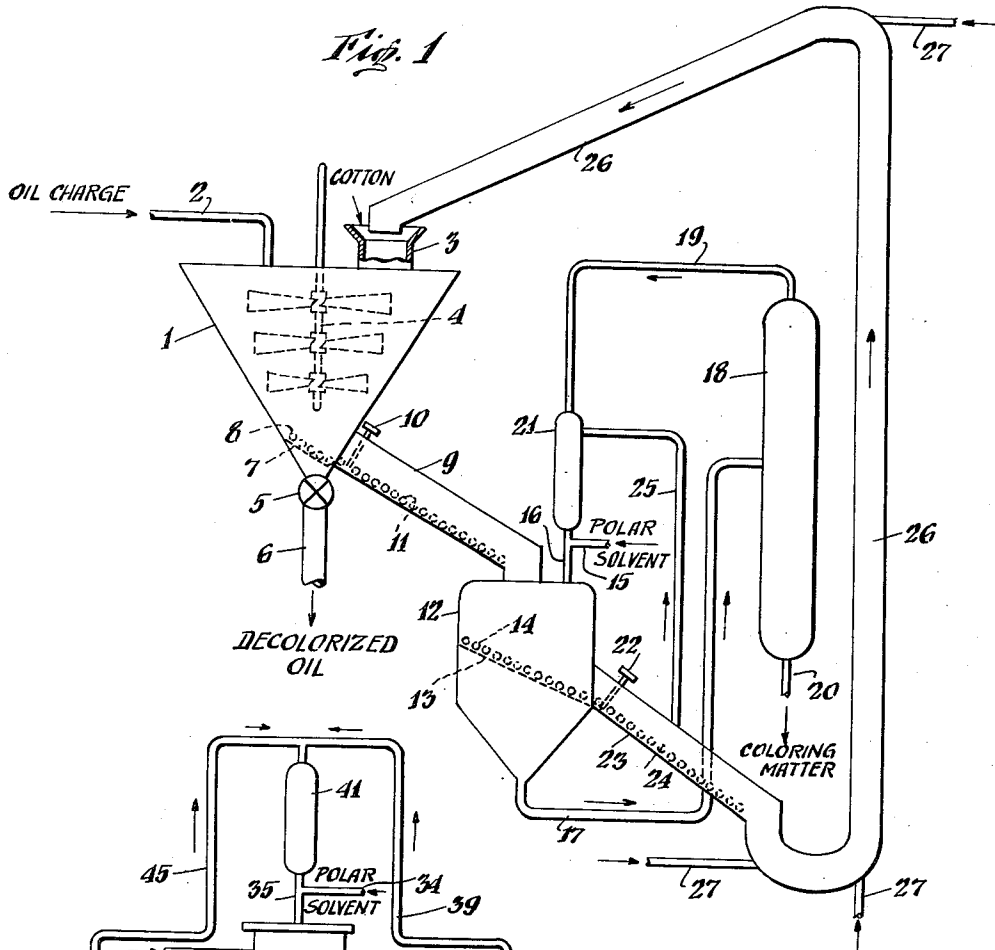
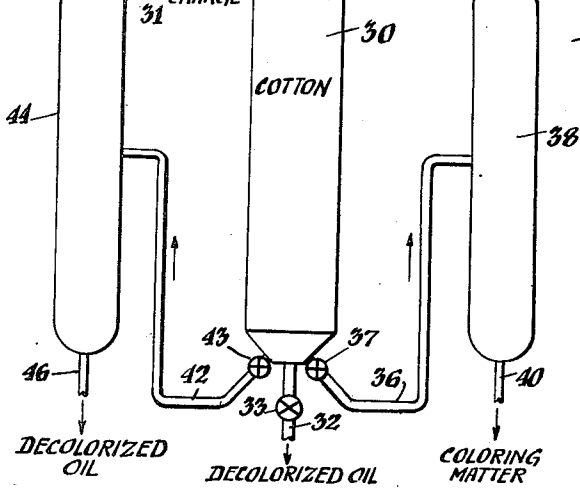


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DECOLORIZATION PROCESS
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DECOLORIZATION PROCESS

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This invention relates to color refining of petroleum fractions. More particularly, the present invention is concerned with a method for decolorizing certain petroleum fractions characterized by the presence of polar colored components and containing a relatively high content of naphthenic acids, i. e., quantities of the order of 0.5 to 3 per cent by weight. Typical of the stocks which may be effectively decolorized by the process of this invention are untreated coastal oil distillates and distillate type fuel oils having an approximate boiling point range of 300 to 800° F.

