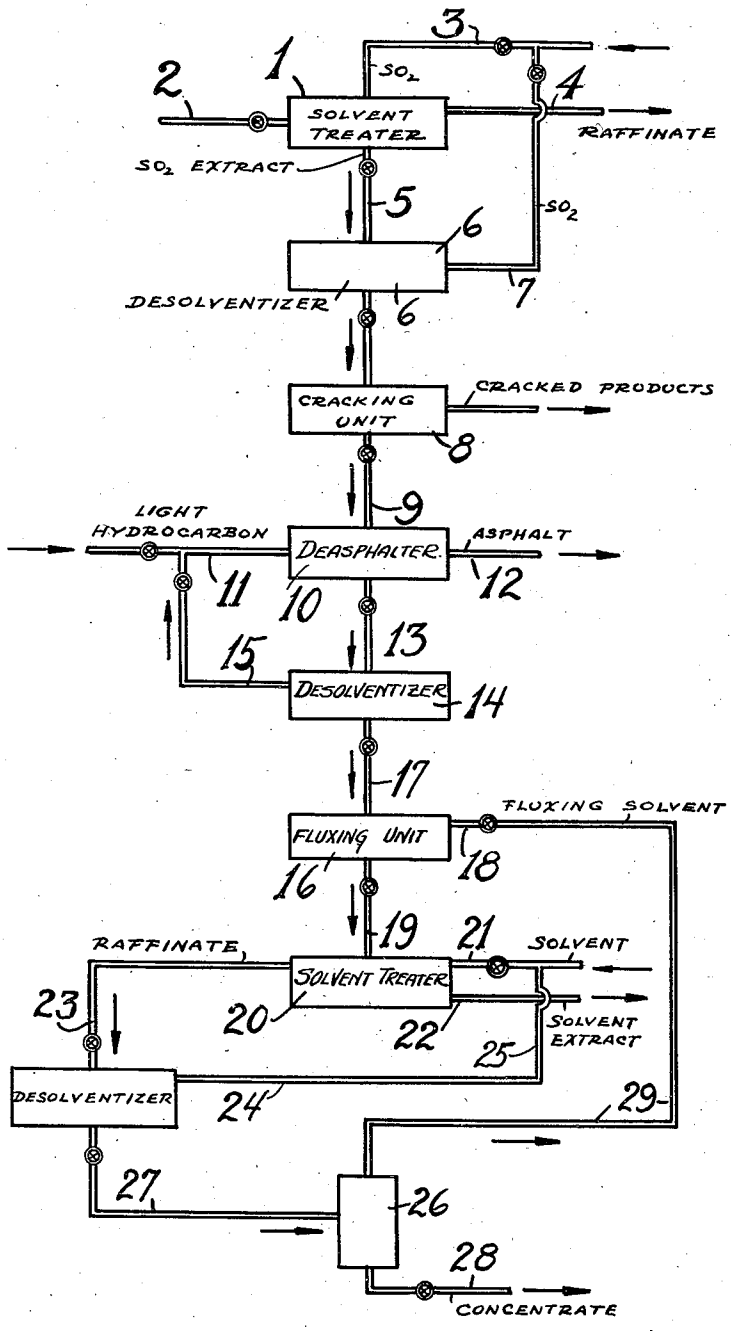
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PROCESS FOR PREPARING LUBRICATING OIL DYES

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PROCESS FOR PREPARING LUBRICATING OIL DYES

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The present invention relates to an improved lubricating oil dye suitable for imparting desirable blooms to petroleum lubricating oils. The dye of the present invention is produced from petroleum oil and will impart a desirable cast to petroleum lubricating oils without producing undesirable detrimental effects on other properties.

Various procedures have been disclosed for the preparation of various dyes suitable for imparting various blooms to petroleum oils. The dyes heretofore secured have been satisfactory in so far as their dyeing properties are concerned. However, in most instances it has been necessary to add a relatively large amount of the dye to secure the desired cast which results in an excessive increase in carbon residue and an increase in the Sligh number of the petroleum oil to which it has been added.

