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REMOVING CORROSIVE SULFUR FROM NAPHTHA WITH ANHYDROUS COPPER SULFATE

Kenneth Lucas, Woodstock, Ill., assignor to The Pure Oil Company, Chicago, Ill., a corporation of Ohio

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This invention is directed to a method for the production of petroleum naphthas characterized by their ability to pass the Distillation-Corrosion test and, more particularly, the invention relates to the production of non-corrosive naphtha hydrocarbons by chemical reaction or treatment with copper sulfate and preferably anhydrous copper sulfate at a temperature of about 400° to 500° F.

Crude petroleum has long been the source of widely known products including gasoline, kerosene, diesel fuels, lubricating oils, and heavy tars. In many instances, the products obtained from petroleum are employed as reactants in the synthesis of additional petroleum derivatives and chemicals and a large number of products of petroleum are used directly without extended treatment or modification. Petroleum naphthas comprise a wide variety of such latter products used extensively in the dyeing, rubber, extraction, protective coating, and allied industries. A large portion of the petroleum naphthas used is the straight-run naphthas which are selected fractions of the lower boiling, more volatile constituents of crude petroleum. The present invention is directed to a method of transforming deleterious sulfur compounds present in hydrocarbon mixtures into forms which are less obnoxious and non-corrosive and will be illustrated by the treatment of straight-run naphthas. The examples given are not to be construed as limiting the invention. The term naphthas as used herein shall mean straight-run petroleum naphthas and other hydrocarbon mixtures or their equivalents containing deleterious sulfur compounds which must be transformed to meet rigid corrosion tests.

Naphthas prepared from petroleum by physical means inevitably contain other types of organic and inorganic compounds due to the complex nature of petroleum which are deleterious as far as certain end uses of the naphthas are concerned and necessitate the application of additional refining steps. Even with such additional refining, it is exceedingly difficult to prepare naphthas which meet the exacting specifications that have been established by the industry. Of these deleterious non-hydrocarbon compounds, the sulfur and sulfur-containing constituents are generally the most persistent and cling tenaciously to any environment in which they exist, imparting objectionable odor, corrosiveness, color, and other physical and chemical properties thereto. The odor of naphthas is important; however, no standard test exists to cover this property and the odor of a well refined naphtha is generally described as sweet.

Tests have been devised to determine both quantitatively and qualitatively the presence of these odious compounds in an attempt to control the properties and quality of naphthas from petroleum sources. For this purpose, various copper strip corrosion tests, the mercury test, the lead acetate test, and the "Doctor" test are used. Procedures established by A. S. T. M. are used to determine the content and distribution of these sulfur compounds. Perhaps the most critical and rigorous qualitative test for determining the presence of corrosive sulfur compounds in naphthas is the Distillation-Corrosion test, known also as the Philadelphia test, the Amsco corrosion test, or the full boiling range corrosion test—by any name, a particularly rigorous species of copper strip corrosion test. The test, widely applied by the manufacturers, distributors, and users of specialty naphthas, is carried out by the addition of a small pure copper coupon to an ordinary A. S. T. M. distillation flask containing 100 cc. of the naphtha to be tested. The copper strip is so positioned in the flask that one end of the strip contacts the residue at the end of the distillation, and the distillation is conducted according to A. S. T. M. D86–38 as described in A. S. T. M. Standards on Petroleum Products and Lubricants, published by the American Society for Testing Materials, Philadelphia, Pennsylvania.

At the completion of the test, wherein the flask has been heated to dryness, the color of the copper strip is an indication of the relative amount of corrosive sulfur compounds present in the naphtha sample. A negative test is shown by the presence of a very slight or moderate tarnish on the strip and stamps the naphtha as satisfactory. If the copper strip becomes moderately blackened, the results are interpreted as positive or unsatisfactory. The production of a slightly tarnished or slightly colored or corroded strip, indicated by a dark orange with peacock colorations thereon, is termed borderline and as such denotes a naphtha which is not acceptable and must be further refined. The market is limited for off-specification naphthas and further refining is expensive since even then there is no assurance that the product will pass the severe Distillation-Corrosion test.

