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PROCESS FOR PRODUCING A HYDROCARBON FLUORESCENT PRODUCT

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This invention relates to hydrocarbon products and to a method for producing same, and more particularly to products derivable from higher boiling or residual fractions of coal tar.

Our products which are not fluid in nature and are usually in the form of a dry powder, when added, for example, to mineral oils of the lubricating range, will impart to the oil a desirable fluorescence, making the oil green by reflected light and shades of red, orange and/or yellow by transmitted light. Also, our products may be employed for lending effects which their purely chemical properties provide, their effect upon the stability of viscous petroleum fractions being exemplary of one of the purposes for which they may be beneficially utilized.

An exemplary method by which our products may be prepared, in view whereof, many obvious modifications within the sphere and scope of their invention will occur to those skilled in the art, is as follows:

A high molecular weight hydrocarbon mixture, such as a fraction from coal tar, for example, a pitch such as is produced by distillation of coal or coal tar, is placed, preferably in finely divided form, in an extracting vessel, and agitated with a suitable solvent. It is preferred that the pitch to be extracted have a melting point of the order of from about 200° F. to about 500° F. Solvents, such as petroleum fractions having a substantial content of aromatics, hydroaromatics, or unsaturates, are more particularly preferred. Other liquids which are good solvents for bitumens in general, may also be employed. It is preferred that the solvents have a boiling range the minimum temperature of which is above 350° F., so that the subsequent steps of the process may be more conveniently and economically carried out. A more important feature, however, is that the solvent be capable of dissolving substantially all of the bitumen, and be of low viscosity so that it will readily serve to extract the soluble portion of the high molecular weight bitumen. The mixture of bitumen and solvent is agitated, and the temperature is preferably maintained somewhat above normal temperature, for example, from about 150° F. to about 250° F., to provide for the more rapid and complete solution of a maximum of the soluble bodies. After substantially complete extraction of the soluble bodies has occurred, as experience will dictate, the portion of the bitumen which has not dissolved in the solvent is separated therefrom, as by decantation and/or filtration. The solution, which is now free from insoluble portions of the extracted material, and contains in solution the desirable components of our product, may next be reduced in volume to concentrate the solute therein, that is, a portion of the solvent may be removed therefrom as by distillation. Whether or not the step of concentration may be employed will depend upon the solvent used, and the concentration desired at this point must be learned by experimentation. In general, for example, where a highly aromatic or unsaturated solvent is employed for the original extraction, some concentration will be desirable. The solution is then admixed with a saturated hydrocarbon diluent, preferably, paraffinic petroleum naphtha, whereby certain constituents of the solute are precipitated from the solution. It is preferable to choose a straight-run naphtha having a boiling range substantially below that of the solvent previously used, that is, having a boiling range preferably between 150° F. and 350° F., and more preferably having a dry point below 350° F. The amount of paraffinic naphtha added is preferably equal to about 5 to 6 times the volume of the solution; however, this quantity may be advantageously increased or decreased depending upon the particular hydrocarbon product being extracted and the particular solvent employed in the extraction, and also depending on whether or not the solution is concentrated prior to treatment with a paraffinic hydrocarbon liquid. Where the solution has been concentrated, the concentrate may be diluted more than 5 or 6 times its volume and possibly to the extent of 10 or 15 times its volume with paraffinic naphtha. However, too great dilution will result in loss of product. The precipitate formed is separated from the supernatant liquid by decantation and/or filtration, whereby our product, free from certain components initially present in the pitch, is produced. This precipitate is preferably further dried and pulverized, thereby producing a fine powder of reddish or reddish brown color. The aromatic solvent and paraffinic diluent mixture, after separation from our precipitated hydrocarbon product, may be fractionally separated, as by distillation, and the separated liquids may be recycled for further extraction and precipitation of fresh pitch.

