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PROCESS FOR PREVENTING CORROSION DURING DISTILLATION BY ADDING AN ORGANIC PHOSPHITE

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This invention relates to the processing of a hydrocarbon admixture containing sulfur compounds which are heat-sensitive and susceptible to the formation of corrosive sulfur compounds at elevated temperatures. It is more specifically concerned with the preparation of industrial naphthas wherein an oxidatively-sweetened, petroleum fraction boiling in the naphtha range is further refined at an elevated temperature.

In the manufacture of industrial solvents from crude petroleum oils, selected fractions of the lighter, more volatile constituents of the crude petroleum are chemically refined and separated into various boiling ranges. In preparing the selected fraction there is concomitantly produced during the fractional distillation of the crude petroleum oil a variety of impurities, including undesirable sulfur compounds. A number of these sulfur compounds boiling in the naphtha range have a deleterious effect 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. It is, therefore, desirable to pretreat the naphtha distillate prior to the separation of the full boiling range naphtha into the selected fraction. Although a variety of desulfurization processes for the refining of light petroleum products are available, conventional refining techniques involve the treatment of the naphtha distillate in an oxidative-sweetening type of process in which the objectionable sulfur compounds, such as mercaptans, are converted or transformed into less noisome sulfur compounds which do not affect the usefulness of the naphthas. Examples of suitable processes which are employed in the oxidative-sweetening of light petroleum distillates include the "doctor" treat employing sodium plumbite, the hypochlorite treatment, treating methods using copper-containing reagents, such as copper chloride, or copper oxide, and other processes.

In the distillation of the crude petroleum oil any hydrogen sulfide which may have been contained in the crude oil feed stock is removed in the natural gas or in refinery off-gases. Accordingly, the objectionable sulfur compounds contained in the naphtha distillate from the standpoint of odor and corrosion are generally the mercaptans. In the oxidative-sweetening process these objectionable sulfur compounds are converted to relatively innocuous organic sulfides or disulfides. In the subsequent distillation step in which the oxidatively-sweetened naphthas are separated into fractions having various boiling ranges, depending upon the end use of the selected distillate, elevated temperatures are employed which result in the reconversion of the unharmed 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. This condition, however, can also occur in the treatment of lower-boiling naphthas or petroleum fractions, even though special designs are em-

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ployed in order to avoid excessive skin temperatures on the walls of fractionating columns or other processing vessels in which the high temperatures which produce the conversion of organic sulfide or disulfides into undesirable sulfur compounds are encountered.

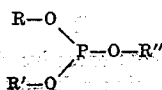
To overcome this problem a number of techniques have been developed, wherein an additive composition is introduced into the refining process, in order to prevent the conversion of the relatively innocuous organic sulfides or disulfides to the undesirable mercaptans which produce conditions of corrosion and odor. Suitable agents for this purpose include glycerin, various organic peroxides, such as tertiary butyl hydroperoxide and benzoyl peroxide, as well as compositions consisting of an admixture of an alkylene oxide and an oil-soluble basic salt of a high-molecular-weight organic acid not reactive with the alkylene oxide. According to this invention, an additional expedient has been found which will permit the treatment of oxidatively-sweetened, hydrocarbon compounds containing organic sulfur compounds, including disulfides, at temperatures normally effective for the conversion of said compounds to produce noxious sulfur compounds which have a deleterious effect on the odor and corrosiveness properties of the treated hydrocarbon fraction.

It is, therefore, an object of this invention to provide a method for the refining of oxidatively-sweetened, hydrocarbon fractions containing organic sulfur compounds, including disulfides, at elevated temperatures which would normally effect the conversion of these compounds to produce undesirable sulfur-containing products. It is another object of this invention to effect the distillation of oxidatively-sweetened, hydrocarbon fractions containing organic sulfur compounds, including disulfides, without converting the organic compounds to undesirable sulfur-containing products. It is another object of this invention to provide a method for preventing the development of odor or corrosiveness in oxidatively-sweetened petroleum liquids during distillation. These and other objects will become more apparent from the following detailed description of this invention.

According to this invention, it has been found that the refining of an oxidatively-sweetened, hydrocarbon fraction containing organic sulfur compounds, including disulfides, can be carried out at elevated temperatures normally effective for the conversion of said sulfur compounds without producing undesirable sulfur-containing products by carrying out the refining process in the presence of an added amount of a non-aromatic, oil-soluble, organic phosphite. In order to effectuate the objectives of this invention it is necessary that not less than about 0.4% by weight of organic phosphite, based on the charge of the hydrocarbon fraction, be employed.

