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STABILIZATION OF ORGANIC COMPOUNDS

William K. T. Gleim, Orland Park, Ill., assignor to Universal Oil Products Company, Des Plaines, Ill., a corporation of Delaware

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This invention relates to the stabilization of organic compounds and more particularly to the use of a novel additive in retarding and/or preventing deterioration of organic compounds in storage.

Various organic compounds are unstable in storage, during shipment, treatment or use, and undergo discoloration, form gums, form sludges or otherwise deteriorate due to various undesirable reactions which may include oxidation, polymerization, condensation, etc. Included among the organic compounds which undergo such deterioration and which may be treated in accordance with the present invention are fuel oil, burner oil, furnace oil, diesel fuel, jet fuel, mineral oil, lubricating oil, gasoline, drying oil, greases, rubber, edible fats and oils, acetylenes, and particularly vinyl acetylenes, butadienes, isoprenes, styrene and other vinyl aromatics, various unsaturated alcohols, acids, ketones, etc.

The invention is particularly applicable to the stabilization of burner oils which undergo discoloration and form undesirable sediment in storage. Burner oils are marketed under various trade names such as fuel oil, furnace oil, burner oil, diesel fuel, etc. and are selected to meet commercial specifications. It is understood that the term "burner oil" is used in the present specification and claims in a generic sense to include hydrocarbon distillates heavier than gasoline. In general, these hydrocarbon distillates will have initial boiling points ranging as low as 300° F. and end boiling points which may range up to about 750° F. Also included are oils having even lower initial boiling points but containing components boiling above gasoline as, for example, jet fuels, etc.

Discoloration of burner oil is undesirable because marketing of the burner oil in most cases includes a color specification, and therefore, it is important that the burner oil does not undergo discoloration in storage. Similarly, the formation of sediment 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 as such in burner oil 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.

At the present time burner oils come primarily from nondestructive distillation of petroleum oil, commercially referred to in the art as straight run distillates, and from catalytic and noncatalytic cracking processes, commonly referred to in the art as cycle stocks. The term "cycle stocks" 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, etc. Regardless of the source, many of the burner oils are unstable in storage and undergo discoloration and sediment formation. This is particularly true in blends of straight run petroleum distillates and cracked hydrocarbon oils, particularly catalytically cracked hydrocarbon oils, all being heavier than gasoline. Because of the increased amount of cycle stocks available, many refiners are marketing blended burner oils and, therefore, require some method of retarding and/or preventing this undesirable deterioration.

In one embodiment the present invention relates to a process for stabilizing organic material against deterioration in storage which comprises adding thereto a hydrocarbon substituted biuret.

In a specific embodiment the present invention relates to a process for retarding discoloration of burner oil in storage which comprises adding thereto not more than about 2% by weight of an alkyl biuret having at least eight carbon atoms per molecule.

In another specific embodiment the present invention relates to a process for retarding discoloration of burner oil in storage, which comprises adding thereto from about 0.0001% to about 1% by weight of di-tertiary-octylbiuret.

In another embodiment the present invention relates to an organic compound tending to deteriorate in storage, and particularly burner oil containing, as a retardant of said deterioration, a minor amount of the additive herein set forth.

In accordance with the present invention, deterioration of the unstable organic compound is retarded by means of a hydrocarbon substituted biuret and more particularly a hydrocarbon substituted biuret containing at least eight carbon atoms per molecule. Biuret contains two carbon atoms and, therefore, the hydrocarbon substituent or substituents should contain at least six carbon atoms. This is necessary in order that the modified biuret is soluble in the substrate, and the number of carbon atoms in the hydrocarbon substituent or substituents shall be sufficient so that the additive is soluble in the particular substrate in which it is to be employed. The number of carbon atoms in the hydrocarbon substituent or substituents may range from a total of six carbon atoms up to a total of 40 and, in some cases, even higher. Preferably the total number of carbon atoms in the substituent or substituents is within the range of from about 10 to 30.

