the mixture in the tower to stratify to separate the product.

We have discovered that although naphthoquinones and certain hydroxy derivatives of naphthalene, which group of compounds is characterized by having the hydroxy groups ortho or para to each other so that they are oxidizable to quinones, are efficient catalysts in the foregoing sweetening operation, they impart an undesirable color to the sweetened gasoline. We have further discovered that by converting the compounds to be used as oxidation promoters to the corresponding sulfonates, loss of the catalyst and development of color in the hydrocarbon can be very largely avoided.

The alkaline treating solution used in accordance with our process is preferably a rather strongly alkaline aqueous solution containing about 5 to 40 per cent of alkali metal hydroxide, such as sodium or potassium hydroxide, and

about 0.05 to 5 per cent of a catalyst for accelerating the oxidation of the obnoxious sulfur compounds. The catalyst, as noted, is preferably a sulfonated naphthoquinone or naphthalene with at least two hydroxy groups attached thereto in positions either ortho or para to each other so that the compound is oxidizable to the quinone form to put the quinone function on the exposed part of the condensed ring. Also, compounds of that type which in addition have one or more alkoxy groups substituted for hydrogen in the ring, the compounds being modified by sulfonation in the aromatic ring to mono-, di-, or polysulfonate, are useful. As examples of compounds, the sulfonates of which are effective oxidation promoters, there may be mentioned naphthohydroquinone, naphthoquinone, and various alkyl, phenyl and alkoxy derivatives thereof, sulfonated to at least the mono- form, such as 1,2-naphthohydroquinone, 1,2-naphthoquinone, 3-methyl-1,4-naphthoquinone, 6-phenyl-1,2-naphthoquinone, 4-methoxy-1,2-naphthoqui-

and 2 per cent by weight of oxidation catalyst. Upon completion of the contact, the mixture was allowed to stand to permit separation of the hydrocarbon. Tests were made to show it was doctor sweet and its color was measured on the NPA or Saybolt scale, depending upon its intensity.

In any sweetening process, the essential operation to be carried out is to bring about reaction between the mercaptan sulfur and the reagent added to convert the sulfur to an innocuous form. Since mercaptans are normally present in hydrocarbons in quite small concentrations, it is necessary to bring about intimate contact between the treating solution and the hydrocarbon. The time required for sweetening will always vary with the apparatus and the technique used for bringing about the contact. Thus, in the evaluation of the process, time required for obtaining a sweet product is only a secondary criterion.

In the following table, the results of a series of tests are presented:

Effectiveness of oxidation catalysts in 10 per cent caustic solution for sweetening sour Stoddard solvent

[Stoddard solvent contained 0.005 percent mercaptan sulfur]

No.	Catalyst	Time Stoddard Contacted With Treating Solution—Shaking (Minutes)	Character of Treated Stoddard		
			Doctor Test	Color	
				NPA	Saybolt
1.....	1,2-Naphthoquinone.....	30	Negative..	1+	-----
2.....	Sodium-1,2-Naphthoquinone-4-Sulfonate.....	180	..do.....	-----	+15
3.....	Hydroquinone.....	15	..do.....	+1½	-----
4.....	Sodium Hydroquinone Sulfonate.....	15	..do.....	+1	-----
5.....	Anthraquinone.....	235	Border-line Neg.	-----	+21
6.....	Sodium Anthraquinone-α-Sulfonate.....	265	..do.....	-----	+24
7.....	No catalyst used (2% water added instead of catalyst).	435	Negative..	-----	+25

		Composition (percent by weight)
Treating solution used:	Sodium hydroxide.....	10
Catalyst.....	Water.....	2
Volume of treating solution used.....cc.		88
Volume of sour Stoddard used.....cc.		150

none, and the corresponding substitution products of the naphthohydroquinones.

Thus, sulfonates of 1,2-naphthoquinone, 1,4-naphthoquinone and especially 5, 6, 7 and 8 sulfonates thereof, together with alkyl and alkoxy derivatives wherein the alkyl or alkoxy groups are attached to the aromatic ring, typify the naphthoquinone type compounds.

To establish the effectiveness of the sulfonation of this class of compounds as a means for improving the operation thereof in the oxidation of obnoxious sulfur compounds in hydrocarbons, various tests were conducted with sour Stoddard solvent and alkaline solutions made up containing the unsulfonated and sulfonated materials.

The experimental procedure for conducting a test was as follows:

Example—A 150 milliliter sample of Stoddard solvent having a boiling range of 304° to 405° F., a mercaptan sulfur content of 0.005 per cent, and color +26 Saybolt was agitated in the presence of a free oxygen-containing gas such as air for 15 minutes with 15 milliliters of a solution containing 10 per cent by weight of sodium hydroxide,

In each test, contact with the treating solution and the hydrocarbon was maintained until the hydrocarbon became essentially sweet. It is to be observed that the aeration process for sweetening hydrocarbons, as a practical matter, is limited to those hydrocarbons which have a relatively low mercaptan sulfur content and are close to being sweet in any case. Thus, the sample treated contained 0.005 per cent of mercaptan sulfur.

Examination of the results tabulated as tests Nos. 1 and 2, comparing the effectiveness of 1,2-naphthoquinone and sodium-1,2-naphthoquinone-4-sulfonate, shows that to develop a sweet product, the sulfonate required about six times as long a period of contact as did the naphthoquinone. However, the product had satisfactory color, and sweetening was effected in less time than required for other promoters which produced a product of satisfactory color.

