PROCESS FOR DECOLORIZING PETROLEUM HYDROCARBONS WITH A PYRROLIDONE

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This invention relates to an improved process for decolorizing petroleum hydrocarbons.

In the customary refining, crude oil is first submitted to fractional distillation by means of which it is separated into four or more main fractions. The distillate coming over up to 150° C. consists of the lower hydrocarbons and is a mobile liquid. By further fractionation, it is separated into petroleum ether having a boiling range of 40–70° C., naphtha having a boiling range of 70–90° C., and lignite having a boiling point of 90–120° C. The fraction distilling between 150 and 300° C. consists of kerosene and light paraffin oil. After the distillation of the crude, the various fractions are treated with sulfuric acid, adsorbents, or with inorganic compounds such as for example, lime, magnesium hydroxide, sulfite dioxide, the so-called Edelanu process, or by treatment with aluminum chloride which acts as a polymerizing and saturating agent.

The color of the foregoing fractions, when well refined, varies in shade with the specific gravity of the petroleum hydrocarbon, being yellow for light gravity oils (0.77–0.789), amber for medium gravity oils (0.792–0.820), and dark for oils of heavy specific gravity. All of these fractions are further purified by fractional distillation to yield substantially pure hydrocarbons which are colorless, but become colored upon oxidation, especially oxidation of the unsaturated members.

For some industrial applications, the color of liquid petroleum hydrocarbons is of significant importance, for example, in the field of insecticidal oils, wherein kerosene and light mineral oils are employed as the dispersing medium, it is essential that the kerosene or mineral oil be almost of water white quality. The same applies to mineral oils used for medicinal purposes, and vaseline oils which find considerable use in the field of cosmetics, especially in the preparation of hair tonics. To supply a product which would be water white, or substantially water white, is the goal of every petroleum refiner. The currently employed refining processes while yielding products which meet this requirement, the products when stored or packaged in bottles or other containers have the tendency to become cloudy. This, as noted above, is due to oxidation of the unsaturated constituents which were not removed either during the distillation process or by any one of the refining or treating processes used.

To provide a simple and inexpensive process for decolorizing liquid and solid petroleum hydrocarbons constitutes the principal object of the present invention.

Other objects and advantages will become apparent from the following description.

I have discovered that various liquid and waxy (solid and semi-solid) petroleum hydrocarbons are readily decolorized by contacting them with a compound having the following formula:

\[
\text{H}_2\text{C} \quad \text{A} \quad \text{H} \text{CH}_2
\]

wherein A represents \(-\text{NH}, \text{-NH} \text{-CH} \text{-CH}_3\) or an \(-\text{N-alkyl} \text{group}, \text{e.g., N-methyl, N-ethyl, N-propyl, N-butyl, etc.}

As illustrative of specific compounds which may be used for this purpose, the following may be mentioned:

2-pyrrolidone
N-methyl-2-pyrrolidone
N-ethyl-2-pyrrolidone
N-isopropyl-2-pyrrolidone
N-vinyl-2-pyrrolidone

Any petroleum hydrocarbon derived from crude oil refining such as petroleum ether, kerosene, naphtha, lubricating oils having a boiling point of approximately 350° C. more or less, including medium and heavy mineral oils, paraffin oil, which are available to the trade under the names of liquid petroleum, “Albolene,” “Stanolax,” “Nujol” and the like, including “Vaseline” or petroleum jelly melting between 38–50° C. and paraffin wax having melting points between 45–65 and 50–80° C. are very readily decolorized by treating with any compound characterized by the foregoing general formula.

In some instances, this treatment may be given in the absence of any one of the above-mentioned compounds in liquid colored petroleum hydrocarbon, and stirring or shaking the hydrocarbon mixture to establish contact and separating the immiscible portions by decantation and separation of the colored layer, which is always the bottom liquid layer, or by allowing it to drain off. The contact time required is very short with instantaneous decolorization and separation into two layers occurring.

In other instances where it is desired to remove color from crude kerosene, crude naphtha, paraffin oil and the like, 2-pyrrolidone is the best and most efficient for largescale decolorization because of its complete immiscibility (or insolubility) in the hydrocarbon, thereby providing complete and simple removal of the colored bodies without change in physical or chemical properties of the product.

The concentration of the 1-vinyl-2-pyrrolidone or its polymers, or of N-methyl-2-pyrrolidone in the liquid hydrocarbon should be sufficient to saturate the hydrocarbon at room temperature.

The unusual feature of the present invention is that by employing 1-vinyl-2-pyrrolidone, N-methyl-2-pyrrolidone or 2-pyrrolidone as the decolorizing medium, these pyrrolidones may contain as much as 40% by weight of water without impairing the decolorizing effect.

