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(54) **Title:** ASHLESS OIL ADDITIVES AND THEIR USE AS TBN BOOSTERS

(57) **Abstract:** Described herein is an ashless oil additive, comprising at least one diazabicyclo or triazabicyclo compound. Also described is a composition comprising an engine oil mixed with an oil additive, wherein the oil additive comprises at least one diazabicyclo or triazabicyclo compound. Further described is a method for boosting the total base number (TBN) of an engine oil composition, comprising adding an oil additive to said engine oil composition, wherein the oil additive comprises at least one diazabicyclo or triazabicyclo compound.



ASHLESS OIL ADDITIVES AND THEIR USE AS TBN BOOSTERS

CROSS-REFERENCE TO RELATED APPLICATION

[0001] The present application claims the benefit of and priority to U.S. Provisional Patent Application No. 61/971,976, filed March 28, 2014, which is incorporated herein by reference in its entirety.

BACKGROUND

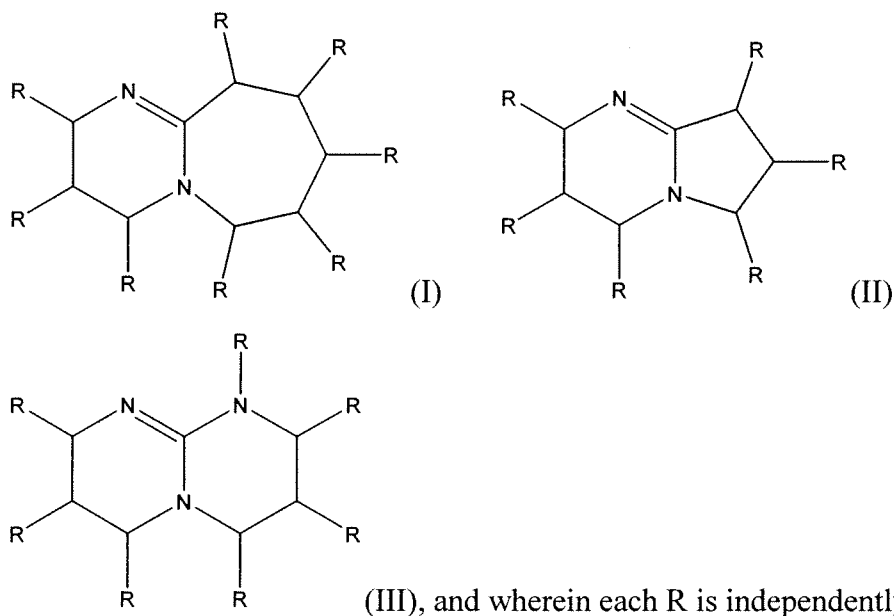
[0002] Current engine oils are not equipped to handle long oil drain intervals in many commercial engines. Metal based TBN (total base number) boosters have been designed to neutralize the acids generated by the combustion process and to ultimately protect the soft metals from increased corrosion. Metal based TBN boosters have limitations – with normal oil consumption levels, the ash-based chemicals participate in the combustion process and eventually decrease the usable life of the after-treatment systems. Servicing and replacing after-treatment systems, however, is time intensive and expensive. Because of their negative impact on the after-treatment filters, it is difficult to include a sufficient concentration of these metallic based chemicals for longer corrosion protection and longer oil drain intervals.

SUMMARY

[0003] By utilizing novel ashless TBN boosters described herein, the acid neutralizing capability of the engine oil can be increased substantially without increasing damage to the after-treatment filters. The TBN boosters described herein are applicable to both diesel and natural gas engines. Indeed, natural gas engines are more susceptible to ash producing additives, with the limit of ash present in natural gas engine oil being 0.6% (vs. 1% for diesel engines), and have struggled to get reasonable oil drain intervals. The TBN boosters described herein would greatly improve the oil drain intervals for both diesel and natural gas engines.

[0004] Many embodiments described herein relate to an ashless oil additive, comprising at least one diazabicyclo or triazabicyclo compound, wherein the diazabicyclo or triazabicyclo compound comprises at least two tertiary amines.

