COMMONWEALTH of AUSTRALIA
Patents Act 1952

619957

## APPLICATION FOR A STANDARD PATENT

I/We

Ethyl Petroleum Additives, Inc.

of

20 South Fourth Street, St. Louis, Missouri, 63102-1886, United States of America

hereby apply for the grant of a Standard Patent for an invention entitled:

**Middle Distillate Fuel Having Improved Storage Stability**

which is described in the accompanying complete specification.

Details of basic application(s):-

| Number | Convention Country | Date |
|---|---|---|
| 318748 | United States of America | 2 March 1989 |

The address for service is care of DAVIES & COLLISON, Patent Attorneys, of 1 Little Collins Street, Melbourne, in the State of Victoria, Commonwealth of Australia.

DATED this FIRST day of MARCH 1990

To: THE COMMISSIONER OF PATENTS

....................................
a member of the firm of
DAVIES & COLLISON for
and on behalf of the
applicant(s)

Davies & Collison, Melbourne

M 016.90 010390

CASE EI-5918

## COMMONWEALTH OF AUSTRALIA

### PATENTS ACT 1952

## DECLARATION IN SUPPORT OF CONVENTION OR NON-CONVENTION APPLICATION FOR A PATENT

Insert title of invention.

In support of the Application made for a patent for an invention entitled: Middle Distillate Fuel Having Improved Storage Stability

Insert full name(s) and address(es) of declarant(s) being the applicant(s) or person(s) authorized to sign on behalf of an applicant company.

~~We~~ I, Philip M. PIPPENGER of,
~~We of~~ Ethyl Petroleum Additives, Inc.
451 Florida Boulevard
Baton Rouge, LA 70801
United States of America

Cross out whichever of paragraphs 1(a) or 1(b) does not apply
1(a) relates to application made by individual(s)
1(b) relates to application made by company; insert name of applicant company.

do solemnly and sincerely declare as follows :–

1. (a) ~~I am~~ ~~We are~~ ~~the applicant for the patent~~

or (b) I am authorized by

Ethyl Petroleum Additives, Inc.

the applicant............ for the patent to make this declaration on its ~~their~~ behalf.

Cross out whichever of paragraphs 2(a) or 2(b) does not apply
2(a) relates to application made by inventor(s)
2(b) relates to application made by company(s) or person(s) who are not inventor(s); insert full name(s) and address(es) of inventors.

2. (a) ~~I am~~ ~~We are~~ ~~the actual inventor of the invention~~

or (b) John Gray Bostick of 144 S. 34th Street, Belleville, Illinois 62221; Larry John Cunningham of 1928 Windyhill, Kirkwood, Missouri 63122; and John Vincent Hanlon, of 2610 Bopp Road, St. Louis, Missouri 63131; all in the United States of America

~~is~~ are the actual inventor s of the invention and the facts upon which the applicant........... ~~is~~ are entitled to make the application are as follows :–

State manner in which applicant(s) derive title from inventor(s)

The actual inventors have assigned the invention to the said applicant

Cross out paragraphs 3 and 4 for non-convention applications. For convention applications, insert basic country(s) followed by date(s) and basic applicant(s).

3. The basic application........... as defined by Section 141 of the Act was ~~were~~ made

in the United States of America on the 2nd of March, 1989
by John G. Bostick, Larry J. Cunningham, and J. Vince Hanlon
in .................................... on the ....................................
by ....................................
in .................................... on the ....................................
by ....................................

4. The basic application.......... referred to in paragraph 3 of this Declaration was ~~were~~ the first application......... made in a Convention country in respect of the invention the subject of the application.

Insert place and date of signature.

Declared at Baton Rouge, Louisiana USA this 7th day of February, 1990

Signature of declarant(s) (no attestation required)

ETHYL PETROLEUM ADDITIVES, INC.

Philip M. Pippenger
Patent Counsel

Note: Initial all alterations.

DAVIES & COLLISON, MELBOURNE and CANBERRA.

**(12) PATENT ABRIDGMENT** (11) Document No. **AU-B-50603/90**
**(19) AUSTRALIAN PATENT OFFICE** (10) Acceptance No. **619957**

(54) Title
**MIDDLE DISTILLATE FUEL HAVING IMPROVED STORAGE STABILITY**

International Patent Classification(s)
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| 318748 | 02.03.89 | US UNITED STATES OF AMERICA |

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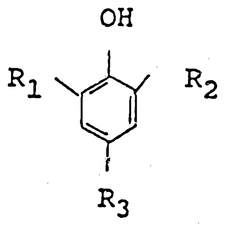
(56) Prior Art Documents
US 4668412
US 3725480
US 3634575

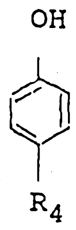
(57) Claim

1. A fuel additive concentrate comprising a mixture of N,N-dimethylcyclohexylamine and a Mannich Base which is the reaction product of an aldehyde, a primary or secondary amine and an alkyl phenol selected from (a) hindered phenol having the formula:



where $R_1$, $R_2$, $R_3$ are independently selected from hydrogen, t-butyl, t-amyl and isoproprpyl, provided that at least one of $R_1$, $R_2$ and $R_3$ is hydrogen and at least one of $R_1$ and $R_2$ is t-butyl, t-amyl or isopropyl; and (b) p-alkyl phenol having the formula:

.../2



where $R_4$ is $C_9$ to $C_{30}$ alkyl; said concentrate containing, based on the total weight of concentrate, from 25 to 95 wt% N,N-dimethylcyclohexylamine from 5 to 75 wt% Mannich Base.

619957

COMMONWEALTH OF AUSTRALIA
PATENTS ACT 1952
COMPLETE SPECIFICATION

NAME & ADDRESS
OF APPLICANT:

Ethyl Petroleum Additives, Inc.
20 South Fourth Street
St.Louis Missouri 63102-1886
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NAME(S) OF INVENTOR(S):

John Gray BOSTICK
Larry John CUNNINGHAM
John Vincent HANLON

ADDRESS FOR SERVICE:

DAVIES & COLLISON
Patent Attorneys
1 Little Collins Street, Melbourne, 3000.