The various petroleum hydrocarbons, particularly the kerosene and light mineral oil fractions are more effectively decolorized than by the distillation and currently employed refining techniques, thereby making available to the petroleum industry a cheap, readily usable method for maintaining water white quality of such products.

Storage tanks containing such liquid hydrocarbon products can be readily treated with 2-pyrrolidone for maintaining them and other petroleum liquid products colorless. Such products, especially the kerosene and light mineral fractions, are readily usable by manufacturers of disinfectants, insecticides, and as solvents for DDT aerosol sprays, without fear of contamination of household effects and other objects sprayed on, due to objectionable color as caused by the same hydrocarbons in a colored state.

The pyrrolidones are of particular advantage in decolorizing crude oil free from asphaltic constituents before processing, i.e., distillation and purification.

Various mineral oils, lubricating oils, vaseline, greases, and the like, containing from 10–22% by weight of 1-vinyl-2-pyrrolidone or from 5–8% of N-methyl-2-pyrrolidone by weight appear to contribute to the depression of the freezing point of these various hydrocarbons.

In
other words, the various pyrrolidones appear to act as pour-point depressants. The following examples will illustrate how the various pyrrolidones may be effectively utilized in decolorizing petroleum hydrocarbon products. It is to be clearly understood that these examples are merely illustrative, and are not to be construed as being

**Example I**

111 grams of N-vinyl-2-pyrrolidone and 111 grams of brown colored kerosene were poured into a 1-liter, 3-neck round-bottom flask equipped with reflux condenser, stirrer and thermometer. To this, 0.56 grams (0.5%) of a’a’-azodisobutyronitrile catalyst was added and the flask and contents heated on a steam bath while stirring. Within 5 minutes, the temperature of the solution sharply rose to 90° C. and continued to rise until a maximum of 110° C. was reached. At this point the temperature quickly dropped of its own accord to 95° C. and a mass of polyvinylpyrrolidone was obtained which settled to the bottom of the flask rendering the colored kerosene used, colorless. Analysis of the supernatant kerosene showed it to be free of nitrogen, but colorless. Its color was also more pleasant than the color-containing kerosene.

**Example II**

50 grams of colored kerosene was poured into a separatory funnel along with 8 grams of N-vinyl-2-pyrrrolidone and shaken vigorously. The separatory funnel was then placed in a vertical position and the solution allowed to stand. Within 1 minute a separation of 1 ml. of N-vinyl-2-pyrrolidone occurred which was brown in color and the kerosene layer containing 7 grams of N-vinyl-2-pyrrolidone was colorless and clear.

**Example III**

50 grams of colored kerosene was poured into a separatory funnel along with 47.5 grams of N-vinyl-2-pyrrolidone and shaken vigorously. The separatory funnel was then placed in a vertical position and the solution allowed to stand. Within 1 minute separation into 2 liquid layers occurred and 33.5 grams of N-vinyl-2-pyrrolidone was recovered. 14 grams of N-vinyl-2-pyrrolidone remained soluble in the kerosene which was also colorless and clear. Analysis of the kerosene layer for nitrogen gave 2.77% which corresponds to 22% N-vinyl-2-pyrrolidone remaining soluble in the kerosene at room temperature.

**Example IV**

100 grams of a solution comprising 50% by weight colored kerosene, 30% N-vinyl-2-pyrrolidone and 20% water (50 grams kerosene and 50 grams of a 60/40 vinylpyrrolidone/water solution) was poured into a separatory funnel and shaken vigorously. Upon standing for about 1 minute a separation into 2 liquid layers occurred and 50 grams of vinylpyrrolidone/water solution was obtained as the bottom layer and contained the color of the kerosene used. In this instance the presence of water in the vinylpyrrolidone prevented the vinylpyrrolidone from dissolving in the kerosene. The kerosene obtained was free of color and clear.

**Example V**

50 grams of colored kerosene and 50 grams of a 70/30 solution of vinylpyrrolidone and water were poured into a separatory funnel and shaken and let separatory funnel and contents stand. Within 1 minute separation into 2 layers occurred and 49 grams of the 70/30 solution of vinylpyrrolidone-water was recovered. The kerosene (top layer) was colorless and clear while the bottom layer (vinylpyrrolidone and water) was colored as was the kerosene used for the experiment. Analysis for nitrogen in the kerosene layer gave 0.86% which corresponds to 6.8% N-vinyl-2-pyrrolidone remaining soluble in the kerosene.

