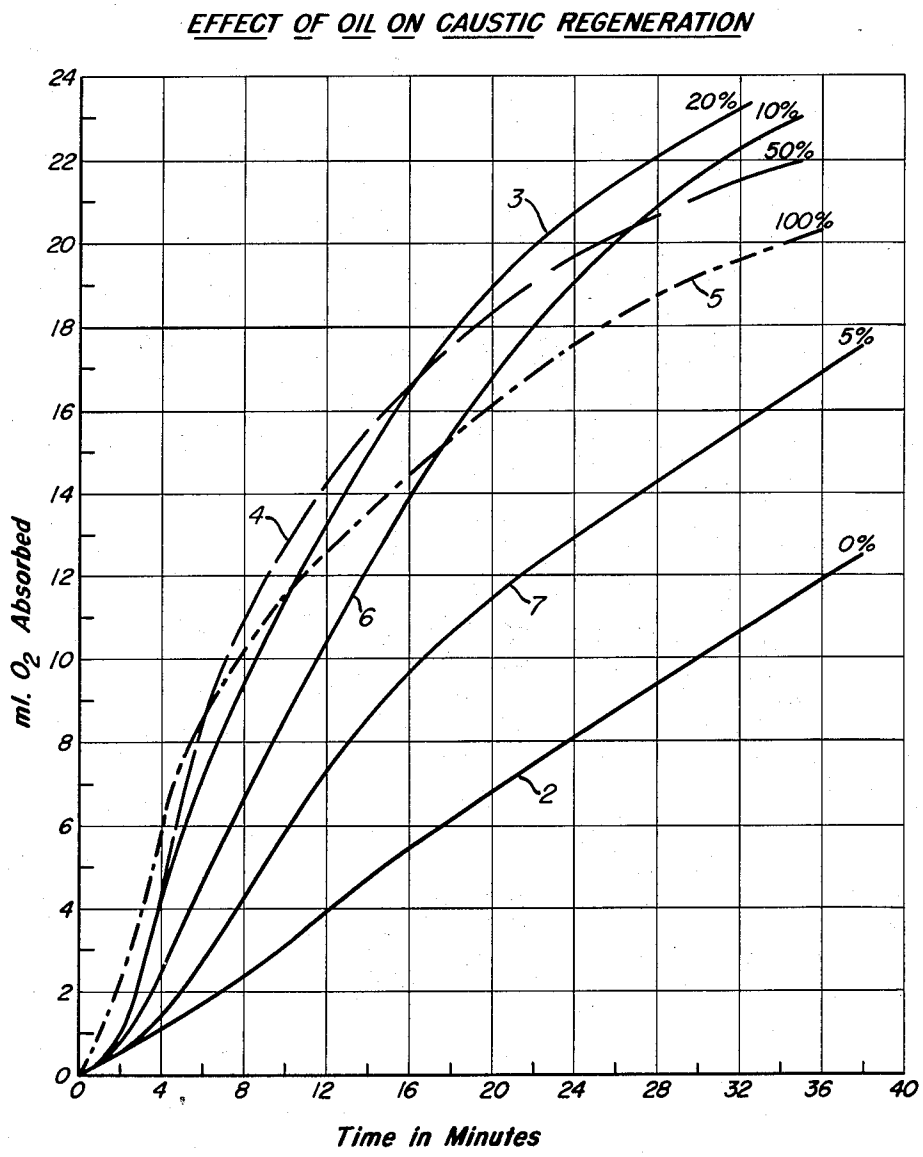
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REGENERATION OF AQUEOUS CAUSTIC-MERCAPTIDE SOLUTIONS WITH OXYGEN AND A LIQUID HYDROCARBON

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# REGENERATION OF AQUEOUS CAUSTIC-MERCAPTIDE SOLUTIONS WITH OXYGEN AND A LIQUID HYDROCARBON

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This invention relates to the oxidation of mercaptans to disulfides. More particularly the invention relates to the regeneration of spent aqueous caustic solutions containing mercaptides.

Virtually all petroleum distillates and hydrocarbon oils from other natural sources such as shale oil and coal carbonization contain objectionable amounts of mercaptans, or are "sour" in the language of the petroleum art. It is necessary to eliminate the mercaptans from the oils prior to commercial use. Most commonly the sour oils are treated to convert the mercaptans to the corresponding disulfides, which disulfides remain in the oil. Thus, even though the oil is now "sweet" there has been no reduction in the sulfur content.

