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METHOD FOR PRODUCING SPECIAL NAPHTHAS OF IMPROVED CHARACTERISTICS BY CONTACTING A REFINED NAPHTHA WITH SILVER MOLYBDATE AT ELEVATED TEMPERATURE

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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 at a temperature of about 400° to 500° F.

Crude petroleum has long been the source of widely known products including gasoline, kerosine, 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 certain silver 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 transformed and there take 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 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. silver molybdate 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 agent, 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 af 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 above 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.

Accordingly, the present invention is primarily directed to the treatment of naphthas or hydrocarbon mixtures containing sulfur contents in the order of about 0.16 percent by weight or less of total sulfur. The total sulfur may comprise elemental sulfur or sulfur compounds or mixtures of sulfur and one or more types of 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 previously desulfurized to bring the sulfur content down to 0.16% or to as low as 0.025 percent or less total sulfur. The 0.025 percent total sulfur may be mercaptan sulfur only and one embodiment of the invention comprises the treatment of naphthas containing substantially only mercaptan sulfur compounds. The chemical treatment with silver molybdate 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.

To illustrate the invention, a sour, corrosive, West Texas naphtha having a boiling range of 100° to 400° F. containing 0.158 percent total sulfur was passed through a treating agent, consisting of silver molybdate supported on alumina, at 450° F., substantially atmospheric pressure, and a space velocity of about 1.0. Analyses of the corrosive naphtha charged and the non-corrosive naphtha produced were as follows:

TABLE I

The production of non-corrosive naphthas using silver molybdate

Sulfur Distribution	Charge	Product
Free—S, Percent W	Nil	Nil
H_2S—S, Percent W	Nil	Nil
RSH—S, Percent W	0.019	Nil
R_2S_2—S, Percent W	0.052	Nil
R_2S—S, Percent W	0.080	0.030
Residual S, Percent W	0.007	0.017
Total—S, Percent W	0.158	0.047
Doctor Test	Positive	Negative
Distillation-Corrosion Test	Positive	Negative

The product was of good color and odor and was non-corrosive when subjected to the critical distillation-corrosion test. The products from this treatment may be fractionated into the various specialty naphthas desired.

Although the invention in its broadest aspects is not to be limited to the treatment of hydrocarbons containing any particular amount or kind of sulfur compounds, some explanation of the relationship of sulfur content and severity of treatment is in order. As previously explained, prior art high temperature desulfurization processes, although greatly reducing the sulfur contents of the products, leave therein those types of sulfur compounds which give a positive distillation-corrosion test.

Naphthas containing about 0.16 wt. percent sulfur are considered to be high sulfur naphthas which are ordinarily difficult to desulfurize by prior art methods. By maintaining the temperature at between about 400–500° F. using silver molybdate as the treating material, no hydrogen sulfide will appear in the product and a successful treatment is obtained. This is also true of the hydrocarbon mixtures containing greater amounts of

sulfur provided the teachings of this invention are followed. Thus by treating a fraction containing as much as 2.0% of sulfur if the temperature does not exceed 500° F., no hydrogen sulfide will appear and a non-corrosive product will be formed. In those instances where hydrogen sulfide is formed, the reaction must be terminated before hydrogen sulfide appears, otherwise a product exhibiting a negative distillation-corrosion test cannot be obtained. If temperatures above 500° F. and as high as 750° F. are used, successful treatment is impossible not only because of the appearance of hydrogen sulfide which forms corrosive sulfur compounds in the products, but because of the general nature of the remaining sulfur compounds, especially a small amount of mercaptans inevitably present. Thus even if the prior art methods of desulfurization at temperatures above 500° F. wherein the reaction is terminated before the appearance of a substantial amount of hydrogen sulfide in the products are used, the results of this invention will not be obtained.

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 experiments 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.

