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METHOD FOR IMPROVING THE STABILITY OF HYDROFINISHED DISTILLATES AND RAFFINATES OF DISTILLATES

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ABSTRACT OF THE DISCLOSURE

The method comprises adding an inhibitor to a hydrofinished distillate or a hydrofinished raffinate from a distillate prior to the time that said distillate or said raffinate is contacted with air. The inhibitor is a member selected from the group consisting of hindered phenols, amines, and metal complexes of Mannich condensation products from phenols, aldehydes, and polyamines. If the distillate has been hydrofinished in a two-stage process under relatively severe conditions, an inhibitor may be added to the effluent from the first stage and an inhibitor may be added to the product from the second stage.

BACKGROUND OF THE INVENTION

In the past, petroleum hydrocarbon distillates and their raffinates have been refined by employing a finishing treatment using clay as a finishing medium or a finishing treatment employing a combination of sulfuric acid and clay as finishing media. The feedstock to such treatment may have been dewaxed and/or solvent extracted. Such finishing treatments provided a treated product which possessed improved color and odor and, in many cases, improved stability to light and oxidation. Generally, stability to oxidation and to light has been maintained by the addition of one or more chemicals to the finished product. In recent years, the qualities of various distillates and their raffinates have been improved by a finishing treatment comprising a relatively severe hydrogenation treatment. This is particularly true for lubricating oils and their derivatives.

The hydrogenation treatment of a distillate, such as a lubricating oil fraction, may comprise either a one-stage process or a two-stage process. In a one-stage process, the distillate is desulfurized and hydrogenated over a sulfactive hydrogenation catalyst under hydrogenation conditions, which may be relatively severe. In the first stage of a typical two-stage process, the selected distillate is desulfurized over a sulfactive hydrogenation catalyst under relatively severe hydrogenation conditions, and the effluent from this first stage is contacted in a second stage with hydrogen under relatively mild conditions with a hydrogenation catalyst comprising a Group VIII metal on a non-acidic or a weakly-acidic support.

Quite often, the product obtained from a hydrofinishing treatment of either a petroleum hydrocarbon distillate or the raffinate obtained from a distillate is rather unstable to both sunlight and to oxidation. Some hydrocracked disillates also possess stabilities to light and to oxidation that are quite poor. Certain inhibitors have been added to these hydrofinished and hydrotreated products to improve the stability of the product to either sunlight or oxidation, or both. There has now been found a method for improving the stability of hydrofinished distillates and hydrofinished raffinates from distillates.

SUMMARY OF THE INVENTION

Broadly, according to the present invention, there is provided a method for improving the stability of a hydrofinished member selected from the group consisting of petroleum hydrocarbon distillates and raffinates obtained

from distillates, said hydrofinished member having been hydrofinished under relatively severe hydrofinishing conditions, which method comprises adding to said hydrofinished member prior to the time that said hydrofinished member is contacted with air an inhibitor which is a member selected from the group consisting of hindered phenols, amines, and metal complexes of Mannich condensation products obtained from phenols, aldehydes, and polyamines. When the member is hydrofinished in a two-stage process, the method comprises adding said inhibitor to the effluent that is obtained from the first stage prior to introduction of said effluent that is obtained from the first stage into the second stage and to the product from the second stage of the hydrofinishing treatment prior to the time that the product from said second stage is contacted with air. Examples of suitable inhibitors are 2,6-di-tertiarybutyl-4-methyl phenol and the calcium salt of the Mannich condensation product from nonyl phenol, formaldehyde, and ethylenediamine.