The subjection of high sulfur content naphthas to various refining and sweetening operations which may include oxidation and extraction methods, or the recycling of rejected off-specification naphthas back through such a process, does not produce acceptable naphthas because the sulfur compounds remaining are the most difficult to remove and the most corrosive. High sulfur content naphthas usually have a poor odor as well as other undesirable properties. If straight-run naphthas from high sulfur crudes are subjected to other more severe refining methods, the resulting products may pass the other tests for sulfur compounds but do not pass the Distillation-Corrosion test. Often naphthas are produced which are negative or borderline to the Distillation-Corrosion test and which exhibit a positive reaction to one or more of the other tests for sulfur compounds. Since naphthas must pass all such tests to be acceptable, further treatment is necessary. Prior art methods of desulfurization when applied to such naphthas may produce a Doctor negative or mercury negative product, but in so doing the end result is a positive Distillation-Corrosion test.

Accordingly, the primary object of this invention is to overcome this problem and provide a process for producing improved naphthas by chemical reaction or treatment with copper sulfate at 400° to 500° F. and preferably at 450° F.

A second object of the invention is to provide a method of producing naphthas which pass the Distillation-Corrosion test from naphthas containing unacceptable amounts of sulfur compounds.

These and other objects of the invention will become apparent as the description thereof proceeds.

In the prior art there are described many methods for desulfurizing and sweetening hydrocarbon mixtures. These processes may be roughly divided into two groups—those involving chemical treatment or adsorptive contact at low temperatures with the main purpose being the removal of free sulfur, hydrogen sulfide, and those organic sulfur compounds which may be adsorbed; the

second group of processes, which include hydrodesulfurization reactions, are conducted at elevated temperatures and involve the breakdown of the organo sulfur compounds into other products including hydrogen sulfide. During these hydrodesulfurization processes, the sulfur compounds present are substantially completely destroyed and there takes place reactions involving hydrogenation, dehydrogenation, reforming, and the like, depending on the particular catalyst used and the operating conditions. In general, especially in the presence of hydrogen under optimum conditions, gasoline products are obtained which have increased octane numbers and good lead susceptibility. Products produced by these methods may have their sulfur contents greatly reduced, and it is not uncommon to reduce the sulfur content to points below 0.01 per cent sulfur.

These prior art processes cannot be depended upon to produce naphthas which are non-corrosive to the Distillation-Corrosion test because the types of organic sulfur compounds remaining after these treatments are the very types that are corrosive to copper and, though present in a very small amount, are deleterious and indicate an unsalable product. Therefore, a sharp distinction must be made between desulfurization generally as meant in the prior art and the desulfurization necessary to produce non-corrosive naphthas. The present invention is directed to the finding that at a temperature of about 400° to 500° F. copper sulfate may be used to contact naphtha hydrocarbons to transform the sulfur compounds therein to forms which are non-corrosive to the Distillation-Corrosion test. It has been found that at temperatures below 400° F., although there may be a large degree of desulfurization, the remaining sulfur compounds are corrosive to the Distillation-Corrosion test. In ordinary gasoline sweetening processes using oxidizing agents, the general object is to convert the mercaptans to disulfides. At temperatures above about 350° F., the disulfides break down and form lesser amounts of corrosive sulfur compounds. Thus, because of the instability of the disulfides, these methods of desulfurization or sweetening cannot be used to produce sweet naphthas. This is especially true in considering crude naphthas which have above about 0.003 per cent mercaptans. If the chemical treatment or desulfurization is carried out according to the prior art at temperatures of above 500° F., there may be adequate desulfurization, but by-products are formed at these elevated temperatures which deleteriously affect the color of the resultant naphthas. This color cannot be removed by ordinary adsorbents, and again the product is unsalable.

