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HYDROCARBON OIL TREATMENT

Wesley H. Sowers, Flossmoor, Ill., assignor to The Pure Oil Company, Chicago, Ill., a corporation of Ohio

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This invention relates to the solvent refining of hydrocarbon oils and is concerned particularly with the refining of distillates of relatively high aromatic content such as coal tar distillates and distillates obtained by the high temperature polymerization of hydrocarbons, especially low molecular weight hydrocarbons.

It is well known in the art to refine mineral hydrocarbon oil containing mixtures of various groups or homologous series of hydrocarbon compounds by contacting the oil with various solvents, the mixtures of solvent and oil being separable into two layers, namely, an upper layer or phase called the raffinate which is relatively richer in those compounds of a paraffinic nature, and a lower layer or phase called the extract which is relatively richer in non-paraffinic compounds. The raffinate generally contains only a small amount of solvent dissolved in the more paraffinic compounds while the extract phase is composed of a relatively large volume of solvent in which are dissolved the non-paraffinic compounds. This characteristic behavior of solvents and mineral hydrocarbon oils is due to the fact that the various series of hydrocarbons present in mineral oils possess different solubilities in the solvents used, the non-paraffinic hydrocarbons usually being much more soluble therein than the paraffinic hydrocarbons. The non-paraffinic hydrocarbons are those hydrocarbons in which the hydrogen to carbon ratio is less than in the paraffin series of hydrocarbons, such as the naphthenic, olefinic or asphaltic hydrocarbons. The separation of the mixture of solvent and oil into raffinate and extract phases is usually readily accomplished by simply allowing the mixture to remain quiescent for a short period of time. The raffinate and extract are usually separated by decantation and the solvent removed from both fractions by distillation. It is an essential characteristic of solvents that they be at least partially miscible with certain types of hydrocarbons and substantially immiscible with other types or series of hydrocarbons that are present in the material being treated, in order that a phase separation will occur subsequent to the mixing of the solvent with the oil which is to be treated.

It is frequently desirable to increase the aromatic content of coal tar distillates or distillates prepared by the polymerization of low molecular weight petroleum hydrocarbons which already contain a relatively large proportion of aromatic hydrocarbons, to a still higher proportion in order that the distillate will have greater solvent power and will approach the solvent power of pure aromatic hydrocarbons; or it may be desirable to prepare substantially pure aromatic hydrocarbons by effecting a separation of the aromatic hydrocarbons from hydrocarbons of other series of the same or approximately the same boiling range. The various individual aromatic hydrocarbon compounds may then be separated from each other by well known means such as distillation.

In the past, efforts to solvent treat distillates containing high proportions of materials completely soluble in the solvent, such as distillates of relatively high aromatic content, prepared by the polymerization of hydrocarbons or obtained from the distillation of coal tar, by the usual methods and solvents such as liquid sulfur dioxide and other polar solvents, have not been successful. In treating such distillates with solvents, no phase separation would occur; or if a phase separation did occur, there was no substantial difference in aromatic content of the two phases. This was apparently due to the high solubility of such hydrocarbon compositions in the solvents used. This is believed to be attributable to the relatively high proportions of aromatic hydrocarbons such as benzene, toluene and xylene that are usually present in such compositions. The difficulty may have been further aggravated by the presence of non-aromatic compounds in such compositions which were so similar in characteristics to the aromatic compounds present that the selectivity of solvents heretofore employed was not sufficiently sharp to successfully separate the aromatic compounds from the non-aromatic compounds.

I have now found that distillates that are relatively high in aromatic hydrocarbon content may be successfully solvent treated to produce a product containing a much higher proportion of aromatics than the original distillate. Furthermore, no difficulty is experienced in obtaining two separate and distinct phases which may be readily separated by decantation. As previously pointed out, highly polar solvents such as sulfur dioxide have been tried in the past, but without success since the distillate is completely miscible with the sulfur dioxide.

I have found that the desired result can be accomplished by using a mixture of liquid sulfur dioxide, water and an anti-freeze miscibility agent such as alcohol. Alcohol suitable for my purpose is preferably aliphatic alcohol, either monohydric or polyhydric, the essential requisites being that the alcohol used must be stable,

at least partially soluble in water and sulfur dioxide and be capable of forming solutions with water, the freezing points of which are below the usual operating temperatures required in a liquid sulfur dioxide extraction process. While there are a number of alcohols, such as methyl alcohol, ethyl alcohol, propyl alcohol, ethylene glycol, glycerine and others, which will meet these requirements, I prefer for purposes of economy to use methyl or ethyl alcohol. It is obvious that a mixture of two or more of these alcohols may also be used. At atmospheric pressure, sulfur dioxide solidifies at −72.7° C. and boils at −10° C. It is obviously impossible to use sulfur dioxide at temperatures below −72.7° C. and at temperatures appreciably above −10° C. the equipment required is very expensive due to the massive construction required to withstand the pressures encountered. The usual temperature of solvent extraction with liquid sulfur dioxide ranges from below zero degrees Centigrade down to almost −70° C. Methyl alcohol solidifies at −97° C., is miscible with water and liquid sulfur dioxide and it forms aqueous solutions, the freezing points of which range from below 0° C. to −97° C., depending upon the proportion of water and methyl alcohol present. For example, a solution of 40% methyl alcohol and 60% water has a freezing point of about −35° C. Other solutions of methyl alcohol and water may have higher or lower freezing points, depending upon the proportion of each present. It will therefore be apparent that solutions of methyl alcohol and water varying over a wide range of methyl alcohol content may be prepared which will have freezing points well below the temperature at which it may be necessary to work with the liquid sulfur dioxide solvent.