We have now discovered a process of producing a concentrated dye which, when used in small proportions, will impart a desirable cast to the petroleum oil. The dye produced by our invention moreover will improve the pour characteristics of the oil and will also act as a cloud inhibitor. The process of producing the dye of the present invention may be readily understood by reference to the attached diagrammatical drawing illustrating one modification of the same.

A petroleum oil preferably boiling in the range between 260° F. and 540° F. and having a gravity in the range between 38° A. P. I. and 43° A. P. I. is introduced into solvent treating unit 1 by means of feed line 2. In solvent treating unit 1 the oil is contacted with a selective solvent selected from the class of solvents which have a preferential selectivity for the more aromatic type hydrocarbons as compared to the more paraffinic type hydrocarbons. Solvents of this class are, for example, phenol, furfural, sulfur dioxide, cresol, nitrobenzene, aniline, beta beta dichlor diethyl ether and the like. For the purposes of illustration, it is assumed that the oil is treated in unit 1 with sulfur dioxide which is introduced by means of line 3. The raffinate is removed from treating unit 1 by means of line 4 while the solvent extract is removed by means of line 5 and introduced into desolventizer 6. Sulfur dioxide is removed from the solvent extract by means of line 7. The extract is then cracked in cracking unit 8 under conditions to produce a heavy cracking coil tar having a gravity in the range from about 1° A. P. I. to 6° A. P. I. The cracking coil tar is removed from cracking unit 8 by means of line 9 and introduced into unit 10 in which the tar is deasphalted by means of a deasphalting solvent which is introduced into unit 10 by means of line 11. For the purposes of illustration, it is assumed that the deasphalting solvent is kerosene. The asphalt is removed by means of line 12 while the kerosene extract is removed by means of line 13 and introduced into desolventizer 14. Kerosene is removed from the deasphalted tar by means of line 15. The deasphalted tar is introduced into fluxing unit 16 by means of line 17. A suitable fluxing petroleum oil is then introduced into unit 16 by means of line 18 and the mixture removed by means of line 19 and introduced into treating unit 20. A solvent of the class of solvents having a preferential selectivity for the more aromatic type compounds as compared to the more paraffinic type compounds, as for example, phenol, is introduced into solvent treating unit 20 by means of line 21 under conditions to form a solvent extract phase and a raffinate phase. The solvent extract phase is removed from treating unit 20 by means of line 22 while the raffinate phase is removed by means of line 23 and introduced into desolventizer 24. The phenol is removed from the raffinate and light oil in desolventizer 24 and recycled to line 21 by means of line 25. The solvent-free raffinate and light oil are then introduced into distillation unit 26 by means of line 27 in which the light oil is removed by means of line 29. The dye concentrate of the present invention is removed from distillation unit 26 by means of line 28.

The process of the present invention may be widely varied. Any cracking coil tar is satisfactory which has a gravity in the range between 1° A. P. I. and 6° A. P. I. However, it is preferred that the cracking coil tar be produced from a cracked solvent extract, preferably a cracked sulfur dioxide extract, and that the tar have a gravity of about 2° A. P. I. to 3° A. P. I.

The heavy tar may be deasphalted in any suitable manner by the use of light kerosene or by the use of liquefied normally gaseous hydrocarbons, as for example, propane, butane and the like. In general, it is preferred to deasphalt the tar by adding approximately 100% of a deasphalting solvent such as light naphtha, propane or the like. The temperature and pressure conditions may vary widely and are adjusted to secure optimum operation. In general, atmospheric temperature and a pressure sufficient to maintain the deasphalting solvent in the liquid state are preferred.