It has been found that at a temperature of about or above 400° F. some of the mercaptans are converted to metal mercaptides instead of disulfides and as the temperature is maintained or raised to about 450° F. the metal mercaptides break down into metal sulfides and organic mono-sulfides which are non-corrosive and stable. This is the type of sweetening reaction which is contemplated by the present invention. There is no minimum sulfur content requirement for naphthas but, since they must meet the Doctor test, contain no hydrogen sulfide or free sulfur, and pass the Distillation-Corrosion test, the amount of total sulfur present in the finished product is necessarily small. The principal factors pertaining to the influences exerted by this small content of sulfur compounds on the various corrosion tests are the boiling points of the sulfur compounds in relation to the boiling range and end point of the naphtha, and the stability of the sulfur compounds at moderately high temperatures. Mercaptans are rather unstable at moderately high temperature and break down into products corrosive to the Distillation-Corrosion test. Disulfides are more unstable and produce very corrosive decomposition products, especially under the conditions present in the distillation residue. High boiling naphthas like Stoddard solvent generally give a more corroded copper strip than lower boiling naphthas, as rubber solvent. Treatment of off-specification naphthas by prior art methods may break down the sulfur compounds into those types which are more corrosive to the Distillation-Corrosion test, especially where low sulfur naphthas are concerned since these sulfur compounds are most difficult to remove and most corrosive.

The present invention is directed primarily to the treatment of naphthas or hydrocarbon mixtures containing relatively low sulfur contents. It has been found that the initial degree of hydration of the copper sulfate affects to a certain extent the efficiency of the desulfurization obtained at a given temperature and time of contact. Especially where the feed stock contains over 0.025 per cent by weight of total sulfur, the best results are obtained by employing anhydrous copper sulfate, that is copper sulfate containing less than one molecule of water per molecule of copper sulfate. This substantially anhydrous form of copper sulfate also is particularly efficient and dependable in forming non-corrosive naphthas from feed stocks containing 0.025 per cent by weight or less of total sulfur. The hydrated forms, such as copper sulfate containing 5 molecules of water per molecule of copper sulfate, can also be used for treating feed stocks which have very small sulfur contents, providing the contacting time at a temperature within 400° to 500° F. is sufficient to substantially dehydrate the copper sulfate.

Crude naphthas having a higher total sulfur content than about 0.025 per cent preferably should be desulfurized prior to treatment in accordance with this invention. The chemical treatment with copper sulfate at 400° to 500° F. in accordance with this invention may effect a considerable reduction in the total sulfur content of the naphthas, as by as much as about 50 per cent, but generally the reaction is one of sweetening or transformation of the sulfur compounds into non-corrosive form.

In order to demonstrate the invention, a series of experiments were conducted in which an intermediate sour West Texas naphtha having a boiling range of 290° to 432° F. was vaporized and passed through a slurry of anhydrous copper sulfate suspended in Number 2 white oil at a temperature of about 450° F. The results are shown in the following table.

TABLE I

Treating Material	Charge Stock #1	Copper Sulfate	Charge Stock #2	Copper Sulfate
Product Sulfur Distribution, Wt. Percent:				
Free—S	Nil	Nil	Nil	Nil
H_2S—S	Nil	Nil	Nil	Nil
RSH—S	0.021	Nil	0.013	Nil
R_2S_2—S	Nil	Nil	0.002	0.001
R_2S—S	0.054	0.023	0.006	0.007
Residual—S	0.005	0.006	0.004	0.009
Total—S	0.080	0.029	0.025	0.017
Doctor Test	Positive	Negative	Positive	Negative.
Mercury Test	do	do	Negative	Do.
Distillation-Corrosion Test.	do	do	Negative to Borderline.	Do.

In order to further demonstrate the invention, the following table is shown wherein various treating agents were investigated as to their ability to transform the corrosive sulfur compounds in a naphtha to non-corrosive forms as evidenced by a good or bad Distillation-Corrosion test. In these tests an intermediate sweet West Texas naphtha having a boiling range of 250° to 400° F. was treated under substantially the same conditions as those recited for the results of Table I. This charge exhibited a negative to borderline Distillation-Corrosion test. In each instance, with the exception of copper nitrate, the materials used gave a product of good color. The table shows whether or not there has been a reduction in sulfur

content and whether or not the product passed the Distillation-Corrosion test.

TABLE II

Treatment of a naphtha with various agents at 450° F.