One method of carrying out my invention is to treat distillate, prepared by the polymerization of hydrocarbon gases under conditions suitable for the formation of substantial proportions of aromatic hydrocarbons, with liquid sulfur dioxide under conditions of temperature and pressure usually required in the extraction of mineral hydrocarbon oils with liquid sulfur dioxide. Such distillates may contain in excess of 50% of non-paraffinic hydrocarbons. The distillate will be found to be completely miscible with the liquid sulfur dioxide. To this solution is added a solution of methyl alcohol and water. The methyl alcohol-water solution may be added in quantities ranging from approximately 10% to approximately 100% by volume of the amount of liquid sulfur dioxide present. The proportion of water to alcohol may range from two parts by volume of water and 98 parts of alcohol to 50 parts of water and 50 parts of alcohol. In general the ratio of solvent to distillate will range from about 1 to 1 to 10 to 1. The exact ratio of solvent to the distillate being treated and the proportions of water, alcohol and sulfur dioxide for optimum results are susceptible to variation depending upon the characteristics of the distillate being treated and the conditions of temperature and pressure at which the extraction may be carried out. These proportions can be determined empirically in each case, less of the water-alcohol solution being required as the solvent-insoluble or paraffinic fraction increases in proportion. The proportion of alcohol to water in any case should not be below that required to form an alcohol-water solution the freezing point of which is below that of the temperature of the process. When the proper quantities of liquid sulfur dioxide, alcohol and water are present, the mixture of solvent and distillate will separate into two phases, the upper or raffinate phase being richer in non-aromatic hydrocarbons, and the lower or extract phase being richer in aromatic hydrocarbons than the original distillate. The separation of the two phases may be accomplished by any suitable procedure—for example, by decantation. The solvent treatment of the raffinate may be repeated any desired number of times with the same composition of solvent or preferably the proportion of the solvent components may be varied so as to be miscible with fractions previously immiscible, thereby increasing the amount of extract obtained. The extract may also be subjected to repeated extractions with solvent of higher water-alcohol solution content or portions of water-alcohol added directly to the extract in order to further increase the separation of non-aromatic components.

The invention will be more clearly understood from the following specific example:

500 cc. of distillate obtained by the polymerization of hydrocarbon gases under conditions suitable for the production of substantial proportions of aromatic hydrocarbons, hereinafter called poly distillate, was added to an equal volume of liquid sulfur dioxide at a temperature of −29° C. The poly distillate was completely soluble in the sulfur dioxide. To this solution was added 100 cc. of a methyl alcohol-water solution composed of 80% methyl alcohol and 20% water. After thorough agitation, the mixture of distillate and solvent was allowed to stand, whereupon it quickly resolved into two layers, the upper layer or raffinate amounting to 300 cc. and the lower layer or extract, 800 cc. The phases were separated by decantation and the extract layer freed from sulfur dioxide by distillation, washed with an aqueous solution of sodium hydroxide, and finally washed with water. The yield of extract was found to be 52% by weight of the original poly distillate. The following table shows the effectiveness of the extraction.

Table I

	Poly distillate	Extract
Gravity	54.8	46.2
Iodine number	122	107
Per cent aromatics	20	46
Refractive index	1.427	1.449

Reference to Table I indicates that a single extraction with only slightly more than an equivalent volume of solvent produced an increase of 26% in the aromatic content of the distillate. This increase in the aromatic content greatly exceeds that which has heretofore been obtainable by any known solvent extraction method. The aromatic content of the extract may be further increased by repeated extractions with solvent in which the water and/or alcohol content is increased. While my solvents may be successfully applied to distillates of low aromatic content, the problem of separating such distillates and liquid sulfur dioxide into two phases does not exist when distillates of low aromatic content are used as a starting material. Such distillates ordinarily readily separate from liquid sulfur dioxide in usual extraction processes.

It is very evident from the foregoing data that a solvent comprised of liquid sulfur dioxide,

methyl alcohol and water in the proportions set forth is well adapted to the preparation of liquids high in aromatic hydrocarbon content from poly distillate.

The foregoing example of one method of carrying out a solvent extraction of poly distillate with my preferred solvent is given merely by way of illustration and is not intended to define the scope of my invention which is intended to cover generally the separation of aromatic from non-aromatic hydrocarbons in solutions difficultly separable from solvents, which is clearly defined in the following claims.