The removal of substances producing color in petroleum fractions is generally understood to be dependent upon the phenomena known as adsorption. The effectiveness of oil refining operations employing adsorbent materials accordingly depends upon the characteristics and properties of the adsorbent materials used as well as upon the particular stock undergoing treatment. An ever present problem in the art is to develop improved adsorbents in order to obtain higher decolorization efficiency and increased commercial value in these operations. In one method for the decolorization of petroleum fractions, the oil to be decolorized is agitated with a finely divided adsorbent material for a suitable period of time, followed by separation of the decolorized oil from the spent adsorbent mass. Such procedures are generally referred to as "contact" methods of decolorization. A second method for decolorizing oil stocks has involved percolating the stock through a column of particle-form adsorbent. These processes are referred to as "percolation" methods of decolorization. In either of the foregoing decolorizing procedures, it is essential that the adsorbent medium employed possess a high sorption capacity for the particular color bodies contained in the specific stock undergoing treatment.

The process of this invention is directed to the decolorization of certain oil distillates boiling between about 300° F. and about 800° F. and containing a naphthenic acid content of about 0.5 per cent by weight and greater. Such stocks have heretofore been decolorized with conventional clay-type adsorbents. Operations utilizing such adsorbents, however, have generally been conducted on a batch basis since the clay, after contact with the foregoing stock is ordinarily not subject to solvent regeneration. This invention accordingly has as its principal object the provision of an improved process for decolorizing petroleum fractions of the above type.

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A further object is to provide a decolorizing method for these petroleum fractions which is rapid and efficient, readily lending itself to commercial operation. A still further object of this invention is the provision of a method for decolorizing the above-described stocks utilizing an adsorbent material capable of easy regeneration, thereby affording a continuous cyclic decolorization process.

These and other objects which will be apparent to those skilled in the art are attained in accordance with the present invention wherein cotton has been found to possess excellent capacity for sorbing color bodies from petroleum distillates having a relatively high naphthenic acid content. It has further been discovered that color bodies thus sorbed can be effectively removed by elutriation with a polar organic solvent and the color sorption capacity of the cotton can thus be regenerated.

Broadly, the present process comprises bringing the oil fraction to be decolorized into contact with the cotton adsorbent for a suitable period of time and thereafter effecting a separation of the decolorized oil from the spent cotton adsorbent. The method of this invention may be carried out either by a "contact" decolorization procedure wherein the cotton adsorbent is immersed and soaked the necessary time within the oil stock and thereafter removed by filtration or other feasible means or alternatively the decolorization may be accomplished in a "percolation" operation wherein the oil fraction undergoing treatment is permitted to percolate through a column packed with cotton. With the use of either procedure, the cotton containing sorbed color bodies may be regenerated by elutriation of the spent adsorbent with an organic polar solvent, after which the cotton adsorbent is again ready for use.

The adsorbent employed in the present process is ordinary cotton, preferably in an unbleached condition, although bleaching of the cotton is not contemplated to affect its sorption capacity for removing color bodies from the particular stocks undergoing treatment. When employed in a percolation type operation, the cotton adsorbent is thoroughly tamped into place to prevent channeling of the oil stock passing therethrough. Generally the density of the cotton column through which the oil fraction percolates will be between about 0.1 and about 0.8 gram per cubic centimeter. The sorbing capacity for color bodies present in the petroleum distillates treated by the method of this inven-

tion appears to be confined to the use of a fibrous adsorbent of cotton. Thus, other organic fibers, including wool, were found to be unsuitable as adsorbents for decolorizing the petroleum stocks treated by the instant process.

The petroleum fractions decolorized by the present method include crude oil distillates containing between about 0.5 and about 3 percent by weight of naphthenic acids, having a boiling point range of 300 to 800° F. and an A. P. I. gravity of between about 20 and about 40. Just as cotton appears to exhibit specific color sorption properties for stocks of the above type, these stocks appear to be particularly susceptible to decolorization by a cotton adsorbent. Thus, it has been noted that certain other petroleum fractions, such as acid-treated stocks, are not appreciably decolorized by the instant process. Treatment of such stocks accordingly is not within the purview of this invention.