COMPLETE SPECIFICATION FOR THE INVENTION ENTITLED:

Middle Distillate Fuel Having Improved Storage Stability

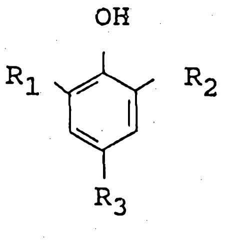
The following statement is a full description of this invention, including the best method of performing it known to me/us:-

This invention relates generally to improving the stability of middle distillate fuels and more particularly to stabilized middle distillate fuel compositions which contain a combination of N,N-dimethylcyclohexyl amine and a Mannich Base.

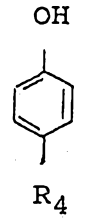
Middle distillate fuels such as diesel oil, fuel oil, jet fuel and kerosene when stored for long periods of time are subject to the formation of color and solid deposits. The deposits accumulate on filters causing the filters to become plugged. Various additives and combinations of additives have been employed to reduce color and deposit formation. For example: U.S. Patent 2,984,550 discloses the use of Mannich bases derived from phenols, formaldehyde and polyamines for stabilization; U.S. Patent 3,490,882 discloses stabilized petroleum distillate fuel oils containing N,N-dimethylcyclohexylamine antioxidant and a N,N'-di(ortho-hydroxyarylidene)-1,2-alkylenediamine metal deactivator such as N,N'-disalicylidene-1,2-propylenediamine; U.S. Patent 4,166,726 discloses a fuel additive which is a mixture of a polyalkylene amine and a Mannich Base; and U.S. Patents 4,501,595 and 4,533,361 disclose diesel oil which contains a condensate of tetraethylene pentamine, paraformaldehyde, a hindered phenol such as 2,6-di-t-butylphenol and polyisobutenyl succinic anhydride.

The effectiveness of any particular type of additive combination can vary with different fuel stocks and combinations which are more effective at the same total additive concentration reduce treatment cost. We have now discovered novel, synergistic additive combinations which include certain Mannich Bases and provide middle distillate fuels having generally improved storage stability compared to fuels containing the same total concentrations of either N,N-dimethylcyclohexylamine antioxidant alone or N,N-dimethylcyclohexylamine in combination with an N,N'-di-(ortho-hydroxyarylidene)-1,2-alkylenediamine metal deactivator.

In accordance with this invention, there is provided a fuel additive concentrate comprising a mixture of N,N-dimethylcyclohexylamine and a Mannich Base which is the reaction product of an aldehyde, an amine and an alkyl phenol selected from (a) hindered phenol having the formula:



where $R_1$, $R_2$, $R_3$ are independently selected from hydrogen, t-butyl, t-amyl and isoproprοpyl, provided that at least one of $R_1$, $R_2$ and $R_3$ is hydrogen and at least one of $R_1$ and $R_2$ is t-butyl, t-amyl or isopropyl; and (b) p-alkyl phenol having the formula:



where $R_4$ is $C_9$ to $C_{30}$ alkyl.

The concentrate can also contain a N,N'-di(ortho-hydroxyarylidene)-1,2-alkylenediamine metal deactivator such as N,N'-disalicylidene-1,2-propylenediamine. Also provided is a stabilized fuel containing from 1 to 1400 mgs/liter of N,N-dimethylcyclohexylamine, from 0.5 to 1100 mgs/liter of Mannich Base and from 0 to 400 mgs/liter of an N,N'-di(ortho-hydroxyarylidene)-1,2-alkylenediamine.

The N,N-dimethylcyclohexylamine component of the compositions of the invention is a commercially available fuel antioxidant.

The N,N'-di(ortho-hydroxyarylidene)-1,2-alkylenediamine component, in which, typically, the arylidene radical contains 6-7 carbon atoms and the alkylene radical contains 2-3 carbon atoms, is a metal deactivator whose presence in combination with the other components provides fuel compositions of the invention having the most improved stability. The preferred metal deactivator is N,N'-disalicylidene-1,2-propylenediamine which is commercially available.

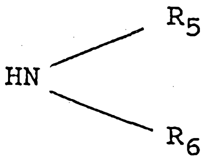
The Mannich Base component of the invention is produced by the Mannich condensation reaction of a hindered or p-alkyl phenol, an aldehyde, such as formaldehyde, ethanal, propanal, and butanal (preferably formaldehyde in its monomeric form or paraformaldehyde) and primary or ~~and~~ secondary amines.

The hindered phenols which are useful in preparing the Mannich Base component of the invention are phenols which are characterized by the presence of at least one and preferably two ortho-t-butyl, t-amyl, and/or isopropyl groups. Specific examples of such hindered phenols include: 2,4-di-t-butylphenol, 2,4-diisopropylphenol, 2,6-diisopropylphenol, 2-t-butylphenol, and 2-t-amylphenol with 2,6-di-t-butylphenol being most preferred.

The p-alkyl phenols which are useful in preparing the Mannich Base component of the invention are those which contain from 9 to 30 carbons which can be arranged in either a straight or a branched chain. Preferred phenols are $C_9$ to $C_{12}$ p-alkylphenols such as, for example, p-nonylphenol and p-dodecylphenol.