I claim:

1. In the process of concentrating the aromatic content of hydrocarbon distillate which is completely miscible with liquid sulfur dioxide, the steps of extracting the distillate at temperatures below the freezing point of water with a solvent comprising sulfur dioxide, alcohol and water in which the volume of alcohol plus water is not substantially less than 10% and not substantially in excess of the volume of liquid sulfur dioxide, the proportion of water to alcohol ranges from 10 parts by volume of water and 90 parts of alcohol, to 50 parts of water to 50 parts of alcohol and the proportion of alcohol to water is never less than that required to produce an alcohol-water mixture of lower freezing point than the temperature at which the extraction is carried out, and removing the solvent from the distillate.

2. Process in accordance with claim 1 in which the temperature at which the extraction is carried out ranges from about 0° C. to —70° C.

3. Process in accordance with claim 1 in which the proportion of solvent to distillate may range from 1 to 1, to 10 to 1 and the composition of the solvent is approximately 84% liquid sulfur dioxide, 13% methyl alcohol and 3% water.

4. Process in accordance with claim 1 where the alcohol is methyl alcohol.

5. In the solvent refining of hydrocarbon distillate completely miscible with liquid sulfur dioxide and containing a substantial proportion of aromatic hydrocarbons, the process which comprises bringing said distillate into contact with solvent at temperatures below the freezing point of water, said solvent consisting of liquid sulfur dioxide, alcohol and water in which the volume of alcohol plus water is not substantially less than 10% and not substantially in excess of the volume of liquid sulfur dioxide, the proportion of water to alcohol ranges from 10 parts by volume of water and 90 parts of alcohol, to 50 parts of water to 50 parts of alcohol and the ratio of alcohol to water is never less than that required to produce an alcohol-water mixture of lower freezing point than the temperature at which the refining is carried out, effecting solution in the solvent of a portion of the distillate which is relatively higher in aromatic hydrocarbon content, separating the solution thus formed from the remainder of the distillate and removing the solvent from both portions of the distillate, thereby obtaining fractions respectively higher in aromatic and non-aromatic hydrocarbon content.

6. Process in accordance with claim 5 in which the temperature of the refining may range from about 0° C. to —70° C.

7. Process in accordance with claim 5 in which the alcohol is a stable aliphatic alcohol which is at least partially soluble in water and liquid sulfur dioxide.

8. Process in accordance with claim 5 in which the ratio of solvent to distillate ranges from 1 to 1, to 10 to 1 and the alcohol is methyl alcohol.

9. Claim in accordance with claim 5 in which the ratio of solvent to distillate is approximately 1 to 1 and the composition of the solvent is approximately 84% liquid sulfur dioxide, 13% methyl alcohol and 3% water.

10. In the solvent refining of hydrocarbon distillates normally completely soluble in liquid sulfur dioxide and containing a substantial proportion of aromatic hydrocarbons, the process which comprises bringing said distillate into contact with liquid sulfur dioxide at temperatures below the freezing point of water whereby to form a homogeneous solution of the distillate in the liquid sulfur dioxide, adding a mixture of water and alcohol, in which the proportion of alcohol is not more than 90% and not less than that required to produce an alcohol-water mixture of lower freezing point than the temperature at which the refining is carried out, to the liquid sulfur dioxide-distillate solution in a quantity not substantially less than 10% and not substantially in excess of the volume of liquid sulfur dioxide present, but sufficient to cause the formation of two liquid phases one of which is richer in aromatic hydrocarbons than the distillate treated, and separating the phases.

11. Process in accordance with claim 10 in which the ratio of solvent to distillate is approximately 1 to 1 and the alcohol is methyl alcohol.

12. Process in accordance with claim 10 in which the alcohol is a stable aliphatic alcohol which is at least partially soluble in water and liquid sulfur dioxide.

13. Process in accordance with claim 10 in which the ratio of solvent to distillate may range from 1 to 1, to 10 to 1.

14. Process in accordance with claim 10 in which the composition of the solvent is approximately 84% by volume liquid SO_2, 13% by volume methyl alcohol and 3% by volume water.

15. In a process of solvent refining hydrocarbon distillate which is normally completely miscible with liquid sulfur dioxide, the steps of mixing the distillate at temperatures below the freezing point of water with a solvent comprising liquid sulfur dioxide, alcohol and water in which the volume of alcohol plus water is not substantially less than 10% and not substantially in excess of the volume of liquid sulfur dioxide, the proportion of water to alcohol ranges from approximately ten parts by volume of water and ninety parts of alcohol to fifty parts of water to fifty parts of alcohol and the proportion of alcohol to water is never less than that required to produce an alcohol-water mixture of lower freezing point than the temperature at which the extraction is carried out, said solvent being capable of effecting separation of the distillate into phases, allowing the mixture to stratify into separate phases, separating the phases from each other and separating the solvent from each phase.

16. Process in accordance with claim 15 in which the alcohol is methyl alcohol and the ratio of solvent to distillate may range from 1 to 1 to 10 to 1.

WESLEY H. SOWERS.