The conditions under which the present process is carried out may vary widely, depending upon the nature and degree of discoloration of the oil stock undergoing treatment and upon whether it is desired to use a contact or a percolation type operation. For a contact operation, the oil stock is brought into contact with cotton adsorbent and said contact is maintained for a sufficient period of time to effect substantial removal of color bodies contained therein. The duration of such contact is dependent upon the relative proportions of oil and adsorbent as well as upon the degree of discoloration of the oil. As a general rule, the larger the amount of cotton adsorbent present, the shorter is the contact time required. Under the usual conditions of practicing the process of this invention, however, employing the contact technique, the period of contact will generally range from about 2 to about 15 hours. In order to bring about a more effective contact between the cotton adsorbent and the oil stock, the mixture is ordinarily agitated by stirring, shaking, or other means during the aforementioned period. Such treatments are effected at substantially atmospheric pressure and may be carried on at ambient or higher temperatures, generally not exceeding about 200° C. The quantity of adsorbent employed may be of the order of from about 10 per cent to about 200 per cent or more by weight based on the quantity of oil stock treated, depending upon the state of the oil stock and upon the qualities desired in the resulting decolorized product. The decolorized oil is thereafter separated from the spent cotton by filtration, centrifuging, or other suitable means.

For a percolation operation, the oil stock is introduced into a vertical column packed with cotton adsorbent and the oil permitted to percolate by gravity therethrough. The packing density and the length of the column are so correlated that oil emerging from the bottom of the column is substantially free of color bodies without necessitating an unduly long time of percolation. Treatment is effected at temperatures ranging from atmospheric to moderately elevated temperatures not exceeding about 200° C. The operation is generally carried out at atmospheric pressure, although the application of pressure during percolation may in some instances be found desirable.

With either of the foregoing techniques, the cotton adsorbent containing sorbed color bodies may be regenerated by elutriation with an organic polar solvent. The solvents useful for this purpose should possess at least some mutual solu-

bility with the oil undergoing treatment and should be sufficiently volatile to be completely separable from the oil by distillation at relatively low temperatures. The solvent employed should be polar in nature since the color bodies removed from the adsorbent therewith are polar. The reason for mutual solubility of solvent and oil resides in the necessity for the polar solvent to penetrate and work off layers of oil adhering to the cotton adsorbent. The elutriation will generally be carried out at atmospheric temperatures although in some instances slightly elevated temperatures not exceeding the boiling point of the particular solvent employed may be helpful in facilitating the removal of color bodies. In particular, it has been found that the lower alcohols and ketones may be used with advantage as elutriants for the sorbed coloring matter. Thus, ethyl, isopropyl, butyl, amyl, and isoamyl alcohols and such ketones as acetone, methylethyl ketone, and methylisopropyl ketone may be used advantageously. These solvents, together with other polar solvents having the above defined characteristics may be used either alone or in combination to provide an effective elutriant medium for regenerating the spent adsorbent by removing sorbed color bodies therefrom. In some instances, it has been found desirable to first wash the cotton adsorbent containing sorbed color bodies with an oil solvent such as carbon tetrachloride, naphtha, etc., to effect removal of oil adhering to the adsorbent and thereafter to remove the sorbed color bodies by extraction with one of the aforementioned polar solvents.

The regenerated cotton adsorbent may be used for further decolorization. The solvent solution containing the coloring matter previously removed is treated to effect recovery of the solvent. Such treatment ordinarily involves fractionating a solution of coloring matter, driving the solvent therefrom as overhead and obtaining the coloring bodies as residue. Solvent vapor removed as overhead is condensed and may then, if desired, be used for further elutriation of the spent adsorbent.

The process described above is conveniently adaptable to continuous operation and suitable systems for carrying out such operation are shown in the attached drawing. Referring more particularly to Figure 1 of the drawing, it will be seen that the oil which is to be treated is conducted into mixing tank 1 through conduit 2. The cotton adsorbent is led into the mixing tank via inlet pipe 3. The tank is provided with a propeller agitator 4 which serves to intimately admix the oil and adsorbent. After thorough admixture has been attained, valve 5 in the bottom of the mixing tank is opened and decolorized oil is permitted to drain from the tank through outlet pipe 6. The cotton adsorbent is retained in the mixing tank on slanted perforated plate 7 having a plurality of rollers 8 affixed thereto to permit movement of the cotton adsorbent through conduit 9 when valve 10 is opened. The spent cotton adsorbent passes along conduit 9, the movement being facilitated by a plurality of rollers 11. The sorbent thereafter passes into tower 12, falling onto a slanted perforated plate 13 likewise provided with a plurality of rollers 14. Polar solvent is introduced into tower 12 through pipes 15 and 16 and flows through the spent adsorbent contained in the tower, removing sorbed color bodies therefrom. The stream of solvent containing the color bodies so removed is conducted from the bottom of tower 12 through out-

let conduit 17 and is led to fractionating column 18. The column is maintained at a temperature such that the solvent passes overhead as a vapor through pipe 19 while the coloring matter previously removed from the oil and the adsorbent collects in the bottom of column 18 and is periodically removed therefrom through pipe 20. The solvent vapor flowing through pipe 19 passes through condenser 21 wherein the solvent vapor is condensed. Liquid solvent ensuing from condenser 21 is recycled to tower 12 through pipe 16.

