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METHOD OF NEUTRALIZING OIL WITH DIAZOMETHANE

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This invention relates to new and useful improvements in processes for the refining of petroleum fractions to reduce the amount of free acid present therein. It is more particularly concerned with the treatment of refined petroleum fractions, such as lubricating oils, to obtain neutral, color-stable products.

Crude oils which contain appreciable quantities of naphthenic acids and other acidic materials cause difficulties during their refining to produce various petroleum products. Distillation to produce lubricating oil stocks may be accompanied by corrosion, necessitating the use of special alloys for caps and trays in the fractionating column. Corrosion difficulties may also be encountered during distillation of extraction solvent from the extract phase from a lubricating oil solvent extraction process. The lubricating oil extracts which are obtained in the solvent refining of lubricating oils also contain large quantities of free naphthenic acids and other acidic materials. Even finished oils, such as neutrals and bright stocks, may have acid neutralization numbers which are objectionable. Other petroleum fractions, such as fuel oils and kerosenes, may also contain objectionable amounts of acidic materials. The problem of acidic materials in petroleum refining is also encountered in the reclaiming of used oils, such as used crankcase oils, where the acids have originated from partial oxidation of the oil during use. The presence of acidic materials in hydrocarbon fractions may also be objectionable from the standpoint of thermal stability and color stability of the finished product. It has been found that lubricating oils containing objectionable amounts of acidic materials have a greater tendency to decompose upon heating and have less color stability. In particular, lubricating oils containing excess acidity have been found to deteriorate in color and darken upon extended storage in the light, or upon storage at moderately elevated temperatures in the dark.

It is therefore one object of this invention to provide a new and improved process for the refining of hydrocarbon fractions which reduces the acidity and improves thermal and color stability of the product.

Another object of this invention is to provide an improved process for treatment of a refined petroleum fraction containing substantial quantities of acidic material by treatment with a reagent which converts acidic materials into neutral esters and ethers.

Another object of this invention is to provide an improved process for reclaiming used lubricating oils in which a used oil, which has been treated to remove asphaltic and tarry materials is treated with a reagent which converts acidic materials into neutral esters and ethers.

A feature of this invention is the provision of an improved process for refining a petroleum fraction in which a partially refined petroleum fraction having a substantial acidity and content of color-forming materials is treated with a solution of diazomethane in an inert, volatile solvent.

Another feature of this invention is the provision of an improved process for the reclaiming of used lubricating oils in which the used oil is treated with a solid adsorbent to remove asphaltic and tarry materials, and then is treated with a solution of diazomethane in a volatile, inert solvent,

such as a low-boiling hydrocarbon, to convert acidic materials into neutral esters and ethers.

Other objects and features of this invention will become apparent from time to time throughout the specification and claims as hereinafter related.

This invention is based upon our discovery that neutral color-stable products can be produced by treating petroleum fractions having substantial acidity in the form of naphthenic acids and other acidic or acid-forming materials, such as oil-soluble phenols, with a solution of diazomethane in an inert, volatile solvent, preferably a low-boiling hydrocarbon, such as hexane. This treatment is primarily useful in the preparation of color-stable, neutral lubricating oils from distilled or solvent-extracted lubricating oils, or from reclaimed oils which have been freed of asphaltic or tarry materials by treatment with a solid adsorbent. In the case of lubricating oil fractions obtained from crude oil, it is preferred that the crude oil, or the lube oil cuts obtained during distillation, be given a preliminary treatment, such as a treatment with an alkyl halide or dialkyl sulfate and alkali, as disclosed in our copending application, Serial No. 47,597, filed August 5, 1960, now U.S. Patent No. 3,061,540, entitled Process, or a clay treatment, to reduce the acidity of the oil so that it can be processed more readily in the process of this invention. The diazomethane may be applied in a relatively low-boiling, inert solvent, such as hexane or kerosine, or may be generated in situ by alkaline decomposition of nitrosomethylurea.

