

1

2,769,764

**METHOD FOR PRODUCING NAPHTHAS OF IMPROVED CHARACTERISTICS FROM HIGHLY REFINED NAPHTHAS BY TREATING THE HIGHLY REFINED NAPHTHAS WITH A COPPER ACETATE**

Weldon Grant Annable, Mundelein, Ill., assignor to The Pure Oil Company, Chicago, Ill., a corporation of Ohio

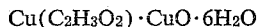
No Drawing. Application April 1, 1954, Serial No. 420,462

7 Claims. (Cl. 196—28)

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 an organo-copper compound, particularly solid cupric acetate having the formulae



and basic cupric acetate having the formulae



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 com-

2

pounds 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 certain copper compounds 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 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 percent 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. solid cupric acetate and basic cupric acetate or their mixtures 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 percent 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 point 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.

Accordingly, the present invention is primarily directed to the treatment of naphthas or hydrocarbon mixtures containing low sulfur contents in the order of 0.025 percent by weight or less of total sulfur. The total sulfur may be in the form of free sulfur or sulfur compounds or mixtures of sulfur and sulfur compounds. Crude naphthas having more than this amount of total sulfur may be treated in accordance with the invention but it is preferred that such naphthas be desulfurized prior to treatment in accordance with the instant method. The 0.025 percent total sulfur may be mercaptan sulfur only and one embodiment of the invention is directed to treating naphthas which contain substantially only sulfur compounds of this type. The chemical treatment with solid cupric acetate and basic cupric acetate or their mixtures at 400° to 500° F., in combination with prior desulfurization as described in accordance with this invention, may effect a considerable reduction in the total sulfur content of the naphthas as by as much as 90 percent, 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 sweet West Texas naphtha having a boiling range of 250° to 400° F. was subjected to vaporization and passage over solid cupric acetate at a temperature of about 450° F. under atmospheric pressure and with a space velocity of 1.0 with a 100 percent liquid recovery. The following table makes a comparison of the sulfur distribution in the charge stock, which gave a negative to borderline distillation-corrosion test, with that of the products after treatment with solid cupric acetate.

TABLE I

Sulfur Distribution	Charge	Product
Percent w.:		
Free S.....	Nil	Nil
H <sub>2</sub> S-S.....	Nil	Nil
RSH-S.....	0.013	Nil
R <sub>2</sub> S-S.....	0.002	0.002
R <sub>3</sub> S-S.....	0.006	0.017
Residual S.....	0.004	0.002
Total S.....	0.025	0.021
Amsco Test.....	Negative to Borderline.	Negative.
Doctor Test.....	Positive.....	Negative.

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, the same West Texas naphtha was used as in the previous experiment and the same reaction conditions were used. 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.

5  
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 acetate.....	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. Fullers 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 used and subjected to treatment with the organo copper compounds of the present invention 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 percent 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 percent 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 210°-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 percent sulfur, as, for example, a naphtha containing from 0.10 to as high as 7.0 percent 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

6

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 100 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 hydrotreating operation preceding the chemical treatment with cupric acetate. The hydrotreating 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. Since these processes of desulfurization and aromatization are well known and merely used as preliminary treatments for the present process, further description is unnecessary.

The contacting of naphthas with the copper treating agents in accordance with this invention may be effected in any suitable manner such as: by filtration of the naphthas through towers containing the copper reagent; by mechanical agitation of the comminuted reagent with the naphtha; or by circulation of a slurry of the reagent suspended in the naphtha. 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 or in contact with the copper treating agent using the aforementioned techniques. 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 0.2 to 100 may be used. Any of the well known percolation, fixed bed, or plural bed 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 chemical agents used herein are available commercially or may be prepared from raw materials. Copper acetate may be formed by reacting a copper salt with acetic acid. Cupric oxide or copper hydroxide may be reacted with acetic acid to form the copper acetates. Variation in the proportions of reactants influences the production of the normal or basic salt as desired. These copper salts may be used alone or in admixture as contact materials.

Although the vapor-solid contact procedures constitute an expedient method of carrying out the invention, one preferred method is to bring the naphtha in either liquid or vapor form into contact with a slurry of the copper reagent in an inert liquid. For this purpose, the inert

liquid should be unreactive and be substantially free of sulfur compounds that may upset the distillation-corrosion test. The inert liquid carrier preferably will have an initial boiling point slightly above the end point of the hydrocarbon mixture or naphtha being treated, and not exhibit an excessively high vapor pressure at temperatures between 400° and 500° F. in order that the necessity of using excessive pressures to maintain the carrier in liquid form may be avoided. The procedure used in the copper oxide slurry treatment may be used. Suitable carrier liquids for the treating agents may comprise high boiling hydrocarbons, gas oils, cracked fractions, cracked gas oil, lubricating oil distillates, residual stocks, or the various organic liquids, all of which are inert under the conditions of treatment. The contacting is continued until the desired degree of sweetening is effected, whereupon the treated product may be separated from the suspended copper reagent either by settling or filtration.

Upon completion of the treatment with copper acetate, 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. After treatment with the copper acetate, the naphtha is washed free of the organic by-products by use of a water wash and any copper sulfide by-product formed may be reclaimed by roasting at temperatures of 1100° to 1300° F. to convert this material to copper oxide. Following this, the treating agent is subjected to reaction with acetic acid in concentrated form to reform the copper acetate. In most instances, it will be found that a given quantity of copper acetate can be economically used for some time to successfully treat naphthas and may be discarded to save the cost of regeneration.

As an alternative procedure, the copper treating agents may be used admixed with an inert carrier to insure intimate contact and simplify handling. The treating agents may be added to such inert carriers as silica, bauxite, pumice, active carbon, alumina, etc., by simple mixing or impregnation. Although the invention has been demonstrated by specific embodiments, the only limitations thereon appear in the appended claims.

What is claimed is:

1. The method of producing special solvent naphthas from highly refined petroleum hydrocarbon mixtures containing small amounts of total sulfur of not more than about 0.025 weight percent which comprises subjecting said hydrocarbon mixtures to contact with a material selected from the group consisting of cupric acetate and basic cupric acetate and their mixtures at temperatures of about 400 to 500° F. and separating special solvent naphthas therefrom characterized by their ability to pass the distillation-corrosion test.
2. The method in accordance with claim 1 in which the contact material is cupric acetate.
3. The method in accordance with claim 1 in which the contact material is basic cupric acetate.
4. The process in accordance with claim 1 in which the contacting is carried out at a temperature of about 450° F., at substantially atmospheric pressure, and with a space velocity of about 1.0.
5. The method in accordance with claim 1 in which the contact material is cupric acetate supported on an inert carrier in an amount such that the copper content of the total mass is less than about 10 per cent.
6. The method in accordance with claim 1 in which the contact material is basic cupric acetate supported on an inert carrier in an amount such that the copper content of the total mass is less than about 10 per cent.
7. The method in accordance with claim 1 in which said highly refined petroleum hydrocarbon mixtures are obtained by catalytic desulfurization of hydrocarbon mixtures containing a high content of sulfur compounds in the presence of a desulfurization catalyst at a temperature of about 700° to 800° F.

References Cited in the file of this patent  
UNITED STATES PATENTS

1,768,683	Gray	July 1, 1930
1,825,861	Gray	Oct. 6, 1931
2,467,429	Hoover	Apr. 19, 1949