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STABILIZATION OF HYDROCARBON DISTILLATES

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This invention relates to the stabilization of hydrocarbon distillates and more particularly to a novel method of retarding deterioration of hydrocarbon distillates heavier than gasoline.

Hydrocarbon distillates heavier than gasoline are utilized primarily for burner oils and lubricating oils. These hydrocarbon distillates tend to undergo deterioration in storage and become discolored, form sediment, and undergo other undesirable reactions. The present invention is directed to a novel method of retarding this undesirable deterioration.

The term "burner oil" is used in the present specification and claims in a generic sense to include hydrocarbon distillates heavier than gasoline. These oils are marketed under various trade names such as fuel oil, furnace oil, burner oil, range oil, diesel fuel, jet fuel, etc., and are selected to meet commercial specifications. In general, the burner oil will have an initial boiling point ranging as low as 300° F. or lower and an end boiling point which may range up to about 750° or higher. Included in the classification of burner oil are jet fuels or other hydrocarbon distillates which may have an initial boiling point as low as 60° F. and an end boiling point within the range of from about 450° F. to about 600° F. or higher.

At the present time burner oils come primarily from non-destructive distillation of petroleum oil, and the burner oil is commonly referred to in the art as straight run distillate, and from catalytic and non-catalytic cracking processes, and the burner oil is commonly referred to in the art as cycle stock. The term cycle stock is used because the burner oil is separated from a fraction which is recycled to the cracking process for further conversion therein. Other sources of burner oil may include those produced by the reaction of carbon monoxide with hydrogen in the process known as the Synthesis Process, Fischer-Tropsch process, etc. Regardless of the source, burner oils, particularly when comprising blends of two or more different oils, tend to undergo discoloration and form sediment in storage, and the present invention is directed to a novel method of retarding this deterioration.

Because of the increasing amounts of catalytic cycle stock available at the present time, refiners have adopted the practice of blending catalytic cycle stock with straight run distillate to produce burner oils. As hereinbefore set forth, these blended burner oils tend to undergo discoloration and sediment formation to an undesirable extent, and require some method of retarding this deterioration. It is apparent that discoloration of burner oil is undesirable because many burner oils are marketed on the basis of a color specification, and discolored oils cannot meet the color specification. Furthermore, sediment formation in burner oil is objectionable because the sediment tends to plug strainers, burner tips, injectors, etc. and, when used as diesel fuel, tends to form varnish and sludge in the cylinders of the diesel engine. The sediment referred to herein is different from the solid material originally contained in burner oils and

referred to in the art as B. S. & W. The sediment with which the present invention is concerned is not contained in the burner oil as produced but forms during storage.

While, as hereinbefore set forth, the present invention is particularly applicable to the treatment of blends of catalytic cycle stock and straight run distillate, there are cases where the straight run distillate itself or the catalytic cycle stock will undergo excessive sediment formation and discoloration in storage. It is understood that the present invention may be used for the purpose of retarding this deterioration. Similarly, the present invention may have an application to the treatment of lubricating oils, transformer oils, turbine oils, etc. which undergo excessive deterioration in storage.

In one embodiment the present invention relates to a method of stabilizing a hydrocarbon distillate heavier than gasoline which comprises incorporating in said distillate a small amount of a nitropyrimidine.

In a specific embodiment the present invention relates to a method of retarding deterioration of burner oil which comprises incorporating therein from about 0.0001% to about 1% by weight of a nitrohexahydropyrimidine.

In still another embodiment the present invention relates to a burner oil containing the nitropyrimidine as herein set forth as an additive to retard deterioration of the burner oil.

The additive for use in accordance with the present invention comprises a nitropyrimidine, including nitropyrimidine, nitrodihydropyrimidine, nitrotetrahydropyrimidine and nitrohexahydropyrimidine.

The particular position of the nitro group on the pyrimidine ring will depend in most cases upon the particular compounds used as starting materials for the preparation of the nitropyrimidine compound.