Particularly preferred hydrocarbon substituted biurets comprise mono- and polyalkyl biurets. Typical compounds in this class include tertiary-hexylbiuret, tertiary-heptylbiuret, tertiary-octylbiuret, tertiary-nonylbiuret, tertiary-decylbiuret, tertiary-undecylbiuret, tertiary-tridecylbiuret, tertiary-tetradecylbiuret, tertiary-pentadecylbiuret, tertiary-hexadecylbiuret, tertiary-heptadecylbiuret, tertiary-octadecylbiuret, tertiary-nonadecylbiuret, tertiary-eicosylbiuret, tertiary-heneicosylbiuret, tertiary-docosylbiuret, tertiary-tricosylbiuret, tertiary-tetracosylbiuret, tertiary-pentacosylbiuret, tertiary-hexacosylbiuret, tertiary-heptacosylbiuret, tertiary-octadecosylbiuret, tertiary-nonadecosylbiuret, etc., 1,5-di-propylbiuret, 1,5-di-tertiary-butylbiuret, 1,5-di-tertiary-amylbiuret, 1,5-di-tertiary-hexylbiuret, 1,5-di-tertiary-heptylbiuret, 1,5-di-tertiary-octylbiuret, 1,5-di-tertiary-nonylbiuret, 1,5-di-tertiary-decylbiuret, 1,5-di-tertiary-undecylbiuret, 1,5-di-tertiary-dodecylbiuret, etc. While the tertiary alkyl substituted compounds are preferred, it is understood that the primary and secondary substituted compounds may be employed but not necessarily with equivalent results. It also is understood that, while the monoalkyl and dialkyl biurets may be preferred, the tri- and tetra-alkyl biurets may be employed, but not necessarily with equivalent results.

The specific compounds hereinbefore set forth comprise the preferred alkyl biurets. Cyclic biurets include, as specific examples of typical compounds, phenylbiuret, tolylbiuret, xylylbiuret, ethylphenylbiuret, propylphenylbiuret,

butylphenylbiuret, amylphenylbiuret, hexylphenylbiuret, heptylphenylbiuret, octylphenylbiuret, etc., 1,5-di-phenylbiuret, 1,5-di-tolylbiuret, 1,5-di-xylylbiuret, 1,5-di-ethylphenylbiuret, 1,5-di-propylphenylbiuret, 1,5-di-butylphenylbiuret, 1,5-di-amylphenylbiuret, 1,5-di-hexylphenylbiuret, 1,5-di-heptylphenylbiuret, 1,5-di-octylphenylbiuret, etc., cyclohexylbiuret, methyl-cyclohexylbiuret, ethyl-cyclohexylbiuret, propyl-cyclohexylbiuret, butyl-cyclohexylbiuret, amyl-cyclohexylbiuret, hexyl-cyclohexylbiuret, etc., 1,5-di-cyclohexylbiuret, 1,5-di-methyl-cyclohexylbiuret, 1,5-di-ethyl-cyclohexylbiuret, 1,5-di-propyl-cyclohexylbiuret, 1,5-di-butyl-cyclohexylbiuret, 1,5-di-amyl-cyclohexylbiuret, 1,5-di-hexyl-cyclohexylbiuret, etc., methyl-cyclopentylbiuret, ethyl-cyclopentylbiuret, propyl-cyclopentylbiuret, butyl-cyclopentylbiuret, amyl-cyclopentylbiuret, hexyl-cyclopentylbiuret, etc., dicyclopentylbiuret, dimethyl-cyclopentylbiuret, di-ethyl-cyclopentylbiuret, dipropyl-cyclopentylbiuret, di-butyl-cyclopentylbiuret, diamy-cyclopentylbiuret, etc.

In the case of the polysubstituted biurets it generally is preferred that the different substituent groups are the same; that is, each of the substituent groups contains the same number of carbon atoms per group and is of the same configuration. However, it is understood that substituted compounds in which the substituents are different in number of carbon atoms and/or configuration may be employed in accordance with the present invention. Furthermore, it generally is preferred that the di-substituted compounds are 1,5-di-substituted compounds. However, it is understood that the 1,1-di-substituted compounds, the 1,1,5-tri-substituted compounds and the 1,1,5,5-tetra-substituted compounds may be employed but not necessarily with equivalent results. It is understood that a mixture of different hydrocarbon substituted biurets may be employed.