[0005] In some embodiments, the diazabicyclo or triazabicyclo compound is represented by formula (I), (II) or (III):



[0006] In some embodiments, the diazabicyclo or triazabicyclo compound is selected from the group consisting of 1,5-Diazabicyclo[4.3.0]non-5-ene (DBN), 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU), 1,5,7-Triazabicyclo[4.4.0]dec-5-ene (TBD), and 7-Methyl-1,5,7-Triazabicyclo[4.4.0]dec-5-ene (MTBD).

[0007] Other embodiments relate to a composition comprising an engine oil mixed with the oil additive described herein.

[0008] Additional embodiments relate to a method for boosting the total base number (TBN) of an engine oil composition, comprising adding the oil additive described herein to the engine oil composition.

[0009] These and other features, together with the organization and manner of operation thereof, will become apparent from the following detailed description when taken in conjunction with the accompanying drawings

BRIEF SUMMARY OF THE FIGURES

[0010] Figure 1 shows the TBN values of fresh engine oils supplemented with various amounts of 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) and 2,2,6,6-tetramethyl piperidine (TMP).

DETAILED DESCRIPTION

[0011] This disclosure relates to the use of amine-based organic bases as oil additives that function as TBN boosters. With the growing number of after-treatment failures due to increased back pressure because of ash loading on the filter, there is an industry wide initiative to evaluate alternative oil additives that are nonmetallic based. Surprisingly, it is discovered that certain tertiary amine chemicals are suitable as oil soluble TBN boosters. These chemicals work by absorbing acidic protons that have formed in the oil. These acid groups would otherwise attack and remove soft metals such as lead from bearings and bushings. The lead could be present to provide a cushion for the bearing and to delay wear. When the metal is removed by acids, it can cause increased wear on the bearing itself and matching crankshaft.

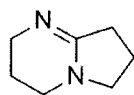
[0012] The tertiary amine chemicals described herein include bicyclic compounds that contain at least two, or at least three, tertiary amines. The bicyclic nature of the molecule affords high basicity and low nucleophilicity. Incorporating poor nucleophiles as oil additives can decrease the chances of side reactions and antagonistic interactions with other lubricant additives and engine components. The core structures of the bicyclic compounds can be functionalized to further minimize the potential of side reactions in lubricating oil.

[0013] The functionalization can also be designed to enhance cold temperature operability. For example, by functionalizing the cyclic amines with long hydrocarbon

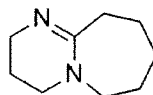
chains, miscibility can be adjusted, and cold weather properties can be improved. With certain functionalization, the TBN boosting power of the nitrogen groups can also be enhanced.

[0014] Additionally, incorporating heteroatoms such as oxygen, sulfur and nitrogen into the alkyl groups allows manipulation of the electronic properties of the parent molecule. Incorporating an oxygen group in various forms can increase or decrease the electron withdrawing and/or electron donating function of the parent molecule depending on its location. Adjusting these parameters can significantly impact the parent molecules basicity or nucleophilicity to favor better efficacy.

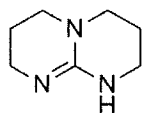
[0015] Exemplary chemical structures of some of the bicyclic tertiary amine chemicals described herein are provided below.



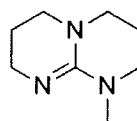
1,5-Diazabicyclo(4.3.0)non-5-ene



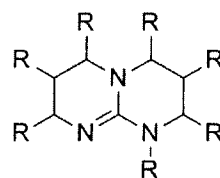
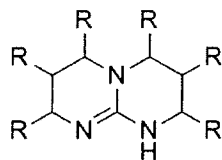
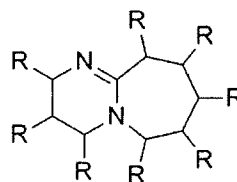
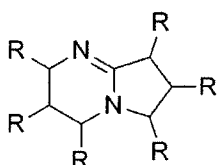
1,8-Diazabicyclo[5.4.0]undec-7-ene



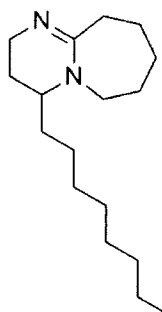
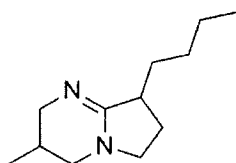
1,5,7-Triazabicyclo[4.4.0]dec-5-ene