DESCRIPTION OF THE INVENTION

Hydrofinished distillates and hydrofinished raffinates obtained from distillates are subject to inferior stability to light and to oxidation. In many cases, such inferior stability can be improved by the addition of an inhibitor or an antioxidant. There has now been found a method for improving the stability of either a hydrofinished distillate or a hydrofinished raffinate obtained from a distillate. This method is particularly suitable for improving the stability of those distillates and their raffinates which have been subjected to a severe or relatively severe hydrofinishing treatment. Severe or relatively severe hydrofinishing conditions comprise a hydrogen partial pressure of at least about 800 p.s.i.g., a temperature that is greater than 600° F., and a maximum liquid hourly space velocity (LHSV) that is not much greater than about 1 volume of hydrocarbon per hour per volume of catalyst.

Broadly, the method comprises adding to the hydrofinished member selected from the group consisting of petroleum hydrocarbon distillates and raffinates obtained from distillates, said hydrofinished member having been hydrofinished under at least relatively severe hydrofinishing conditions, prior to the time that said hydrofinished member is contacted with air an inhibitor which is a member selected from the group consisting of hindered phenols, amines, and metal complexes of Mannich condensation products obtained from phenols, aldehydes, and polyamines.

It is well known that uninhibited oils that have been hydrofinished under severe or relatively severe conditions are less stable towards attack by oxygen or light. It has now been found that the method of the present invention will improve the stability of distillates and raffinates from distillates that have been subjected to severe or relatively severe hydrofinishing conditions. This method comprises adding a selected inhibitor to the hydrofinished product prior to the time that said product is contacted with air. This method is adaptable to either a one-stage process or a two-stage process. When the hydrofinishing treatment is carried out in a two-stage process, the method of the invention may comprise adding the selected inhibitor to the product of the first stage prior to the introduction of that product to the second stage of the hydrofinishing treatment and prior to the time that such product is contacted with air. In addition, an inhibitor is also added to the product obtained from the second stage of the hydrofinishing treatment prior to the time that the product from the second stage is contacted with air.

The selected inhibitor that is employed in the method of the present invention is a member selected from the group consisting of hindered phenols, amines, and metal complexes of Mannich condensation products obtained from phenols, aldehydes, and polyamines.

Examples of hindered phenols are those phenols which have undergone substitution in either or both of the positions ortho to the hydroxyl group. Such hindered phenols are 2,6 - di - tertiary - butyl-4-methylphenol (sometimes called dibutylparacresol or butylated hydroxy toluene); α-tocopherol; bis(3,5 - di-tertiary-butyl-4-hydroxyphenyl) methane; and bis(2 - hydroxy - 3-tertiary butyl-5-methylphenyl) methane.

Certain amines may be used suitably as antioxidants. Both aromatic amines and aliphatic amines may be employed. Examples of such aromatic amines are phenyl-α-naphthylaine; 2,2-bis(4-dimethylamino phenyl) propane; phenyl β - naphthylamine; and bis(4-octylphenyl) amine. An example of a suitable aliphatic amine is the tertiary alkyl primary aliphatic amine that is commercially available from Rohm and Haas Co. under the tradename Primene 81–R.

In addition, certain metal complexes of Mannich condensation products obtained from phenols, aldehydes, and polyamines may be used as antioxidants. An example of a suitable metal complex is a calcium salt of the Mannich condensation product from nonyl phenol, formaldehyde, and ethylenediamine.

According to the present invention, the selected inhibitor is added in an amount that will provide a concentration of the inhibitor that falls within the range of about 1 p.p.m. to about 1 wt. percent. The preferred concentration range is about 6 p.p.m. to about 100 p.p.m.

If the hydrofinished or hydrotreated material has been obtained from a one-stage hydrofinishing process, the method of the present invention comprises adding the inhibitor to the product obtained from the process prior to the time that said product is contacted with air. If the material is hydrofinished in a two-stage process, two embodiments of the method are available. In one embodiment, the method comprises adding the inhibitor to the product obtained from the second stage of the hydrofinishing process prior to the time that said product is contacted with air. In the typical two-stage process, no air has contacted the product of the first stage, which product is introduced into the second stage. In another embodiment, the method comprises adding a small amount of the inhibitor to the effluent that is obtained from the first stage prior to its use in the second stage, as well as adding a small amount of the inhibitor to the product that is obtained from the second stage of the two-stage hydrofinishing process. "Small amount" comprises any amount that will provide the concentrations presented hereinabove. In any of these embodiments, the addition of the inhibitor is to be made prior to the time that the hydrocarbon material is contacted with air.