	Desulfurization	Good Distillation-Corrosion Test
1. Aluminum chloride	Yes	No.
2. Cobalt oxide	Yes	No.
3. Cobalt molybdate	Yes	No.
4. Copper sulfate	Yes	Yes.
5. Copper oxalate		No.
6. Copper nitrate		No.
7. Copper chloride		No.
8. Active carbon	Yes	No.
9. Porocel (regenerated)	Yes	No.
10. Fuller's earth	Yes	No.
11. Filtrol X-417	Yes	No.
12. Filtrol X-466	Yes	No.
13. Nickel vanadate	Yes	No.
14. Sea Sorb (MgO)	Yes	No.
15. Ammonium molybdate		No.
16. Borax glass		No.
17. Sodium bicarbonate		No.
18. Lithium carbonate		No.
19. Molybdenum oxide	Yes	No.
20. Vanadium pentoxide	Yes	No.
21. Chromic oxide	Yes	No.

In practicing the present invention, any hydrocarbon material from which naphthas or solvents or similar products may be obtained can be subjected to treatment with copper sulfate or anhydrous copper sulfate at 400° to 500° F. wherein the objective is to overcome the tendency of the product toward the formation or carry-over of those types of sulfur compounds which cause a positive Distillation-Corrosion test. Fractionation into various specialty naphthas may precede or follow treatment in accordance with the invention. To prolong the life of the treating agents, it is preferred that the more volatile components and the high boiling residues present be removed by fractionation or other methods prior to treatment in accordance with the invention. For example, a crude oil containing from 1.0 to 3.0 or as high as 7.0 weight per cent of sulfur is fractionated to obtain a wide boiling range virgin or straight-run naphtha having an end boiling point of about 500° F. A gas oil fraction may be used which may boil between about 500° and 700° F. Kerosene fractions may also be used. Preferably a straight-run naphtha fraction having up to 0.025 per cent of total sulfur and boiling between 110° and 450° F. is used.

The boiling range of the particular fraction removed for treatment or after treatment in accordance with this invention may be varied somewhat from the boiling ranges given depending upon the relative amounts of specialty naphtha, rubber solvent, V. M. & P. naphthas desired. By narrowing the boiling range of the virgin naphtha to within 100° to 250° F., the process may be directed to obtaining rubber solvents almost exclusively. On the other hand, by starting with a fraction boiling between 200° and 400° F., the process may be directed to production of V. M. & P. solvents and specialty naphthas. In one specific embodiment of the invention, the treatment of the entire first fraction boiling up to 500° F. or more to produce a wide variety of products ranging from rubber solvents up to high boiling specialty naphthas including, for example, petroleum ether 90°–140° F., special textile spirits 180°–210° F., light mineral spirits 290°–330° F., Stoddard solvent 310°–385° F., and High Flash dry cleaning solvent 360°–400° F., all being non-corrosive, odorless, and meeting the rigorous requirements of the industry, is contemplated.

In treating naphtha fractions or hydrocarbon mixtures from which naphtha fractions may be separated, which contain above 0.025 per cent sulfur, as, for example, a naphtha containing from 0.10 to as high as 7.0 per cent sulfur, it is desirable to subject the naphtha to a desulfurization reaction before treatment in accordance with the invention. For this purpose, the naphtha may be vaporized and passed over a bauxite catalyst at 700° to 800° F. A hydrodesulfurization reaction may be employed if the naphtha contains a considerable portion of sulfur compounds. Treatment with such desulfurization catalysts as molybdates, sulfides, and oxides of iron group metals and mixtures, including cobalt molybdate, chromic oxide, vanadium oxide with molybdena and alumina, and sulfides of tungsten, chromium or uranium, with or without the presence of hydrogen at temperatures from 500° F. to 800° F. and under pressures from 20 to 500 pounds per square inch will effectively desulfurize the naphthas as a pretreatment. A particularly efficient catalyst for this purpose is cobalt oxide-molybdena-alumina or a chromia-molybdena-alumina catalyst employed at about 750° F. under 250 pounds pressure of hydrogen. After such treatment it is customary to subject the naphtha to stripping at about 400° F. and 240 p. s. i. g. to remove the hydrogen and hydrogen sulfide.