Tests 3 and 4 indicate the reason why the single ring quinones are inadequate for the purposes of the invention. Hydroquinone by itself is an excellent oxidation catalyst in that

it causes the mercaptan sulfur to be oxidized very rapidly, and on this basis, can be used to some extent. However, it has the serious disadvantage that it is a strong color-forming compound, is quickly extracted into the hydrocarbon phase, and although the product obtained is sweet, it is highly colored as indicated by the NPA value given in the table. Similarly, the sodium hydroquinone sulfonate is a very effective catalyst, but apparently because the sulfonic acid ring is attached to the same ring as the hydroquinone groups and perhaps due to some inherent instability of the compound, it appears that oxidation causes gradual but continuous decomposition of the sodium hydroquinone sulfonate with the result that almost as much color development is obtained therewith as results from the use of hydroquinone.

Anthraquinone is a reasonably good oxidation catalyst in that it does not impart objectionable color to the gasoline, but is slower acting than the sulfonates of the naphthoquinones and hydroquinones. It has the minor disadvantage that it is relatively insoluble in aqueous solution and must be used in conjunction with alcohols to obtain a sufficient effective amount in solution. If the anthraquinone is reduced to the hydroquinone form, it is useful as a catalyst. The anthroquinone sulfonate is sufficiently soluble in the alkali solution to be useful and to that extent, possesses an advantage over the unsulfonated compound. Tests 5 and 6 point up the fact that the color-forming problem is substantially non-existent with the anthraquinone type compounds.

Test No. 7 shows the length of time which was required to develop a sweet colorless product without the use of a catalyst or promoter. On this absolute basis, it is clear that the sulfonated naphthoquinone type of compound not only brings about a substantially increased rate of reaction, but that it develops a good commercial product, for it is sweet and colorless. On the other hand, colors developed in hydrocarbons sweetened in operations employing unsulfonated catalysts are such as to lessen the commercial value of the sweetened product. Thus, the process by employing sulfonated catalysts turns from the production of sweet discolored products to commercial competitive essentially water-white products.

Though the process has been described with a limited number of examples, it should be understood that they are to be interpreted as illustrative and not in a limiting sense.

What is claimed is:

1. The method of oxidizing mercaptans contained in substantially water-white hydrocarbon liquids to polysulfides comprising, agitating the hydrocarbon containing the mercaptan with an alkaline treating solution containing as a catalyst a sulfonated compound capable of promoting the oxidation of mercaptans to polysulfides from the group consisting of naphthoquinone, naphthohydroquinone, and alkyl, phenyl and alkoxy derivatives of the several compounds in amount sufficient to accelerate said oxidation, aerating the mixture and separating from the mixture a sweetened hydrocarbon having substantially the same water-white color as the untreated mercaptan containing hydrocarbon liquid.

2. The method of oxidizing mercaptans contained in substantially water-white hydrocarbon liquids to polysulfides comprising, agitating the hydrocarbon containing mercaptan with an

alkaline treating solution containing about 5 to 40 per cent of alkali and, as a catalyst, about 0.1 to 3 per cent of a sulfonated compound capable of promoting the oxidation of mercaptans to polysulfides from the group consisting of naphthoquinone, naphthohydroquinone, and alkyl, phenyl and alkoxy derivatives thereof, sufficient to accelerate said oxidation, aerating the mixture and separating from the mixture the sweetened hydrocarbon having substantially the same water-white color as the untreated mercaptan containing hydrocarbon liquid.

3. The method in accordance with claim 2 in which the alkaline solution contains about 5 to 40 per cent of alkali and about 0.1 to 3 per cent of a sulfonate of a naphthoquinone.

4. The method in accordance with claim 2 in which the alkaline solution contains about 5 to 40 per cent of alkali and about 0.1 to 3 per cent of a sulfonate of a naphthohydroquinone.

5. The method of oxidizing mercaptans contained in substantially water-white hydrocarbon liquids to polysulfides comprising, agitating the hydrocarbon containing the mercaptan with an alkaline treating solution to which has been added as a catalyst a sulfonated compound capable of promoting the oxidation of mercaptans to polysulfides from the group consisting of naphthoquinone, naphthohydroquinone, and alkyl, phenyl and alkoxy derivatives of the several compounds in amount sufficient to accelerate said oxidation, aerating the mixture and separating from the mixture a sweetened hydrocarbon having substantially the same water-white color as the untreated mercaptan containing hydrocarbon liquid.

6. The method of oxidizing mercaptans contained in substantially water-white hydrocarbon liquids to polysulfides comprising, agitating the hydrocarbon containing the mercaptan in an alkaline treating solution containing about 5 to 40 per cent of alkali to which has been added as a catalyst about 0.1 to 3 per cent of a sulfonated compound capable of promoting the oxidation of mercaptans to polysulfides from the group consisting of naphthoquinone, naphthohydroquinone, and alkyl, phenyl and alkoxy derivatives thereof, sufficient to accelerate said oxidation, aerating the mixture and separating from the mixture the sweetened hydrocarbon having substantially the same water-white color as the untreated mercaptan containing hydrocarbon liquid.

7. The method in accordance with claim 6 in which the alkaline solution contains about 5 to 40 per cent of alkali and about 0.1 to 3 per cent of a sulfonate of a naphthoquinone.

8. The method in accordance with claim 6 in which the alkaline solution contains about 5 to 40 per cent of alkali and about 0.1 to 3 per cent of a sulfonate of a naphthohydroquinone.

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