Whileit is not known what occurs in the second stage of a two-stage hydrogenation process when, pursuant to the present invention, the inhibitor is added to the first-stage effluent of that process prior to the introduction of the first-stage effluent into the second stage, the following theory is proposed for the method when employed in a two-stage process using a second-stage catalyst containing a Group VIII noble metal. However, there is no intention that the scope of the present invention be limited by such theory. It is theorized that the inhibitor in some way affects or augments the activity of the Group VIII noble metal catalyst in the second stage. Such activity modification is demonstrated by the improved oxidation stability of the severely hydrofinished material.

The method of the present invention may be employed to improve the stability to oxidation and the stability to sunlight of petroleum hydrocarbon distillates and of raffinates from distillates. Such hydrocarbon materials may be dewaxed. They will boil within the range of about 600° F. to about 1,100° F. and will possess viscosities of about 50 Saybolt Universal Seconds (SUS) at 100° F. to about 1,000 SUS at 100° F. Such petroleum hydrocarbon distillates may contain small amounts of impurities, such as sulfur, nitrogen, and oxygen.

Embodiments of the present invention are presented in the following examples, which are given for the purpose of illustration only and are not intended to limit the scope of the invention.

Example I

A dewaxed distillate was subjected to a severe hydrofinishing treatment in a commercial hydrotreating unit. This distillate, prior to hydrofinishing, had a viscosity of 224 SUS at 100° F., a sulfur content of 0.72 wt. percent, and a nitrogen level of 890 p.p.m. nitrogen. This distillate also possessed an aromatic carbon content of 17.0 wt. percent, as measured by the n-d-M method, which is described by K. Van Nes and H. A. Van Westen in Aspects of the Constitution of Mineral Oils, Elsevier (1951). The hydrofinishing treatment was carried out with a cobalt-molybdenum-on-alumina catalyst at an average catalyst bed temperature of 683° F., a hydrogen partial pressure of about 800 p.s.i.g., and a LHSV of 0.47 volume of hydrocarbon per hour per volume of catalyst. The hydrofinished distillate had a viscosity of 191 SUS at 100° F., a sulfur content of 0.08 wt. percent, a nitrogen content of 470 p.p.m., and an aromatic carbon content of 13.0 wt. percent.

A sample of the hydrofinished distillate, hereinafter identified as Sample No. 1, was subjected to an Indiana Oxidation Test.

The Indiana Oxidation Test may be described as follows: one hundred cc. of oil are held at 341° F. for 24 hours while air is passed through the oil at a rate of 3.3 liters per hour. Ten grams of the oxidized oil are diluted with 100 cc. of precipitation naphtha and filtered through a fine-mesh fritted glass filter. Results are reported as milligrams of sludge collected on the filter per 10 grams of oil.

To two other samples of the hydrofinished distillate were added inhibitors after the samples had been exposed to air. To one sample, identified hereinafter as Sample No. 2, was added 0.1 wt. percent 2,6-di-tertiary-butyl-4-methyl phenol, hereinafter identified as Inhibitor No. 1. To the other sample, identified hereinafter as Sample No. 3, was added 0.1 wt. percent of a calcium complex of a Mannich condensation product from nonyl phenol, formaldehyde, and ethylenediamine. This inhibitor, the calcium salt of N,N' bis (2-hydroxy-5 nonyl benzyl) ethylenediamine, is hereinafter identified as Inhibitor No. 2. The inhibited samples were subjected to Indiana Oxidation Tests.

The results obtained from these tests are presented in Table I.

