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2,768,885

COPPER SWEETENING OF CRACKED NAPHTHAS AND STABILIZING THE SWEETENED NAPHTHA WITH AN AMINE

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Application August 27, 1953, Serial No. 376,906

4 Claims. (Cl. 44—74)

This invention relates to the sweetening of cracked naphthas which contain objectionable amounts of mercaptans. More particularly, it relates to the sweetening of sour cracked naphthas by means of a supported cupric chloride catalyst.

The sweetening of naphthas which contain objectionable amounts of mercaptans, i. e., commonly known as sour naphthas by treatment with a supported $CuCl_2$ catalyst is of considerable commercial importance. Probably the best known copper sweetening process is the so-called Linde slurry process. In this process a catalyst comprising essentially $CuCl_2$, water and a carrier in the form of free flowing granules is dispersed into the sour naphtha and the dispersion is maintained until a substantially sweet naphtha has been obtained whereupon the sweet product naphtha is separated from the catalyst. Normally the contacting is carried out in the presence of free-oxygen in an amount sufficient to regenerate the catalyst. The carrier may be either an adsorbent material such as fuller's earth or acid treated clay or an essentially non-adsorbent material such as pumice or diatomaceous earth. The adsorbent materials, preferably finely divided fuller's earth, are commonly used in commercial operation.

The slurry process works very well when treating virgin sour naphthas. The oxidation stability of the sweet virgin naphtha as measured by the ASTM induction period method is excellent even in the absence of metal deactivator. However, the solid copper chloride process cannot be used on sour cracked naphthas because, at the same conditions used for virgin naphthas, the sweet naphtha has unsatisfactory oxidation stability and poorer color.

It is an object of this invention to sweeten sour cracked naphthas using a supported $CuCl_2$ catalyst. Another object is a copper chloride sweetening process for sweetening sour cracked naphthas, whereas the sweet naphtha has an acceptable oxidation stability as measured by the induction period method. Other objects will become apparent in the course of the detailed description.

A sweet cracked naphtha of improved oxidation stability is obtained by contacting a sour cracked naphtha, in the presence of free-oxygen, at a temperature below about 120° F., preferably about 70–90° F., with a supported copper chloride sweetening catalyst wherein the weight ratio of carrier to $CuCl_2$ is about 10:1 or more, for example, 12:1. It is preferred to add to the sweet naphtha an effective amount of an oxidation inhibitor and a metal deactivator.

The invention is described in relation to the annexed figure which forms a part of this specification. The figure shows one illustrative embodiment of the process of this invention. Numerous pumps, valves and other items of equipment have been omitted from the embodiment shown in the figure; these items may be readily added by those skilled in the art.

The feed stock to the process is a sour naphtha derived from the thermal or catalytic cracking of gas oils, reduced crudes and heavy naphthas. The feed may consist of a

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mixture of cracked naphtha and virgin naphtha wherein the cracked naphtha is the predominant component. The feed may be a cracked naphtha which has been subjected to prior treatment for reduction in mercaptan content or sulfur content, e. g., the effluent from the treatment of a sour cracked naphtha by one of the well known solutizer processes, which effluent is sour to the doctor test even though said effluent has a copper number of 2 or 3. The sour oil should be H_2S-free. If the feed contains H_2S, the H_2S should be removed by washing with a dilute aqueous caustic solution or other method of removing H_2S that does not also remove all the mercaptans.

Caustic solution reacts with the copper catalyst and deactivates it. Therefore, it is necessary to remove any caustic which may be present in the feed. The sour oil feed in this illustration, a naphtha derived from the thermal cracking of a virgin gas oil which has a mercaptan No. of 5 and an ASTM boiling range from 130° to 400° F., is passed from source 11 through line 12, into salt filter 13. Salt filter 13 consists of a cylindrical vessel filled with crushed rock salt. The rock salt removes any aqueous caustic that may be occluded in the feed. Instead of using a salt drum, a vessel filled with steel wool, gravel, sand or other coalescing medium may be used.

The naphtha is passed from salt filter 13 by way of line 14, into heat exchanger 16. In heat exchanger 16 the temperature of the sour cracked oil is raised to about 80° F. Although the temperature of operation may be as high as about 120° F., better results are obtained by operating below about 90° F. From heat exchanger 16 the oil is passed by way of line 17 into mixer 18. Mixer 18 may be any form of agitating device. In this case mixer 18 is provided with knothole orifice plates. Free-oxygen from source 21 is passed through line 22 into line 17 where it meets the main stream of sour cracked naphtha. The free-oxygen and the sour cracked naphtha are thoroughly intermingled in mixer 18.

