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PREVENTION OF SOURNESS OF SWEET NAPHTHAS DURING DISTILLATION BY DISTILLING IN THE PRESENCE OF AN ALKYLENE OXIDE AND A SALT OF AN ORGANIC ACID

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This invention relates to the preparation of industrial naphthas. It is more specifically concerned with the distillation of a sulfur-containing hydrocarbon mixture which is susceptible to the formation of corrosive sulfur compounds at the elevated temperatures encountered in the distillation process.

The inherent qualities and advantages of naphthas, such as non-toxicity, good solvent properties, low cost, and availability, permit the application of these substances in many industrial services. Naphthas are generally defined as "selected fractions of the lighter, more volatile constituents of crude petroleum chemically refined and separated into various boiling ranges." Although highly aromatic petroleum naphthas are readily available, the subject invention is only concerned with straight-run petroleum naphthas or equivalent hydrocarbon mixtures.

Although naphthas consist essentially of mixtures of low-boiling hydrocarbons, there are present in the crude oils from which these hydrocarbon mixtures are derived various impurities which are retained in the distillates during the fractional distillation of the crude. The nature of these impurities varies and includes, among others, organic and inorganic acids, nitrogen compounds, and sulfur compounds. Because of the relatively high-boiling range of most of these materials, they are found only in the heavier petroleum distillates. However, boiling within the naphtha range are a number of sulfur compounds whose presence is deleterious because they impart to the naphtha distillate certain undesirable odors as well as corrosive properties which cause metal corrosion or the darkening of paints or varnishes. Specific applications of naphtha compositions make it necessary to refine naphthas in order to control their properties and insure uniform quality. As was pointed out in the definition of a naphtha, naphtha preparation processes generally involve chemical refining followed by distillation of the chemically treated product to produce naphthas having a selected boiling range. Although refining processes are available, which remove substantial amounts of obnoxious sulfur compounds from admixture with hydrocarbons, these processes generally do not reduce the sulfur content sufficiently to produce a non-corrosive and substantially odor-free naphtha. In the refining of petroleum naphthas, processes referred to as "sweetening" processes are employed in which the objectionable sulfur compounds, such as mercaptans, are converted or transformed into acceptable ones without altering the sulfur content of the oil. The presence of the less noisome sulfur compounds does not affect the usefulness of the naphthas as industrial products as long as these sulfur compounds are non-corrosive and substantially odor-free. Examples of suitable processes which are employed in the "sweetening" of light petroleum products are the doctor-treat using sodium plumbite, the hypochlorite treatment, and treating methods employing copper-containing reagents, such as copper chloride or copper oxide. Other suitable "sweetening" processes are comprehensively discussed by V. A. Kalichevsky in a series of articles entitled "Sweetening and desulfurization of light petroleum products," Petroleum Refiner, 30, (1951).

There are a variety of processes which may be employed as the complementary fractionation step in the naphtha preparation process. In some instances, such as the vapor-phase treatment of petroleum distillates with copper oxide-oil slurries, the treated vaporous distillate is reintroduced into the crude oil distillation tower and recovered as a conventional side-stream cut. Other recovery processes employ special naphtha re-run units in which the naphtha is fractionated in a separate fractionating system. Where particularly close boiling-range fractions are desired with a minimum overlap of boiling ranges, superfractionators having a large number of plates are employed. In units of this nature, due to the height of a column necessary to accommodate the large number of plates, the column is split into two sections with the overhead from the first section passing into the base of the second section. Reflux from the second section is returned to the top of the first section. Regardless of the combination of refining and distillation processes employed, these sequential steps occur in naphtha preparation processes. As a result, it has been found that even though the chemical refining step produces a naphtha free from objectionable sulfur compounds by converting them to relatively innocuous organic sulfides or disulfides, the elevated temperatures employed in subsequent distillation steps cause the reconversion of the unharmful sulfur compounds into noxious sulfur compounds which are corrosive and odorous. This problem is particularly prevalent in the preparation of naphthas which contain components boiling above about 300° F. However, this condition may also occur in the treatment of the lower-boiling naphthas because even though special designs are employed in order to avoid excess skin temperatures on the walls of the fractionation columns, high temperatures which facilitate the conversion of the organic sulfide or disulfides into undesirable sulfur compounds frequently are encountered. As a result, the naphtha products produced in this manner containing these obnoxious sulfur compounds do not conform to established specifications relative to the presence of corrosive and odorous sulfur-containing materials.