TABLE I.—INDIANA OXIDATION TEST RESULTS

Sample number	Inhibitor number	Sludge, mg.	Percent reduction
1		50	
2	1	43	12
3	2	44	14

Although the inhibitor had been added after the severely hydrofinished distillate had been exposed to air, appreciable resistance to oxidation was obtained.

Example II

Another dewaxed distillate was severely hydrofinished; in this case, the hydrofinishing was performed over a cobalt-molybdenum-on-alumina catalyst in a hydrofinishing pilot plant. The dewaxed distillate had a viscosity of 78.3 SUS at 100° F., a sulfur level of 0.59 wt. percent sulfur, a nitrogen content of 450 p.p.m. nitrogen, and an aromatic carbon content of 16.3 wt. percent. The hydrofinishing was carried out at a temperature of 680° F., a hydrogen partial pressure of 800 p.s.i.g., and a LHSV of 0.47 volume of hydrocarbon per hour per volume of catalyst. The hydrofinished material possessed a viscosity of 73.7 SUS at 100° F., a sulfur content of 0.03 wt. percent, a nitrogen content of 220 p.p.m., and an aromatic carbon

content of 12.4 wt. percent. A sample of the severely hydrofinished material, identified as Sample No. 4, was subjected to an Indiana Oxidation Test. Three other samples were inhibited with a selected inhibitor prior to the time that the hydrofinished material was contacted with air. Such treatment constituted embodiments of the method of the present invention. Sample No. 5 was inhibited with 45 p.p.m. of Inhibitor No. 1; Sample No. 6, was inhibited with 51 p.p.m. of Inhibitor No. 2 Sample No. 7 was inhibited with 0.09 wt. percent Primene 81–R, hereinafter identified as Inhibitor No. 3. Three additional samples of the severely hydrofinished material were inhibited about one week after they had been exposed to air. Sample No. 8 was inhibited with 0.1 wt. percent Inhibitor No. 1; Sample No. 9, with 0.1 wt. percent Inhibitor No. 2; and Sample No. 10, with 0.1 wt. percent Inhibitor No. 3. All of the inhibited samples were subjected to the Indiana Oxidation Test. Results of these tests are presented in Table II.

TABLE II.—INDIANA OXIDATION TEST RESULTS

Sample number	Inhibitor number	Sludge, mg.	Percent reduction
4		101	
5	1	64	37
6	2	74	27
7	3	36	64
8	*1	58	43
9	*2	125	−24
10	*3	117	−16

* Added after exposure to air.

The results of these tests indicate that the addition of any of the inhibitors prior to the time that the hydrofinished distillate was contacted with air improved the stability of the distillate to oxidation. A comparison of these results with the results obtained in Example I hereinabove reveals that the inhibition resulting from the addition of the inhibitor to the distillate prior to contact with air was much more effective than the inhibition resulting from the addition of the inhibitor to the hydrofinished distillate after the distillate had been contacted with air. It is believed that this comparison of the results obtained in the two examples is a valid comparison even though the distillate employed in Example I and the distillate employed in Example II possessed different viscosities, since both of the distillates were hydrofinished at approximately the same degree of severity.

Moreover, the addition of the inhibitors in this example after the hydrofinished material had been exposed to air for about a week is not an effective way of inhibiting the hydrofinished material. Although Inhibitor No. 1 appears to give a greater reduction of sludge when added after air exposure than prior to air exposure, please consider that the amount of the inhibitor that was added after exposure to air was about 20 times greater than the amount of the inhibitor that was added prior to exposure to air.

These results demonstrate the superiority of the method of the present invention, which method is depicted in Example II by the embodiments employed to obtain Samples Nos. 5, 6, and 7.