In carrying out the process of this invention, the selected organic phosphite is added to the sulfur-containing hydrocarbon distillate prior to fractionation in the event that a batch-wise distillation process is used. This same procedure can be used if the distillation process is carried out continuously. In this instance, however, it is preferred that the necessary amounts of refining agent in the form of organic phosphite be introduced into and admixed with the incoming feed by the continuous injection of the selected phosphite before the feed stock enters the fractionating tower. The organic phosphite which is added to the sulfur-containing hydrocarbon fraction prior to or during the fractionation or refining at an elevated temperature can be any oil-soluble, non-aromatic organic phosphite having a boiling point at least as high as the end boiling point of the hydrocarbon

fraction being distilled or refined at an elevated temperature. Organic phosphites having the general formula:



where R, R', and R'' are selected from the group consisting of alkyl or alicyclic radicals having one to ten carbon atoms or more.

Suitable reagents include, but are not limited to, trimethyl phosphite, triethyl phosphite, tri-n-propyl phosphite, tri-2-propyl phosphite, tributyl phosphite, tri-isobutyl phosphite, triamyl phosphite, trihexyl phosphite, tri-2-ethylhexyl phosphite, triisooctyl phosphite, and tri-cyclohexyl phosphite. Unsymmetrical aliphatic or alicyclic phosphites, such as propyl di-n-butyl phosphite, can also be used.

To facilitate the handling of the organic phosphite treating agent employed in the process of this invention, it is preferred that the selected phosphite be a normally liquid product. In the event, however, that solid organic phosphites are available and are preferred for use, a concentrate obtained by dissolving a sufficient amount of the organic phosphite in a portion of the hydrocarbon charge being distilled or refined can be used.

The amount of organic phosphite utilized will, of course, depend upon the type of hydrocarbon fraction being treated, as well as upon the nature and concentration of the sulfur compounds. Although amounts not less than about 0.4% by weight are required to effectuate the objectives of this invention, the optimum quantity of organic phosphite is best determined experimentally by making tests on small samples obtained from the hydrocarbon fraction which is to be distilled or refined at an elevated temperature. In general, amounts up to about 1.0% by weight are effective. On the other hand, quantities as high as 5.0% by weight may be required in exceptional cases.

To illustrate the instant invention, a petroleum naphtha derived from a Mid-Continent crude, having an ASTM boiling range of about 100–400° F. was initially sweetened in an oxidative-sweetening type process by contacting it with an Attapulugus clay in the presence of cupric chloride, employing a ratio of treating agents of 10 grams 200 mesh Attapulugus clay, to 0.50 gram of cupric chloride per 700 ml. of naphtha. The treated naphtha was subjected to the well-known "doctor" test (ASTM designation D484-40) and gave a negative test. The naphtha was divided into a number of samples and these samples were redistilled at atmospheric pressure, either in the absence of or the presence of various additive materials, including the organic phosphites employed in the process of this invention. The results of these distillations are summarized in tabular form in Table I.

Table I

Volume Percent Overhead		10	20	30	40	50	60	70	80	90	95	First Doctor-sour Cut
Run No.	Material added to charge naphtha	Overhead Temperature at Cut Point (° F.)										
1.....	None.....	157	181	201	215	246	264	290	-----	-----	-----	7 (264-290)
2.....	5.0 ml. tri-n-butyl phosphite.	146	170	182	206	232	243	282	306	340	-----	9 (306-340)
3.....	Residue from Run 2	156	176	206	236	236	259	283	300	323	-----	9 (300-323)
4.....	0.5 ml. tri-n-butyl phosphite.	146	182	202	222	240	263	288	315	345	-----	9 (315-345)
6.....	0.1 ml. tri-n-butyl phosphite.	160	180	205	219	232	269	290	-----	-----	-----	6 (232-269)
8.....	5.0 ml. tri-n-butyl phosphate.	161	181	202	217	231	262	292	-----	-----	-----	6 (231-262)
10.....	5.0 ml. tri-tolyl phosphate.	163	187	208	231	249	270	290	305	-----	-----	7 (270-290)
11.....	0.3 ml. tri-butyl phosphite.	158	182	205	220	234	262	292	307	340	-----	6 (234-262)
12.....	5.0 ml. tri-phenyl phosphite.	64	181	199	221	236	266	280	292	-----	-----	6 (236-266)
13.....	0.4 ml. tri-butyl phosphite.	65	180	202	217	252	275	292	318	352	-----	9 (318-352)
5.....	Residue from Run 4	143	171	202	213	223	262	290	-----	-----	-----	6 (223-262)