Our process may be illustrated by the following example:

758 lbs. of granulated coal tar pitch having a melting point of 400° F., was introduced into an extraction vessel, together with 380 gallons of recycle gas oil having an A. P. I. gravity of 16°, and a distillation range of from 350° F. to 750°

F. The mixture of pitch and solvent was thoroughly agitated at a temperature of about 220° F., and the residue and solution was passed to a series of settling vessels, wherein the undissolved residue was separated from the solution and withdrawn from the vessels. During this settling process, the temperature of the solution was reduced to about 70° F. to 80° F., and the solution free of residue was then admixed with 1700 gallons of naphtha having an A. P. I. gravity of 58°, and a distillation range of from 165° F. to 340° F. This dilution caused a precipitation of insoluble material, and the mixture of solvent, diluent and precipitate was then passed into a filter press, whereby the precipitate was freed of hydrocarbon solvent and diluent. The filter cake was subsequently washed with 1800 gallons of clean naphtha to remove traces of gas oil solvent, and the cake was finally dried and pulverized, the yield of dry powder being 204 pounds, based on the weight of pitch charged to the system.

It may be desirable, in certain cases, to employ our product for a use in which a slight amount of naphtha or solvent adhering to the product is not undesirable; the product may, without drying, be employed directly for such purposes. For example, if our product is employed to stabilize, or lend a distinguishing color to a light petroleum fraction, it may often be employed directly for such purpose without first being dried; or where it is desirable to make up a concentrated solution of our product in an oil, portions of which concentrate may be subsequently added to oils to impart fluorescence thereto, the drying step may be dispensed with.

Furthermore, it may, in certain cases, be desirable to further purify our product. This may be accomplished by redissolving the product in the aforementioned aromatic or unsaturated solvent and reprecipitating it by the addition of a paraffinic diluent, whereby certain undesirable components will remain in solution and the desired product will precipitate. Or, the high molecular weight hydrocarbon mixture, such as coal tar pitch, may be first extracted with the aromatic or unsaturated solvent, and the solution, freed of insoluble residue, may be filtered thru or contacted with fuller's earth or clay to remove undesirable color-imparting bodies therefrom, prior to the precipitation of our bloom compound by the addition of paraffinic naphtha, as above described.

As set forth in the literature, and particularly in U. S. patents to Black et al., Nos. 1,708,602 and 1,842,856 and to Hanna et al. No. 1,566,000, materials which add the desirable green fluorescence, i. e., bloom, to an oil, are also of utility in rendering the oil more stable. Our products may be employed to provide these advantages without incurring the disadvantages incident to the addition of undesirable impurities, such as are introduced in accordance with the teaching of the prior art. Such introduction of impurities along with the fluorescent compound necessitates a subsequent distillation and/or treatment, which is costly and time consuming, to bring the physical properties of the oil within the specified standards. The more important physical properties of an oil which are deleteriously affected by blooming or fluorescent rendering operation taught by the prior art, are; color, flash point, fire point, viscosity, gravity, pour point and Conradson carbon. For example, where blooming constituents are supplied to a lubricating oil dissolved in benzol, the benzol, even in small quantities, very seriously affects the flash and fire point characteristics of the oil. Again, where bloom is added to a lubricating oil by directly dissolving certain residues in the oil, the color of the oil is darkened, and other characteristics of the oil are deleteriously affected, especially when the properties of the oil before the addition of bloom compounds are only narrowly within specification limits. In sharp contrast with this procedure, an oil may be given a satisfactory bloom by addition thereto of our product, without discernibly, or at least to any substantial extent, varying the physical properties by which the oil is gaged.

In the foregoing description of the process, among other modifications, it is obvious that any liquid which possesses a high solvent power for bituminous bodies, for example, those derived from coal tar, may be employed in lieu of the highly cracked or aromatic petroleum distillates hereinbefore referred to. Again, in lieu of a straight-run naphtha for precipitating the components of our product from the aromatic extract thereof, any other dilluent which is readily miscible with the aromatic or unsaturated solvent in which the desired components are dissolved, and which will thereby form a homogeneous liquid in which such components are substantially insoluble, especially at reduced temperatures, may be employed as a substitute for such naphtha.

By means of our process, a non-fluid or semi-solid product is provided or there is produced a solid, which by grinding or other well known procedure may be reduced to powder form. Our product may be employed for the uses suggested or may be employed for other purposes for which its physical and/or chemical properties make it adaptable. The use of our product in hydrocarbon oil, particularly petroleum hydrocarbons, such as lubricating oil fractions and also motor fuel, such as gasoline, to render the same of improved quality, is primarily contemplated.

While the preferred form of our product is a dry powder, it is to be understood that where the components thereof, without drying, for example, are to be mixed with a small amount of solvent with a view to subsequent use of our material in such form, such material is within the spirit and scope of our invention.