In order to simultaneously sweeten the oil and to reduce the sulfur content, frequently the sour oils are treated to physically remove the mercaptans from the oil. The most common method of doing this is by treatment of the sour oil with an aqueous caustic solution. The caustic reacts with the mercaptans to form mercaptides which are soluble in the aqueous caustic solution. Economy in the operation of these processes requires that the spent solution be regenerated by removal of the mercaptides. This is ordinarily accomplished by contacting the spent solution with oxygen or air in the presence of a mercaptan oxidation catalyst; or by operating at slightly elevated temperatures in the absence of a catalyst. These regeneration processes require prolonged times and are one of the bottlenecks in sweetening procedures by the extraction technique.

An object of the invention is the conversion of mercaptans to disulfides. Another object of the invention is the regeneration of aqueous caustic-mercaptide solutions by oxidizing the mercaptides to the corresponding disulfides. A particular object is a more rapid regeneration process wherein the aqueous caustic-mercaptide solution is contacted with free oxygen. Still another object is a refining process wherein a sour petroleum distillate is sweetened by extracting mercaptans with an aqueous caustic solution; the spent aqueous caustic solution is regenerated and the regenerated solution is recycled to the extraction step.

It has been discovered that the rate of free oxygen oxidation of the mercaptides present in an aqueous caustic-mercaptide solution can be markedly accelerated by the presence of between about 10 and about 100 volume percent based on aqueous caustic solution of a liquid hydrocarbon in the oxidation zone. The preferred liquid hydrocarbon is a petroleum distillate boiling below about 700° F.; for example, heavy naphtha, kerosene, and light gas oil.

In a mercaptan extraction process, the sour oil is contacted with aqueous caustic solution. The aqueous caustic solution may be simply a solution of alkali metal-hydroxide in water; the most commonly used alkali metal-hydroxide is sodium hydroxide. In order to improve the efficiency of the extraction, the aqueous caustic solution usually contains mercaptan solubility promoters.



These promoters generally are slightly acidic materials with high solubility in the aqueous caustic solution. Examples of the more common solubility promoters are cresol, xylenol and isobutyric acid. The alkoxyalkanoic acids such as ethoxypropionic acid are also excellent solubility promoters. The most commonly used solubility promoters are the so-called cresols and heavy xylenols derived by aqueous caustic extraction of naphthas and light gas oils respectively. It is to be understood that aqueous caustic as used in this specification includes not only the simple water-alkali metal hydroxide solution, but also solutions of water, alkali-metal hydroxide and mercaptan solubility promoter.

The aqueous caustic solutions used may contain between about 5 and 50 weight percent of caustic and preferably between about 10 and 25 percent.

It is to be understood that the aqueous caustic solutions described above are those conventionally used in this art wherein mercaptans are removed from sour oils by treatment with either aqueous caustic alone or aqueous caustic in conjunction with a mercaptan solubility promoter.

The sour oil is contacted with the aqueous caustic solution either in a batch-wise operation or in a continuous countercurrent process. The treated oil is separated, usually after gravity settling, from the spent aqueous solution which consists essentially of the aqueous caustic solution and dissolved mercaptides.

The spent solution is regenerated by contacting the solution with free oxygen, i. e., oxygen or air. Although it is possible to completely convert the mercaptides present to the corresponding disulfides, normally less than this amount of conversion is carried out. Normally, satisfactory mercaptan extraction does not require the use of a completely regenerated solution. Sufficient free oxygen is added to the regeneration zone to accomplish the degree of conversion desired. Theoretically, one-quarter mol of oxygen is necessary per mol of mercaptan to be converted.

The regeneration can be carried out at temperatures between about 50° and about 250° F. However, it is preferred to operate at temperatures within the range of about 80° to about 130° F. when using a mercaptan oxidation catalyst. When operating in the absence of a catalyst, it is preferred to operate between about 175° and 200° F.

These higher temperatures needed for regeneration without a catalyst impose an economic disability on the process because the extraction is normally carried out at temperatures on the order of 80° to130° F. It is most common to regenerate in the presence of a mercaptan oxidation catalyst. Many catalysts for this purpose are known to this art. The more common catalysts are the polyhydroxybenzenes and alkylphenols. Examples of the polyhydroxybenzenes are hydroquinone, pyrogallol and 1,2,4-trihydroxybenzene. Examples of the commonly used alkylphenols are cresol, heavy xylenols and t-butylcatechol. In addition to these, acids and esters of polyhydroxybenzenes are used as catalysts. Examples of these are gallic acid, commercial tannic acid and various tannins. In addition to these organic catalysts, inorganic salts, such as copper salts and nickel salts can be used.