The unusual or unexpected results which are produced by the process of this invention are clearly seen from a review of the data presented in Table I. It will be noted that, in the absence of a selected organic phosphite, the oxidatively-sweetened naphtha became doctor positive in the fractions that were recovered above 60 volume percent (about 270° F.); however, when a portion of the doctor negative naphtha was distilled in the presence of 5% by volume of tri-n-butyl phosphite, 80% by volume was recovered before the overhead evinced a negative test with respect to the doctor test.

In these distillations, a triaryl phosphite, a triaryl phosphate, a trialkyl phosphite and a trialkyl phosphate were utilized. However, only the trialkyl phosphite gave a beneficial result. The results shown in Table I also indicate that at least a minimum amount is required in order to produce the beneficial effect in accordance with the process of this invention. This is shown by the distillations in which 0.1 volume percent and 0.3 volume percent of tri-n-butyl phosphite were employed. In these distillations, the yields of doctor negative distillate were not increased. On the other hand, 0.4 volume percent was fully effective.

In the distillation which was carried out in the absence of an added selected organic phosphite, the residue remaining in the still after 90% by volume had been distilled was very malodorous and contained black solid material which was difficult to remove. In contradistinction, the residue remaining in the still pot wherein the distillation was carried out in the presence of 0.4 volume percent of tri-n-butyl phosphite was clear, mild smelling and a liquid, free of solid materials, which was easily handled for disposal purposes. This leads to a collateral feature of this invention. In run 3, a second portion of oxidatively-sweetened naphtha was admixed with the residue obtained in the distillation of an oxidatively-sweetened naphtha in the presence of 5 volume percent of tri-n-butyl phosphite. This admixture was distilled in the manner employed in the foregoing investigation, and the results which were obtained were identical with those of the first run. In other words, 80% by volume was taken overhead before a positive effect with respect to the doctor test was evinced in the distillation effluent. Therefore, if desired, the initial amount of selected organic phosphite employed in a batch distillation process can be utilized for more than one distillation.

It is necessary when re-using the still pot residue to employ a large excess of phosphite in the first run (see run 5). In a continuous distillation, the best procedure would be to feed the minimum effective amount of phosphite continuously.

Although the subject invention is especially adaptable to the production of industrial naphthas by the distillation of an oxidatively-sweetened, full-boiling-range naph-

tha or naphtha fraction, the invention has application in the refining or distillation of other light petroleum distillates boiling up to about 750° F. at atmospheric pressure, which have been previously oxidatively-sweetened. These include the light distillates, such as industrial petroleum naphthas and solvents; gasoline-type motor fuels and motor fuel blending components; kerosenes, etc.; and the middle distillates, such as diesel fuels, heater and furnace oils, etc., which are subjected to elevated temperatures whereby the sulfur constituents of the hydrocarbon fraction are decomposed to form sulfur compound which impart undesirable odor and corrosive properties to the fraction. Although the foregoing illustrative example has been directed to the use of the instant invention in a batch-wise distillation process, it is evident that the invention has application in the treatment of sulfur-containing hydrocarbon fractions in refining processes which are carried out at elevated temperatures conducive to the decomposition of the sulfur compounds contained in said fraction to produce undesirable sulfur-containing products. Accordingly, a number of modifications and variations of the instant invention can be made by those skilled in the art to which this invention pertains without departing from the scope of this invention as defined in the appended claims.

Accordingly, we claim as our invention:

1. In the fractional distillation of an oxidatively-sweetened, hydrocarbon fraction boiling within the naphtha boiling range and containing organic sulfur compounds, including disulfides, at an elevated temperature normally effective for the conversion of said compounds to produce doctor-positive products, the improvements wherein said conversion is minimized which comprises carrying out the distillation at said temperature in the presence of an added amount of an oil-soluble, saturated organic phosphite from the group consisting of alkyl and cycloalkyl phosphites and having a boiling point at least as high as the end boiling point of the hydrocarbon fraction being distilled, the amount of said organic phosphite being not less than about 0.4% by weight, based on the amount of said hydrocarbon fraction being fractionally distilled.