It will be noted that a considerable number of compounds may be prepared and utilized in accordance with the present invention. It is understood that these compounds will not necessarily be equivalent in all substrates and that the particular compound to be employed will depend upon the particular substrate to be treated.

The hydrocarbon substituted biurets may be prepared in any suitable manner. The specific preparation of tertiary-octylbiuret will be described in the following examples. It will be noted that in this specific preparation sulfuric acid in glacial acetic acid was utilized and that the reaction was effected at 0° C. Room temperature or elevated temperatures may be employed with different acids as, for example, phosphoric acid, hydrochloric acid, etc.

As hereinbefore set forth, the novel process of the present invention is particularly applicable for the stabilization of burner oils. However, it is understood that this process also may be used for the stabilization of other organic materials which undergo deterioration in storage. Specifically, the present invention may be utilized for the stabilization of gasoline and more particularly unsaturated gasoline, including cracked gasoline, polymer gasoline, etc., as well as to the treatment of aviation gasoline which tends to undergo deterioration due to the addition of tetraethyl lead fluid or other components in the gasoline. Furthermore, the process may be used for the stabilization of petroleum waxes, adhesives, rubber, greases, etc., as well as animal and vegetable fats and oils including, linseed oil, menhaden oil, cod liver oil, castor oil, olive oil, rapeseed oil, coconut oil, palm oil, corn oil, sesame oil, peanut oil, babassu oil, butter, fat, lard, beef tallow, waxes, etc.

The additive of the present invention is generally added to the organic material in an amount of less than about 2% by weight and more generally within the range of from about 0.0001% to about 1% and preferably of from about 0.001% to about 0.1% by weight. It is understood that these additives may be used alone or in conjunction with other additives employed for specific

purposes depending upon the particular organic material being treated. For example, in the treatment of burner oil, these additives may be used in conjunction with antioxidants which may comprise aliphatic amines, amino-alcohols, imidazolines, etc., metal deactivators, dyes, detergents, drying agents, etc. When used in gasoline, the additive may be employed along with antioxidants, particularly of the phenolic, amino phenolic or phenylene diamine type, metal deactivators, dyes, anti-knock agents including tetraethyl lead, etc. When used in edible fats and oils, the additive may be employed along with synergists, such as citric acid, ascorbic acid, phosphoric acid, etc.

When desired, the additive may be utilized in a suitable solvent, including hydrocarbons, alcohols, glycols, ethers, ketones, etc. and, in such cases, the additive may be prepared as a solution in the solvent and marketed in this manner alone or along with any other component to be included in the mixture as hereinbefore set forth.

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

Tertiary-octylbiuret used in this example was prepared by the reaction of di-cyandiamide and di-isobutylene in the following manner. 0.2 mol of sulfuric acid in glacial acetic acid was added over a period of 1½ hours to a mixture of 0.2 mol of di-cyandiamide and 0.2 mol of di-isobutylene at a temperature of 0° C. and with mechanical stirring. The mixture was allowed to stand for one hour at 20° C. and then stirred for one hour at 20° C. The mixture was heated for four hours at 60–67° C. and then allowed to cool. The cooled solution was then neutralized with ammonium and the resultant oil was recovered in ether.

The additive as prepared in the above manner was utilized as an additive to prevent discoloration of burner oil. Discoloration of the burner oil was determined in an accelerated test, which avoids the necessity of running long time storage tests in order to determine the effect of the additive. In other runs it has been found that this accelerated test correlates quite satisfactorily with long time storage tests and, therefore, gives a true picture of the stability of the fuel. The samples of the fuel oil were stored at 100° C. for 20 hours. The color was determined in a Lumitron, model 402–E, Spectrophotometer, and the results are reported as the per cent transmittance. It is apparent that the percent transmittance is inversely proportional to discoloration, and that high per cent transmittance means low discoloration.