Owing to the fact that the phenolic catalysts described above can be oxidized with free oxygen in the presence of aqueous caustic, it is necessary to operate in a manner to avoid substantial loss of the catalyst. According to the well known procedure in this art, the regeneration is not carried out to completion. That is, a sufficient amount of mercaptans are left unconverted in order to prevent oxidation of the phenolic catalysts. In general, only about 50% of the mercaptide is converted, although with loss

of catalyst, operation at 80–90% conversion is feasible. An aqueous caustic-mercaptide solution containing about 50% of the mercaptides originally charged to the regenerator is suitable for use in the extraction zone and is considered a "regenerated solution."

At least a catalytically effective amount of mercaptan oxidation catalyst must be present. When using the phenolic catalysts, between about 0.005 and 1 weight percent based on spent solution are generally used.

It has been discovered that the presence of a liquid hydrocarbon in the regeneration zone may have a favorable effect on the amount of time needed to carry out the desired degree of mercaptan conversion. In order to obtain a beneficial effect on the regeneration time, it is necessary to control the amount of oil present in the regeneration zone. When regenerating to the extent of at least about 50% conversion of the mercaptans, the amount of liquid hydrocarbon present must be between about 10 and about 100 volume percent based on aqueous caustic portion of the spent solution, i. e., the spent solution less the mercaptan solubility promoter present. When 80% conversion is desired, the usage of liquid hydrocarbon should be between about 10 and about 50 volume percent. When about 90% conversion of the mercaptans is desired, the useage of liquid hydrocarbon is between about 15 and about 25 volume percent.

The liquid hydrocarbon used in the process of this invention may be any hydrocarbon that is liquid under the conditions of temperature and pressure existing in the regeneration zone. Examples of suitable hydrocarbons are hexane, octane, naptha, kerosene, virgin gas oil, light thermally cracked gas oil, light catalytically cracked gas oil, toluene, xylene and tetralin. It is preferred to operate with petroleum distillates boiling below about 700° F. The most effective hydrocarbons are the paraffins. However, in general for a particular operation the type of hydrocarbon used will be dependent upon the degree of improvement in regeneration time obtainable and also the value of the hydrocarbon itself.

The hydrocarbons used in the process may be either sweet or sour. It is preferred to use a hydrocarbon that is sweet or substantially so.

The results obtainable with the process of this invention are illustrated below. In these tests, a measured amount of aqueous caustic-mercaptide solution was added to a 50 ml. round bottomed flask. A few glass beads were added to the flask to aid in agitation. The flask was clamped to a shaker arm in such a way that the contents of the flask were immersed in a constant temperature bath set at 31° C. (88° F.). Oxygen was introduced into the top of the flask at a pressure of 1 atmosphere. This pressure was maintained by adding oxygen to the flask at the same rate that oxygen was absorbed by the solution. The rate of oxygen absorption was measured in order to determine the relative effectiveness of the addition of various amounts of liquid hydrocarbon. In order to obtain agitation of the flask and improve the oxygen-liquid contacting, since the oxygen was not bubbled through the liquid, the flask was shaken at 100 vibrations per minute.

In all the tests the spent solution was made up by dissolving n-butyl mercaptan in aqueous sodium hydroxide. The aqueous solution contained 4 weight percent sodium hydroxide. 10 ml. of this aqueous caustic-mercaptide solution were introduced into the flask in each test.

In each test gallic acid was used as the mercaptan oxidation catalyst. The catalyst was present to the extent of 0.005 weight percent based on aqueous caustic solution.

*Example I*

In this example, six tests were carried out using 10 ml. of the above described spent solution. A standard test was made to determine the rate of mercaptan oxidation in the absence of n-octane, which was the liquid hydrocarbon. The other tests were carried out with various amounts of n-octane present in the oxidation zone. In these tests, 12.6 ml. of oxygen absorption corresponded to 50% mercaptan conversion; 21 ml. corresponded to 80% conversion and 23.5 ml. corresponded to 90% conversion. The results of these tests are set out graphically in the annexed drawing. The numbers assigned to each curve correspond to the test number set out hereafter. In tabular form following there is set out the percent mercaptan oxidized at 25 minutes and also at 32 minutes.

| Test | Volume Percent n-octane | Mol Percent Mercaptan Oxidized | |
|---|---|---|---|
| | | 25 minutes | 32 minutes |
| 2 | none | 30 | 40 |
| 3 | 20 | 80 | 90 |
| 4 | 50 | 75 | 81 |
| 5 | 100 | 68 | 75 |
| 6 | 10 | 72 | 85 |
| 7 | 5 | 49 | 60 |

It is noteworthy that tests 4 and 6 show a reversal in effectiveness when going from 25 minutes time to 32 minutes time. The figure clearly shows that when using 50% of liquid hydrocarbon, the slope of the oxygen absorption curve decreases very rapidly after about 16 minutes of time and when using 100% of liquid hydrocarbon, the slope decreases rapidly after about 12 minutes of time. These data clearly show that at least about 10% of hydrocarbon is needed; at hight conversion the amount tolerable decreases to about 50%; and still further to about 25%. This, in spite of the fact that the data show that large improvements in regeneration efficiency can be obtained when using very small amounts of liquid hydrocarbon and also very large amounts of liquid hydrocarbon.

