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PRODUCTION OF DOCTOR-SWEET NON-CORROSIVE NAPHTHAS

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This invention relates to a method for preparing improved petroleum naphthas and more particularly to production of naphthas which are doctor-sweet and give a negative full-flask distillation-corrosion test.

The naphthas prepared by this invention are those produced from crude petroleum oils and boil within the range of about 200° F. to about 450° F.

A major problem in the commercial preparation of naphthas has been the sour and corrosive characteristics of the naphthas derived from the distillation of crude petroleum because of the presence of certain undesirable mercaptans, sulfides and free sulfur. The industry has developed various tests to determine the sourness and corrosive effect of dissolved mercaptans, free sulfur or sulfur compounds present in said naphthas produced. Among the most common tests are the doctor test, copper-strip corrosion test and the distillation-corrosion test. The doctor test and the copper-strip test are widely used throughout the petroleum industry and have been provided with ASTM designations D484 and D130, respectively, and descriptions thereof may be found in the publication "ASTM Standards on Petroleum Products and Lubricants." The distillation-corrosion test is to be found in an article by L. M. Henderson et al., entitled, "The Effect of Sulfur and Sulfur Compounds in Naphtha Upon Certain Corrosion Tests," Industrial Engineering Chemistry, Analytical Edition, 12, (1) 1. The test in essence employs a modification of the standard method of test for distillation of gasoline, naphtha, kerosene and similar petroleum products, ASTM designation D86, wherein a clean strip of polished pure sheet copper about ½" x 3" and of sufficient thickness to stand lengthwise without buckling, is placed in the regulation distilling flask and exactly 100 cc. of the naphtha to be tested is placed therein. The naphtha sample is distilled in accordance with the manner prescribed in the foregoing ASTM distillation test D86, the strip remaining in the flask during the entire distillation. At the completion of the distillation, the copper strip is allowed to cool in the flask to room temperature before it is taken from the apparatus. In the interpretation of the results of this distillation-corrosion test a slight tarnish on the copper strip does not indicate that the material has not satisfactorily met the test. However, any marked blackening of the copper strip means that the material is unsatisfactory. In accordance with the condition of the copper strip, if the naphtha tested is not corrosive, the result is reported as "negative," and if it is corrosive, the result is reported as "positive."

Many processes have been developed for the sweetening of sour naphthas, such as the Linde process involving oxidation with oxygen in the presence of clay impregnated with cupric chloride. However, a wide-naphtha-cut stock sweetened by a conventional process, such as the Linde process, usually contains sufficient aliphatic and naphthenic disulfides so that when distilled at temperatures above 300° F., the distillate is slightly sour and gives a positive test when the distillate is subjected to the distillation-corrosion test. The distillate boiling below 300° F. is usually satisfactory with respect to the doctor test, copper-strip test and distillation-corrosion test.

An object of this invention is to provide a method for preparing naphtha which is negative to the distillation-corrosion test.

A further object of this invention is to manufacture several naphthas from a single wide-cut naphtha stock, which naphthas are non-corrosive to the distillation-corrosion test.

A further object of this invention is the removal of disulfides from straight-run naphtha so that the treated naphtha will be both doctor-sweet and give a negative distillation-corrosion test. These and other objects will be made apparent in the following detailed discussion of my invention.

It has been found that if most or all of the aliphatic and/or alicyclic disulfides boiling at and above 300° F. are removed from the sweetened wide-range naphtha stock, the naphtha fraction boiling above, as well as below, 300° F. will pass the distillation-corrosion test. The process of this invention consequently involves a supplementary sweetening treatment of an already sweetened, wide-range naphtha stock.

In accordance with this invention, naphtha which has been rendered sweet to the doctor test and contains fractions boiling above 300° F., including small amounts of aliphatic and/or alicyclic disulfides, is treated with a thiophenol such as thiophenol, o-, m- and p-thiocresols or thioxylenols, or their mixtures, in amounts sufficient to react with the aliphatic and/or alicyclic disulfides present in the fraction, and the mixture maintained at a temperature of approximately 300° F. until the effluent distilling over is essentially mercaptan-free. The bottoms are then washed with caustic soda solution, e. g., a 10% solution, until any remaining aromatic mercaptans are removed. The resulting bottoms are again sweetened to convert any mercaptans to higher boiling disulfides which will remain in the bottoms when the naphtha is distilled to its desired end-point.

The basically novel step in this process involves a mercaptan-disulfide interchange according to the equation:

$$2RSH + R'S—SR' \rightarrow RS—SR + 2R'SH$$

wherein R is a hydrocarbon aryl radical and R's are hydrocarbon aliphatic or alicyclic radicals. RSH must be selected so that its boiling point is higher than the boiling points of R'SH.