In a preferred embodiment of this invention, a crude oil is treated with an aqueous caustic soda solution and then with dimethyl sulfate just prior to desalting. Then the crude oil is passed through the desalter and salts are removed therefrom. By this step, a large part of the naphthenic acids, particularly the more acidic material, is converted to neutral methyl naphthenates. Crude oil containing these methyl naphthenates is processed in the usual manner yielding products, such as finished neutrals and bright stocks, which have relatively low neutralization numbers, compared to those obtained when the crude oil is not methylated in this manner. Next, the essentially finished oils produced from the treated crude oil are treated with a solution of diazomethane in a low-boiling, inert solvent in an amount sufficient to convert substantially all of the remaining naphthenic acids present to methyl naphthenates. Where other acidic or acid-forming materials, such as oil-soluble phenols are present, they are converted into ethers or other methylated products by the diazomethane. The finished oils which are obtained in this manner have a substantially zero neutralization number, show resistance to oxidation and heat breakdown, and are very stable against color deterioration on extended storage.

By this combination of steps, improved results are obtained which are not produced by the use of either of the process steps alone. The application of the first step to the crude oil, even when carried out in its most extreme manner, does not produce a zero-acid-number lubricating oil stock, nor is the stability of the oil increased as with the diazomethane treatment. The application of only the diazomethane treatment to the finished lubricating oil stocks decreases the acid neutralization number and improves the stability of the stock, but so much diazomethane is required in the case of highly acid fractions, such as solvent extracts obtained in the solvent refining of lubricating oil, that the use of diazomethane is prohibitively costly. Likewise, the use of diazomethane in treatinng the crude oil before the desalter will produce a drastic decrease in the acid neutralization number, but at a prohibitive cost. In the operation of this process, the corrosion of refining equip-

ment is minimized, since the most active naphthenic acids in the crude oil are the first to be methylated in the preliminary treatment of the crude oil.

In our two-step process, we prefer to treat the crude oil with 0.5–2 mols of aqueous caustic soda solution per mol of organic acid present in the crude oil, followed by treatment with 0.5–2 mols of dimethyl sulfate (or alkyl halide) per mol of organic acid, followed by desalting to remove the by-products and naturally occurring salts. This treatment is carried out, as described in our copending application, at temperatures up to about 200° F., preferably at ambient temperature. In the initial treatment of the crude oil, it is preferred that the treatment with caustic soda solution be carried out for a time sufficient to convert the acids into alkali salts prior to treatment with the dimethyl sulfate or alkyl halide.

The diazomethane used in the final step of the process is formed in situ in a low-boiling, inert solvent, preferably a paraffinic hydrocarbon, such as hexane, odorless mineral spirits, or deodorized kerosine. The diazomethane is formed in situ in a hydrocarbon solvent by alkaline decomposition (with aqueous sodium hydroxide or sodium carbonate) of nitrosomethylurea, followed by settling and separation of the by-product salt. The diazomethane solution is added to the hydrocarbon fraction being treated, in an amount of 1–18 mols of diazomethane per mol of acid in the hydrocarbon product, from ambient temperatures up to about 160° F. The treatment with diazomethane in solution provides a more convenient and safer method of handling diazomethane. Diazomethane is shock-sensitive and tends to detonate at high temperatures or high pressures. By forming the diazomethane in hydrocarbon solution, it may be stored for extended periods of time, if necessary, or may be generated just prior to use. By using a hydrocarbon solution of diazomethane as the treating material, the hydrocarbon solvent may be left in the finished product or may be removed by blowing the oil with an inert gas, or by distillation.

The following non-limiting examples are illustrative of the scope of this invention.

Example I

An East Texas crude oil having an acid neutralization number of 1.3 is mixed thoroughly with 1.1 mols of caustic soda solution per mol of organic acid in the oil and heated at about 120° F. for 30 minutes. The oil is then mixed with 1 mol of dimethyl sulfate per mol of organic acid present, at about 120° F., after which it is washed with water in a desalter and the aqueous material settled out under high electrical potential. The desalted crude, which now has an acid neutralization number of 0.3, is processed in the usual manner to produce low-boiling distillates and residual lubricating oil stocks. The finished neutral oil is obtained from the lubricating oil fraction and has an acid neutralization number of 0.01. This oil is treated with a hexane solution of diazomethane in the proportion of 3 mols of diazomethane per mol of organic acid in the oil. The neutralization number of the oil is reduced to 0.0, and the resulting product has substatnially improved oxidation stability and is improved in color stability. The diazomethane-treated neutral oil is lighter in color by about 0.5 ASTM color unit and is stable for periods up to 30 days, or more, at room temperature and at elevated temperatures, both in the dark and when exposed to sunlight.