One sample of the fuel oil did not contain an additive and, therefore, may be considered as a blank or control sample. 0.002% by weight of the octylbiuret prepared in the above manner was added to another sample of the fuel oil, and 0.004% by weight of the octylbiuret was added to a third sample. The samples were subjected to accelerated storage as described above and the percent transmittences of the samples are shown in the following table.

Table I

Additive	Percent Transmittence
None	0
0.002% tertiary-octylbiuret	68
0.004% tertiary-octylbiuret	82

It will be noted that the sample not containing the additive became very dark in color after aging at 120° C. for 20 hours. On the other hand, the samples containing the additive had high percent transmittances and, therefore, discoloration was considerably retarded by the additive.

EXAMPLE II

Dodecylbiuret may be prepared by the reaction of propylene tetramer with di-cyandiamide. The resultant additive may be used in a concentration of 0.005% in burner oil to retard discoloration thereof.

EXAMPLE III

The dodecylbiuret described in Example II may be utilized in a concentration of 0.001% in cracked gasoline to retard discoloration of the gasoline in storage.

EXAMPLE IV

1,5-di-tertiary-dodecylbiuret may be utilized in a concentration of 0.4% by weight in lubricating oil to retard discoloration and other undesirable deterioration thereof.

EXAMPLE V

Tertiary-decylbiuret may be incorporated in lard in a concentration of 0.006% by weight to retard rancidity development.

I claim as my invention:

1. Organic material tending to deteriorate in storage containing, in a small but sufficient amount to retard said deterioration, a hydrocarbon substituted biuret containing at least 8 carbon atoms per molecule and having a hydrocarbon substituent selected from the group consisting of alkyl, aryl and alkaryl radicals.

2. Hydrocarbon oil subject to deterioration in storage containing an alkyl biuret having at least 8 carbon atoms per molecule in a small but sufficient amount to retard said deterioration.

3. Burner oil subject to deterioration in storage containing an alkyl biuret having at least 8 carbon atoms per molecule in a small but sufficient amount to retard said deterioration.

4. Burner oil subject to discoloration in storage containing at least 0.0001% but not more than about 2% by weight of an alkyl biuret containing at least eight carbon atoms.

5. A blend of straight run petroleum distillate and cracked hydrocarbon oil both heavier than gasoline containing from about 0.0001% to about 1% by weight of an alkyl biuret containing at least eight carbon atoms.

6. Burner oil containing from about 0.0001% to about 1% by weight of tertiary-octylbiuret.

7. Burner oil containing from about 0.0001% to about 1% by weight of tertiary-nonylbiuret.

8. Burner oil containing from about 0.0001% to about 1% by weight of tertiary-decylbiuret.

9. Burner oil containing from about 0.0001% to about 1% by weight of tertiary-dodecylbiuret.

10. Burner oil containing from about 0.0001% to about 1% by weight of tertiary-pentadecylbiuret.

11. Motor fuel subject to deterioration in storage containing, as an additive to retard said deterioration, not more than about 2% by weight of an alkyl biuret having at least eight carbon atoms.

12. Gasoline subject to discoloration in storage containing, as an additive to retard said deterioration, from about 0.0001% to about 1% by weight of an alkyl biuret having at least eight carbon atoms.

13. Lubricating oil subject to deterioration in storage containing, as an additive to retard said deterioration, not more than about 2% by weight of an alkyl biuret having at least eight carbon atoms.

14. Rubber subject to deterioration in storage containing, as an additive to retard said deterioration, not more than about 2% by weight of an alkyl biuret having at least eight carbon atoms.

15. Fatty material subject to deterioration in storage containing, as an additive to retard said deterioration, not more than about 2% by weight of an alkyl biuret having at least eight carbon atoms.

16. Organic material normally subject to oxidative deterioration containing an anti-oxidizing amount of an alkyl biuret having at least 6 carbon atoms in the alkyl substitution.

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