The cotton adsorbent so regenerated in tower 12, upon opening valve 22, moves by gravity from plate 13 along rollers 14 and passes through conduit 23 provided with a plurality of rollers 24 to facilitate movement of the cotton. Conduit 23 is heated by coils or other suitable means not shown, driving solvent from the cotton adsorbent passing therethrough as overhead vapor. This vapor passes through pipe 25 to condenser 21. The dried regenerated cotton passes from conduit 23 into an air-lift 26 provided with a plurality of inlets 27 for the introduction of high air pressure. The cotton is thus pneumatically elevated through air-lift 26 and recycled to mixing tank 1, passing through inlet pipe 3.

Referring more particularly to Figure 2 of the drawing, wherein a suitable continuous percolation process is shown, 30 designates a tower packed with cotton adsorbent. The oil charge to be treated is conducted into tower 30 through conduit 31. The oil so charged percolates down through the tower and decolorized oil flows from the bottom of the tower through outlet pipe 32 provided with valve 33. After the oil charge has drained from the tower, valve 33 is closed and polar solvent is introduced into the tower through pipes 34 and 35. The solvent passes down through the spent cotton adsorbent contained in the tower, removing sorbed color bodies therefrom, and passes from the bottom of the tower through conduit 36 provided with a control valve 37. The solvent containing sorbed coloring matter is then conducted into fractionating column 38. The column is maintained at a temperature such that the solvent passes overhead as vapor through pipe 39 while the coloring matter previously removed from the oil and the adsorbent collects in the bottom of column 38 and is periodically removed therefrom through pipe 40. The solvent vapor flowing through pipe 39 passes into condenser 41, wherein the solvent vapor is condensed. Liquid solvent ensuing from condenser 41 is recycled to tower 30 through pipe 35. After regeneration of the cotton adsorbent, a further oil charge is introduced through conduit 31 and the oil percolates down through the tower, removing a certain amount of solvent from the wet adsorbent during its course of flow. This oil, after percolation, is removed from the bottom of the tower through conduit 42 provided with control valve 43. The admixture of oil and solvent is led into fractionating column 44, which is maintained at a temperature such that the solvent passes overhead as vapor through pipe 45 while decolorized oil collects in the bottom of column 44 and is periodically removed therefrom through pipe 46. The solvent vapor flowing through pipe 45 passes into condenser 41 and then is recycled to tower 30 through pipe 35.

Having described the nature of this invention, the following specific but non-limiting examples will serve to illustrate the improved results attained in accordance with the instant process.

Example 1

Eight hundred grams of a coastal distillate having an A. P. I. gravity of 25.7, a boiling range from 500° F. to 700° F., and a naphthenic acid content approximating 1 per cent by weight was percolated through a column 2 inches in diameter and 24 inches high, containing 160 grams of unbleached cotton. The temperature was maintained at about 20° C. and the rate of flow was about 1 fluid ounce per hour.

The oil before contact with the cotton adsorbent had a color (Lovibond) of 5 and after passing through the column of cotton adsorbent had a color (Lovibond) of 2.7.

Example 2

Five hundred c. c. of an oil having an A. P. I. gravity of 25.7, a boiling range of from 500 to 700° F., and a naphthenic acid content approximating 1 per cent by weight was percolated through 80 grams of cotton contained in a column two inches in diameter and 24 inches high. Percolation was carried out at room temperature and the rate of flow was about 1 fluid ounce per hour.

The oil before contact with the cotton adsorbent had a color (Lovibond) of 5 and after percolation through the column of cotton had a color (Lovibond) of 3.2.

Two hundred c. c. of carbon tetrachloride were passed through the column of cotton adsorbent to remove oil adhering to the surface of the cotton. Thereafter, 500 c. c. of isopropyl alcohol were passed through the adsorbent column, removing the sorbed color bodies. The cotton so treated was thereafter dried. Five hundred c. c. of fresh oil stock were again passed through the same column and the color of the oil after percolation was found to be 3 on the Lovibond scale.

Example 3

Two hundred seventy-five c. c. of a fuel oil boiling between about 330 and about 640° F. and having an A. P. I. gravity of about 31.3 and a naphthenic acid content of about 0.5 per cent by weight were percolated through a column 2 inches in diameter and 24 inches deep, containing 40 grams of unbleached cotton. Percolation was carried out at room temperature and the rate of percolation was about 1 fluid ounce per hour. The oil after percolation through the column had a color (Lovibond) of 17. The charge stock had a color (Lovibond) of 30.