A finished bright stock, obtained from a lubricating oil fraction which has been solvent-extracted, dewaxed and clay-treated, and having an acid neutralization number of 0.05, is treated by adding a solution of diazomethane in deodorized kerosine in the proportion of 6 mols of diazomethane per mol of acid in the oil. The acid neutralization number of the bright stock is reduced to 0.00, and the oil is greatly improved in oxidation and color stability.

In the preparation of solvent-refined oils from a lubricating oil fraction, an aromatic extract oil is obtained as a by-product in the production of 170-vis. neutral, which extract has an acid neutralization number of 1.1. The solvent extraction process tends to concentrate naphthenic acids and other acidic materials in the extract phase. This solvent-extract oil is treated with a solution of diazomethane in deodorized kerosene in the proportion of 3 mols diazomethane per mol of organic acid. This reduces the acid neutralization number to 0.08 and improves the stability of the oil substantially.

When the crude oil (Example I) is processed without the preliminary treatment with alkali and dimethyl sulfate, and the final treatment with diazomethane, the finished lubricating oils obtained have substantially greater acidity. The 170-vis. neutral has an acid neutralization number of about 0.03 and the bright stock has an acid neutralization number of about 0.07. The extract obtained in the solvent refining of the neutral oil has an acid neutralization number of about 4.1. From these examples, it is seen that the two-step treatment results in a very substantial reduction in acid neutralization number of the finished petroleum products and produces products of enhanced stability.

Example II

Texas crude oil was desalted and then fractionated into distillate and residual fractions. The bright stock was obtained by a conventional finishing process, including solvent extraction, dewaxing, and clay-treating, and had an acid neutralization number of 0.08. A portion of this bright stock was treated with a solution of diazomethane in hexane, prepared by the decomposition of nitrosomethylurea with sodium hydroxide. The solution contained 0.178 g. of diazomethane per cc. of hexane and was added to the bright stock at ambient temperature in an amount equal to 6 mols of diazomethane per mol of organic acid in the oil. After this treatment, the acid neutralization number of the bright stock had decreased to 0.02. Another portion of the finished bright stock was treated with an amount of the diazomethane solution sufficient to provide 18 mols of diazomethane per mol of organic acid in the oil. This treatment was carried out at room temperature and reduced the acid neutralization number of the bright stock to 0.00. Samples of the treated bright stock were about 0.5 ASTM color unit lighter in color than the untreated bright stock, and were stable against color deterioration for a period up to at least 30 days, both in the dark and in sunlight, at room temperature and at 165° F.

A portion of the bright stock which had been solvent-treated and dewaxed, but had not been given a finishing clay-treatment, had an acid neutralization number of 0.18. This bright stock was treated with the hexane solution of diazomethane (0.178 g./cc.) in an amount sufficient to provide 2.6 mols of diazomethane per mol of acid. The acid neutralization number of the bright stock decreased to 0.10 after this treatment. Another portion of the solvent-extracted and dewaxed bright stock, having an initial acid neutralization number of 0.18, was treated with the hexane solution of diazomethane in the proportion of 8 mols of diazomethane per mol of acid in the oil. After this treatment, the acid neutralization number of the oil decreased to less than 0.01. Samples of this bright stock before and after treatment with diazomethane were tested for color stability using ASTM Method D 1500–58 T as the procedure for the color determination. The diazomethane-treated bright stocks were about 0.5 color unit lighter in color than the untreated bright stocks and were stable against color deterioration for periods up to at least 30 days. The untreated bright stock darkened by about 0.5 color unit on extended storage.

In another experiment, a solvent-extract oil obtained as by-product in the phenol extraction of a lube oil stock

in the production of 170-vis. neutral oil was treated with diazomethane in the form of a hexane solution. The solvent-extract oil had an initial acid neutralization number of 6.5, and after treatment with a solution containing 3 mols of diazomethane per mol of acid present in the oil had an acid neutralization number of 0.18. If this oil is given a further treatment with diazomethane, the acid neutralization number can be reduced to substantially zero. In this experiment, and in the previous experiments using a hexane solution of diazomethane, it appears that it is necessary to use a substantial excess of diazomethane to reduce the acid neutralization number of oil to substantially zero. It appears that the necessity of using an excess of diazomethane arises from the presence of other acidic materials in the oil which react with the diazomethane. It therefore appears that the diazomethane not only converts acids to methyl esters in the oil, but also converts phenols to ethers, and may even methylate some hydrocarbons which contain a reactive hydrogen atom.