The steps in my process are as follows:

(1) The wide naphtha cut (such as a 200–415° F. cut or a 250–420° F. cut) is first sweetened by a conventional process, such as the Linde or Doctor process, which converts all of the mercaptans present to disulfides. The wide naphtha cut is usually given a pretreatment with caustic solution before Linde or other treatment to remove phenols and thiophenols. After the sweetening operation the naphtha may be washed with water, or with sodium sulfide solution and water, if desired. (2) The sweetened, wide naphtha cut is fractionally distilled to give, for example, a high-flash V. M. and P. naphtha boiling at 250–288° F., if a 250–420° F. cut is taken as the starting wide naphtha cut, or a fraction boiling at 212–238° F. plus a high-flash V. M. and P. naphtha boiling at 250–288° F., if a 212–415° F. wide naphtha cut is processed. If the fractional distillation is continued to obtain a cut boiling above 300° F. as, for example, a 307–340° F. or a 310–394° F. cut, the distillate obtained above 300° F. begins to come over slightly sour and contains sufficient aliphatic and/or naphthenic disulfides to make the naphtha fraction over 300° F. fail to pass the distillation-corrosion test. The distillate boiling below 300° F. is satisfactory, however, with respect to doctor-sweetness and

distillation-corrosion test. (3) The residue remaining after removal of the distillate boiling below approximately 300° F. is treated with an amount of a thiophenol, such as thiophenol, thiocresols and thioxylenols, sufficient to react with the aliphatic and/or alicyclic disulfides therein according to the equation:

$$2RSH+R'S-SR'\rightarrow RS-SR+2R'SH$$

where R' represents hydrocarbon aliphatic and/or alicyclic radicals and R represents a hydrocarbon aryl radical. In other words, an amount of thiophenol, thiocresols or thioxylenols, or their mixtures, is added to the fraction boiling over 300° F. so that the amount of aryl mercaptan sulfur added is equal to the amount of aliphatic or alicyclic disulfide sulfur present in the fraction. (4) The mixture of the naphtha boiling over 300° F. and the thiophenolic-type mercaptan, or mercaptans, is maintained at an elevated temperature below about 300° F. sufficient to cause reaction between the disulfides and thiophenols and then subjected to a slow distillation at approximately 300° F., or slightly lower, until the mercaptans formed therein, boiling at or below approximately 300° F., have substantially all distilled from the bottoms, as demonstrated by a sharp drop in the mercaptan content of the distillate. The temperature of distillation may be about 300° F. at atmospheric pressure, or, if vacuum or stripping gas is used, the temperature may be accordingly lower. The object is to get rid of mercaptans overhead without distilling any more than necessary of the hydrocarbons. The bottoms are then washed with caustic soda solution, e. g., 10% sodium hydroxide solution, to remove excess aromatic mercaptan. The caustic-washed bottoms are then treated by the Linde, Doctor or other sweetening process to convert residual mercaptans to disulfides and then fractionally distilled to give a distillate boiling under 400° F., preferably 394° F., such as mineral spirits, which boil at 310–394° F. The distillate is doctor-sweet and passes the distillation-corrosion test. Since the disulfides boil at considerably higher temperatures than the mercaptans, they are concentrated in the residue from this fractionation.

Since the disulfides usually boil at least 100° F. higher than the corresponding aliphatic and/or alicyclic mercaptans, the mercaptans in the 200–300° F. portion of the naphtha are converted during sweetening into disulfides boiling above 300° F. and concentrate in the heavy naphtha (boiling above 300° F.). They decompose at temperatures above 300° F. to affect adversely the distillation-corrosion test. Heating with thiophenol, thiocresols or thioxylenols reduces the aliphatic and/or alicyclic disulfides to the corresponding mercaptans, boiling below 300° F., and which are removed in the slow distillation step. Any remaining high-boiling mercaptans, after removal of excess thiophenol, thiocresols or thioxylenols by caustic soda solution, are converted into disulfides which boil above the end-point of the high-boiling naphtha to be manufactured and are therefore left in the bottoms after removal of this high-boiling naphtha by distillation. Any aromatic disulfides formed during the conversion of the aliphatic and/or alicyclic disulfides are likewise high in boiling point. Consequently, fractional distillation of the final sweetened material gives a naphtha, such as mineral spirits, which is doctor-sweet, contains little or no disulfides, and passes the distillation-corrosion test. Moreover, aromatic disulfides in which sulfur is directly connected to the aromatic ring, are far more stable to heat than are the aliphatic and/or alicyclic disulfides and do not decompose to discolor a copper strip at approximately the end of the distillation in the distillation-corrosion test.