The amines which are useful in preparing the Mannich Base component of the invention are primary and secondary amines which can be selected from one or more of:

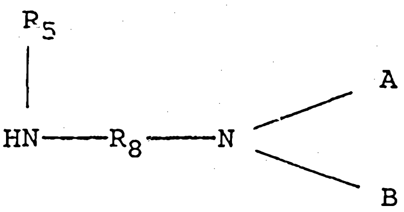
A. alkyl monoamines of the formula;



$$HN\begin{cases} R_5 \\ R_6 \end{cases}$$

where $R_5$ is selected from H and $C_1$ to $C_5$ alkyl, and $R_6$ is selected from $C_1$ to $C_{14}$ alkyl and the group $-(CH_2)n-OR_7$ where n = 1 to 10 and $R_7$ is $C_1$ to $C_{20}$ alkyl,

B. alkyl diamines of the formula;



$$\overset{R_5}{\overset{|}{HN}}-R_8-N\begin{cases} A \\ B \end{cases}$$

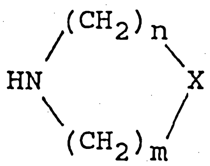
where $R_5$ is selected from H and $C_1$ to $C_5$ alkyl, $R_8$ is $C_1$ to $C_6$ alkylene and A and B are independently selected from H, $C_1$ to $C_5$ alkyl, monohydroxysubstituted $C_1$ to $C_5$ alkyl, and the group $(CH_2)_n-OR_7$ where n = 1 to 10 and $R_7$ is $C_1$ to $C_{20}$ alkyl,

C. ethylene polyamines of the formula;

$H_2N{\leftarrow}(CH_2)_2NH{\rightarrow}_nH$

where n = 2 to 10, and

D. cyclic amines of the formula;

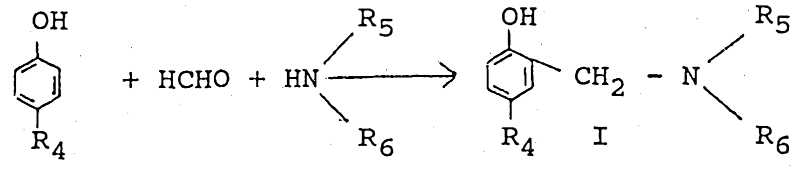


where n and m are independently integers from 1 to 3, X is selected from $CH_2$, O, S and $NR_9$ where $R_9$ is H, $C_1$ to $C_{10}$ alkyl, or the group $(CH_2)_n-NH_2$ where n is 1 to 10. The alkyl groups can have a branched chain.

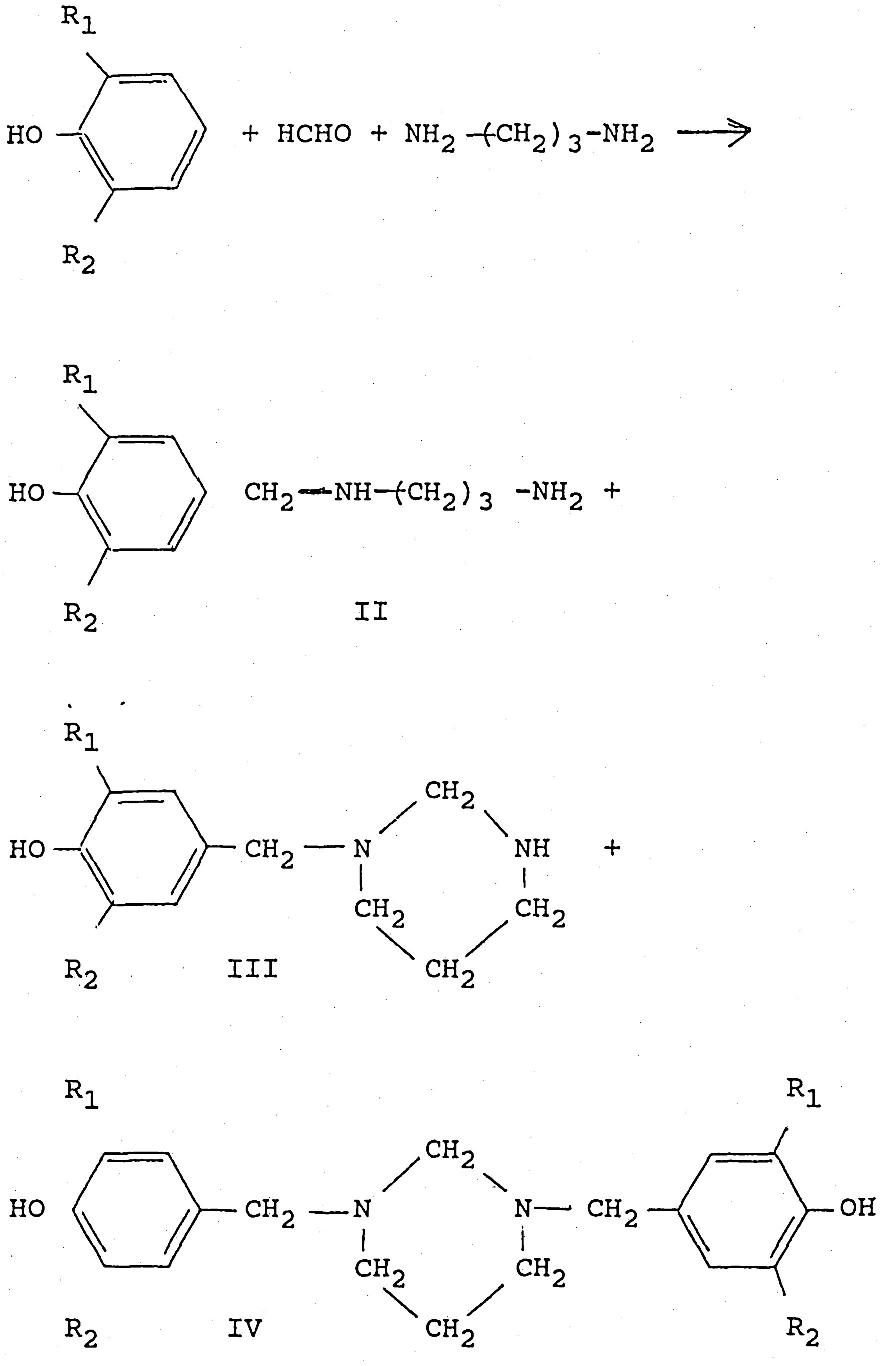
Specific examples of such amines include 1,3-diaminopropane, 1,2 diaminopropane, dimethylamine, diethylamine, dipropylamine, dibutylamine, N,N-dimethyl-1,3-diaminopropane, 1,1-dimethyldodecylamine, mixed $C_{12}$-$C_{14}$ t-alkyl amines, 2-methyl-1,5-pentadiamine, ethylenediamine; cyclic amines such as piperazine, aminoethylpiperazine, morpholine and thiomorpholine; and ethylene polyamines such as diethylene triamine and triethylene tetraamine.