While this invention is primarily concerned with the treatment of virgin oil fractions, it is also applicable to the reclamation of used oils. Used oils, such as crankcase oils, have been reclaimed by various methods, including distillation to remove crankcase dilution, percolation through adsorbents to remove asphaltic and tarry materials, and distillation over alkali to remove most of the organic acids. Where the oils contain a substantial amount of bright stock or other non-distillable lubricating fractions, it has been difficult to reclaim all of the oil satisfactorily. When bright stock is present in the oil, distillation in the presence of alkali to remove acids (produced by partial oxidation of the oil during use) is not feasible. Thus, most reclaimed oils have relatively high organic acidities and may give trouble during use with certain types of bearings. In the following example, it is seen how our process can be applied to the production of reclaimed oils having substantially zero acid number and containing substantially no asphaltic or tarry matter, regardless of whether bright stock is present in the oil.

Example III

A used crankcase oil, black in color and having an acid neutralization number of 1.4, is percolated through fuller's earth to remove asphaltic and tarry materials. The percolated oil is greenish-red in color and has an acid neutralization number of 1.1. After percolation through the fuller's earth, the percolated oil is treated with a 3% solution of diazomethane in hexane in an amount corresponding to 1–18 mols of diazomethane per mol of organic acid present in the oil. This treatment is carried out at room temperature and converts all of the acid present into methyl esters. The reclaimed oil obtained after this treatment has an acid neutralization number of 0.00. This reclaimed oil is more stable to color deterioration and has a lighter color (about 0.5 ASTM color unit lighter) than the oil before treatment with diazomethane.

The used crankcase oil which was treated in accordance with this process cannot be converted to a zero-acid-neutralization-number product by percolation through fuller's earth, or by distillation in the presence of caustic, or by a combination of the two steps. This oil is only 40% distillable in the presence of caustic without substantial cracking.

While we have described our invention fully and completely with special emphasis upon several preferred embodiments, we wish it to be understood that within the scope of the appended claims, this invention may be practiced otherwise than as specifically described herein.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A method of preparing a color-stable lubricating oil, having substantially zero acid neutralization number, which comprises treating a petroleum lubricating oil having substantial acidity with a solution of diazomethane in an inert solvent to convert acidic materials in the oil into neutral, stable products.

2. A method according to claim 1 in which the diazomethane is added in solution in a low-boiling hydrocarbon.

3. A method according to claim 2 in which the diazomethane is prepared in situ in the hydrocarbon solvent.

4. A method according to claim 3 in which the diazomethane is formed by alkaline decomposition of methylnitrosourea in the presence of a light hydrocarbon.

5. A method according to claim 1 in which the lubricating oil is pretreated to reduce its acidity to a low value prior to treatment with diazomethane.

6. A method according to claim 5 in which the oil is given an initial clay treatment.

7. A method according to claim 5 in which the oil is treated initially with another neutralizing agent.

8. A method according to claim 1 in which the oil treated is a dewaxed, clay-treated bright stock.

9. A method according to claim 1 in which the oil treated is a dewaxed, clay-treated neutral oil.

10. A method according to claim 1 in which the oil treated is a solvent-extract oil obtained in the solvent refining of lubricating oils.

11. In a method of reclaiming used crankcase oil in which the used oil is percolated through a granular adsorbent to remove asphaltic and tarry impurities, the improvement which comprises treating the percolated oil with a solution of diazomethane in an inert solvent to convert acidic components of the oil into neutral stable products.

12. A method according to claim 11 in which the diazomethane is added in solution in a low-boiling hydrocarbon.

13. A method according to claim 11 in which the percolated oil is treated with a solution containing 1–18 mols of diazomethane per mol of acid in the oil.

14. A method according to claim 7 in which the oil is treated initially with aqueous alkali and then with an agent selected from the group consisting of lower alkyl sulfates and lower alkyl halides.

15. A method according to claim 14 in which the oil is desalted subsequent to the initial treatment but prior to the treatment with diazomethane.

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