**Example VI**

90 grams of colored kerosene and 10 grams of N-vinyl-2-pyrrolidone were poured into a separatory funnel and shaken. A solution was obtained. The separatory funnel containing the solution was placed in an ice bath at 0° C.-5° C. and within 1 hour 5.5 grams of vinylpyrrolidone containing the color of the kerosene separated as the bottom layer. The supernatant layer, kerosene plus 4.5 grams of vinylpyrrolidone was clear and colorless.

**Example VII**

75 grams of colored kerosene and 25 grams of N-vinyl-2-pyrrolidone were poured into a separatory funnel and shaken. Within 1 minute, 2.5 grams of vinylpyrrolidone was recovered as a dark brown bottom layer. Upon standing at room temperature for several hours no further separation occurred. The kerosene layer containing 22.5 grams of vinylpyrrolidone was colorless and clear.

**Example VIII**

50 grams of colored kerosene and 50 grams of N-methyl-2-pyrrolidone were poured into a separatory funnel and shaken. Upon standing for a few minutes a 2-layer separation occurred with the bottom layer, N-methyl-2-pyrrolidone being dark brown in color and the top layer kerosene plus some N-methyl-2-pyrrolidone being colorless and clear. Analysis of the kerosene layer for nitrogen showed it to contain 0.56% N or about 4% N-methyl-2-pyrrolidone on a weight basis remained soluble in the kerosene.

**Example IX**

70 grams of colored kerosene and 30 grams of N-methyl-2-pyrrolidone were poured into a separatory funnel and shaken. Upon standing for a few minutes a 2-layer separation occurred, the bottom layer being N-methyl-2-pyrrolidone plus the color contained in the kerosene used. The kerosene layer was clear and colorless. Analysis for nitrogen gave 0.96% N which corresponds to about 8% N-methyl-2-pyrrolidone dissolved in the kerosene.

**Example X**

25 grams of colored kerosene and 25 grams of 2-pyrrolidone were poured into a separatory funnel and shaken. Upon standing, 2 layers separated immediately with the decolorized kerosene being the top layer and the 2-pyrrolidone containing all the color of the colored kerosene as the bottom layer. Analysis for nitrogen in the kerosene layer yielded a trace of nitrogen indicating that none of the 2-pyrrolidone was dissolved in the kerosene. (Analysis for nitrogen on the colored kerosene used in these experiments yielded a trace of nitrogen also.)

**Example XI**

The colored (yellow-brown) kerosene used in the above experiments had the following analyses:

- Percent nitrogen—trace
- Percent H2O—<0.1
- Percent ash or carbon residue —<0.01

The decolorized kerosene obtained in each experiment above contained the same amount of water (<0.1%) and same amounts of ash (<0.01%). They differed only in nitrogen content, with those samples in which 1-vinyl-2-pyrrolidone or N-methyl-2-pyrrolidone were used containing nitrogen due to their solubility in kerosene (1-vinyl-2-pyrrolidone 22% soluble, N-methyl-2-pyrrolidone 8% soluble).

**Example XII**

Example X was repeated with the exception that 25 grams of colored kerosene were replaced by 25 grams of
light lubricating oil having a yellow color and a boiling point over 300° C. Upon standing, 2 layers separated immediately with the decolorized mineral oil being the top layer, and the 2-pyrrolidone containing all the color of the mineral oil as the bottom layer.

Example XIII

150 grams of paraffin wax having a melting point of 50–80° C. was dissolved in 500 cc. of ethylene dichloride by the application of gentle heat until complete solution was effectuated. The solution was allowed to reach room temperature and 100 grams of 2-pyrrolidone added, and the mixture shaken vigorously for several minutes. Thereafter the mixture was placed in “Dry Ice” until a temperature of approximately −15° F. was attained. Within a few seconds the wax precipitated from the cold solution, was collected and pressed in a filter press to yield a pure white wax.

I claim:

1. The process of decolorizing hydrocarbons which comprises contacting said hydrocarbon with a pyrrolidone having the following general formula:

   \[
   \begin{array}{c}
   \text{H}_2\text{O} \\
   \text{CH}_3 \\
   \text{O}=\text{O} \\
   \end{array}
   \]

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wherein A represents a member selected from the group consisting of NH, N-vinyl and N-alkyl groups.

2. The process according to claim 1 wherein the pyrrolidone is 1-vinyl-2-pyrrolidone.

3. The process according to claim 1 wherein the pyrrolidone is N-methyl-2-pyrrolidone.

4. The process according to claim 1 wherein the pyrrolidone is 2-pyrrolidone.

5. The process according to claim 1 wherein the pyrrolidone is N-ethyl-2-pyrrolidone.

6. The process according to claim 1 wherein the pyrrolidone is N-isopropyl-2-pyrrolidone.

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