Theoretically, the amount of free-oxygen needed in the process to insure substantially complete regeneration of the catalyst is 1 mol for each 4 mols of mercaptan present. However, normally a 100 or 200% excess is desirable. In general, from about 3 to about 9 standard cubic feet of free-oxygen or an equivalent amount of air are used in the process per pound of mercaptan sulfur. Herein 4.5 s. c. f. of free-oxygen are used.

A side stream of the sour cracked naphtha is withdrawn from line 17 by way of line 24 and is passed into slurry tank 26. Slurry tank 26 is a cone-bottomed vessel provided with an agitator not shown. Fresh catalyst from source 27 is added by way of line 28 to slurry tank 26. The slurry of catalyst and sour cracked naphtha is passed from tank 26 through line 29 by way of pump 31 into line 32. The main stream of sour cracked naphtha is passed from mixer 18 by way of line 34 and pump 36 into line 37 where it meets the makeup catalyst slurry from line 32.

The catalyst comprises essentially $CuCl_2$, water and a carrier. Herein, the carrier consists essentially of a finely powdered mixture, having a screen size of less than about 80 mesh of Attapulgus clay. Adsorbed on the carrier is an aqueous solution of $CuCl_2$. Based on the total catalyst, the catalyst should contain between about 5 and 30 weight percent of water. A water content of 15 to 25% is preferred to minimize catalyst carryover.

The $CuCl_2$ may be added by using either the anhydrous salt. Or, the $CuCl_2$ may be made by reacting in aqueous solution cupric sulfate and sodium chloride or ammonium chloride. When forming the $CuCl_2$ by this reaction, it is preferred to use a small excess of the chloride salt. The weight ratio of carrier to $CuCl_2$ must be at least about 10:1 and may be as high as 20:1. It is preferred to use a ratio between about 12:1 and 15:1.

In this illustration the Attapulgus clay to $CuCl_2$ weight

ratio is 13:1 and the total catalyst mass contains 20 weight percent of water. The naphtha-oxygen-catalyst dispersion in line 37 is passed into eductor 38 and from eductor 38 it is passed through line 39 into reactor 41. In some cases the edutor may be by-passed and the dispersion passed into line 39 by way of by-pass line 42. In reactor 41 the naphtha and the catalyst are maintained in the dispersed condition until the naphtha is substantially sweet.

Reactor 41 has a conical shaped lower portion into which the catalyst settles. The dense slurry of catalyst and naphtha is withdrawn from the bottom of reactor 41 through line 46 and is passed into eductor 38 by way of line 47. In eductor 38 the recycle catalyst meets the stream of sour naphtha and makeup catalyst. Catalyst circulation rate may be between about 10 and 30 volume percent, based on naphtha; rates between 10 and 20% are preferred to reduce carryover. When the catalyst has become substantially inactive, catalyst is sent to recovery by way of lines 46 and 49.

The sweet naphtha usually contains a very slight amount of catalyst (carryover). The copper in the catalyst has an adverse effect on the oxidation and color stability of the naphtha. The catalyst-containing sweet naphtha is withdrawn from reactor 41 through line 51 and is passed into line 52 where it meets water from source 53 in line 54. The amount of wash water used is dependent upon the amount of catalyst carried over from the reactor. In general the amount of wash water may be between about 10 and 100 volume percent based on sweet naphtha. The mixed stream of water and sweet naphtha is passed into mixer 56. From mixer 56 the stream of sweet naphtha and water is passed by way of line 57 into settler 58. The wash water separates in settler 58 and is sent to a sewer by way of line 59. The washed sweet naphtha from settler 58 is passed into line 61. The washing operation may be by-passed by way of lines 51 and 62. The washed naphtha from line 61 is passed through line 63, through cooler 64 and line 66 into salt filter 67. Cooler 64 lowers the temperature of the washed naphtha in order to reduce the amount of water dissolved in the naphtha, and salt filter 67 dehydrates the washed naphtha. Brine from vessel 67 is passed to the sewer by way of line 68. Salt filter 67 is similar in construction to salt filter 13.

Sweet naphtha is withdrawn from the filter by way of line 69. A solution of phenylene diamine-type inhibitor and copper metal deactivator from source 71 is introduced by way of line 72 into line 69. The PDA-MD solution and the sweet naphtha are intermingled in mixer 73. The stabilized naphtha is passed to product storage by way of line 74.

The phenylene diamine inhibitors may be N,N'-dialkyl-p-phenylene diamines in which the alkyl groups contain from 1 to about 12 carbon atoms per molecule including such compounds as N,N'-di-iso-propyl-p-phenylene diamine, N,N'-di-amyl-p-phenylene diamine, N,N'-di-hexyl-p-phenylene diamine, etc., as well as those in which the alkyl groups are different as, for example, in such compounds as N-propyl-N'-butyl-p-phenylene diamine, N-butyl-N'-amyl-p-phenylene diamine, N-hexyl-N'-octyl-p-phenylene diamine, etc. Generally between about 0.5 and 10 pounds of inhibitor are used per 1000 barrels (42 gals.) of oil. Herein, 1 lb./M. bbls. (42) of N,N'-di-sec-butyl-p-phenylene diamine is used.