7-Methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene

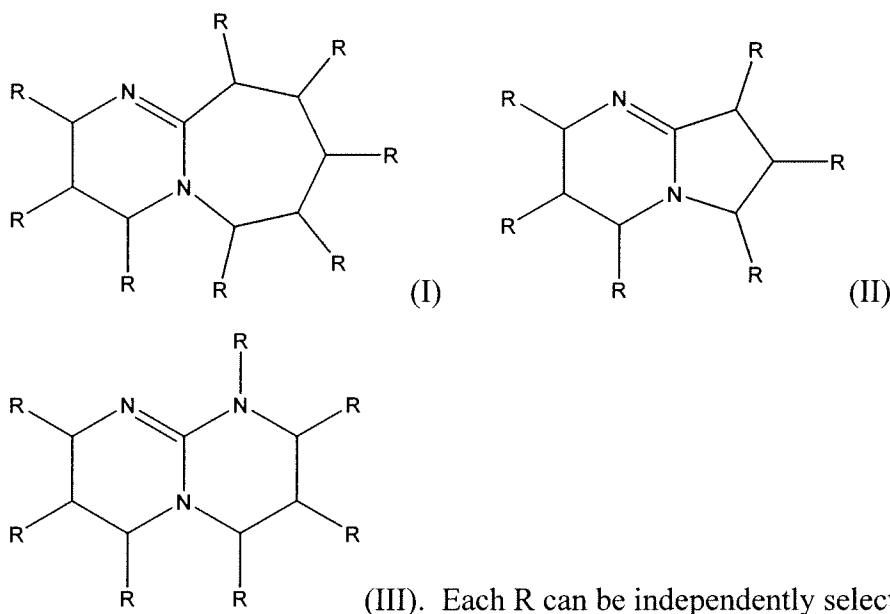


R = C1-C20. Every position does not need to be functionalized. Drawing is meant to show that each location could be. See below for an example.



[0016] The ashless oil additive described herein can comprise, for example, at least one diazabicyclo or triazabicyclo compound. The diazabicyclo or triazabicyclo compound can comprise, for example, at least two or at least three tertiary amines. The diazabicyclo or triazabicyclo compound can be, for example, optionally substituted with at least one linear or branched C1-C20, C1-C12, or C1-C6 organic group containing zero or at least one heteroatom, such as oxygen, sulfur or nitrogen.

[0017] The diazabicyclo or triazabicyclo compound can be represented by, for example, formula (I), (II) or (III):



example, hydrogen, or a linear or branched C1-C20, C1-C12, or C1-C6 alkyl group, containing zero or at least one heteroatom, such as oxygen, sulfur or nitrogen.

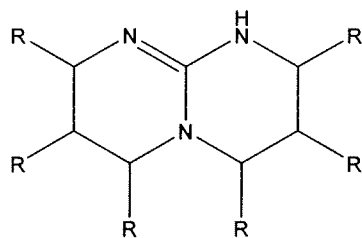
[0018] In some embodiments, the ashless oil additive comprises a diazabicyclo compound represented by formula I. In one embodiment, each R is hydrogen, and the diazabicyclo compound is 1,8-Diazabicyclo[5.4.0]undec-7-ene. In another embodiment, at least one R is a C1-C20, C1-C12, or C1-C6 alkyl group. In another embodiment, the R group can contain zero or at least one heteroatom, such as oxygen, sulfur or nitrogen, in the alkyl group.

[0019] In some embodiments, the ashless oil additive comprises a diazabicyclo compound represented by formula II. In one embodiment, each R is hydrogen, and the

diazabicyclo compound is 1,5-Diazabicyclo[4.3.0]non-5-ene. In another embodiment, at least one R is a C1-C20, C1-C12, or C1-C6 alkyl group. In another embodiment, the R group can contain zero or at least one heteroatom, such as oxygen, sulfur or nitrogen, in the alkyl group.