A number of tests have been devised as criteria to determine the effect of sulfur and sulfur compounds in naphtha. These tests, which are qualitative in nature, include the copper strip corrosion test, the doctor test, and the distillation corrosion test. This latter test is also variously known as the Amsco corrosion test, the full flask distillation test, or the full corrosion test. These tests are standards in the petroleum industry and are described in an article entitled "Effect of sulfur and sulfur compounds in naphtha upon certain corrosion tests," L. M. Henderson et al., Industrial and Engineering Chemistry, Analytical Edition, 12 (1), 1 et seq. The distillation corrosion test is particularly severe as compared with other corrosion tests used in the petroleum industry, and there is no correlation between the results of this test and those of other corrosion tests. The naphtha products which in the course of the distillation step are transformed into off-specification products with regard to these tests, cannot be repurified by a simple washing of the distillate with an aqueous solution of caustic soda and it is necessary to re-treat the contaminated distillate in a "sweetening" process. This, of course, is uneconomical and unsatisfactory refining practice. However, according to this invention it has been found that by carrying out the distillation step in the presence of a stablizer, the undesirable deterioration of the organic sulfides or disulfides is prevented and the development of the undesirable properties avoided. It is therefore an object of this

invention to provide a method for stabilizing "sweetened" hydrocarbon distillates during distillation. It is another object of this invention to provide a method for preventing the development of odor or corrosiveness in "sweetened" petroleum liquids during distillation. These and other objects and advantages will be made more apparent from the following detailed description of this invention.

According to this invention it has been found that if the distillation of a "sweetened" hydrocarbon mixture containing petroleum sulfur compounds, including disulfides, is carried out in the presence of an alkylene oxide and an oil-soluble basic salt of a high molecular weight organic acid, not reactive with the alkylene oxide, a satisfactory noncorrosive product as determined by the aforementioned test methods will be obtained without requiring additional treating for the removal or conversion of obnoxious sulfur compounds. The essence of the invention is shown by the following illustrative but nonlimiting examples in which a petroleum naphtha distillate was first sweetened by contacting the distillate with an admixture of finely divided fuller's earth and cupric chloride using the Linde Sweetening Process. The admixture was agitated until the petroleum distillate was made "doctor sweet." The sweetened petroleum distillate was recovered and separated into a plurality of 100 ml. portions, which were then subjected to the standard ASTM distillation test. Each distillation was carried out employing a different additive combination admixed with the distillate charged to the distllaton flask. A series of 10 ml. fractions were taken for each distillate, each fraction being subjected to the scrutiny of the doctor test. The data obtained in these distillations are listed in Table 1. The naphtha which was treated was from a mixture of sour and sweet crudes and had the following characteristics:

Distillation

I. B. P.	5%	50%	95%	E. P.
111° F.	136° F.	260° F.	392° F.	414° F.

Sulfur distribution, percent weight

Sulfur, total	0.077
Sulfur, free	0.008
Sulfur, H_2S	None
Sulfur, RSH	0.030
Sulfur, R_2S_2	0.004
Sulfur, R_2S	0.028
Sulfur, resid	0.007

um distillates. In these sweetening processes no correlation is required between the boiling range of the distillate being treated and the boiling point of the alkylene oxide treating agent. However, according to the instant invention, it has been found that in order to effectuate the objectives of this invention, it is necessary to employ an alkylene oxide having a boiling point at least as high as the end boiling point of the naphtha fraction being distilled. This requirement is seen from the data in Table 1 wherein it is shown that neither ethylene oxide (B. P. 51° F.) nor propylene oxide (B. P. 95° F.) provides the advantages that are obtained when an alkylene oxide, viz., dodecene epoxide (B. P. 520° F.) having the aforementioned boiling point characteristics is employed. The data also shows that it is necessary to employ the combination treating agent of this invention as it is shown that the constituents of the composite, when used separately, are not effective.