From the foregoing examples, it will be seen that cotton possesses a high color sorptive capacity for removing color bodies from mineral oil fractions characterized by a boiling point within the range of 300 to 800° F., an A. P. I. gravity within the range of 20 to 40 and a naphthenic acid content of between about 0.5 and about 3 per cent by weight.

It is to be understood that the above description is merely illustrative of preferred embodiments of the invention, of which many variations may be made within the scope of the following claims by those skilled in the art without departing from the spirit thereof.

I claim:

1. A method for removing color bodies from an oil containing the same characterized by a boiling point range of between about 300 and about 800° F., an A. P. I. gravity of between about 20 and about 40, and a naphthenic acid content of between about 0.5 and about 3 per cent by weight, which comprises agitating said oil with ordinary cotton adsorbent to insure thorough admixture

of cotton and oil, removing the oil so treated from the cotton and elutriating the spent cotton with a polar solvent.

2. A method for removing color bodies from an oil containing the same characterized by a boiling point range of between about 300 and about 800° F., an A. P. I. gravity of between about 20 and about 40, and a naphthenic acid content of between about 0.5 and about 3 per cent by weight, which comprises percolating said oil through a column packed with ordinary cotton adsorbent, collecting the oil issuing from said column and elutriating the spent cotton with a polar solvent.

3. A method for removing color bodies from an oil containing the same characterized by a boiling point range of between about 300 and about 800° F., an A. P. I. gravity of between about 20 and about 40, and a naphthenic acid content of between about 0.5 and about 3 per cent by weight, which comprises contacting said oil with ordinary cotton adsorbent, separating the oil so treated from said adsorbent and elutriating the spent cotton with a polar solvent.

4. A method for removing color bodies from an oil containing the same characterized by a boiling point range of between about 300 and about 800° F., an A. P. I. gravity of between about 20 and about 40, and a naphthenic acid content of between about 0.5 and about 3 per cent by weight, which comprises contacting said oil with ordinary cotton adsorbent, separating the oil so treated from said adsorbent, removing oil adhering to said adsorbent with a solvent therefor and thereafter elutriating the cotton adsorbent with a polar solvent.

5. A continuous process for removing color bodies from an oil containing the same and characterized by a boiling range of between about 300 and 800° F., an A. P. I. gravity of between about 20 and about 40 and a naphthenic acid content of between about 0.5 and about 3 per cent by weight, which comprises contacting said oil with ordinary cotton adsorbent, filtering the decolorized oil from said cotton adsorbent, elutriating the spent cotton with a polar solvent, drying the cotton adsorbent so regenerated, recycling the regenerated cotton to further contact with the original oil, separating the solvent solution of color bodies and recycling said separated solvent to contact with the aforesaid spent cotton.

6. A continuous process for removing color bodies from an oil containing the same and characterized by a boiling range of between about 300 and 800° F., an A. P. I. gravity of between about 20 and about 40 and a naphthenic acid content of between about 0.5 and about 3 per cent by weight, which comprises agitating said oil with ordinary cotton adsorbent for a suitable period of time to

sorb color bodies therefrom; filtering the oil so decolorized from said cotton, elutriating the spent cotton with a polar solvent, drying the cotton so regenerated, recycling the regenerated cotton to further contact with the original oil, separating the solvent solution of color bodies and recycling said separated solvent to contact with the aforesaid spent cotton.

7. A continuous process for removing color bodies from an oil containing the same and characterized by a boiling range of between about 300 and 800° F., an A. P. I. gravity of between about 20 and about 40 and a naphthenic acid content of between about 0.5 and about 3 per cent by weight, which comprises percolating said oil through a column packed with ordinary adsorbent cotton, collecting the decolorized oil issuing from said column, elutriating the spent cotton with a polar solvent, separating the solvent solution of color bodies, and recycling said separated solvent to said column.

8. A continuous process for removing color bodies from an oil containing the same and characterized by a boiling range of between about 300 and 800° F., an A. P. I. gravity of between about 20 and about 40 and a naphthenic acid content of between about 0.5 and about 3 per cent by weight, which comprises percolating said oil through a column packed with ordinary cotton adsorbent, collecting the decolorized oil issuing from said column, elutriating the spent cotton with a polar solvent, separating the solvent solution of color bodies so obtained, contacting the regenerated cotton adsorbent with a fresh charge of oil, separating the mixture of oil and solvent issuing from said column, collecting the decolorized oil obtained as a result of said separation and recycling the separated solvent to contact with the spent cotton adsorbent.

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