The deasphalted tar, after removal of the deasphalting solvent, is then fluxed with a suitable petroleum oil. It has been found that desirable results are secured if the deasphalted tar is fluxed with a paraffinic light petroleum oil having a gravity in the range from about 27° A. P. I. to 40° A. P. I. The fluxed tar is then treated, preferably with phenol, under conditions to form a solvent extract phase and a raffinate phase. The raffinate phase is separated from the solvent extract phase and treated in any suitable manner to

remove the selective solvent. The solvent-free oil comprising the light fluxing oil and the dye is then treated in a manner, preferably by distillation, to remove the light oil. The distillation operation is preferably conducted under vacuum at an absolute pressure from about 1 mm. to 10 mm. and at a temperature not exceeding about 500° F. to 650° F. in order to prevent decomposition of the dye. The dark brown dye concentrate is removed as a residue after distilling overhead the fluxing oil. Under certain operations the deasphalted tar might be solvent treated while the tar is dissolved in the deasphalting medium. However, in general, it is preferred to remove the light petroleum deasphalting solvent and then to flux the tar with a relatively light petroleum oil of the desired gravity, preferably in the range from about 27° A. P. I. to 29° A. P. I.

The dark brown dye concentrate of the present invention may be utilized in any oil to impart a green fluorescence thereto. The dye concentrate of the present invention, however, is particularly applicable for imparting a green fluorescence to refined petroleum oils boiling in the lubricating oil range. The amount of dye used may vary considerably and will depend to a large extent upon the character of the oil to which it is added. In general, it is preferred to add from 0.25% to 0.75% and not over 1% of the dye, based upon the volume of oil.

The process of the present invention may be readily understood by reference to the following examples which are given for the purposes of illustration.

EXAMPLE 1

A petroleum oil boiling in the range from about 360° F. to 540° F. and having a gravity of about 38° A. P. I. was extracted with sulfur dioxide. The sulfur dioxide extract, after removal of the solvent, was cracked under conditions in which a 3° A. P. I. gravity cracking coil tar was produced. The cracking coil tar was deasphalted by diluting with an equal volume of light kerosene having a gravity of about 41° A. P. I. The kerosene was removed from the deasphalted tar by distillation with fire and steam. The deasphalted tar was then fluxed with a light paraffinic oil having an A. P. I. gravity of about 28°. The mixture was then solvent treated with 100% of phenol under conditions to form a solvent extract phase and a raffinite phase. The respective phases were separated and the phenol removed. The solvent-free raffinate phase was then distilled under vacuum conditions in order to remove overhead the light fluxing oil and to recover as a residue the dark brown dye concentrate of the present invention.

The dye concentrate, when added in concentrations of 0.5% and 1.0%, had the following effect upon the characteristics of a refined Coastal lubricating oil of approximately 570 seconds Saybolt viscosity at 100° F.

Table I

Percent dye	0	0.5	1.0
Color, Robinson	12	7½	4¾
Color, N. P. A.	1½	3½	4
Colorhold, Robinson	9½	4¼	2½
Colorhold, N. P. A.	2½	4	5
Carbon residue percent	0.04	0.05	0.05
Neutralization value	0.013	0.014	0.03
Cast	Blue	Olive green	Olive green

The data show that the color of the original oil was darkened by the dye and the cast was improved but the carbon residue was not appreciably increased.

EXAMPLE 2

100 volumes of cracking coil tar having a gravity of about 3° A. P. I. were deasphalted by treating said tar with 75 volumes of light crude naphtha at room temperature, resulting in a yield of 75 volumes of asphalt-free tar on a solvent-free basis.

The asphalt-free tar, after separtion from the asphalt but before removal of the naphtha, was further diluted with 150 volumes of paraffin gas oil and was then treated with 75 volumes of phenol. The temperature of the treat was approximately 120° F. The raffinate phase comprising approximately 292.5 volumes was separated from the extract phase of about 82.5 volumes. The raffinate phase was then vacuum distilled to remove overhead the phenol, naphtha and gas oil and to secure as a residue approximately 39 parts by volume of a dark brown dye concentrate of the present invention.