The alkylene oxide which is added to the sulfur-containing hydrocarbon distillate prior to fractionation can be any alkylene oxide having a boiling point at least as high as the end boiling point of the naphtha being distilled. Specific examples of useful alkylene oxides include but are not limited to aliphatic alkylene oxides having suitable boiling points, as well as derivatives thereof, such as epoxides of unsaturated fatty acid esters, e. g. methyl oleate; epoxides of unsaturated hydroxy acid esters, e. g. methyl ricinoleate; epoxides of unsaturated alcohols, e. g., 2-octen-1-ol; epoxides of unsaturated branched chain hydrocarbons, e. g. diisobutylene, triisobutylene and tetraisobutylene; epoxides of alicyclic olefins, e. g. α-pinene; epoxides of arylalkenes, e. g. styrene.

In carrying out this invention the amount of alkylene oxide which should be present in the distillation zone while conducting the preparation of the special naphthas will depend upon the amount of sulfur compounds which are contained in the distillate undergoing distillation. In treating conventionally "sweetened" petroleum distillates, between about 1.0 to 3.0 weight percent of alkylene oxide stabilizer should be used. The optimum quantity, however, should be determined experimentally by making tests on samples of the naphtha which are to be subjected to processing in the distillation unit. In some instances as much as 5% may be necessary but in others the presence of amounts as low as 0.5% sometimes may be effective.

The basic salt which is employed as an essential part of the distillation additive combination may be any oil-soluble basic salt of an organic acid, having a positive base number, which is non-reactive with alkylene oxide and has a boiling point at least as high as the end boiling

TABLE 1

Run Number	Material Added to Charge Naphtha	Volume Percent Overhead: 10	20	30	40	50	60	70	80	90	95	First Doctor Sour Cut
		Overhead Temperature at Cut Point (°F.)										
1	None	144	169	196	214	235	250	275	286	334	------	7(250-275)
2	Ethylene Oxide	167	183	194	226	241	259	282	289	------	------	7(259-282)
3	Bentonite plus Ethylene Oxide	151	190	212	250	270	284	304	322	------	------	7(284-304)
4	2 ml. Dodecene Epoxide	156	178	205	221	234	270	295	------	------	------	7(270-295)
5	1.2 g. Barium Sulfonate [1]	151	183	201	216	226	262	275	------	------	------	7(262-275)
6	2 ml. Dodecene Epoxide plus 1.9 g. Barium Sulfonate [1]	158	189	205	230	255	271	309	329	356	363	9(329-356)
7	1.2 g. Barium Sulfonate plus Propylene Oxide	164	198	216	234	250	270	302	324	352	------	6(250-270)
8	Ethylene Oxide plus 1.2 g. Barium Sulfonate	------	------	------	------	254	286	326	349	375	------	6(254-286)

[1] Basic oil-soluble barium sulfonate containing 12.7% ash as sulfate and having a 30 base number, prepared by sulfonating a medium neutral oil followed by reacting the sulfonated oil with excess barium hydroxide.

