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(54) Mannich bases useful in middle distillate fuel having improved storage stability.

(57) Mannich Bases derived from a hindered phenol, formaldehyde and an amine are useful as stabilizers for middle distillate fuels.

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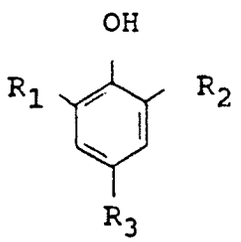
MANNICH BASES USEFUL IN MIDDLE DISTILLATE FUEL HAVING IMPROVED STORAGE STABILITY

This invention relates generally to Mannich Bases useful for improving the stability of middle distillate fuels, more particularly when used in combination with N,N-dimethylcyclohexyl amine. This Application is a divisional of our Application No. 90301791.1 (Publication No. 0385633).

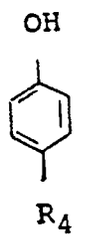
Middle distillate fuels such as diesel oil, fuel oil, jet fuel and kerosene when stored for long periods of time are subject to the formation of colour and solid deposits. The deposits accumulate on filters causing the filters to become plugged. Various additives and combinations of additives have been employed to reduce colour 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. In our aforesaid present Application No. 90301791.1 we have described and claimed 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.

The Mannich Base component of the compositions of our aforesaid Application is produced by the Mannich condensation reaction of a (a) hindered phenol having the formula:

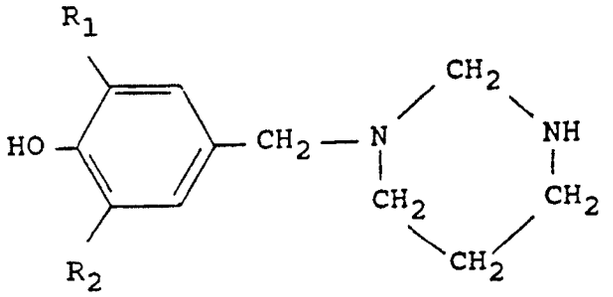


where R_1, R_2, R_3 are independently selected from hydrogen, t-butyl, t-amyl and isopropyl, provided that at least one of R_1, R_2 and R_3 is hydrogen and at least one of R_1 and R_2 is t-butyl, t-amyl or isopropyl; or a (b) p-alkyl phenol having the formula:

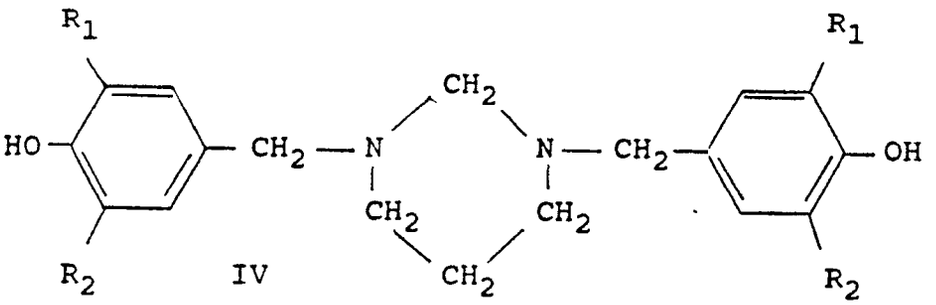


where R_4 is C_9 to C_{30} alkyl, an aldehyde, such as formaldehyde, ethanal, propanal, and butanal (preferably formaldehyde in its monomeric form or paraformaldehyde) and primary and secondary amines.

Of these Mannich Bases, those 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 of the formula:



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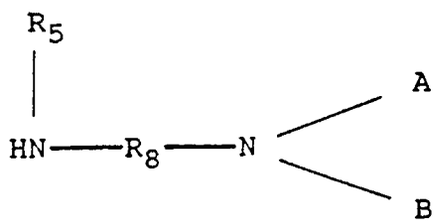
where R_1 and R_2 are independently selected from hydrogen, t-butyl, t-amyl and isopropyl provided that at least one of R_1 and R_2 is t-butyl, t-amyl, or isopropyl are novel compounds.

The hindered phenols which are useful in preparing the Mannich Bases of the invention are phenols which are characterised 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.