In a preferred embodiment, at least one nitro group is attached to at least one of the carbon atoms of the pyrimidine ring. In some cases nitropyrimidine compounds having a nitro group attached to the nitrogen atom in the pyrimidine ring may be employed but not necessarily with the equivalent results.

Preferred nitropyrimidine compounds comprise 1,3-dicycloalkyl-5-nitro-5-methyl-hexahydropyrimidine and 1,3-dialkyl-5-nitro-5-methyl-hexahydropyrimidine. These compounds may be prepared in any suitable manner. In one method of manufacture, 1,3-dicyclohexyl-5-nitro-5-methylhexahydropyrimidine may be prepared by reacting cyclohexylamine, formaldehyde and nitroethane. When dialkyl substituted compounds are desired, the desired alkylamine is employed in place of the cyclohexylamine. Thus for example, the alkylamine may comprise methylamine, ethylamine, propylamine and particularly isopropylamine, butylamine, amylamine, hexylamine, heptylamine, octylamine and particularly tertiaryoctylamine, nonylamine, decylamine, etc. Similarly, in place of cyclohexylamine, cyclopropylamine, cyclobutylamine, cyclopentylamine may be employed and, in some cases, cyclohexenylamines, cyclohexadinenylamines and phenyl amines may be employed. It is understood that the cyclic amines may contain aliphatic side chains attached thereto and also that the cyclic amines and the alkyl amines may have attached thereto one or more substituents containing oxygen, nitrogen and/or sulfur. Thus, for example, the cyclic amine or alkyl amine may contain one or more nitro groups attached thereto.

In place of nitroethane as a starting material for the preparation of these additives, other suitable nitroalkanes may be employed, including nitromethane, nitropropane, nitrobutane, nitropentane, nitrohexane, etc. When nitromethane is employed along with formaldehyde and cyclohexylamide, for example, the resultant pyrimidine compound will be 1,3-dicyclohexyl-5-nitro-5-hexahydropyrimidine. Similarly, when nitropropane is utilized, the

pyrimidine compound will be 1,3-dicyclohexyl-5-nitro-5-ethyl-hexahydropyrimidine.

It is understood that these various nitropyrimidine compounds are not necessarily equivalent but that all of them will serve to retard deterioration of burner oils.

The additive of the present invention generally is added to the burner oil in an amount of less than about 1% by weight and preferably from about 0.001% to about 1% by weight. It is understood that these additives may be used alone or in conjunction with other additives employed for specific purposes, such as metal deactivators, antioxidants, preferably of the phenolic type, synergists, cetane improvers, rust inhibitors, etc.

The following examples are introduced to illustrate further the novelty and utility of the present invention but not with the intention of unduly limiting the same.

Example I

1,3-dicyclohexyl-5-nitro-5-methyl -hexahydropyrimidine was prepared by reacting 99 grams of cyclohexylamine, 112.5 ml. of 36% aqueous formaldehyde and 37.5 ml. of nitroethane, with constant stirring, at 10° C. The product was extracted with ether, dried over sodium sulfate, the solvent evaporated and the product was recrystallized. The product had a melting point of 79–80° C.

0.02% by weight of 1,3-dicyclohexyl-5-nitro-5-methyl-hexahydropyrimidine was incorporated in a fuel oil blend comprising catalytically cracked and straight run fuel oil. The samples of fuel oil were subjected to accelerated aging at 100° C. for 20 hours, and the color of the different samples was determined in a Lumitron, model 402–E, Spectrophotometer. Distilled water is rated as 100 and a very dark oil is rated as 0 in this analysis.

The fuel oil had an original color of 88. After accelerated aging, the color of the fuel oil dropped to 23. The sample of the fuel oil containing the 1,3-dicyclohexyl-5-nitro-5-methyl-hexahydropyrimidine, after such aging, had a color of 51.

It will be noted that after the accelerated aging, the sample, to which the hexahydropyrimidine compound was added, was of considerably better color than the sample of the fuel oil without this additive.

Example II

0.02% by weight of 1,3-ditert-octyl-5-nitro-5-methyl-hexahydropyrimidine was added to another sample of the fuel oil described in Example I. After the accelerated aging, the sample containing the additive had a color of 47. Here again it will be noted that the hexahydropyrimidine compound served to considerably retard discoloration of the fuel oil.