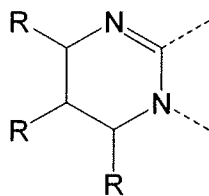
[0020] In some embodiments, the ashless oil additive comprises a triazabicyclo compound represented by formula III. In one embodiment, the N-R group comprises a C1-C20, C1-C12, or C1-C6 alkyl substituent group, optionally comprising at least one heteroatom such as oxygen, sulfur, or nitrogen. In another embodiment, the N-R group comprises a methyl substituent group, while each other R is hydrogen, and the triazabicyclo compound is 7-methyl-1,5,7-triazabicyclo[4,4,0]dec-5-ene. In another embodiment, the N-R group comprises a methyl substituent group, and at least one other R is a C1-C20, C1-C12, or C1-C6 alkyl group. In another embodiment, the R group can contain zero or at least one heteroatom, such as oxygen, sulfur or nitrogen, in the alkyl group.

[0021] In some embodiments, the ashless oil additive comprises a triazabicyclo



compound represented by formula (IV): (IV). In one embodiment, each R is hydrogen, and the triazabicyclo compound is 1,5,7-triazabicyclo[4,4,0]dec-5-ene. In another embodiment, at least one R is a C1-C20, C1-C12, or C1-C6 alkyl group. In another embodiment, the R group can contain zero or at least one heteroatom, such as oxygen, sulfur or nitrogen, in the alkyl group.

[0022] In some embodiments, the diazabicyclo or triazabicyclo compound comprises a first, six membered ring comprising at least two nitrogen atoms fused to a second, five-to-seven membered ring. In some embodiments, the first ring is represented



by formula (V): (V), wherein each R is independently hydrogen, a C1-C20, C1-C12 or C1-C6 alkyl group. In another embodiment, the R group can contain zero or at least one heteroatom, such as oxygen, sulfur or nitrogen, in the alkyl group.

[0023] In one embodiment, the second ring is a five membered ring. It is also possible for the second ring to be a six membered ring or a seven membered ring. In one embodiment, the second ring comprises no additional heteroatom in the ring. In one embodiment, the second ring comprises at least one additional heteroatom in the ring. In one embodiment, the second ring comprises at least one additional tertiary amine group, optionally in the meta position. In one embodiment, the second ring comprises one or more substituents selected from C1-C20, C1-C12, or C1-C6 organic groups. In another embodiment, the organic group can contain zero or at least one heteroatom, such as oxygen, sulfur or nitrogen, in the alkyl group.

[0024] The diazabicyclo or triazabicyclo compound can have, for example, inherent or neat base numbers of 300-650 mg KOH/g, or 350-600 mg KOH/g, or 400-550 mg KOH/g, or 450-500 mg KOH/g. The higher the latent base number, the more proton accepting the molecule can be.

[0025] Embodiments described herein also relate to a composition comprising an engine oil mixed with any of the ashless oil additive described above. The amount of the diazabicyclo or triazabicyclo compound mixed in the engine oil composition can be, for example, up to 10% (w/w), up to 5% (w/w), up to 3% (w/w), up to 2% (w/w), or up to 1% (w/w). In one embodiment, the composition is used in a diesel engine. In another embodiment, the composition is used in a natural gas engine.

[0026] The ashless oil additive can be, for example, substantially free of metal species. The ashless oil additive can be, for example, substantially free of any amine-based cyclic compound that comprises only secondary amine.

[0027] Embodiments described herein also relates to a method for boosting the TBN of an engine oil composition, comprising adding any of the ashless oil additive described above to the engine oil composition. In one embodiment, the inclusion of the diazabicyclo or triazabicyclo compound can increase the initial TBN of a fresh oil composition by, for example, at least 1 mg KOH/g, or at least 2 mg KOH/g, or at least 3 mg KOH/g, or at least 4 mg KOH/g. In another embodiment, the inclusion of the diazabicyclo or triazabicyclo compound can increase the initial TBN of a used oil composition by, for example, at least 1 mg KOH/g, at least 2 mg KOH/g, at least 3 mg KOH/g, or at least 4 mg KOH/g.

[0028] In one embodiment, the use of the ashless oil additive described above increases standard oil drain intervals for a diesel or natural gas engine by, for example, at least 10%, or at least 20%, or at least 50%, or at least 100%, compared to an oil additive based on one or more metallic TBN boosters. In another embodiment, the use of the ashless oil additive described above increases standard oil drain intervals for a diesel or natural gas engine by, for example, at least 10%, or at least 20%, or at least 50%, or at least 100%, compared to an oil additive based on 2,2,6,6-tetramethyl piperidine as TBN booster.