The Mannich Base can be formed by reacting from 1 to 5 moles of aldehyde, from about 1 to 2 moles of amine and from 1 to 4 moles of phenol at a temperature of from 0°C to 150°C for 0.5 to 10 hours. An inert solvent such as isopropanol can be used which is distilled from the product along with water formed in the reaction.

The Mannich Base product is usually a mixture of materials which may contain unreacted ingredients, especially the phenol. The Mannich Bases can be isolated from the product mixture but the product mixture itself can conveniently be used in forming the compositions of the invention. Examples of Mannich reactions and products are illustrated below:


OH
R4
+ HCHO + HN
R5
R6
OH
CH2 - N
R5
R6
R4
I

or


R1
HO
R2
+ HCHO + NH2 -(CH2)3-NH2
R1
HO
CH2-NH-(CH2)3 -NH2 +
R2
II
R1
HO
CH2
N
NH
CH2
CH2
CH2
+
R2
III
R1
HO
CH2
N
CH2
N
CH2
OH
CH2
CH2
CH2
R1
R2
IV
R2

where $R_1$, $R_2$, $R_4$, $R_5$ and $R_6$ are as defined above.

The additive mixtures of the invention are usually prepared and marketed in the form of concentrates for addition to the fuel by the customer although the individual components could be added directly into the fuel. Suitable proportions of additives in the concentrates of the invention, based on the total weight of concentrate, include from 25 to 95 wt% N,N-dimethylcyclohexylamine, from 0 to 25 wt% N,N'-di(ortho-hydroxyarylidene)-1,2-alkylenediamine and, from 5 to 75 wt% Mannich Base.

The concentrates are added to the fuel in effective amounts to provide improved stability. Suitable amounts of additive concentrate in the fuel are from 1 to 500 pounds per thousand barrels (Ptbs) (3 to 1500 mgs/liter, preferred 2.5 to 100 Ptbs or 8 to 300 mgs/liter). This will provide a stabilized fuel containing from 1 to 1400 mgs/liter (preferred 2 to 250 mgs/liter) N,N-dimethylcyclohexylamine, from 0 to 400 mgs/liter (preferred 0 to 100 mgs/liter) N,N'-di(ortho-hydroxyarylidene)-1,2-alkylenediamine metal deactivator and from 1 to 1100 mgs/liter (preferred 1 to 250 mgs/liter) of Mannich Base. When used, the metal deactivator is preferably present in amounts of 1.0% to 25 wt% of concentrate or .3 to 400 mgs/liter of fuel. The concentrates can also contain an inert diluent or solvent which can be, for example, an aliphatic hydrocarbon such as kerosene or an aromatic hydrocarbon such as xylene.

The middle distillate fuels whose stability is improved by the invention typically include those boiling within a temperature range of 150°-400°C which may commonly be labeled as kerosene, fuel oil, diesel oil, No. 1-D, or No. 2-D.

The compositions of the invention are further illustrated by, but are not intended to be limited to, the following examples wherein parts are parts by weight unless otherwise indicated.

### Example 1

A Mannich Base reaction product of formaldehyde, 1,3-diaminopropane and 2,6-di-t-butylphenol is prepared by the following process.

Dissolve 103 grams (0.5 mole) of 2,6-di-t-butylphenol in 100 grams of isopropyl alcohol (IPA) in a 500 ml round bottom flask. Add 18.5 grams (0.25 mole) of 1,3-diaminopropane dropwise over 15 minutes while the contents of the flask are stirred. There is an exotherm observed as the amine is added. Cool the contents of the flask to below 30°C and add a 10% excess, (44.6 grams 0.55 mole) of 37% aqueous formaldehyde solution dropwise over 30 minutes while maintaining the temperature below 30°C. Heat the contents of the flask to reflux and continue to reflux for one hour. Switch from reflux to distillation and distill off IPA/water mixture to 105°C. Apply 28 in. Hg vacuum to remove residual materials. The total product yield is 122.2 or 96% of theory which contains compounds of the Structure III and IV.

Additive blends of the reaction product were prepared and tested in different fuels using both the D 4625 43°C (110°F) Storage Stability Test, in which the color change (using ASTM D1500) and the total insolubles in the fuel (reported in mg/100 ml) are determined on 400 ml samples stored for 13 weeks in the dark and the F-21-61 149°C (300°F) Accelerated Stability Test in which the color change and insoluble gums are determined on 50 ml samples heated to 149°C for a selected time, which was 90 minutes, allowed to cool in the dark, tested for color (ASTM D1500), and then filtered (using a 4.25 cm Whatman #1 filter paper) and the filtrate discarded. The filter is washed clean of fuel with isooctane and measured for deposits by comparison with a set of reference papers. The blend compositions and test results in comparison to untreated fuel and blends without the Mannich Base product are reported in Table I below.