The tabular summary in Table 1 shows the various cut points at which the distillate went off specification with regard to the doctor test used as the criterion and illustrates the unusualness of the instant invention. The prior art in U. S. Patents 2,530,561 and 2,575,989 discuss the effectiveness of ethylene oxide alone or in combination with an alkaline catalyst for sweetening petroleum distillates. In these sweetening processes no correlation is required between the boiling range of the distillate being treated and the boiling point of the alkylene oxide treating agent. However, according to the instant invention, it has been found that in order to effectuate the objectives of this invention, it is necessary to employ an alkylene oxide having a boiling point at least as high as the end boiling point of the naphtha fraction being distilled. This requirement is seen from the data in Table 1 wherein it is shown that neither ethylene oxide (B. P. 51° F.) nor propylene oxide (B. P. 95° F.) provides the advantages that are obtained when an alkylene oxide, viz., dodecene epoxide (B. P. 520° F.) having the aforementioned boiling point characteristics is employed. The data also shows that it is necessary to employ the combination treating agent of this invention as it is shown that the constituents of the composite, when used separately, are not effective.

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In carrying out this invention the amount of alkylene oxide which should be present in the distillation zone while conducting the preparation of the special naphthas will depend upon the amount of sulfur compounds which are contained in the distillate undergoing distillation. In treating conventionally "sweetened" petroleum distillates, between about 1.0 to 3.0 weight percent of alkylene oxide stabilizer should be used. The optimum quantity, however, should be determined experimentally by making tests on samples of the naphtha which are to be subjected to processing in the distillation unit. In some instances as much as 5% may be necessary but in others the presence of amounts as low as 0.5% sometimes may be effective.

The basic salt which is employed as an essential part of the distillation additive combination may be any oil-soluble basic salt of an organic acid, having a positive base number, which is non-reactive with alkylene oxide and has a boiling point at least as high as the end boiling range of the naphtha distillate being fractionally distilled. This constituent is defined in the appended claims as a "basic salt of a high molecular weight organic acid." The use of such oil-soluble basic salts constitutes an essential part of the subject invention because a uniform and complete distribution of the additive combination in the hydrocarbon fraction can be effected, the hydrocarbon frac-

tion is not subjected to contact with any extraneous immiscible alkali solutions which require subsequent treatment steps, the unsatisfactory distillation of heterogeneous admixtures produced by the presence of an aqueous phase is avoided, and minimum amounts of basic materials are employed. Examples of suitable basic salts of high molecular weight organic acids which may be employed as a constituent of the additive combination include the oil-soluble alkali and alkaline earth metal salts of naphthenic acids, sulfonic acids, and high molecular weight fatty acids. Specific basic compounds which may be employed include sodium naphthenate, barium naphthenate, sodium petroleum sulfonate, calcium oleate, magnesium stearate, potassium naphthalene sulfonate, etc. Salts of petroleum sulfonates are preferred, especially barium and calcium salts.

In formulating the composite distillation additive of this invention the amount of the basic salt employed will depend upon the character of the oil being treated, as well as the nature and concentration of the sulfur compounds present. It is preferable to employ from about 1.0 to 5.0%, by weight, and preferably 1.0–2.0%, by weight, of the basic constituent, based on the naphtha. Although the illustrative examples of this invention describe the use of a batch-wise distillation process, the instant invention may be carried out continuously. In the event that the former technique is employed, the composite additive is admixed with the naphtha charge and the distillation effected. It is preferred, however, that the distillation process be carried out continuously, in which instance the necessary amounts of composite additive may be introduced into and admixed with the incoming feed.

Another important feature of the instant invention is illustrated by the condition of the still pot after the batch distillation has been substantially completed. In employing the instant invention the residue remaining in the still pot even after about 95% by volume or more of the original charge has been distilled is a clear, mild smelling liquid as opposed to the extremely odorous and adherent black solid material which remains in the still pot after a conventional batch fractional distillation has been effected. Accordingly, the use of this invention eliminates a cleaning and disposal problem of noxious still-pot residues normally remaining in a fractional distillation unit after a sulfur-containing hydrocarbon fraction has been distilled.