In the appended claims, the term "unsaturated hydrocarbon liquid" comprehends hydrocarbon liquid containing primarily aromatics, hydroaromatics, and/or olefinic hydrocarbons, while the term "saturated hydrocarbon liquid" comprehends hydrocarbon liquid composed primarily of hydrocarbons which are non-aromatic and non-olefinic, i. e., substantially paraffinic hydrocarbons. Also, the terms "derivatives of coal tar" and "derivative" are to be understood to comprehend coal tar residues and/or high boiling fractions of coal tar.

What we claim is:

1. The process for producing a hydrocarbon product capable of rendering a hydrocarbon oil fluorescent from high molecular weight derivatives of coal tar which comprises, commingling said derivative with an unsaturated hydrocarbon liquid, separating the undissolved portions of said derivative from the solution formed with other portions thereof, and adding to such solution sufficient saturated hydrocarbon liquid to precipitate at least a portion of the solute.

2. The process for producing a hydrocarbon product capable of rendering a hydrocarbon oil fluorescent from high molecular weight deriva-

tives of coal tar which comprises commingling said derivative with an unsaturated hydrocarbon liquid at a temperature sufficiently high to readily dissolve the soluble portions of said derivative, separating the undissolved portions of said derivative from the solution formed with the other portions thereof, and then adding to such solution at a reduced temperature sufficient saturated hydrocarbon liquid to precipitate at least a portion of the solute.

3. The process for producing a hydrocarbon product capable of rendering a hydrocarbon oil fluorescent from high molecular weight derivatives of coal tar which comprises commingling said derivative with an unsaturated hydrocarbon liquid at a temperature sufficiently high to readily dissolve the soluble portions of said derivative, separating the undissolved portion of said derivative from the solution formed with the other portion thereof, concentrating the solute in said solution to substantial extent by vaporizing a portion of the solvent therefrom, and then adding to such solution at a reduced temperature sufficient saturated hydrocarbon liquid to precipitate at least a portion of the solute from said solution.

4. The process for producing a hydrocarbon product capable of rendering a hydrocarbon oil fluorescent from a coal tar residue which comprises commingling said residue with an unsaturated hydrocarbon liquid at a temperature sufficiently high to readily dissolve the soluble portion of said residue, separating the undissolved portions of said residue from the solution formed with the other portions thereof, and adding to such solution at a reduced temperature sufficient saturated hydrocarbon liquid to precipitate at least a portion of the solute from the solution.

5. The process for producing a hydrocarbon product capable of rendering a hydrocarbon oil fluorescent from high molecular weight derivatives of coal tar which comprises, commingling said derivative with an unsaturated hydrocarbon liquid, separating the undissolved portions of said derivative from the solution formed with other portions thereof, adding to such solution sufficient saturated hydrocarbon liquid to precipitate a substantial portion of the solute, separating the precipitate from the liquid, redissolving said precipitate in fresh unsaturated hydrocarbon liquid, reprecipitating therefrom at least a portion of the solute by the addition of a saturated hydrocarbon liquid, and separating said precipitate from the hydrocarbon liquid.

6. The process for producing a hydrocarbon product capable of rendering a hydrocarbon oil fluorescent from a coal tar residue which comprises commingling said residue with an unsaturated hydrocarbon liquid at a temperature sufficiently high to readily dissolve the portion of said residue, soluble therein, separating the undissolved portions of said residue from the solution formed with the other portions thereof, concentrating the solute in such solution by vaporizing a portion of the solvent therefrom, and adding to such solution at a reduced temperature sufficient saturated hydrocarbon liquid to precipitate at least a portion of the solute from the solution.

7. The process for producing a hydrocarbon product capable of rendering a hydrocarbon oil fluorescent from a coal tar residue which comprises commingling said residue with an unsaturated hydrocarbon liquid at a temperature sufficiently high to readily dissolve the soluble portion of said residue, separating the undissolved portions of said residue from the solution formed with the other portions thereof, concentrating the solute in said solution to substantial extent by vaporizing a portion of the solvent therefrom, adding to such solution at a reduced temperature sufficient saturated hydrocarbon liquid to precipitate at least a portion of the solute from the solution, and separating the precipitate from the hydrocarbon liquid.

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