WORKING EXAMPLES

EXAMPLE 1

[0029] The TBN of fresh engine oils supplemented with various amounts of either 1,5-diazabicyclo[4.3.0]non-5-ene or a secondary-amine-based additive were tested.

[0030] As shown in FIG. 1, the addition of 1% (w/w) of 1,5-diazabicyclo[4.3.0]non-5-ene increased the initial TBN of fresh oil by ~3 points. . In comparison, the addition of 1% (w/w) of 2,2,6,6-tetramethyl piperidine increased the initial TBN of fresh oil by ~2.5 points.

EXAMPLE 2

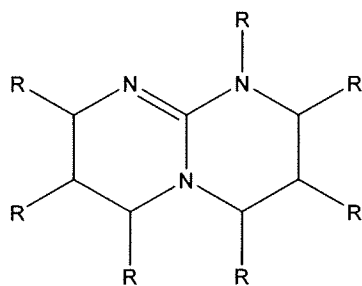
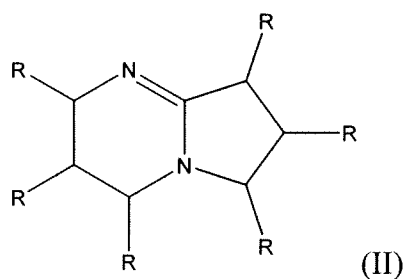
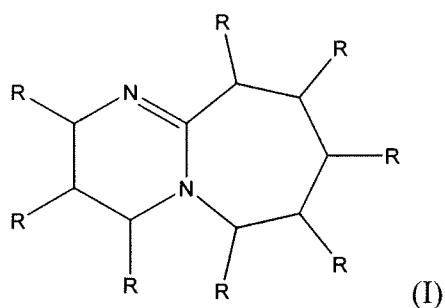
[0031] The TBN of [1,8]diazabicyclo and [1,5]diazabicyclo were tested either neat or in 9 g of mineral oil. The results are shown in the table below.

Sample	Sample Size	TBN (mg KOH/g)
[1,8] Diazabicyclo (neat) in 100 mL of TBN solvent run 1	0.012g	636.27
[1,8] Diazabicyclo (neat) in 100 mL of TBN solvent run 2	0.016g	346.77
[1,8] Diazabicyclo (neat) in 100 mL of TBN solvent run 3	0.014g	421.15
1 g of [1,8] Diazabicyclo (in 9 g of mineral oil) in 100 mL of TBN solvent run 1	0.112g	42.02
1 g of [1,8] Diazabicyclo (in 9 g of mineral oil) in 100 mL of TBN solvent run 2	0.106g	40.54
[1,5] Diazabicyclo (neat) in 100 mL of TBN solvent run 1	0.018g	577.21
[1,5] Diazabicyclo (neat) in 100 mL of TBN solvent run 2	0.011g	318.75
[1,5] Diazabicyclo (neat) in 100 mL of TBN solvent run 3	0.013g	543.31
1 g of [1,5] Diazabicyclo (in 9 g of mineral oil) in 100 mL of TBN solvent run 1	0.142g	42.67
1 g of [1,5] Diazabicyclo (in 9 g of mineral oil) in 100 mL of TBN solvent run 2	0.160g	42.32

[0032] In the foregoing description, it will be readily apparent to one skilled in the art that varying substitutions and modifications may be made to the invention disclosed herein without departing from the scope and spirit of the invention. The invention illustratively described herein suitably may be practiced in the absence of any element or elements, limitation or limitations which is not specifically disclosed herein. The terms and expressions which have been employed are used as terms of description and not of limitation, and there is no intention that in the use of such terms and expressions of excluding any equivalents of the features shown and described or portions thereof, but it is recognized that various modifications are possible within the scope of the invention. Thus, it should be understood that although the present invention has been illustrated by specific embodiments and optional features, modification and/or variation of the concepts herein disclosed may be resorted to by those skilled in the art, and that such modifications and variations are considered to be within the scope of this invention.