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. Silver molybdate	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 used and subjected to treatment with silver molybdate at 400° to 500° F. wherein the objective is to overcome the tendency of the product toward the formation of 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. Although the present process may be applied to products boiling up to 700° F. with adequate results as far as desulfurization is concerned, for those materials boiling over 400° F. the distillation-corrosion test is not applied and only those products boiling under 400° F. must meet this severe test. Products boiling above 400° F. must meet this severe test. Products boiling above 400° F. must pass the less severe immersion corrosion tests. Accordingly, to prolong the life of the treating agents, it is preferred that the more volatile components and the high boiling residues or products boiling above about 400° F. that are present be removed by fractionation or other methods prior to treatment in accordance with the invention. As another example, a crude oil containing from 1.0 to 3.0 or as high as 7.0 weight percent of sulfur may be fractionated to obtain a wide boiling range virgin or straight-run naphtha having an end boiling point of about 500° F. which may be treated in accordance with the invention. A gas oil fraction may be used which may boil between about 500° and 700° F. Kerosine fractions may also be used. Preferably a straight-run naphtha fraction having up to 0.16 percent of total sulfur and boiling between 110° and 450° F. or a previously desulfurized fraction having 0.05 percent sulfur, especially as mercaptan sulfur, is treated in accordance with this invention.

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 0.16 percent sulfur, as, for example, a naphtha containing from 0.20 to as high as 7.0 percent total 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.

Although preferred treating conditions for low sulfur naphthas are temperatures of about 450° F., pressures approximately atmospheric, and space velocities around 1.0, operation in general may be carried out at temperatures between about 400° and 500° F., super- or sub-atmospheric pressures, and space velocities between about 0.2 and 10. In another variation of the process to produce non-corrosive naphthas by treatment with silver molybdate, treatment under the less severe conditions also may be used as the second step of an over-all process wherein the first step is a desulfurization carried out with either silver molybdate as the catalyst or with a different catalyst, as mentioned above, known for the purpose. The preferred treating agent is co-precipitated silver molybdate and alumina, and may be regenerated by heating at temperatures between 900° and 1500° F. to reduce the sulfur content to below 1 percent.

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 silver molybdate. 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. Since these processes of desulfurization and aromatization are well known and merely used as preliminary treatments for the present process, further description is unnecessary.

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 silver 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 silver 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 10 may be used. Any of the well known percolation, fixed bed, fluidized reaction zone, 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.

Silver molybdate is available commercially or may be prepared from raw materials. Silver molybdate may be formed by reaction of a water-soluble silver salt, such as silver nitrate, silver acetate, silver salicylate, silver fluoride, silver perchlorate, with ammonium molybdate. It is preferred that the silver treating agents be used with a carrier to insure intimate contact and simplify handling. Such carriers as silica, bauxite, titania, zirconia, chromia, kieselguhr, bentonite, activated carbon, clays, pumice, and alumina may be used. The various well known co-precipitation, separate precipitation, impregnation, and simple mixing processes may be used to prepare the silver compound and inert carrier for use in the process. In general between about 5 to 10% by weight of silver is the desired amount to be incorporated with the carrier. Calculated as silver molybdate the amount will be correspondingly higher.

Upon completion of the treatment with silver molybdate, the products may sometimes have a slight acrid odor. The odor may be removed by caustic wash since it is apparently due to a trace of sulfur dioxide. The used treating material may be regenerated by passing an oxygen-containing gas through the bed of material at 1100° to 1300° F. The methods of regeneration described in United States Patents 2,506,552, 2,506,545, and 2,506,542 as applicable to spent contact masses of this type may be used. The term "space velocity" as used herein may be defined as the liquid volumes of feed per unit of time per unit volume of reactor.

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 0.16% by weight which comprises subjecting said hydrocarbon mixtures to contact with silver molybdate at a temperature 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 temperature of contact is about 450° F.

3. The method in accordance with claim 1 in which the petroleum hydrocarbon mixture comprises a straight-run naphtha containing up to about 0.16 weight percent of total sulfur.

4. The method in accordance with claim 1 in which the petroleum hydrocarbon mixture comprises a straight-run naphtha containing up to about 0.025 weight percent of mercaptan sulfur.

5. The method in accordance with claim 1 in which the silver molybdate is supported on alumina in an amount of about 5 to 10% by weight of silver based on the total weight of alumina.

6. The method in accordance with claim 1 in which the hydrocarbon mixtures to be treated are obtained from crude naphthas containing more than about 0.16 weight percent of total sulfur and said crude naphthas are desulfurized at temperatures between about 700 to 800° F. in the presence of a desulfurizing catalyst prior to treatment with said silver molybdate.

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