Blends were then prepared, using various percentages of the dye concentrate with a refined Colombian and with a refined Coastal lubricating oil, with the following results:

Table II

Oil	Colombian	Colombian	Coastal	Coastal
Percent dye	0	0.5	0	0.25
Gravity, °A. P. I.	23.0	22.9	22.6	22.5
Flash, °F.	425	430	395	390
Fire, °F.	485	480	455	450
Viscosity at 100° F.	501	501	518	517
Viscosity at 210° F.	55.5	55.5	55.9	56.0
Color, Robinson	11½	3¼	13	5
Colorhold, Robinson	9¾	3	11¼	4
Cloud, °F.	34	26	28	16
Pour, °F.	—25	—30	—20	—25

When viewed under reflected light the above blended oils had a distinct olive green fluorescence which was superior to the fluorescence of the unblended oils. Furthermore the blended oils were deep red in color when viewed with transmitted light. It is to be noted that the dye of the present invention improved the cloud and pour characteristics of the oil.

The present invention is not to be limited by any theory or mode of operation, but only by the following claims in which it is desired to claim all novelty in so far as the prior art permits.

We claim:

1. Process for the preparation of an improved petroleum oil dye comprising extracting a petroleum oil boiling in the range from about 360° F. to 540° F. with sulfur dioxide under conditions to form a solvent extract phase and a raffinate phase, removing the solvent extract phase, separating the sulfur dioxide therefrom and cracking the extract to produce a cracking coil tar having a gravity in the range from about 2° to 6° A. P. I., deasphalting said cracking coil tar by the addition thereto of a diluent, separating said deasphalted tar and extracting the same with a selective solvent of the class which has a preferential selectivity for the more aromatic type compounds as compared to the more paraffinic type compounds under conditions to form a solvent extract phase and a raffinate phase, separating said raffinate phase and removing the solvent therefrom, distilling said solvent-free raffinate phase under conditions to remove overhead said diluent and to recover as a residue said improved petroleum oil dye.

2. Process in accordance with claim 1 in which

said diluent is kerosene and in which said solvent is phenol.

3. The process of producing lubricating oil addition agents having the properties of blending with lubricating oils to impart a deep red color by transmitted light and an olive green fluorescence and to improve the pour and cloud characteristics which comprises extracting a petroleum oil boiling in the range from about 360° F. to 540° F. with liquid sulfur dioxide under conditions to form a solvent extract phase and a raffinate phase, removing the solvent extract phase, removing the sulfur dioxide therefrom and cracking the extract to produce a cracking coil tar having a gravity in the range from about 2° to 6° A. P. I., deasphalting said cracking coil tar by the addition thereto of a diluent, separating said deasphalted tar and treating the same with a selective solvent of the class which has preferential solubility for the relatively aromatic type compounds as compared to the relatively paraffinic compounds under conditions to form a solvent extract phase and a raffinate phase, separating said raffinate phase and removing the solvent therefrom, distilling the said solvent free raffinate under conditions to remove overhead said diluent and to recover as a residue the said lubricating oil addition agent.

4. A process in accordance with claim 3 in which said diluent is kerosene and in which said solvent is phenol.

5. Process for the preparation of an improved petroleum oil dye comprising diluting a deasphalted petroleum oil tar obtained by cracking the extract of a petroleum oil treated with a selective solvent having a preferential selectivity for the more aromatic type constituents as compared to the more paraffinic type constituents under conditions to form a solvent extract phase and a raffinate phase and having an A. P. I. gravity in the range from about 2° to 6°, diluting the said tar with a suitable diluent, extracting the diluted tar with a selective solvent having a preferential selectivity for the more aromatic type constituents as compared to the more paraffinic type constituents under conditions to form a solvent extract phase and a raffinate phase, separating the raffinate phase and removing the solvent therefrom, then distilling the solvent free raffinate phase under conditions to remove overhead the diluent and to recover as residue said improved dye.

6. Process in accordance with claim 5 in which the said tar is obtained by cracking a sulfur dioxide extract.

7. Process in accordance with claim 5 in which the diluent is kerosene and the selective solvent for treating the diluent tar is phenol.

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