The 1,3-ditert-octyl-5-nitro-5-methyl-hexahydropyrimidine was prepared in substantially the same manner as described in Example I except that 129 grams of tert-octylamine were utilized instead of the dicyclohexylamine.

Example III

1,3-diisopropyl-5-nitro-5-methyl - hexahydropyrimidine was prepared in the same manner as described in Example I except that 60 grams of isopropylamine were used instead of the cyclohexylamine. This product had a melting point of 44–45° C.

0.02% by weight of the 1,3-isopropyl-5-nitro-5-methyl-hexahydropyrimidine were added to another sample of the fuel oil described in Example I and, after the accelerated aging, the fuel oil had a color of 43. Here again it will be noted that the color of the fuel oil was considerably improved by the addition of the hexahydropyrimidine compound.

Example IV

1,3-dihexyl-5-nitro -5- propylhexahydropyrimidine may be prepared by the reaction of hexylamine, formaldehyde and nitrobutane. The resultant compound may be added in a concentration of 0.05% by weight to a West Coast catalytically cracked burner oil to retard discoloration thereto.

I claim as my invention:

1. A hydrocarbon oil heavier than gasoline and normally subject to sediment formation in storage containing, in a small but sufficient amount to retard said sediment formation, a nitropyrimidine.

2. A hydrocarbon oil heavier than gasoline and normally subject to sediment formation in storage containing, in a small but sufficient amount to retard said sediment formation, a nitrohydropyrimidine.

3. A hydrocarbon oil heavier than gasoline and normally subject to sediment formation in storage containing, in a small but sufficient amount to retard said sediment formation, a nitrodihydropyrimidine.

4. A hydrocarbon oil heavier than gasoline and normally subject to sediment formation in storage containing, in a small but sufficient amount to retard said sediment formation, a nitrotetrahydropyrimidine.

5. A hydrocarbon oil heavier than gasoline and normally subject to sediment formation in storage containing, in a small but sufficient amount to retard said sediment formation, a nitrohexahydropyrimidine.

6. A hydrocarbon oil heavier than gasoline and normally subject to sediment formation in storage containing, in a small but sufficient amount to retard said sediment formation, a di-substituted nitropyrimidine in which the substituents are selected from the group consisting of alkyl and cycloalkyl radicals.

7. A hydrocarbon oil heavier than gasoline and normally subject to sediment formation in storage containing, in a small but sufficient amount to retard said sediment formation, a 1,3-dicycloalkyl-5-nitro-5-methyl-hexahydropyrimidine.

8. A hydrocarbon oil heavier than gasoline and normally subject to sediment formation in storage containing, in a small but sufficient amount to retard said sediment formation, a 1,3-dialkyl-5-nitro-5-methyl-hexahydropyrimidine.

9. A hydrocarbon oil heavier than gasoline and normally subject to sediment formation in storage containing, in a small but sufficient amount to retard said sediment formation, 1,3-di-cyclohexyl-5-nitro-5-methyl-hexahydropyrimidine.

10. A hydrocarbon oil heavier than gasoline and normally subject to sediment formation in storage containing, in a small but sufficient amount to retard said sediment formation, 1,3-dioctyl-5-nitro-5-methyl-hexahydropyrimidine.

11. A hydrocarbon oil heavier than gasoline and normally subject to sediment formation in storage containing, in a small but sufficient amount to retard said sediment formation, 1,3-diisopropyl-5-nitro-5-methyl-hexahydropyrimidine.

12. A hydrocarbon oil heavier than gasoline and normally subject to sediment formation in storage containing, in a small but sufficient amount to retard said sediment formation, 1,3-diisopropyl-5-nitro-5-ethyl-hexahydropyrimidine.

13. A hydrocarbon oil heavier than gasoline and normally subject to sediment formation in storage containing, in a small but sufficient amount to retard said sediment formation, 1,3-dihexyl-5-nitro-5-propyl-hexahydropyrimidine.

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