## TABLE I

### Composition in Pounds Per Thousand Barrels

| | Fuel #1 | | | | | Fuel #2 | | | Fuel #3 | | | Fuel #4 | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Components | 1 | 2 | 3 | 4 | 5 | 1 | 2 | 3 | 1 | 2 | 3 | 1 | 2 | 3 | 4 | 5 |
| DMCA[1] | 0.0 | 5.0 | 4.0 | 4.75 | 3.80 | 0.0 | 4.75 | 3.8 | 0.0 | 9.5 | 7.6 | 0.0 | 2.38 | 1.90 | 4.75 | 3.80 |
| MDA[2] | 0.0 | 0.0 | 0.0 | 0.25 | 0.25 | 0.0 | 0.25 | 0.24 | 0.0 | 0.5 | 0.5 | 0.0 | 0.12 | 0.12 | 0.25 | 0.24 |
| Mannich Base | 0.0 | 0.0 | 1.0 | 0.00 | 0.95 | 0.0 | 0.0 | 0.96 | 0.0 | 0.0 | 1.9 | 0.0 | 0.00 | 0.48 | 0.00 | 0.96 |
| Total Additives | 0.0 | 5.0 | 5.0 | 5.0 | 5.0 | 0.0 | 5.0 | 5.0 | 0.0 | 10.0 | 10.0 | 0.0 | 2.5 | 2.5 | 5.0 | 5.0 |

### Test Results

### 149°C (F-21-61)

| | Fuel #1 | | | | | Fuel #2 | | | Fuel #3 | | | Fuel #4 | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Components | 1 | 2 | 3 | 4 | 5 | 1 | 2 | 3 | 1 | 2 | 3 | 1 | 2 | 3 | 4 | 5 |
| Color | L7 | L3.5 | 2.5 | L3 | 2 | 8 | 3 | 3 | 8 | L2.5 | 2 | L2.5 | 2 | 2 | 2.5 | L2.5 |
| Deposit | 13 | 5 | 4 | 4 | 2 | 17 | 10 | 5 | 17 | 5 | 3 | 6 | 4 | 4 | 4 | 4 |

### 43°C (D 4625)

| | Fuel #1 | | | | | Fuel #2 | | | Fuel #3 | | | Fuel #4 | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Components | 1 | 2 | 3 | 4 | 5 | 1 | 2 | 3 | 1 | 2 | 3 | 1 | 2 | 3 | 4 | 5 |
| Color | L5 | 4 | 4 | 4 | L4 | L3.5 | L3.5 | L3.5 | L3.5 | L3.5 | L3.5 | 2.5 | L2.5 | L2.5 | L2.5 | L2.5 |
| Deposit | 6.8 | 3.2 | 2.4 | 2.5 | 1.8 | 7.9 | 4 | 4.7 | 6.7 | 3 | 2.1 | 2.2 | 2 | 1.6 | 1.3 | 1 |

L = less than

[1] N,N-dimethylcyclohexylamine

[2] N,N'-disalicylidene-1,2-propylenediamine

Fuel #1 is Midwest Refinery

Fuel #2 is Mid-Continent #2 Diesel (Corning Crude)

Fuel #3 is Mid-Continent #2 Diesel (Ill. Basin Crude)

Fuel #4 is Midwest #2 Diesel (KS/Tx Crude)

A significant difference in stability at 149°C is indicated by a color difference of about 1/2 number and/or a deposit difference of 2 numbers and a significant difference in stability at 43°C is indicated by a color difference of about 1/2 number and a deposit difference of 20%. The results in Table I show that the blends of the invention which contain Mannich Base in addition to DMCA or DMCA and MDA gave significantly better overall stability when compared to comparable blends which did not contain the Mannich Base, for example, blend 3 vs blend 2 and blend 5 vs blend 4 of Fuel #1.

## Example 2

A Mannich Base reaction product of formaldehyde, dimethylamine, and 2,6-di-t-butylphenol is prepared by the following process.

Dissolve 103 grams (0.5 mole) of 2,6-di-t-butylphenol in 100 grams of IPA in a 500 ml round bottom flask and add 72 grams (0.64 mole) of a 40% aqueous dimethylamine solution. Cool the mixture to about 30°C and add dropwise with stirring 44.6 grams (0.55 mole) of 37% formaldehyde while keeping the mixture at a temperature below 40°C. Heat the mixture to reflux and reflux for 4 hours. Remove IPA/water by distillation and apply vacuum to remove residual materials. The product yield is 113 grams or 86% of theory which contains N,N-dimethyl-3,5-di-t-butyl4-hydroxybenzylamine.

Additive blends of the above reaction product were prepared and tested in different fuels using the test procedures described in Example 1. The blend compositions and test results in comparison to untreated fuel and blends which did not contain the Mannich Base product are reported in Table II below.

# TABLE II

## Composition in Pounds Per Thousand Barrels

| | Fuel #1 | | | | | Fuel #2 | | | Fuel #3 | | | Fuel #4 | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Components | 1 | 2 | 3 | 4 | 5 | 1 | 2 | 3 | 1 | 2 | 3 | 1 | 2 | 3 | 4 | 5 |
| DMCA | 0.0 | 5.0 | 4.0 | 4.75 | 3.80 | 0.0 | 9.5 | 7.6 | 0.0 | 28.5 | 22.8 | 0.0 | 2.38 | 1.90 | 4.75 | 3.80 |
| MDA | 0.0 | 0.0 | 0.0 | 0.25 | 0.25 | 0.0 | 0.5 | 0.5 | 0.0 | 1.5 | 1.5 | 0.0 | 0.12 | 0.12 | 0.25 | 0.24 |
| Mannich Base | 0.0 | 0.0 | 1.0 | 0.00 | 0.95 | 0.0 | 0.0 | 1.9 | 0.0 | 0.0 | 5.7 | 0.0 | 0.00 | 0.48 | 0.00 | 0.96 |
| Total Additives | 0.0 | 5.0 | 5.0 | 5.0 | 5.0 | 0.0 | 10.0 | 10.0 | 0.0 | 30.0 | 30.0 | 0.0 | 2.5 | 2.5 | 5.0 | 5.0 |