The invention is broadly directed to the production of high quality naphthas and provides an improved method of distilling "doctor sweet" naphthas whereby increased yields of higher boiling, sweet distillates are obtained without further treating. Sweetened sulfur-containing hydrocarbon fractions boiling between about 100° F. and 500° F. may be treated in accordance with this invention. However, the invention has particular application in the treatment of straight-run, aliphatic petroleum distillates boiling between about 100° F. and 400° F. In carrying out the instant invention it is not necessary that the distillation effluent be further treated in order to provide a satisfactory non-corrosive product.

We claim as our invention:

1. In the distillation of an oxidatively sweetened hydrocarbon fraction containing organic sulfur compounds, including disulfides, at temperatures normally effective for the conversion of said compounds to produce doctor-positive products, the improvement which comprises carrying out the distillation in the presence of sufficient amounts of an admixture of an alkylene oxide having a boiling point at least about as high as the end boiling point of said fraction and an oil-soluble, basic salt of a high molecular weight organic acid to prevent said conversion and the development of a doctor-positive distillation effluent.

2. A distillation in accordance with claim 1 in which said basic salt is an alkaline earth metal sulfonate.

3. A distillation in accordance with claim 2 in which said basic salt is barium petroleum sulfonate.

4. In the distillation of an oxidatively sweetened hydrocarbon fraction containing organic sulfur compounds, including disulfides, at temperatures normally effective for the conversion of said compounds to produce doctor-positive products, the improvement which comprises carrying out the distillation in the presence of 0.5–5% by weight, based on the charge of said fraction, of an alkylene oxide having a boiling point at least about as high as the end boiling point of said fraction, and 1–5% by weight, based on the charge of said fraction, of an oil-soluble, basic salt of a high molecular weight organic acid to prevent said conversion and the development of a doctor-positive distillation effluent.

5. In the distillation of light petroleum distillate boiling between about 100 and 500° F., containing organic sulfur compounds, including disulfides, at temperatures normally effective for the conversion of said compounds to produce doctor-positive products, the improvement which comprises carrying out the distillation in the presence of 0.5–5% by weight, based on the charge of said distillate, of an admixture of an alkylene oxide having a boiling point at least about as high as the end boiling point of said fraction, and 1–5% by weight, based on the charge of said distillate, of an oil-soluble, basic salt of a high molecular weight organic acid to prevent said conversion and the development of a doctor-positive distillation effluent.

6. A sweetening process for producing doctor-sweet petroleum naphtha distillate which comprises contacting a doctor-positive, sulfur-containing, light petroleum distillate in an oxidative sweetening process under conditions to produce a doctor-negative petroleum distillate containing organic sulfur compounds, including disulfides, distilling said doctor-negative petroleum distillate, at temperatures normally effective for the conversion of said sulfur compounds to produce doctor-positive products, in the presence of 0.5–5% by weight, based on the charge of said distillate, of an admixture of an alkylene oxide, having a boiling point at least about as high as the end boiling point of said fraction, and 1–5% by weight, based on the charge of said distillate, of an oil-soluble, basic salt of a high molecular weight organic acid to prevent said conversion and the development of a doctor-positive distillation effluent, and recovering doctor-negative distillate products.

7. A method for fractionally distilling an oxidatively sweetened petroleum naphtha containing organic disulfides susceptible to decomposition under distillation conditions which comprise fractionally distilling said naphtha in the presence of 0.5–5% by weight, based on the naphtha charge of dodecene epoxide and 1–5% by weight, based on the naphtha charge, of basic barium petroleum sulfonate to prevent the decomposition of said disulfides and the development of a doctor-positive distillation effluent.

8. In the thermal treatment of oxidatively sweetened hydrocarbon fractions containing organic compounds, including disulfides, at temperatures effective for the decomposition of said organic compounds, the improvement which comprises carrying out the thermal treatment in the presence of sufficient amounts of an alkylene oxide having a boiling point at least about as high as the end boiling point of said fraction and a basic salt of a high molecular weight organic acid to prevent the decomposition of said organic compounds and the development of a doctor-positive distillation effluent.

No references cited.