The thiophenols, thiocresols and thioxylenols are readily obtained from spent refinery caustic soda solution which has been used in gasoline treating and has been regenerated by steam many times. This spent caustic soda solution,

containing the sodium salts of thiophenol, thiocresols and thioxylenols along with various phenols, is acidified and the oily layer which separates is washed with water and distilled to give a product containing essentially thiophenol, thiocresols and thioxylenols, with the corresponding phenolic compounds. This distillate can be used directly in the process of my invention since phenolic compounds are removed from the naphtha during the subsequent caustic soda wash.

A specific example of my invention is described as follows:

One hundred cc. of Linde-sweetened, wide naphtha cut of 250–415° F. distillation range which passed the Doctor test, was fractionally distilled to give approximately 35% by volume of high-flash V. M. and P. naphtha boiling at 250–288° F. and a residue. The high-flash V. M. and P. naphtha was doctor-sweet and gave a satisfactory distillation-corrosion test. The residue contained 0.048% disulfide sulfur. To this residue was added 0.5 cc. of a thiophenolic fraction from spent caustic solution from the treatment of petroleum naphtha (which contained 15% thiophenolic sulfur). The mixture was maintained at a temperature just sufficient to insure boiling at atmospheric pressure under reflux (about 300° F.) for thirty minutes, after which it was distilled slowly. As soon as a withdrawn sample of the condensing vapors showed a sharp drop in mercaptan content, distillation was stopped. The residue was washed with 50 cc. of 10% sodium hydroxide solution, then Linde-sweetened with solid copper chloride and clay in the presence of oxygen, and finally fractionally distilled. The portion of the distillate boiling between 310–394° F. was collected as mineral spirits (42% of the wide naphtha cut). It was doctor-sweet and gave a negative result with respect to the distillation-corrosion test.

It will be apparent that in the caustic washing step the concentration of the solution may be different from that given in the example. A solution of from 5 to 30% concentration is effective to remove any thiophenols remaining in the naphtha.

I claim:

1. The method for preparing naphtha having a negative distillation-corrosion test comprising treating a sweetened naphtha containing fractions boiling above 300° F. with a thiophenol in amount such that the amount of sulfur therein is at least equal to the disulfide content of the naphtha, maintaining the temperature of the mixture below about 300° F. until upon distillation the overhead shows a sharp decrease in mercaptan content, washing the treated naphtha with caustic alkali solution, sweetening the caustic-washed naptha and then distilling to obtain desired fractions having end-points below about 400° F.

2. Method in accordance with claim 1 in which the naphtha is one which is sweetened by treatment with oxygen in the presence of clay impregnated with cupric chloride.

3. Method in accordance with claim 1 in which the thiophenol is obtained from spent caustic alkali solution from the treatment of petroleum distillate.

4. Method in accordance with claim 3 in which the naphtha is washed with caustic alkali solution prior to treatment with the thiophenol.

5. The method for preparing naphtha negative to the distillation-corrosion test from a sweetened, wide-boiling-range naphtha having fractions boiling below and above 300° F. comprising separating from said naphtha the fractions boiling up to about 300° F., mixing with a fraction boiling above 300° F. a thiophenol-containing substance in an amount such that the thiophenol sulfur content is at least equivalent to the disulfide sulfur content of the naphtha, maintaining the mixture at elevated temperature not substantially above 300° F. until the vapor issuing therefrom shows a sharp drop in mercaptan content, washing the treated naphtha fraction with caustic

alkali solution, sweetening the washed naphtha fraction and distilling the last-mentioned sweetened naphtha fraction under conditions to distill off those fractions boiling below 400° F.

6. Method in accordance with claim 5 in which the fractions boiling above 300° F. are washed with caustic alkali solution prior to treatment with the thiophenol-containing substance.

7. Method in accordance with claim 5 in which the thiophenol-containing substance is the material recovered by acidification of spent alkali solution from the treatment of thiophenolic-containing petroleum distillates.

8. The method of rendering petroleum naphtha, sweetened by contact with oxygen in the presence of cupric chloride-impregnated clay and boiling within the range of about 250–415° F., negative to the distillation-corrosion test, comprising fractionating said naphtha to

separate a cut boiling between about 250–288° F., adding to the residual naphtha thiophenol-containing oil, recovered from spent caustic alkali from the treatment of phenol and thiophenol-containing petroleum distillates, in an amount such that the thiophenol sulfur content is substantially equal to the disulfide sulfur content of the residual naphtha, maintaining the mixture for thirty minutes at the temperature at which the residual naphtha begins to boil, then slowly distilling the naphtha until the distillate shows a sharp drop in mercaptan content, thereafter washing the residual naphtha with 10% sodium hydroxide solution followed by sweetening with oxygen in the presence of cupric chloride-impregnated clay and finally distilling the last-mentioned sweetened naphtha to obtain a cut boiling between about 310 and 394° F.

No references cited.