## Test Results

### 149°C (F-21-61)

| | Fuel #1 | | | | | Fuel #2 | | | Fuel #3 | | | Fuel #4 | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Components | 1 | 2 | 3 | 4 | 5 | 1 | 2 | 3 | 1 | 2 | 3 | 1 | 2 | 3 | 4 | 5 |
| Color | L7 | L3.5 | 3 | L3 | L3 | 8 | 3 | 3 | 4.5 | L4 | 3.5 | L2.5 | 2 | L2.5 | 2.5 | L2.5 |
| Deposit | 13 | 5 | 6 | 4 | 4 | 17 | 10 | 6 | 5 | 3 | 3 | 6 | 4 | 5 | 4 | 3 |

### 43°C (D 4625)

| | Fuel #1 | | | | | Fuel #2 | | | Fuel #3 | | | Fuel #4 | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Components | 1 | 2 | 3 | 4 | 5 | 1 | 2 | 3 | 1 | 2 | 3 | 1 | 2 | 3 | 4 | 5 |
| Color | L5 | 4 | 4 | 4 | 4 | L3.5 | L3.5 | L3.5 | -- | -- | -- | 2.5 | L2.5 | L3 | L2.5 | L2.5 |
| Deposit | 6.8 | 3.2 | 2.8 | 2.5 | 2 | 6.7 | 4 | 3.9 | -- | -- | -- | 2.2 | 2 | 1.9 | 1.3 | 0.9 |

The fuels were the same as in Example 1 except that Fuel #3 is a fuel containing unhydrotreated residual cracked stock.

The results indicated that the blends containing Mannich Base gave fuels having significantly improved stability except in the case of Fuel #4 where the results were mixed.

## Example 3

A Mannich Base reaction product of formaldehyde, $C_{12}$-$C_{14}$ t-alkyl amine mixture (Primene 81R) and 2,6-di-t-butyl phenol is prepared by the process described in Example 2 using 95.5 grams (0.5 mole) of Primene 81R in place of the dimethylamine. The product yield is 200 grams or 82% of theory which contains N-[3,5-di-t-butyl-4-hydroxybenzyl]-mixed $C_{12}$-$C_{14}$ t-alkyl amines.

Additive blends of the above reaction product were prepared and tested in #2 diesel fuel using the test procedures described in Example 1. The blend compositions and test results are reported in Table III below.

TABLE III
Composition Pounds Per Thousand Barrels

| Components | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|---|---|---|---|---|---|---|---|
| DMCA | 0.0 | 9.5 | 0.0 | 4.75 | 19.0 | 0.0 | 9.5 |
| MDA | 0.0 | 0.5 | 0.5 | 0.50 | 1.0 | 1.0 | 1.0 |
| Mannich Base | 0.0 | 0.0 | 9.5 | 4.75 | 0.0 | 19.0 | 9.5 |
| Total Additives | 0.0 | 10.0 | 10.0 | 10.0 | 20.0 | 20.0 | 20.0 |

### Test Results
### 149°C (F-21-61)

| Components | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|---|---|---|---|---|---|---|---|
| Color | L5.5 | L4.5 | L5 | L4.5 | L4.5 | L5 | L4.5 |
| Deposit | 8 | 6 | 4 | 3 | 4 | 3 | 2 |

### 43°C (D 4625)

| Components | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|---|---|---|---|---|---|---|---|
| Color | L6.5 | L6 | 6 | L6 | 5.5 | L6 | L5.5 |
| Deposit | 8.3 | 3.2 | 5 | 2.8 | 3.3 | 5 | 3 |

The results indicate that blends 4 and 7 according to the invention which contain the Mannich Base in addition to DMCA and MDA have better stability at the same total additive levels compared to blends 2 and 5 containing only DMCA and MDA.

## Example 4

A Mannich Base reaction product of formaldehyde, 1,2-diaminopropane, and 2,6-di-t-butyl phenol is prepared by the following process.

Dissolve 103 gm (0.5 mole) of 2,6-di-t-butyl phenol in 100 grams of IPA in a 500 ml roundbottom flask and add 18.5 grams (0.25) moles of 1,2-diaminopropane. Cool this mixture to about 30°C and add dropwise with stirring 44.6 grams (0.55 mole) of 37% formaldehyde while keeping the temperature of the mixture below 40°C. Heat the mixture to reflux and reflux for 1 hour. Remove IPA/water by distillation and apply vacuum to remove residual materials.

Additive blends of the above reaction product were prepared and tested in Fuel #1 fuel using the test procedures described in Example 1. The blend compositions and results are reported in Table IV below.

TABLE IV
Composition Pounds Per Thousand Barrels

| Components | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| DMCA | 0.0 | 5.0 | 4.75 | 4.0 | 3.8 |
| MDA | 0.0 | 0.0 | 0.25 | 0.0 | 0.25 |
| Mannich Base | 0.0 | 0.0 | 0.00 | 1.0 | 0.95 |
| Total Additives | 0.0 | 5.0 | 5.0 | 5.0 | 5.0 |

Test Results
149°C (F-21-61)

| Components | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| Color | L7 | L3.5 | L3 | L3 | L2.5 |
| Deposit | 13 | 5 | 4 | 3 | 3 |

43°C (D 4625)

| Components | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| Color | L5 | 4 | 4 | 4 | L4 |
| Deposit | 6.8 | 3.2 | 2.5 | 2.6 | 1.7 |

The results indicate that blend 4 of the invention containing the Mannich Base has improved stability compound to blend 2 which containing DMCA alone. Blend 5 containing the Mannich Base has improved stability over blend 3 which contained DMCA and MDA alone.

## Example 5

A Mannich Base reaction product of formaldehyde, N,N-dimethyl-1,3-diaminopropane, and p-dodecylphenol was prepared by the following procedure.