It is to be understood that other types of oxidation inhibitors may be used, e. g., butylcatechol.

The metal deactivator may be any one of the classes of compounds set out in Ind. and Eng. Chem. 41, 918 (May 1949). Usually between about 0.5 and 10 pounds of metal deactivator per 1000 barrels (42 gals.) of oil are used. Herein, 2 lbs./M bbls. (42) of N,N'-disalicylidine-1,2-diamino-propane are added.

It is to be understood that the above-described embodiment is illustrative only and is not intended to limit the scope of this invention. Many variations thereon can be readily made by those skilled in the art.

In order to illustrate the results obtainable with this invention, tests were made on a thermally cracked sour naphtha having a mercaptan number of 5 and a boiling range between 130° and 400° F. These tests were carried out in a laboratory size continuous pilot plant which closely simulates the operation of a large scale commerical unit. In each run 6 liters of sour cracked naphtha were passed through the apparatus.

The catalyst consisted of $CuCl_2$, water and Attapulgus clay fines carrier. The catalyst mass was prepared using hydrated cupric chloride, i. e., $CuCl_2 \cdot 2H_2O$. In each case the catalyst contained, on a weight percent basis, about 20% of water.

In each run about 200% of the theoretical requirement of free-oxygen was used—in the form of commercial cylinder oxygen. The dispersion was agitated for a time sufficient to obtain a doctor sweet naphtha. The sweet naphtha was washed with 20 volume percent of water at 85° F. to remove occluded catalyst.

The oxidation stability of the sweet naphtha was determined by the induction period method ASTM D525–49. Prior to each oxidation test N,N'-di-sec-butyl-p-phenylene diamine, 1 lb./M bbl. (42) and N,N'-di-salicylidine-1,2-diaminopropane, 2 lbs./M bbl. (42), were added to the sweet cracked naphtha.

The results of these tests are shown below in the table.

TABLE

Test No.	Clay: $CuCl_2$ Wt. Ratio	Temperature, °F.	Induction Period, Min.
1	6.3:1	110	260
2	6.3:1	110	190
3	12.6:1	110	365
4	12.6:1	110	385
5	12.6:1	90	400
6	12.6:1	90	420

Test 7

A sour virgin naphtha boiling between about 100° and 350° F. with a mercaptan number of about 12 was sweetened under the conditions of Test 1, except that no inhibitor and no metal deactivator was added. The sweet naphtha had an induction period of 1400 minutes. This test shows that the problem of stability of copper chloride sweetened naphthas is limited to cracked naphthas.

The cracked naphtha that had been sweetened at 90° F. had a much better Saybolt color than did the naphtha sweetened at 110° F.

The data in the table must be considered in the light of the requirements of commerce. It is generally accepted that a gasoline of satisfactory commercial storage stability must have an induction period of at least 270 minutes. Better quality commercial gasolines have induction periods of about 400 minutes or more. These data clearly show that the conventional sweetening process does not produce an acceptable product, whereas the process of this invention is substantially equal to better quality commercial gasoline.

Thus having described the invention, what is claimed is:

1. A process for sweetening a sour cracked naphtha, which process comprises dispersing in a sour cracked naphtha an effective amount of a granular catalyst consisting of cupric chloride, water and a carrier, wherein the water content is between about 15 and 25 weight percent of the catalyst and the weight ratio of carrier to cupric chloride is between about 12:1 and 15:1, at a temperature between about 70° F. and about 90° F. in the presence of an amount of free oxygen sufficient to convert essentially all the mercaptans in said sour naphtha and thereby produce an essentially sweet naphtha,

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maintaining said dispersion for a time sufficient to render said naphtha essentially sweet, separating essentially sweet naphtha from said catalyst and adding to said sweet naphtha a phenylene diamine inhibitor and a copper metal deactivator in an amount between about 0.5 and 5 lbs. per 1000 bbls. (42 gals.) of sweet naphtha respectively, whereby a product sweet naphtha is produced which is characterized by an induction period of at least about 400 minutes.

2. The process of claim 1 wherein said sour naphtha is a thermally cracked naphtha.

3. The process of claim 1 wherein said phenylene diamine inhibitor is N,N'-di-sec-butyl-p-phenylene diamine.

4. The process of claim 1 wherein said deactivator is N,N'-disalicylidine-1,2-diaminopropane.

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