2. In the fraction distillation of an oxidatively-sweetened, hydrocarbon fraction boiling within the naphtha boiling range and containing organic sulfur compounds, including disulfides, at an elevated temperature normally effective for the conversion of said compounds to produce doctor-positive products, the improvement wherein said conversion is minimized which comprises carrying out the distillation at said temperature in the presence of an added amount of an oil-soluble, saturated organic phosphite from the group consisting of alkyl and cycloalkyl phosphites and having a boiling point at least as high as the end boiling point of the hydrocarbon fraction being distilled, the amount of said organic phosphite being about 0.4–1% by weight, based on the amount of said hydrocarbon fraction being fractionally distilled.

3. In the distillation of an oxidatively-sweetened, hydrocarbon fraction boiling within the naphtha boiling range and containing organic sulfur compounds, including disulfides, at an elevated temperature normally effective for the conversion of said compounds to produce doctor-positive products, the improvements wherein said conversion is minimized which comprises carrying out the distillation at said temperature in the presence of an added amount of an oil-soluble, alkyl phosphite having a boiling point at least as high as the end point of the hydrocarbon fraction being distilled, the amount of said organic phosphite being not less than about 0.4% by weight, based on the amount of said hydrocarbon fraction being distilled.

4. In the fractional distillation of an oxidatively-sweetened hydrocarbon fraction boiling within the naphtha boiling range and containing organic sulfur com-

pounds, including disulfides at an elevated temperature normally effective for the conversion of said compounds to produce doctor-positive products, the improvement wherein said conversion is minimized which comprises carrying out the fractional distillation at said temperature in the presence of an added amount of an oil-soluble, alkyl, phosphite having a boiling point at least as high as the end boiling point of the hydrocarbon fraction being fractionally distilled, the amount of said aliphatic phosphite being within the range of about 0.4–1% by weight of the amount of hydrocarbon fraction being distilled.

5. In a fractional distillation process in accordance with claim 4 in which said alkyl phosphite is tributyl phosphite.

6. In the fractional distillation of an oxidatively-sweetened, hydrocarbon fraction boiling within the naphtha boiling range and containing organic sulfur compounds, including disulfides, at an elevated temperature normally effective for the conversion of said compounds to produce doctor-positive products, said fraction having been oxidatively-sweetened in a copper chloride sweetening process, the improvement wherein said conversion is minimized which comprises carrying out the distillation at said temperature in the presence of an added amount of an oil-soluble, saturated organic phosphite from the group consisting of alkyl and cycloalkyl phosphites and having a boiling point at least as high as the end boiling point of the hydrocarbon fraction being distilled, the amount of said organic phosphite being not less than about 0.4% by weight, based on the amount of said hydrocarbon fraction being fractionally distilled.

7. In the fractional distillation of an oxidatively-sweetened, hydrocarbon fraction boiling within the naphtha boiling range and containing organic sulfur compounds, including disulfides, at an elevated temperature normally effective for the conversion of said compounds to produce doctor positive products, said fraction having been oxidatively sweetened in a copper chloride sweetening process, the improvement wherein said conversion is minimized which comprises carrying out the fractional distillation at said temperature in the presence of an added amount of an oil-soluble, alkyl phosphite having a boiling point at least as high as the end boiling point of the hydrocarbon fraction being fractionally distilled, the amount of said alkyl phosphite being within the range of about 0.4–1% by weight of the amount of hydrocarbon fraction being distilled.

8. In a fractional distillation process in accordance with claim 7 in which said alkyl phosphite is tributyl phosphite.

9. In the fractional distillation of a hydrocarbon fraction boiling within the naphtha boiling range and oxidatively sweetened by contact with an admixture of copper chloride and an acid treated, montmorillonite type clay whereby there is produced a doctor-sweet hydrocarbon fraction containing organic sulfur compounds, including disulfides, susceptible to decomposition at an elevated temperature, the improvement which comprises carrying out the fractional distillation at an elevated temperature in the presence of an added amount of an oil-soluble, saturated phosphite from the group consisting of alkyl and cycloalkyl phosphites and having a boiling point at least as high as the end boiling point of the hydrocarbon fraction being fractionally distilled, the amount of said organic phosphite being within the range of about 0.4–1% by weight of said hydrocarbon fraction.

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