Example III

The raffinate of a dewaxed distillate was hydrofinished over a cobalt-molybdenum-on-alumina catalyst in a pilot plant unit and at a temperature of 610° F., a hydrogen partial pressure of 800 p.s.i.g., and a LHSV of 1.05 volumes of hydrocarbon per hour per volume of catalyst. The hydrocarbon stream being fed to the pilot plant had a viscosity of 175 SUS at 100° F. and a sulfur level of 0.26 wt. percent. The hydrofinished material had a viscosity of 172 SUS at 100° F. and a sulfur content of 0.016 wt. percent. Daily samples of product were obtained from the pilot plant. Samples obtained in the sequence shown are identified hereinafter as Samples Nos. 11 through 14. Each of the samples was subjected to the Alcoa Oxidation Uptake Test (OUT). In each case, prior to the oxidation test, the sample was inhibited with 0.25 wt. percent of Inhibitor No. 1, 0.05 wt. percent 2,2-bis(4-dimethylamino phenyl) propane, and 0.10 wt. percent dodecenyl succinic acid. For Sample No. 13, 18 p.p.m. of Inhibitor No. 1 was added prior to the sample being exposed to air.

For the Alcoa Oxidation Uptake Test, 13 cc. of the hydrocarbon material are introduced into a 120-cc. flask equipped with a manometer. The remainder of the flask is filled with oxygen (1 atmosphere at ambient temperature). The flask is then placed in an oil bath at 125° C. and the time is recorded for the pressure to drop 60 mm. of mercury from the maximum value that is reached shortly after the flask has been placed in the bath. This amount of time corresponds to the time that is required for a given oxygen consumption. The results of the Alcoa OUT are expressed in terms of hours. The results of the test in this example are presented hereinbelow in Table III.

TABLE III

Sample number	Inhibitor prior to air contact	Alcoa OUT, hours
11		171.5
12		165
13	1	185.5
14		167

Sample No. 13 provides results obtained when an embodiment of the method of the present invention is employed and clearly demonstrates the superiority of this method over the technique of adding an inhibitor to the hydrofinished distillate after it has been in contact with air. Samples Nos. 11, 12, and 14 were inhibited only by the latter technique.

Example IV

The raffinate obtained from a dewaxed distillate having a viscosity corresponding to that of an SAE–5 oil was hydrofinished in a pilot plant unit. Hydrofinishing was carried out in a two-stage process. The catalyst in the first stage of the hydrofinishing process was a nickel-molybdenum-on-alumina catalyst and the catalyst employed in the second stage of the hydrofinishing process was a palladium-on-alumina catalyst. The operating conditions in the first stage included a temperature of 700° F., a hydrogen partial pressure of 3,000 p.s.i.g., and a LHSV of 0.24 volume of hydrocarbon per hour per volume of catalyst. The operating conditions in the second stage of the hydrofinishing process included a temperature of 450° F., a pressure of 1600 p.s.i.g., and a LHSV of 0.24–0.25 volume of hydrocarbon per hour per volume of catalyst. During the production of one hydrofinished sample, Sample No. 15, 20 p.p.m. of Inhibitor No. 1 were added to the effluent from the first stage, while 6 p.p.m. of Inhibitor No. 1 were added to the product obtained from the second stage prior to contact with air. For another sample, Sample No. 16, 20 p.p.m. of Inhibitor No. 1 were added to the effluent from the first stage, while no inhibitor was added to the effluent from the second stage. These two samples were subjected to the USP Acid Test and to the BT Peroxide Test.

The USP Acid Test, a test for carbonizable substances, is described in both the Regulations for Mineral Oil in the United States Pharmacopeia XVIII (1970), pp. 436–437, and the Regulations for Light Mineral Oil in the National Formulary XIII (1970), pp. 461–462. This test was modified by measuring the color of the acid extract by the ASTM color method, rather than by comparing the color to the suggested standard color. The ASTM color method has ASTM designation D1500–64 and IP designation 196/66. The approximate ASTM color value of the standard color referred to in the USP Acid Test is 2.5. Therefore, to pass the test, the color of the acid extract could not be more than 2.5 ASTM. The USP Acid Test is not an oxidation test. However, oxidation of the hydrocarbons can result in an increased amount of carbonizable sub-

stances. Hence, the test indirectly may demonstrate the occurrence of oxidation.