In certain instances, it may be desirable to increase the solvency of the naphthas produced. For this purpose, the naphthas may be first subjected to a mild reforming or hydroreforming operation preceding the chemical treatment with copper sulfate. The hydroreforming may be conducted using a cobalt molybdate or copper molybdate catalyst and the sour naphtha passed thereover at temperatures between 825° and 850° F. The aromatization may be promoted by a platinum-containing catalyst at 800° to 825° F. In order to demonstrate this aspect of the invention, the following table is given.

TABLE III

Increasing the solvency of Amsco naphthas

	Charge Stock	Mild Dehydrogenation	Sweetening
Catalyst or Treating Material		Baker's Platinum.	Copper Sulfate.
Average Reactor Temp., °F		882	450.
Reactor Pressure, p. s. i. g.		500	3.
LVHSV, Vol./Vol./hr.		6.06	1.0.
Liquid Recovery, Vol. Percent		97	100.
Distillation-Corrosion Test	Positive	Positive	Negative.
Vol. Percent Aromatics	13	35	34.
Aniline Point, °F	137.8	102.6	101.1.
Sulfur Distribution, Wt. Percent:			
Free—S	Nil	0.001	Nil
H_2S—S	Nil	0.004	Nil
RSH—S	0.021	Trace	Nil
R_1S_2—S	Nil	Nil	Nil
R_2S—S	0.054	0.006	0.003
Residual—S	0.005	0.005	0.004
Total—S	0.080	0.016	[1] 0.007

[1] Product sweetened and redistilled to 400° F. end point.

In carrying out the reaction, the naphtha to be treated is heated to a temperature of about 400° to 500° F. and preferably 450° F. and the vapors passed through the copper treating agent. Adequate conversion of the sulfur compounds to non-corrosive form may be obtained by passing the hot liquid naphtha under pressure through the copper treating agent. The vapor treatment is preferred because of the ease with which the reaction may be carried out. Space velocities of from 1.0 to 100 may be used. Any of the well known percolation, fixed bed, plural bed, or fluidized solids vapor-solid contact methods of the prior art may be used as long as intimate contact is obtained at a temperature within 400° to 500° F. Since the degree of treatment depends somewhat on the correlation between temperature and time of contact as in all such chemical transformations, it is usually desirable to conduct the treatment at relatively high space velocities when temperatures above 450° F. are used and at lower space velocities when temperatures below 450° F. are used. In general, the space velocity is selected to give results corresponding

to those obtained at a vapor space velocity in the range of about 0.2 to 3.0 at 20 pounds per square inch pressure at about 450° F. These conditions consistently give satisfactory results.

The copper sulfate used herein may be any commercial grade of such product, although it is preferred that the anhydrous form containing substantially no water of crystallization be used. Copper sulfate (hydrocyanite) existing in green-white rhombic crystals having a specific gravity of about 3.606 at 15° C. is one preferred form. Blue vitriol or chalcanthite having the formula $CuSO_4 \cdot 5H_2O$ is only recommended for use on feed stocks containing less than 0.025 weight per cent of total sulfur, and then only if the contacting time is sufficiently long to permit substantial dehydration of the copper sulfate.

Such carriers as silica, bauxite, titania, zirconia, chromia, kieselguhr, bentonite, activated carbon, clays, pumice, and alumina may be used with the copper treating agents. The various well known co-precipitation, separate precipitation, impregnation, and simple mixing processes may be used to prepare the copper compound and inert carrier for use in the process. To avoid the danger of fusing during use or regeneration, it has been found that a maximum of about 8 to 10 per cent by weight of the copper compound should be used in the carrier material.