Combine 262.4 grams (1.0 mole) of the alkyl ($C_{12}$) phenol with 102.2 grams (1.0 mole) of N,N-dimethyl-1,3-diamino-propane and add 89.2 grams (1.1 mole) of 37% formaldehyde with stirring while keeping the temperature below 40°C. Heat the mixture to 100°C for two hours and then remove water by distillation (100°C - 28 in vacuum). The product yield is 176 grams or 93% of theory which contains N,N-dimethyl-N'-[2 hydroxy-5-dodecylbenzyl]-1,3-diamino-propane.

Additive blends of the above reaction product were prepared and tested in midcontinent #2 diesel fuel using the test procedures described in Example 1. The blend compositions and results are reported on Table V below.

TABLE V
Composition Pounds Per Thousand Barrels

| Components | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| DMCA | 0.0 | 4.75 | 2.05 | 9.5 | 4.5 |
| MDA | 0.0 | 0.25 | 0.25 | 0.5 | 0.5 |
| Mannich Base | 0.0 | 0.00 | 2.70 | 0.0 | 5.4 |
| Total Additives | 0.0 | 5.0 | 5.0 | 10.0 | 10.0 |

### Test Results
### 149°C (F-21-61)

| Components | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| Color | 8 | 3 | L3 | L2.5 | L2.5 |
| Deposit | 13 | 10 | 5 | 5 | 5 |

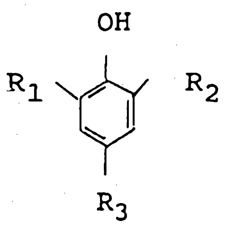
### 43°C (D 4625)

| Components | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| Color | L3.5 | L3.5 | 3 | L3.5 | L3.5 |
| Deposit | 6 | 4 | 3.5 | 3 | 2.4 |

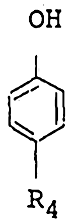
The results indicate that blends 3 and 5 of the invention have over-all improved stability compared to blends at the same total additive level which did not include the Mannich Base.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:-

1. A fuel additive concentrate comprising a mixture of N,N-dimethylcyclohexylamine and a Mannich Base which is the reaction product of an aldehyde, a primary or secondary amine and an alkyl phenol selected from (a) hindered phenol having the formula:



where $R_1$, $R_2$, $R_3$ are independently selected from hydrogen, t-butyl, t-amyl and isoproprropyl, provided that at least one of $R_1$, $R_2$ and $R_3$ is hydrogen and at least one of $R_1$ and $R_2$ is t-butyl, t-amyl or isopropyl; and (b) p-alkyl phenol having the formula:

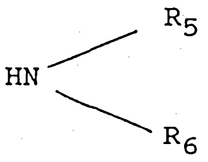


where $R_4$ is $C_9$ to $C_{30}$ alkyl; said concentrate containing, based on the total weight of concentrate, from 25 to 95 wt% N,N-dimethylcyclohexylamine from 5 to 75 wt% Mannich Base.

2. The concentrate of claim 1 wherein the concentrate also contains from 1 to 25 wt% N,N'-di(ortho-hydroxyarylidene)-1,2-alkylenediamine metal deactivator.

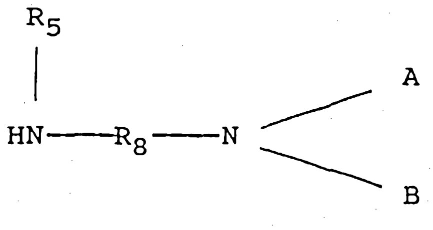
3. The concentrate of claim 1 or 2 wherein the aldehyde is formaldehyde, and the amine is selected from one or more of:

A. alkyl monoamines of the formula;



where $R_5$ is selected from H and $C_1$ to $C_5$ alkyl, and $R_6$ is selected from $C_1$ to $C_{14}$ alkyl and the group $-(CH_2)n-OR_7$ where n = 1 to 10 and $R_7$ is $C_1$ to $C_{20}$ alkyl,

B. alkyl diamines of the formula;



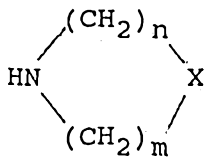
where $R_5$ is selected from H and $C_1$ to $C_5$ alkyl, $R_8$ is $C_1$ to $C_6$ alkylene and A and B are independently selected from H, $C_1$ to $C_5$ alkyl, mono-hydroxysubstituted $C_1$ to $C_5$ alkyl, and the group $(CH_2)_n\text{-}OR_7$ where n = 1 to 10 and $R_7$ is $C_1$ to $C_{20}$ alkyl,

C. ethylene polyamines of the formula;

$H_2N\text{-}((CH_2)_2NH)_nH$

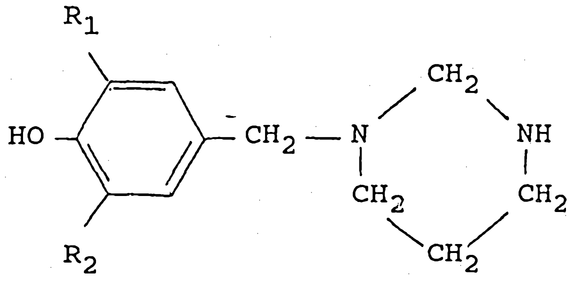
where n = 2 to 10, and

D. cyclic amines of the formula;

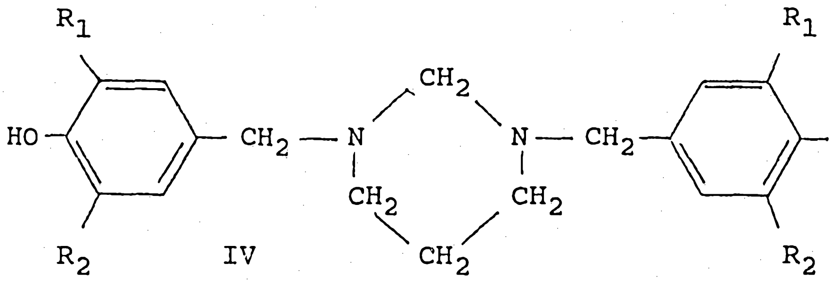


where n and m are independently intergers from 1 to 3, X is selected from $CH_2$, O, S and $NR_9$ where $R_9$ is H, $C_1$ to $C_{10}$ alkyl, or the group $(CH_2)_n\text{-}NH_2$ where n is 1 to 10.