In the BT Peroxide Test, a 5-cc. sample of oil is heated in a 15 x 150 mm. test tube in an oil bath at 300° F. After the sample is removed from the bath, a reagent solution is added to determine the presence of peroxide. This reagent solution is prepared by dissolving 2 grams of C.P. ammonium thiocyanate in 100 cc. of distilled water and adding 200 cc. of C.P. acetone and about 0.5 gram of pure powdered iron. A pink coloration indicates the formation of peroxide. The time interval in minutes for the formation of peroxide, recorded as the BT Peroxide Number, is obtained. The specification for a white oil such as that employed in this example is 40 minutes.

Sample No. 15 passed the BT Peroxide Test and had an acid test value of 0–0.05. Sample No. 16 failed the BT Peroxide Test and had an acid test value of 1.5–2. The results of this sample demonstrate that in a two-stage process, even though an inhibitor is added to the first-stage effluent, this may not be sufficient for inhibition of oxidation and that additional inhibitor may be required after the second stage and prior to exposure to air.

Example V

A blend comprising 75 volume percent raffinate obtained from a dewaxed distillate having a viscosity corresponding to that of an SAE–20 oil and 25 volume percent raffinate obtained from a dewaxed distillate having a viscosity corresponding to that of a SAE–40 oil was hydrofinished in a pilot plant unit. Hydrofinishing was carried out in a two-stage process. The catalyst in the first stage of the hydrofinishing process was a nickel-molybdenum-on-alumina catalyst and the catalyst employed in the second stage of the hydrofinishing process was a palladium-on-alumina catalyst. The operating conditions in the first stage included a temperature of 700° F., a hydrogen partial pressure of 3,000 p.s.i.g., and a LHSV of 0.24–0.25 volume of hydrocarbon per hour per volume of catalyst. The operating conditions in the second stage of the hydrofinishing process included a temperature of 450° F., a pressure of 1,600 p.s.i.g., and a LHSV of 0.24–0.26 volume of hydrocarbon per hour per volume of catalyst. During the production of a hydrofinished sample, Sample No. 17, no inhibitor was added to the effluent from the first stage, while 6 p.p.m. of Inhibitor No. 1 were added to the product obtained from the second stage prior to contact with air. For another hydrofinished sample, Sample No. 18, 20 p.p.m. of Inhibitor No. 1 were added to the effluent from the first stage, while 6 p.p.m. of Inhibitor No. 1 were added to the effluent from the second stage. These two samples were subjected to the BT Peroxide Test. Sample No. 17 failed the BT Peroxide Test, while Sample No. 18 passed the BT Peroxide Test. The results of this example demonstrate that the addition of the Inhibitor No. 1 to the effluent obtained from the first stage of a two-stage hydrofinishing process prior to exposure to air improved appreciably the stability of the hydrofinished material to oxidation.

The method of the present invention for improving the stability of petroleum hydrocarbon distillates and raffinates from distillates that have received a severe hydrofinishing treatment or a relatively severe hydrofinishing treatment provides improved stability to oxidation for the particular distillate or particular raffinate from a distillate. This improved stability is clearly demonstrated by the above examples.

What is claimed is:

1. A method for improving the stability of a hydrofinished member selected from the group consisting of petroleum hydrocarbon distillates and raffinates obtained from distillates, said hydrofinished member having been hydrofinished under relatively severe hydrofinishing conditions, which method comprises adding to said hydrofinished member prior to the time that said hydrofinished member is contacted with air an inhibitor which is a member selected from the group consisting of hindered phenols, amines, and metal complexes of Mannich condensation products obtained from phenols, aldehydes, and polyamines.

2. The method of claim **1** wherein said inhibitor is added to said hydrofinished member in an amount within the range of about 1 p.p.m. to about 1 wt. percent, based on the amount of said hydrofinished member.