Another form of contact material is the pelleted or tablet form. The copper sulfate may be pelleted with an inert carrier. When the copper content of the treating agent exceeds about 10 per cent, it may tend to fuse during use and the fused mass may become more difficult to handle. Regeneration also may be more difficult since the material loses its free flowing properties. Consequently, it is recommended that the copper content of the completed mass or pellets be below about 10 per cent. In preparing the pellets the copper salts, in powder form, are admixed in proportions such that less than 10 per cent by weight based on copper is present and the mixture is subject to compression into pellets or tablets. Following this, the pellets are calcined at 900° to 1200° F. The methods of pelleting described in United States Patents 2,499,675, 2,592,016, and 2,606,159 may be used. It is probable that during the treatment the copper compounds act to convert the mercaptans present to copper mercaptides, which in turn are converted to organic disulfides and copper oxide. It is known that portions of the copper mercaptides are decomposed to organic sulfides and cupric sulfide, but water and cuprous oxide are also products of the reaction.

Upon completion of the treatment with copper sulfate, the products may sometimes have a slight acrid odor. This odor may be removed by caustic wash since it is due to a trace of sulfur dioxide.

Since the treating agent used herein is relatively inexpensive, it is not contemplated that regeneration is necessary for its use on a commercial basis. Effective treatments of naphtha can be conducted at relatively low cost per barrel. Approximately 1500 barrels of naphtha containing 0.083% w. total sulfur and 6000 barrels of naphtha containing 0.025% w. total sulfur could be effectively treated per ton of anhydrous copper sulfate. Regeneration and reclamation of the spent treating agent could be effected if necessary by oxidation with an oxygen-containing gas at 1100° to 1300° F. to form copper oxide, followed by treatment with sulfuric acid to reform the copper sulfate.

What is claimed is:

1. The method of transforming hydrocarbon mixtures containing sulfur compounds which give a positive Distillation-Corrosion test into products which pass that test, comprising subjecting said hydrocarbon mixtures to contact with copper sulfate at a temperature between about 400° and 500° F. and separating non-corrosive hydrocarbon products therefrom.

2. The method in accordance with claim 1 in which the copper sulfate is in anhydrous form.

3. The method in accordance with claim 2 in which the copper sulfate contains no more than one molecule of water per molecule of copper sulfate.

4. The method in accordance with claim 1 in which the temperature of contact is about 450° F.

5. The method in accordance with claim 1 in which the hydrocarbon mixture is vaporized and passed through a slurry of said copper sulfate in a refined mineral oil having a boiling point greater than the boiling point of the hydrocarbon mixture.

6. In the process for producing naphthas from hydrocarbons having a high content of corrosive sulfur compounds wherein said hydrocarbons are subjected to vapor phase desulfurization in the presence of a desulfurizing catalyst at a temperature of about 700 to 800° F., the improvement comprising conducting said desulfurization reaction for a time sufficient to reduce the total sulfur content of said hydrocarbons to not more than about 0.025 weight percent and thereafter subjecting said desulfurized hydrocarbons to treatment with copper sulfate at a temperature of between about 400° to 500° F. and recovering a naphtha which is characterized by its ability to pass the Distillation-Corrosion test.

7. The process in accordance with claim 6 in which the copper sulfate-treating step is carried out at a temperature of about 450° F., at substantially atmospheric pressure, and with a space velocity of about 1.0.

8. The method in accordance with claim 6 in which the copper sulfate is in anhydrous form.

9. The method in accordance with claim 6 in which the copper sulfate contains no more than one molecule of water per molecule of copper sulfate.

10. The method in accordance with claim 6 in which the copper sulfate is in the form of a slurry with refined mineral oil.

11. In the process for producing naphthas from hydrocarbons having a high content of corrosive sulfur compounds wherein said hydrocarbons are subjected to vapor phase desulfurization in the presence of a desulfurizing catalyst at a temperature of about 700° to 800° F. and subjected to a hydroreforming reaction in the presence of an aromatization catalyst at a temperature of between about 800° to 850° F. the improvement comprising conducting the desulfurization reaction for a time sufficient to reduce the total sulfur content of said hydrocarbons to not more than about 0.025 weight percent and finally treating said desulfurized and hydroreformed hydrocarbons to treatment with substantially anhydrous copper sulfate at a temperature of about 450° F., at substantially atmospheric pressure and using a space velocity of about 1.0 to thereby recover a naphtha of increased solvency which is further characterized by its ability to pass the Distillation-Corrosion test.

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