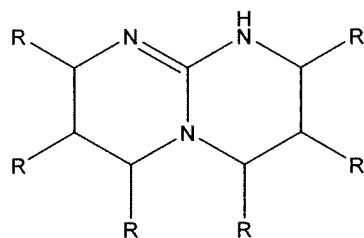
WHAT IS CLAIMED IS:

1. An ashless oil additive, comprising at least one diazabicyclo or triazabicyclo compound, wherein the diazabicyclo or triazabicyclo compound comprises at least two tertiary amines.
2. The oil additive of claim 1, wherein the diazabicyclo or triazabicyclo compound is represented by one of formula (I), (II) or (III):



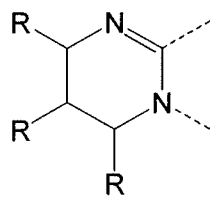
or a C1-C12 alkyl group optionally containing at least one heteroatom selected from Oxygen, Sulfur and Nitrogen.

3. The oil additive of claim 2, wherein the diazabicyclo or triazabicyclo compound is a diazabicyclo compound represented by formula (I).
4. The oil additive of claim 2, wherein the diazabicyclo or triazabicyclo compound is a diazabicyclo compound represented by formula (II).
5. The oil additive of claim 2, wherein the diazabicyclo or triazabicyclo compound is a triazabicyclo compound represented by formula (III).
6. The oil additive of claim 5, wherein the diazabicyclo or triazabicyclo compound is a triazabicyclo compound represented by formula (IV):



, wherein each R is independently hydrogen or a C1-C12 alkyl group optionally containing at least one heteroatom selected from Oxygen, Sulfur and Nitrogen.

7. The oil additive of claim 1, wherein the diazabicyclo or triazabicyclo compound is selected from the group consisting of 1,5-Diazabicyclo[4.3.0]non-5-ene, 1,8-Diazabicyclo[5.4.0]undec-7-ene, 1,5,7-Triazabicyclo[4.4.0]dec-5-ene, and 7-Methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene.
8. The oil additive of claim 1, wherein the diazabicyclo or triazabicyclo compound comprises at least three tertiary amines.
9. The oil additive of claim 1, wherein the diazabicyclo or triazabicyclo compound comprises a first, six membered ring comprising at least two nitrogen atoms fused to a second, five-to-seven membered ring.
10. The oil additive of claim 9, wherein the first ring is represented by



, and wherein each R is independently hydrogen or a C1-C12 alkyl group optionally containing at least one heteroatom selected from Oxygen, Sulfur and Nitrogen.

11. The oil additive of any of claims 1 to 10, wherein the oil additive has a base number of 300-650 mg KOH/g.
12. The oil additive of any of claims 1 to 11, wherein the oil additive is substantially free of any metal species.

13. The oil additive of any of claims 1 to 12, wherein the oil additive is substantially free of any amine-based cyclic compound comprising only secondary amines.
14. A method for boosting the total base number (TBN) of an engine oil composition, comprising adding the oil additive of any of claims 1 to 13 to said engine oil composition.
15. The method of claim 14, wherein the engine oil composition comprises a fresh oil composition.
16. The method of claim 14, wherein the engine oil composition comprises a used oil composition.
17. The method of any of claims 14 to 16, wherein the oil additive increases the total base number of the engine oil composition by at least 1 mg KOH/g.
18. The method of any of claims 14 to 17, wherein the oil additive increases oil drain intervals of the engine oil composition by at least 10%.
19. A composition comprising an engine oil mixed with the oil additive of any of claims 1 to 13.
20. An engine system, comprising an engine configured to operate using diesel or natural gas as a fuel, the engine including the composition of claim 19.
21. The oil additive of claim 2, wherein each R is independently hydrogen or a C1-C12 alkyl group containing no heteroatom.
22. The oil additive of claim 2, wherein each R is independently hydrogen or a C1-C12 alkyl group containing at least one heteroatom selected from Oxygen, Sulfur and Nitrogen.
23. The oil additive of claim 6, wherein each R is independently hydrogen or a C1-C12 alkyl group containing no heteroatom.

24. The oil additive of claim 6, wherein each R is independently hydrogen or a C1-C12 alkyl group containing at least one heteroatom selected from Oxygen, Sulfur and Nitrogen.
25. The oil additive of claim 10, wherein each R is independently hydrogen or a C1-C12 alkyl group containing no heteroatom.
26. The oil additive of claim 10, wherein each R is independently hydrogen or a C1-C12 alkyl group containing at least one heteroatom selected from Oxygen, Sulfur and Nitrogen.

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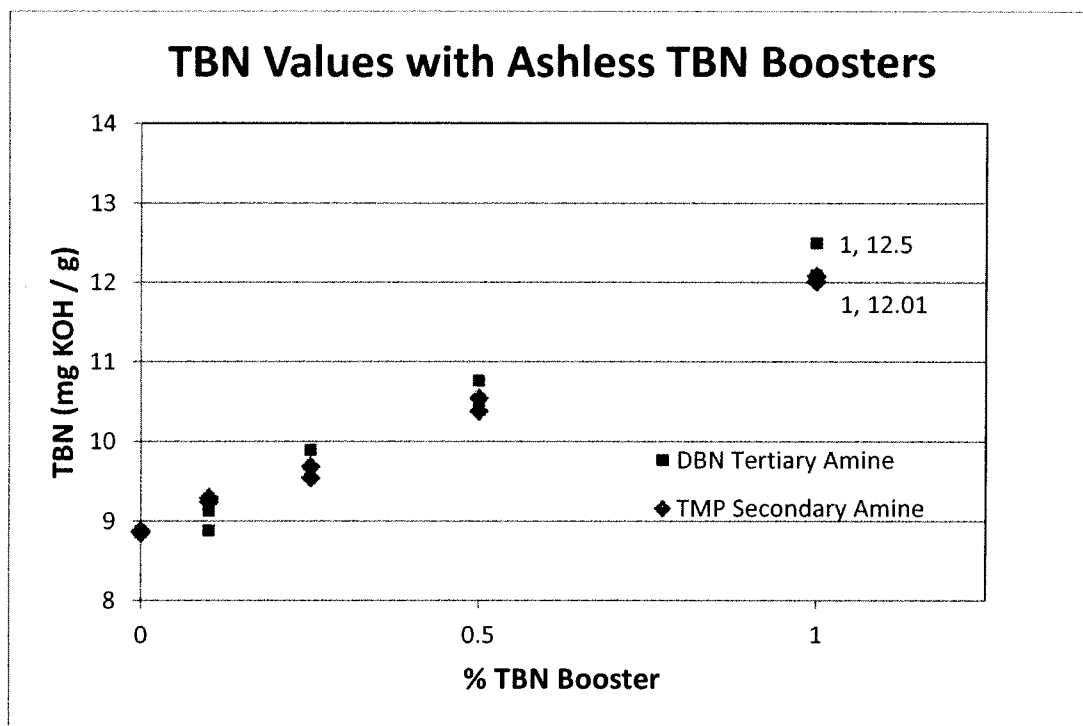


FIGURE 1

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US15/21733

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☒ Claims Nos.: 12-20
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US15/21733

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - C10M 169/04, 141/10 (2015.01)

CPC - C10M 169/04, 141/10

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC(8): C10M 169/04, 141/10 (2015.01)

CPC: C10M 169/04, 141/10

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

PatSeer (US, EP, WO, JP, DE, GB, CN, FR, KR, ES, AU, IN, CA, INPADOC Data); ProQuest; Scifinder; Google/Google Scholar;

KEYWORDS: ashless, oil, additive, diazabicyclo, triazabicyclo, tertiary, amine, KOH

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 2003/000652 A1 (WYETH) 03 January 2003; paragraphs [10]-[11]	1-10, 11/1-10, 21-26
Y	US 2012/0291737 A1 (MATHUR, N et al.) 22 November 2012; abstract	1-10, 11/1-10, 21-26
Y	US 2010/0147238 A1 (KURIHARA, I et al.) 17 June 2010; paragraph [0042]	11/1-10
A	US 2013/0102728 A1 (YANG, Y et al.) 25 April 2013; entire document	1-10, 11/1-10, 21-26
A	US 2009/0087788 A1 (KANCHIKU, SF) 02 April 2009; entire document	1-10, 11/1-10, 21-26
A	US 2013/0101840 A1 (YANG, Y et al.) 25 April 2013; entire document	1-10, 11/1-10, 21-26
A	US 2013/0230929 A1 (NAKAMURA, T et al.) 05 September 2013; entire document	1-10, 11/1-10, 21-26



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T"

later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X"

document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y"

document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&"

document member of the same patent family

Date of the actual completion of the international search

17 May 2015 (17.05.2015)

Date of mailing of the international search report

19 JUN 2015

Name and mailing address of the ISA/

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