4. The concentrate of any one of the preceding claims wherein the phenol is a hindered phenol, and the Mannich Base comprises N-[3,5-di-t-butyl-4-hydroxybenzyl]-mixed $C_{12}$ to $C_{14}$ t-alkyl amines, N,N-dimethyl-3,5-di-t-butyl-4-hydroxybenzylamine, a compound of the formula:



where $R_1$ and $R_2$ are independently selected from hydrogen, t-butyl, t-amyl and isopropyl provided that at least one of $R_1$ and $R_2$ is t-butyl, t-amyl, or isopropyl, or a compound of the formula:


IV

where $R_1$ and $R_2$ are independently selected from hydrogen, t-butyl, t-amyl and isopropyl provided that at least one of $R_1$ and $R_2$ is t-butyl, t-amyl, or isopropyl.

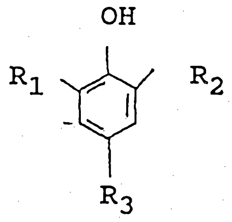
5. The concentrate of any one of claims 1-3 wherein the phenol is a p-alkylphenol, and the Mannich Base comprises N,N-dimethyl-N'-[2-hydroxy-5-dodecylbenzyl]-1,3-diaminopropane.

6. The concentrate of claim 2 wherein the metal deactivator is N,N'-disalicylidene-1,2-propylenediamine and the Mannich Base is the reaction product of formaldehyde, 2,6-di-t-butyl phenol and an amine selected from 1,3-diaminopropane, 1,2-diaminopropane, mixed $C_{12}$-$C_{14}$ t-alkyl amines, and dimethylamine.

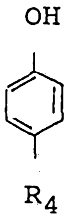
7. The concentrate of claim 2 wherein the metal deactivator is N,N'-disalicylidene-1,2-propylenediamine and the Mannich Base is the reaction product of formaldehyde, p-dodecyl phenol, and N,N-dimethyl-1,3-diaminopropane.

8. A fuel composition comprising middle distillate fuel containing from 3 to 1500 mgs/liter of the concentrate of any one of claims 1-7.

9. A fuel composition comprising a middle distillate fuel and from 1 to 1400 mgs/liter N,N-dimethylcyclohexylamine, from 0 to 400 mgs/liter N,N-di(ortho-hydroxyarylidene)-1,2-alkylenediamine and from 1 to 1100 mgs/liter of a Mannich Base which is the reaction product of an aldehyde, an amine and an alkyl phenol selected from (a) hindered phenol having the formula:



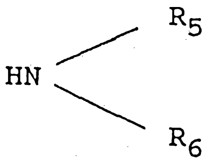
where $R_1$, $R_2$, $R_3$ are independently selected from hydrogen, t-butyl, t-amyl and isoproprop yl, provided that at least one of $R_1$, $R_2$ and $R_3$ is hydrogen and at least one of $R_1$ and $R_2$ is t-butyl, t-amyl or isopropyl; and (b) p-alkyl phenol having the formula:



where $R_4$ is $C_9$ to $C_{30}$ alkyl.

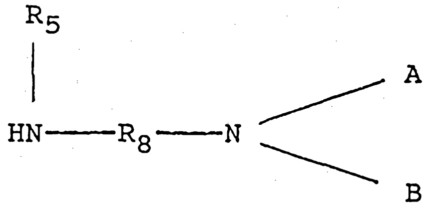
10. The fuel composition of claim 9 wherein the aldehyde is formaldehyde and the amine is selected from one or more of:

A. alkyl monoamines of the formula;



where $R_5$ is selected from H and $C_1$ to $C_5$ alkyl and $R_6$ is selected from $C_1$ to $C_{14}$ alkyl and the group $-(CH_2)n-OR_7$ where n = 1 to 10 and $R_7$ is $C_1$ to $C_{20}$ alkyl,

B. alkyl diamines of the formula;



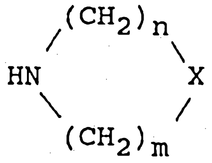
where $R_5$ is selected from H and $C_1$ to $C_5$ alkyl $R_8$ is $C_1$ to $C_6$ alkylene and A and B are independently selected from H, $C_1$ to $C_5$ alkyl, monohydroxysubstituted $C_1$ to $C_5$ alkyl, and the group $(CH_2)_n-OR_7$ where n = 1 to 10 and $R_7$ is $C_1$ to $C_{20}$ alkyl,

C. ethylene polyamines of the formula;

$H_2N\!-\!((CH_2)_2NH)_nH$

where n = 2 to 10, and

D. cyclic amines of the formula;



where n and m are independently intergers from 1 to 3, X is selected from $CH_2$, O, S and $NR_9$ where $R_9$ is H, $C_1$ to $C_{10}$ alkyl, or the group $(CH_2)_n$-$NH_2$ where n is 1 to 10.

11.
~~10.~~ Fuel additive concentrate or compositions containing them, substantially as hereinbefore described with reference to the Examples.

~~11. The steps, features, compositions and compounds disclosed herein or referred to or indicated in the specification and/or claims of this application, individually or collectively, and any and all combinations of any two or more of said steps or features.~~

DATED this FIRST day of MARCH 1990

Ethyl Petroleum Additives, Inc.

by DAVIES & COLLISON
Patent Attorneys for the applicant(s)