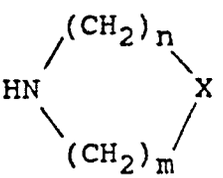
The amines which are useful in preparing the Mannich Base component of the invention include:

A. 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, and

B. cyclic amines of the formula;

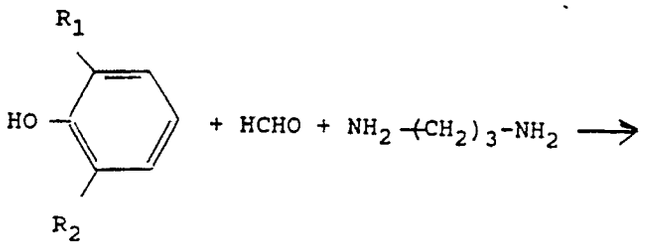


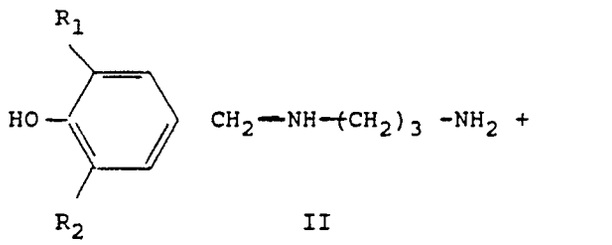
where n and m are independently integers from 1 to 3, and X can be NH.

Specific examples of such amines include 1,3-diaminopropane.

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. A 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:





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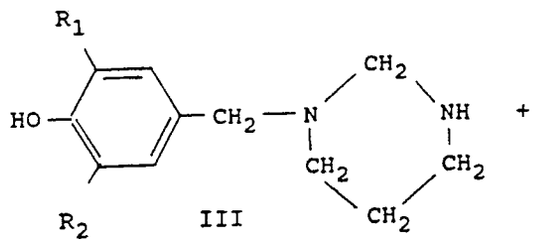
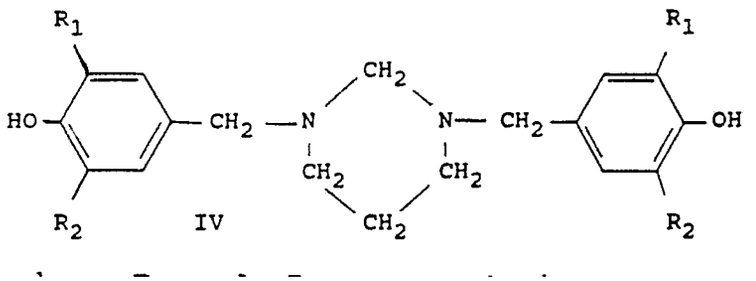


III



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where R_1 and, R_2 are as defined above.

The invention is further illustrated by, but is 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 colour 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 colour 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 colour (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	0.0	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)

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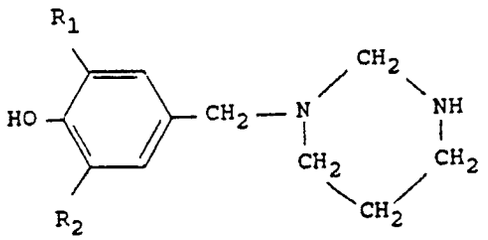
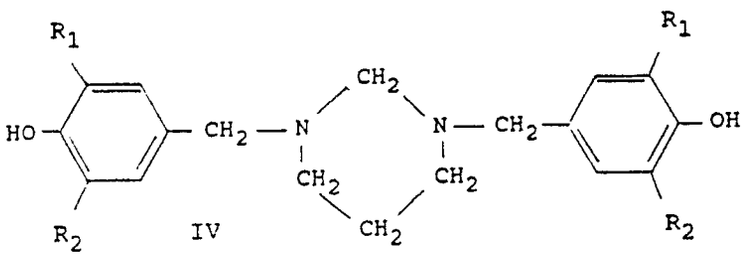
A significant difference in stability at 149° C is indicated by a colour difference of about 1/2 number and/or a deposit difference of 2 numbers and a significant difference in stability at 43° C is indicated by a colour difference of about 1/2 number and a deposit difference of 20%. The results in Table 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.

Claims

1. A Mannich Base 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 of the formula:



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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.

2. A Mannich Base according to claim 1 wherein R_1 and R_2 are both t-butyl.

3. A Mannich Base according to claim 1 which is the reaction product of formaldehyde, 2,6-di-t-butyl phenol and 1,3-diaminopropane.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 90 11 6830

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	US-A-4 025 316 (STOVER) * Whole document *	1,3	C 07 D 239/04 C 10 L 1/22
A	US-A-3 725 480 (TRAISE et al.) * Whole document *	1,3	
A	US-A-3 634 515 (PIASEK et al.) * Whole document *	1,3	
A	BE-A- 660 155 (COMMERCIAL SOLVENTS CORP.) * Claims 1,7; page 2 *	1,3	
A	US-A-4 668 412 (HART et al.) * Column 8 *	1-3	
A	US-A-3 787 416 (CYBA) * Column 2,3 *	1	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5) C 07 D 239/00 C 10 L C 10 M

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	01-10-1990	DE LA MORINERIE B.M.S.B.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

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