*Example III*

In this example, the effectiveness of various liquid hydrocarbons in improving oxidation time was determined. Tests were carried out with 10 volume percent of liquid hydrocarbon present and the test was continued for 39 minutes. The liquid hydrocarbons used were (*a*) tetralin, (*b*) n-octane, and (*c*) a light catalytically cracked cycle oil. This LCCO was obtained from the liquid product of the fluid catalytic cracking of gas oils and had an API gravity of 30.3, an ASTM initial of 420° F., and an ASTM max. of 600° F., a sulfur content of 0.7 weight percent, and was sweet to the Doctor Test. The results of these tests are tabulated below.

| Test | Oil Type | Percent Mercaptans Oxidized |
|---|---|---|
| 8 | none | 50 |
| 9 | tetralin | 58 |
| 10 | LCCO | 74 |
| 11 | n-octane | 85 |

These tests show a remarkable increase in effectiveness when using a petroleum distillate as the liquid hydrocarbon and that highly paraffinic hydrocarbons are most effective.

In all cases, the hydrocarbon separated readily from the aqueous solution and was decanted off to recover the regenerated aqueous caustic solution.

Thus having described the invention, what is claimed is:

1. In the process for the regeneration of aqueous caustic-mercaptide wherein the aqueous caustic-mercaptide solution is contacted with free-oxygen in an amount and for a time sufficient to convert at least about one-half of said mercaptide to disulfide, the improvement wherein said contacting is carried out in the presence of a liquid hydrocarbon in an amount between about 10 and about 100 volume percent, based on aqueous caustic solution.

2. The process of claim 1 wherein said hydrocarbon is a petroleum distillate boiling below about 700° F.

3. A regeneration process which comprises contacting an aqueous solution comprising caustic and mercaptides with free-oxygen, in an amount and for a time sufficient to convert at least about one-half of said mercaptides to disulfide, at a temperature between about 50 and 250° F., in the presence of a liquid hydrocarbon, in an amount between about 10 and about 100 volume percent based on said aqueous solution, and separating an aqueous solution substantially free of disulfides from said hydrocarbon.

4. The process of claim 3 wherein said hydrocarbon is a petroleum distillate boiling below about 700° F.

5. The process of claim 4 wherein said distillate is kerosene.

6. The process of claim 4 wherein said distillate is a catalyticallly cracked oil boiling between about 420° and about 600° F.

7. The process of claim 3 wherein a mercaptan oxidation catalyst is present in the contacting zone.

8. The process of claim 3 wherein said aqueous solution contains a mercaptan solubility promoter.

9. The process of claim 3 wherein said hydrocarbon usage is between about 10 and 50 volume percent.

10. A regeneration process which comprises contacting, at a temperature between about 80° and about 130° F., a substantially spent aqueous caustic-mercaptide solution with free-oxygen, in an amount and for a time sufficient to convert about 80% of said mercaptide to disulfide, in the presence of a liquid petroleum distillate boiling below about 700° F., in an amount between about 10 and about 50 volume percent, based on said spent solution, in the presence of a catalytic amount of a phenolic mercaptan oxidation catalyst, and separating a regenerated aqueous caustic solution from said distillate.



11. A refining process which comprises (1) contacting, in the absence of free-oxygen, a sour petroleum distillate with an aqueous solution comprising caustic and a phenolic solubility promoter for mercaptans, (2) separating a distillate reduced in mercaptan content from a spent aqueous solution comprising mercaptides, caustic and promotor, (3) contacting said spent solution, at a temperature between about 80° and 130° F., in the presence of a phenolic mercaptan oxidation catalyst, with free-oxygen, in an amount and for a time sufficient to convert mercaptides to disulfides without substantial oxidation of said catalyst, and in the presence of a liquid petroleum distillate boiling below about 700° F., in an amount between about 10 and about 100 volume percent based on aqueous caustic in said spent solution, (4) separating distillate from regenerated aqueous solution and (5) recycling said regenerated solution to step (1).

12. The process of claim 11 wherein said promoter consists of petroleum cresols.

13. The process of claim 11 wherein said catalyst is hydroquinone.

14. The process of claim 11 wherein said liquid petroleum distillate is a catalytically cracked oil boiling between about 420° and about 600° F.


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