3. The method of claim **1** wherein said hydrofinished member is obtained from a two-stage hydrofinishing process, which method comprises adding a small amount of said inhibitor to the effluent that is obtained from the first stage of the two-stage process prior to the introduction of said effluent that is obtained from the first stage into the second stage, and adding a small amount of an inhibitor to the product that is obtained from the second stage of said two-stage hydrofinishing process.

4. The method of claim **1** wherein said inhibitor is a hindered phenol.

5. The method of claim **1** wherein said inhibitor is an amine.

6. The method of claim **1** wherein said inhibitor is a metal complex of the Mannich condensation product from a phenol, an aldehyde, and a polyamine.

7. The method of claim **2** wherein said hydrofinished member is obtained from a two-stage hydrofinishing process, which method comprises adding a small amount of said inhibitor to the effluent that is obtained from the first stage of the two-stage process prior to the introduction of said effluent that is obtained from the first stage into the second stage, and adding a small amount of an inhibitor to the product that is obtained from the second stage of said two-stage hydrofinishing process.

8. The method of claim **2** wherein said inhibitor is a hindered phenol.

9. The method of claim **2** wherein said inhibitor is an amine.

10. The method of claim **2** wherein said inhibitor is a metal complex of the Mannich condensation product from a phenol, an aldehyde, and a polyamine.

11. The method of claim **3** wherein the inhibitor that is added to the effluent that is obtained from the first stage and the inhibitor that is added to the product that is obtained from the second stage are the same.

12. The method of claim **4** wherein said hindered phenol is 2,6-di-tertiary-butyl-4-methyl phenol.

13. The method of claim **6** wherein said inhibitor is a calcium salt of the Mannich condensation product from nonyl phenol, formaldehyde, and ethylenediamine.

14. The method of claim **7** wherein the inhibitor that is added to the effluent that is obtained from the first stage and the inhibitor that is added to the product that is obtained from the second stage are the same.

15. The method of claim **7** wherein the inhibitor added to the effluent from the first stage is a hindered phenol.

16. The method of claim **7** wherein the inhibitor added to the effluent from the first stage is an amine.

17. The method of claim **7** wherein the inhibitor added to the effluent from the first stage is a metal complex of the Mannich condensation product from a phenol, an aldehyde, and a polyamine.

18. The method of claim **8** wherein said hindered phenol is 2,6-di-tertiary-butyl-4-methyl phenol.

19. The method of claim **10** wherein said inhibitor is a calcium salt of the Mannich condensation product from nonyl phenol, formaldehyde, and ethylenediamine.

20. The method of claim **14** wherein said inhibitor is a hindered phenol.

21. The method of claim **14** wherein said inhibitor is an amine.

22. The method of claim **14** wherein said inhibitor is a metal complex of the Mannich condensation product from a phenol, an aldehyde, and a polyamine.

23. The method of claim 15 wherein said hindered phenol is 2,6-di-tertiary-butyl-4-methyl phenol.

24. The method of claim 17 wherein said metal complex is a calcium salt of the Mannich condensation product from nonyl phenol, formaldehyde, and ethylenediamine.

25. The method of claim 20 wherein said hindered phenol is 2,6-di-tertiary-butyl-4-methyl phenol.

26. The method of claim 22 wherein said inhibitor is a calcium salt of the Mannich condensation product from nonyl phenol, formaldehyde, and ethylenediamine.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,756,943 Dated September 4, 1973

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It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 3, line 12, "naphthylaine" should be -- naphthylamine --.

Column 5, line 9, "No. 2" should be -- No. 2. --.

Column 7, line 18, "sample" should be -- example --.

Column 9, lines 5 and 6, "ethyleneidamine" should be -- ethylenediamine --.

Signed and sealed this 30th day of July 1974.

(SEAL)
Attest:

McCOY M. GIBSON, JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents