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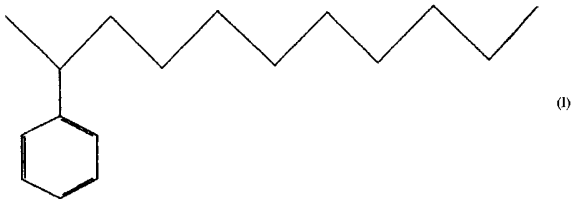
(54) Title: USE OF DIMERIZED FISCHER-TROPSCH PROCESS PRODUCTS AND VINYLIDENE DERIVATIVES THEREOF



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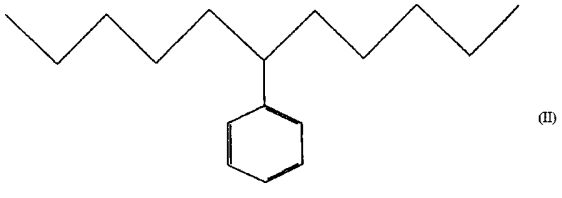

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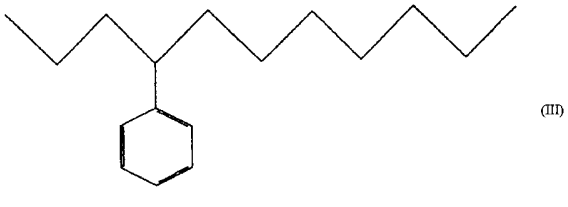

(III)

(57) Abstract: The invention provides and alkyl benzene and a drilling fluid derived from vinylidene. The vinylidene may be derived from olefins by dimerization. The olefins may be Fischer-Tropsch olefins.

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USE OF DIMERIZED FISCHER-TROPSCH PROCESS PRODUCTS AND VINYLIDENE DERIVATIVES THEREOF

Field of the Invention

The invention relates to the use of a feedstock having the general formula R'R"C=CH_2 (vinylidene) obtained by dimerization of Fischer-Tropsch process products.

Background to the Invention

The dimerization of shorter hydrocarbons to form longer chain hydrocarbons, and thereafter to further process the thus obtained longer chain hydrocarbons, for example, to form aldehydes and alcohols is well known. Furthermore, the dimerization of cracked hydrocarbons having from 5 to 7 carbons to form vinylidene, and thereafter to use said vinylidene having from 10 to 14 carbons in the alkylation of benzene to form AB has also recently been disclosed. The AB thus obtained is highly linear as the vinylidene used in the production thereof is highly linear.

In this specification, unless the context clearly indicates to the contrary, the term "dimerization" is to be understood to include both dimerization where two molecules of equal carbon length are added together as well as cross-dimerization, where two molecules of unequal carbon length are added together.

Summary of the Invention

The inventors have now found that an acceptable Alkyl Benzene (AB) composition having at least a substantial proportion of non-linear AB may be obtained by dimerization of Fischer-Tropsch olefins to obtain a Fischer-Tropsch derived vinylidene having both a linear and a branched fraction. Such AB composition is suitable where a less linear AB is desired but does not require delinearization.

Thus, according to a first aspect of the invention, there is provided an alkyl benzene (AB) composition including AB of which the alkyl chain is derived from a vinylidene obtained by dimerization of Fischer-Tropsch olefins, said AB composition including between 10% and 90% branched alkyl chain AB derived from said vinylidene.

The Fischer-Tropsch olefins may be the products of a high temperature Fischer-Tropsch reaction or a low temperature Fischer-Tropsch reaction.

The vinylidene from which the AB is derived may be a dimerization product of one or more of a 5 to 9 carbon olefin from the Fischer-Tropsch process and thus the alkyl chain of the AB may include one or more AB having a 10 to 18 carbon atom alkyl chain.

The branched alkyl chain of the AB may have branches of from 1 to 2 carbons.

Generally, the AB composition includes predominantly linear alkyl chain AB.

The branched alkyl chain AB of the composition may be between 10% and 49% of the AB composition.

Generally, the branched alkyl chain AB is between 15% and 35% of the AB composition.

The branches of the branched alkyl chain of the AB may be mono-methyl, di-methyl,and/or tri-methyl.

The branched alkyl chain of the AB of the AB composition has at least one additional branch when compared to the conventional (non-Fischer-Tropsch) vinylidene derived AB.

Typically the additional branch is a methyl branch. Usually the additional branch forms a di-methyl branch.

The AB of the invention is derived from vinylidene which is obtained by dimerization of Fischer-Tropsch olefins having from 5 to 9 carbons and having both linear and branched olefins in the dimerization feedstock.

The alkyl chain of the AB of the invention has from 10 to18 carbons.

According to a second aspect of the invention, there is provided a vinylidene derived drilling fluid.

The vinylidene may be derived from any source.

The vinylidene may be a dimerization product of an alpha-olefin.

The olefin from which the vinylidene is dimerized may be a crack-olefin or a Fischer-Tropsch olefin, or any other suitable olefin.

Typically the olefins of the dimerization feedstock are of from 7 to 9 carbon atom length.

Where the vinylidene is dimerized Fischer-Tropsch olefin, the drilling fluid derived from the vinylidene has both linear and branched fractions.

Generally, the Fischer-Tropsch derived drilling fluid is predominantly linear, however, the branched fraction may be between 10% and 90% of the drilling fluid.

The branched fraction of the Fischer-Tropsch derived drilling fluid is between 10% and 49% of the drilling fluid.

Typically the branched fraction is between 15% and 35% of the drilling fluid.

The branching of the branched fraction is typically from 1 to 2 carbon atoms in length.

The branching is predominantly methyl branching, however, di-methyl, and/or tri-methyl.

An example of a dimerization process used to obtain vinylidene which may be used as a feedstock in the production of AB and/or drilling fluids broadly in accordance with the invention, uses a metallocene/aluminoxane catalyst and a feedstock of at least 50% alpha olefins under oligomerisation reaction conditions of between –60°C and 280°C and pressures of up to 500 atmospheres, or more. It will however be clear to those skilled in the art that the present invention is not limited to any particular dimerization process and vinylidene produced by any dimerization process of alpha-olefins falls within the scope and spirit of the invention.

EXAMPLES

EXAMPLE 1 – ALKYL BENZENE

A mixture of vinylidene olefins and methyl branched vinylidene olefins, derived from cross-dimerisation of Fischer-Tropsch (C_7 and C_9 olefins, was used. The two main products were 2-pentyl-1-undecene and 2-heptyl-1-nonene and methyl branched vinylidene olefins ~ 25%.

1 mole of the mixture of vinylidene olefins, 10 mole of benzene and 10 wt% based on the olefin mixture of a shape selective beta-zeolite catalyst were added to a stainless steel autoclave. The autoclave was purged with N_2 and then charged to 1000 psig N_2. The mixture was stirred and heated to 150°C for 16 hours. It was then cooled and removed from the autoclave. The reaction mixture was filtered to remove the catalyst and the unreacted benzene was removed in vacuo using a rotary evaporator.

The product mixture contained methyl, di-methyl, tri-methyl and methyl branching.

An analysis of the AB obtained is shown in tables 1 and 2 below.

Table 1: Mass % of Components in Alkyl Benzene Product

Component	Mass%
Branched C_{10} benzene	0.51
Branched C_{10} benzene	0.12
Branched C_{10} benzene	0.14
Branched C_{10} benzene	0.20
Branched C_{10} benzene	0.29
Branched C_{10} benzene	0.39
5-Decylbenzene	2.91
4-Decylbenzene	2.79
Branched C_{10} benzene	0.17
Branched C_{10} benzene	0.76
3-Decylbenzene	4.34
Branched C_{10} benzene	0.25
Branched C_{10} benzene	0.82
Branched C_{11} benzene	1.23
2-Decylbenzene	6.87
Branched C_{11} benzene	0.70
Branched C_{11} benzene	0.57
Branched C_{11} benzene	0.88
5+6-Decylbenzene	7.95
Branched C_{11} benzene	0.52
4-Undecylbenzene	4.59
Branched C_{11} benzene	1.78
3-Undecylbenzene	8.49
Branched C_{11} benzene	1.10
Branched C_{12} benzene	0.41
Branched C_{12} benzene	0.93
2-Undecylbenzene	10.22
Branched C_{12} benzene	0.59
Branched C_{12} benzene	0.94
6-Dodecylbenzene	4.57
5-Dodecylbenzene	3.83
Branched C_{12} benzene	0.71
4-Dodecylbenzene	3.85
Branched C_{12} benzene	0.49
Branched C_{12} benzene	0.54
Branched C_{12} benzene	0.82
3-Dodecylbenzene	5.96
Branched C_{12} benzene	0.66
Branched C_{13} benzene	0.74
2-Dodecylbenzene	7.92
5+6-Tridecylbenzene	1.04
4-Tridecylbenzene	0.73
3-Tridecylbenzene	1.42
2-Tridecylbenzene	1.38
Branched C_{14} Benzenes	0.46
Branched C_{14} Benzenes	1.45
5+6-Tetradecylbenzene	0.50
4-Tetradecylbenzene	0.21
3-Tetradecylbenzene	0.51
2-Tetradecylbenzene	0.77

Table 2: Linear and Branched Analysis of Alkyl Benzene Product

Component	%
C_{10}	
2-Decylbenzene	6.87
3-Decylbenzene	4.34
4-Decylbenzene	2.79
5-Decylbenzene	2.91
Total linear	16.90
Total branched	3.65
C_{11}	
2-Undecylbenzene	10.22
3-Undecylbenzene	8.49
4-Undecylbenzene	4.59
5+6-Undecylbenzene	7.95
Total linear	31.26
Total branched	6.78
C_{12}	
2-Dodecylbenzene	7.92
3-Dodecylbenzene	5.96
4-Dodecylbenzene	3.85
5-Dodecylbenzene	3.83
6-Dodecylbenzene	4.57
Total linear	26.13
Total branched	6.08
C_{13}	
2-Tridecylbenzene	1.38
3-Tridecylbenzene	1.42
4-Tridecylbenzene	0.73
5+6-Tridecylbenzene	1.04
Total linear	4.56
Total branched	0.74
C_{14}	
2-Tetradecylbenzene	0.77
3-Tetradecylbenzene	0.51
4-Tetradecylbenzene	0.21
5+6-Tetradecylbenzene	0.50
Total linear	1.98
Total branched	1.91

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The product mixture contained methyl and di-methyl branching on the alkyl chain portion of the AB. The phenyl group of the AB's was predominantly on the C2 carbon of the alkyl chain.

As shown in the accompanying Figures numbered I to XVI, the AB's obtained included:

I	1- methyldecyl benzene
II	1-pentylhexylbenzene
III	1-propyloctylbenzene
IV	1-butylheptyl benzene
V	1-ethylnonylbenzene
VI	1,1-dimethylnonylbenzene
VII	1,3- dimethylnonylbenzene
VIII	1,6,7-trimethyloctylbenzene
IX	1,4- dimethylnonylbenzene
X	1,5- dimethylnonylbenzene
XI	1,6- dimethylnonylbenzene
XII	1,7- dimethylnonylbenzene
XIII	1,8- dimethylnonylbenzene
XIV	1,1,3-trimethyloctylbenzene
XV	1,3,7-trimethyloctylbenzene
XVI	1,1,4-trimethyloctylbenzene

The AB product was sulfonated with an equivalent of chlorosulfonic acid using methylene chloride as solvent. The methylene chloride was distilled away. The sulfonated product was neutralized with sodium methoxide in methanol and the methanol was evaporated to give alkyl benzene sulfonate, sodium salt mixture.

EXAMPLE 2

The same procedure as in example 1 was used except that the vinylidene olefins were different. The mixture of vinylidene olefins consists of 2-hexyl-1-decene (2 - 40%) and methyl and dimethyl branched vinylidene olefins derived from a C_8 Fischer-Tropsch feed stream.

The alkyl benzene mixture contained methyl, di-methyl and tri-methyl branching.

EXAMPLE 3 - Drilling Fluid

7 carbon and 9 carbon Fischer-Tropsch olefins were dimerized (cross-dimerization) and a product composition was obtained. This product composition was a drilling fluid composition.

The drilling fluid composition included:

A linear component, 2-pentyl-1-undecene and 2-heptyl –1- nonene together making up about 75.1% of the composition; and

A mono-methyl branched component, 2-(2-methylhexyl)-1-nonene, 2-(1-methylbutyl)-undecene, 2-(3-methylhexyl)-1-nonene, 2-(2-methylbutyl)-1-undecene, 2-(-4-methylhexyl)-1-nonene, 2-(3-methylbutyl)-1-undecene, 2-(5-methylhexyl)-1-nonene, 2-pentyl-4-methyl-1-decene, 2-(1-methylhexyl)-1-nonene, 2-pentyl-5-methyl-1-decene, 2-(2-methylhexyl)-1-nonene, 2-pentyl-6-methyl-1-decene, 2-(3-methylhexyl)-1-nonene, 2-pentyl-7-methyl-1-decene, 2-(4-methylhexyl)-1-nonene, 2-pentyl-8-methyl-1-decene, 2-(5-methylhexyl)-1-nonene and 2-pentyl-9-methyl-1-decene, together making up about 24.9% of the drilling fluid composition.

8 carbon Fischer-Tropsch olefins were dimerized and a product composition was obtained. This product composition was used as drilling fluid composition.

The drilling fluid composition included:

A linear component of mainly 2-hexyl-1-decene in amounts of between 2 and 40%, depending on process conditions; and

A mono-methyl branched component including 2-hexyl-8-methyl-1-nonene, 2-hexyl-7-methyl-1-nonene, 2-hexyl-6-methyl-1-nonene, 2-hexyl-5-methyl-1-nonene, 2-hexyl-4-methyl-1-nonene, 2-(4-methylpentyl)-1-decene, 2-(3-methylpentyl)-1-decene, 2-(2-methylpentyl)-1-decene, 2-(1-methylpentyl)-1-decene, 2-hexyl-4-methyl-1-nonene, 2-(4-methylpentyl)-8-methyl-1-nonene, 2-(3-methylpentyl)-7-methyl-1-nonene, 2-(2-methylpentyl)-6-methyl-1-nonene, 2-(1-methylpentyl)-5-methyl-1-nonene, 2-(4-methylpentyl)-7-methyl-1-nonene, 2-(3-methylpentyl)-6-methyl-1-nonene, 2-(3-methylpentyl)-5-methyl-1-nonene, 2-(3-methylpentyl)-4-methyl-1-nonene, 2-(2-methylpentyl)-7-methyl-1-nonene, 2-(1-methylpentyl)-8-methyl-1-nonene, 2-(2-methylpentyl)-5-methyl-1-nonene, 2-(2-methylpentyl)-4-methyl-1-nonene, 2-(2-methylpentyl)-7-methyl-1-nonene, 2-(3-methylpentyl)-8-methyl-1-nonene, 2-(1-methylpentyl)-7-methyl-1-nonene, 2-(4-methylpentyl)-6-methyl-1-nonene, 2-(4-methylpentyl)-5-methyl-1-nonene, 2-(4-methylpentyl)-4-methyl-1-nonene, 2-(1-methylpentyl)-6-methyl-1-nonene, and 2-(1-methylpentyl)-4-methyl-1-nonene together making up between 60% and 98% of the drilling fluid composition.

The drilling fluid compositions in accordance with the invention had the following physical properties:

The properties are for a typical C_{12}-C_{16} internal linear and branched combination of olefinic product made in accordance with the present invention:

Viscocity: 1-2 cSt @ 100'C
Flash point: >90'C
Linear:branch ratio 1:1 to 5:1
Pour Point: < 0'C

Claims:

1. An alkyl benzene (AB) composition including AB of which the alkyl chain is derived from a vinylidene obtained by dimerization of Fischer-Tropsch olefins, said AB composition including between 10% and 90% branched alkyl chain AB derived from said vinylidene.

2. An alkyl benzene composition as claimed in claim 1, wherein the Fischer-Tropsch olefins are the products of a high temperature Fischer-Tropsch reaction.

3. An alkyl benzene composition as claimed in claim 1, wherein the Fischer-Tropsch olefins are the products of a low temperature Fischer-Tropsch reaction.

4. An alkyl benzene composition as claimed in any one of the preceding claims, wherein the vinylidene from which the AB is derived is a dimerization product of one or more of a 5 to 9 carbon olefin from the Fischer-Tropsch process.

5. An alkyl benzene composition as claimed in any one of the preceding claims, including AB having a 10 to 18 carbon alkyl chain.

6. An alkyl benzene composition as claimed in any one of the preceding claims, wherein the branched alkyl chain of the AB has branches of from 1 to 2 carbons.

7. An alkyl benzene composition as claimed in any one of the preceding claims, which includes predominantly linear alkyl chain AB.

8. An alkyl benzene composition as claimed in any one of the preceding claims, wherein the branched alkyl chain AB of the composition is between 10% and 49% of the AB composition.

9. An alkyl benzene composition as claimed in any one of the preceding claims, wherein the branched alkyl chain AB of the composition is between 15% and 35% of the AB composition.

10. An alkyl benzene composition as claimed in any one of the preceding claims, wherein the branching of the branched alkyl chain of the AB is mono-methyl, di-methyl,and/or tri-methyl.

11. An alkyl benzene composition as claimed in any one of the preceding claims, which includes AB whereof the branched alkyl chain has at least one additional branch when compared to non-Fischer-Tropsch vinylidene derived AB.

12. An alkyl benzene composition as claimed in claim 11, wherein the additional branch is a methyl branch.

13. An alkyl benzene composition as claimed in claim 11, wherein the additional branching is in the form of di-methyl branching.

14. An alkyl benzene composition as claimed in any one of the preceding claims, wherein at least some of the AB is derived from vinylidene which is obtained by dimerization of Fischer-Tropsch olefins having from 5 to 9 carbons and having both linear and branched olefins in the dimerization feedstock.

15. A vinylidene derived drilling fluid.

16. A vinylidene derived drilling fluid as claimed in claim 15, wherein the vinylidene is derived from any source.

17. A vinylidene derived drilling fluid as claimed in claim 15 or claim 16, wherein the vinylidene is a dimerization product of an alpha-olefin.

18. A vinylidene derived drilling fluid as claimed in claim 17, wherein the olefin from which the vinylidene is dimerized is selected from a crack-olefin or a Fischer-Tropsch olefin.

19. A vinylidene derived drilling fluid as claimed in any one claims 17 or 18, wherein the olefins of the dimerization feedstock are of from 7 to 9 carbon atom length.

20. A vinylidene derived drilling fluid as claimed in claim 18, wherein the vinylidene is a dimerized Fischer-Tropsch olefin, and the drilling fluid derived from the vinylidene has both linear and branched fractions.

21. A vinylidene derived drilling fluid as claimed in claim 20, wherein the drilling fluid is predominantly linear.

22. A vinylidene derived drilling fluid as claimed in claim 20, wherein the branched fraction is between 10% and 90% of the drilling fluid.

23. A vinylidene derived drilling fluid as claimed in claim 20, wherein the branched fraction is between 10% and 49% of the drilling fluid.

24. A vinylidene derived drilling fluid as claimed in claim 20, wherein the branched fraction is between 15% and 35% of the drilling fluid.

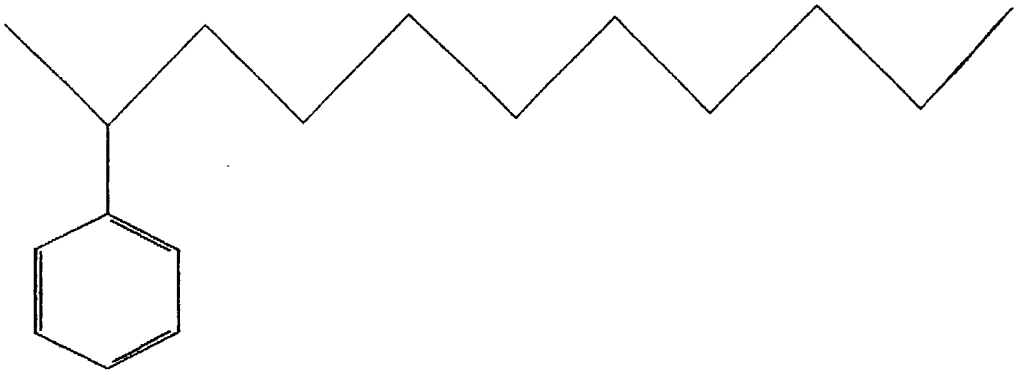
25. A vinylidene derived drilling fluid as claimed in any one of claims 20 to 24, wherein the branching is predominantly methyl branching.

26. A vinylidene derived drilling fluid as claimed in any one of claims 20 to 25, including di-methyl and/or tri-methyl branching.

27. An alkyl benzene composition, substantially as herein described and illustrated.

28. A vinylidene derived drilling fluid, substantially as herein described and illustrated.

29. A new alkyl benzene composition, or a new vinylidene derived drilling fluid, substantially as herein described.



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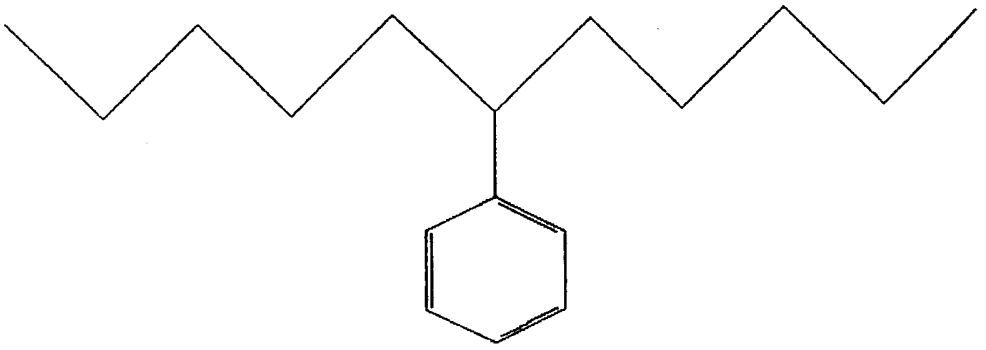

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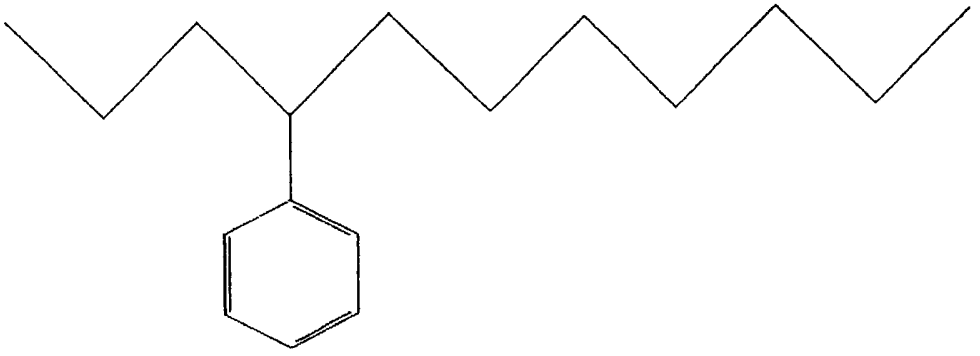

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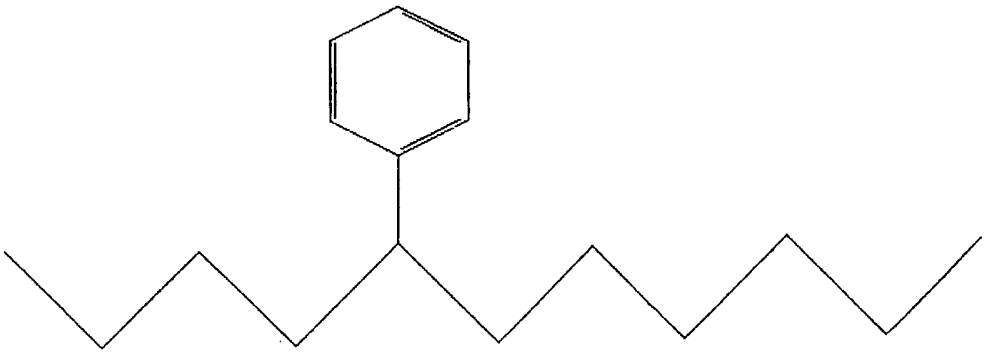

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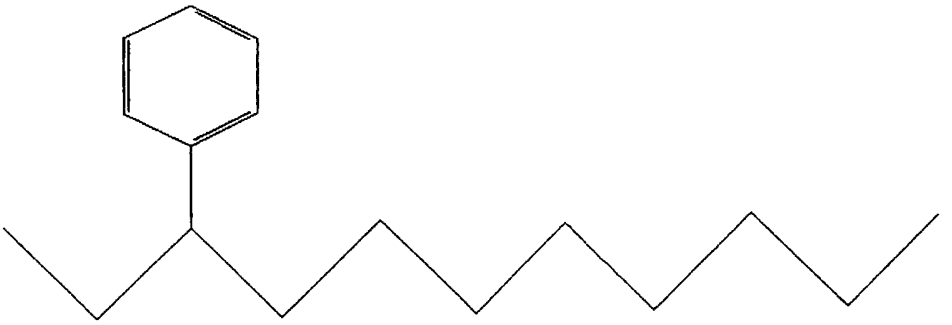

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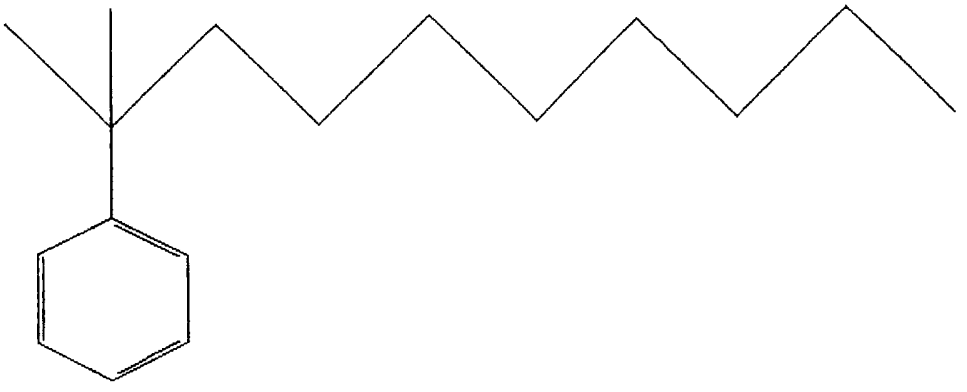

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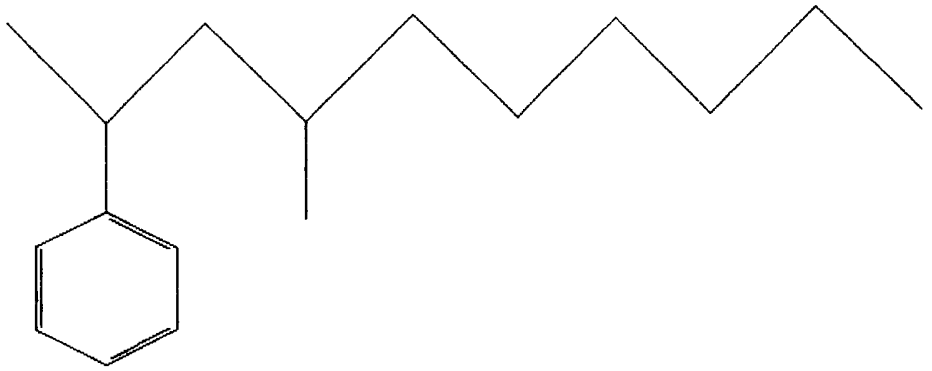

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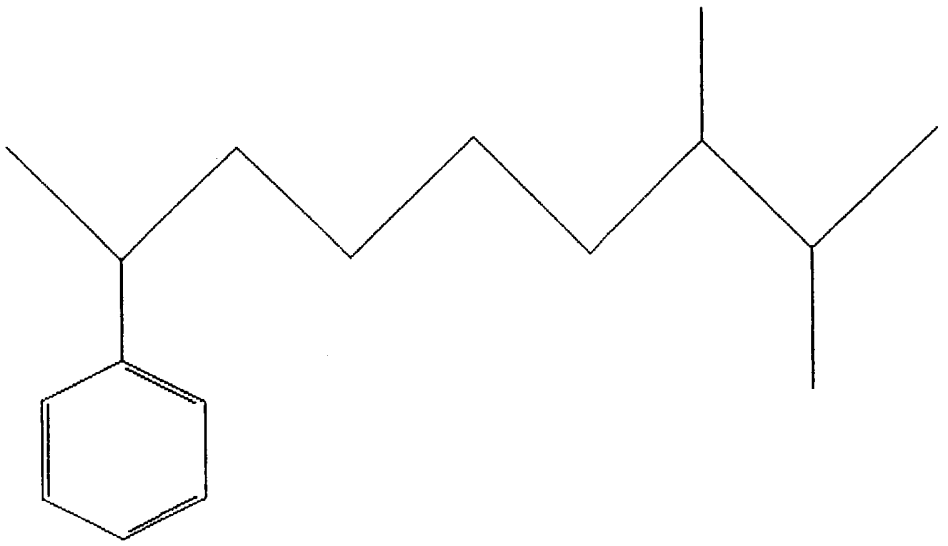

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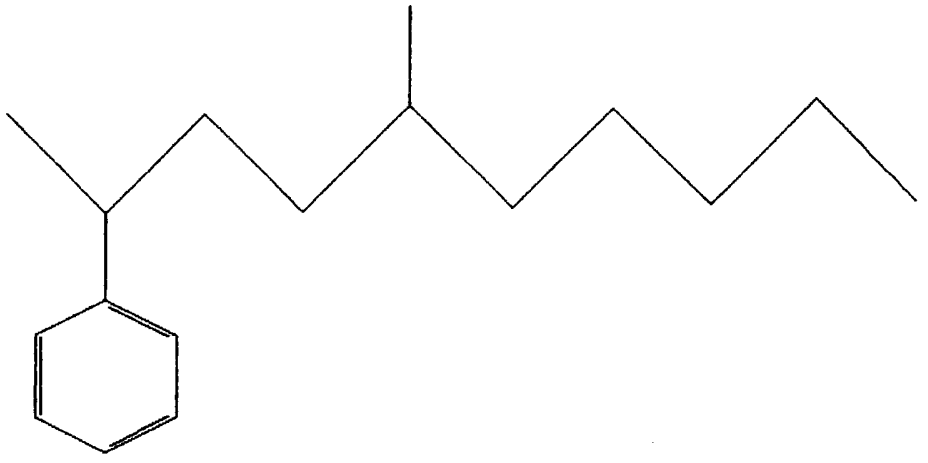

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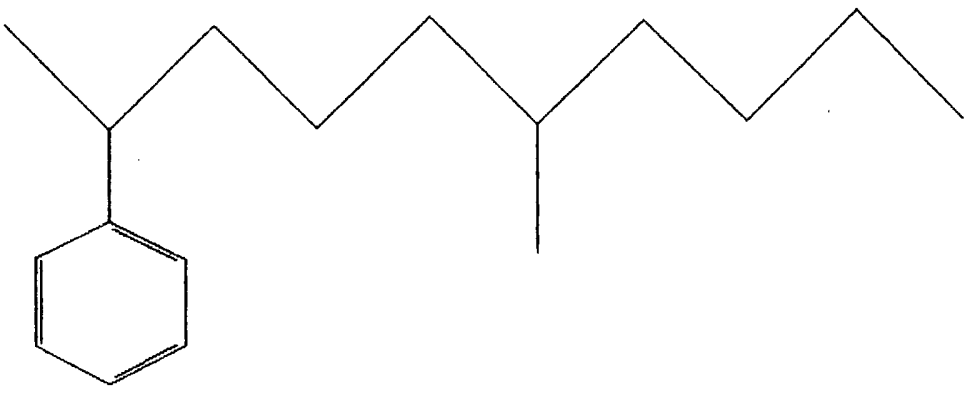

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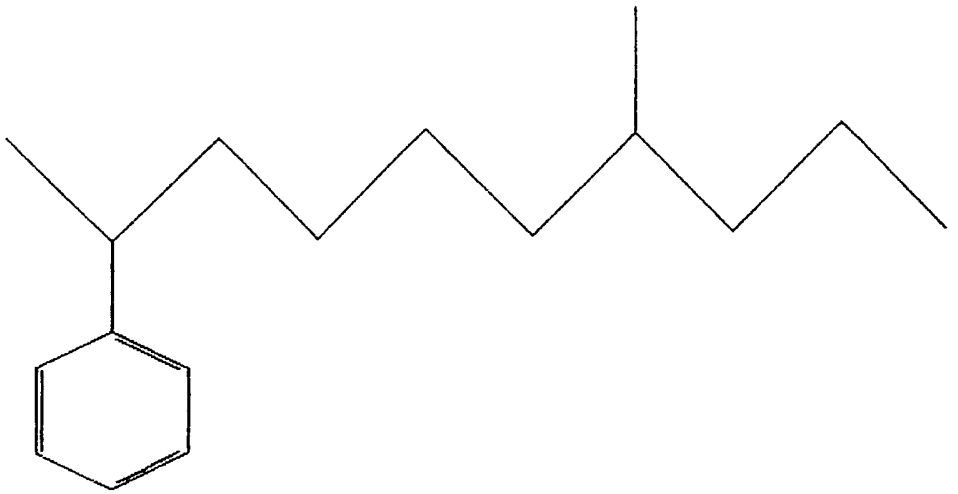

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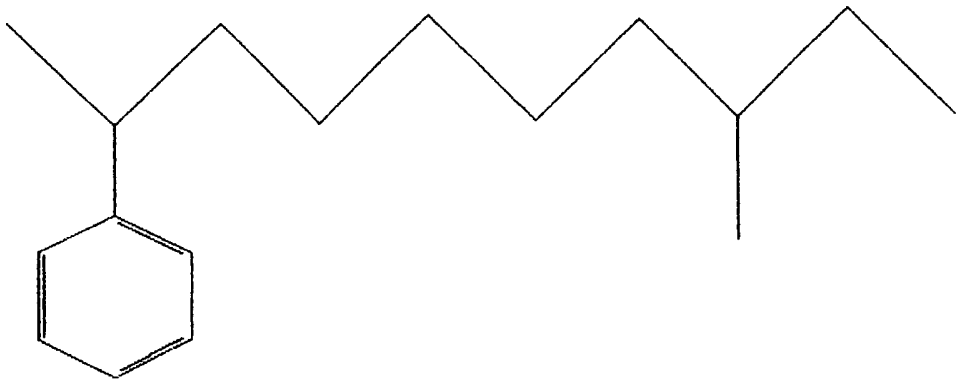
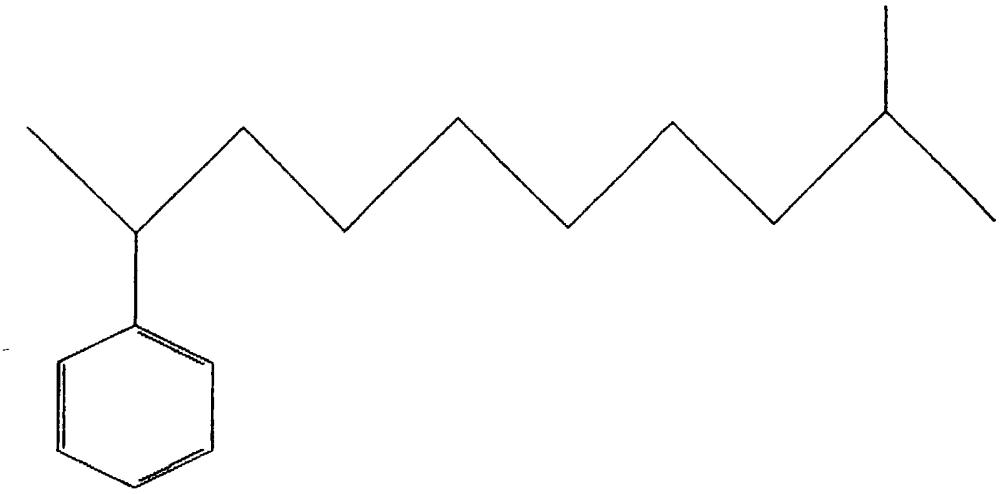


XII



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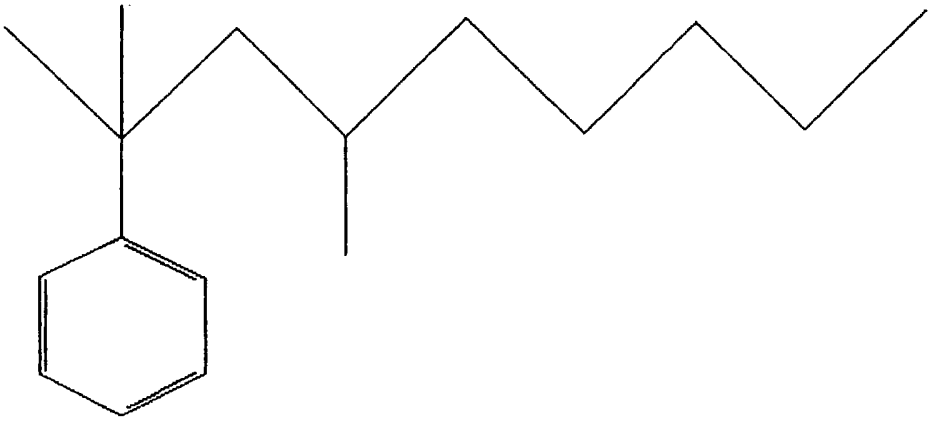
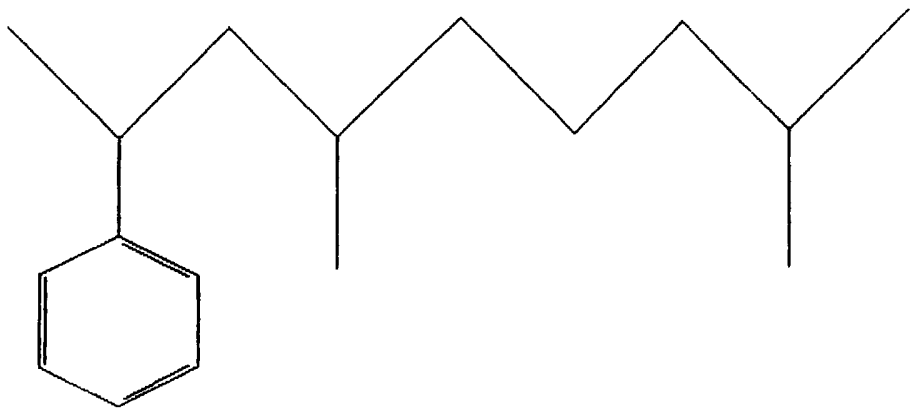
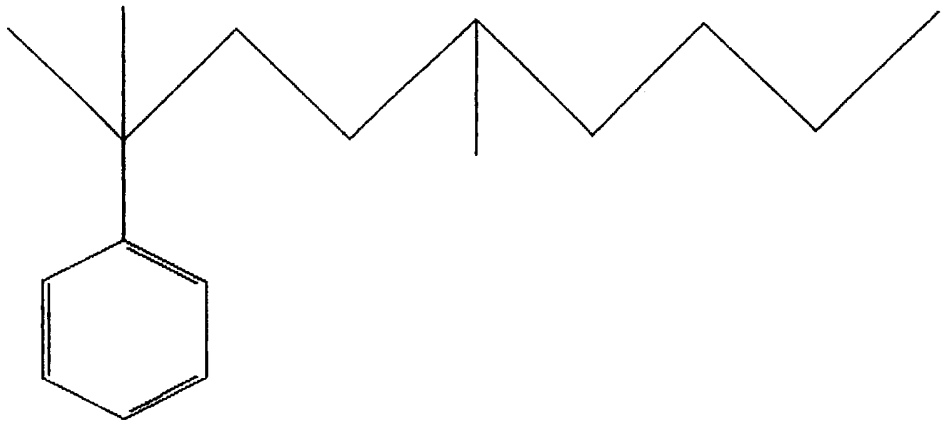


XIV



XV



XVI

INTERNATIONAL SEARCH REPORT

Intern nal Application No
PCT/ZA 00/00121

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C09K7/06 C10G2/00 C07C15/107 C07C2/12 C07C1/04

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 7 C09K C10G C07C

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 practical, search terms used)
EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5 196 625 A (KURKOV VICTOR P ET AL) 23 March 1993 (1993-03-23) examples 1-4 ---	1-14,27, 29
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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
17 November 2000	24/11/2000

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	olde Scheper, B

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Interr. nal Application No
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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X	EP 0 449 257 A (MI DRILLING FLUIDS CO) 2 October 1991 (1991-10-02) page 5, line 46 -page 6, line 36 page 6, line 55 -page 8, line 42; claims 1-13; examples 1,4,5,8,14	15-17, 19,28,29
Y		15-26, 28,29
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