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(54) Dialkylaromatic and hydrogenated dialkylaromatic synthetic lubricating and specialty oils.

(57) A synthetic dialkylaromatic hydrocarbon is described which is useful as synthetic specialty oil and lubricating oil base stock or base stock additive. The synthetic dialkyl aromatic hydrocarbon is characterized by possessing two pendant alkyl side chain groups of significantly different lengths, one short and preferably linear, on the order of 2 to 4 carbons, preferably 2 carbons, and the other long, on the order of 14 to 18 carbons, preferably 15–17, most preferably 15–16 carbons (and mixtures thereof) and linear, the aromatic group to which the two pendant alkylside chain groups are appended being a phenyl moiety. The synthetic dialkyl aromatics of the present invention which are useful as synthetic lubricant base stocks or base stock additives are characterized as possessing in total about 23 to 28 carbons preferably about 23 to 26 carbons most preferably 24 carbons and having kinematic viscosities at 100 °C of approximately 2.2 to 3.7 cSt. These synthetic stocks also have high viscosity indices (VI greater than about 95) and low pour points (less than − 40 °C). The hydrogenated forms of the dialkylaromatic materials are also good synthetic specialty and lubricating oil base stocks and base stock additives.

DESCRIPTION OF THE INVENTION

A synthetic dialkylaromatic hydrocarbon is described which is useful as synthetic specialty oil and lubricating oil base stock or base stock additive. The synthetic dialkyl aromatic hydrocarbon is characterized by possessing two pendant alkyl side chain groups of significantly different lengths, one short and preferably linear, on the order of 2 to 4 carbons, preferably 2 carbons, and the other long, on the order of 14 to 18 carbons, preferably 15-17, most preferably 15-16 carbons (and mixtures thereof) and linear, the aromatic group to which the two pendant alkylside chain groups are appended being a phenyl moiety. The synthetic dialkyl aromatics of the present invention which are useful as synthetic lubricant base stocks or base stock additives are characterized as possessing in total about 23 to 28 carbons preferably about 23 to 26 carbons most preferably 24 carbons and having kinematic viscosities at 100°C of approximately 2.2 to 3.7 cSt. These synthetic stocks also have high viscosity indices (VI greater than about 95) and low pour points (less than -40°C). The hydrogenated forms of the dialkylaromatic materials are also good synthetic specialty and lubricating oil base stocks and base stock additives.

DESCRIPTION OF THE FIGURES

Figure 1 shows the boiling point curves of 2 dialkylbenzenes and 2 polyalpholefins.

The dialkyl benzene synthetic specialty oil and lubricant (or base stock additive) is produced by employing an aromatic stream of benzene, toluene, ethyl benzene, n propyl benzene, isopropyl benzene, n-, sec- or tert butyl benzene and mixtures thereof, preferably benzene, toluene, ethyl benzene and mixtures, most preferably ethyl benzene and alkylating such stream using a catalyst and an alkylating agent which alkylating agent is chosen from linear and slightly branched C_2-C_4 and/or C_{14}-C_{18} olefins (both α, random internal and mixtures thereof), preferably C_3-C_4 and/or C_{14}-C_{18}, more preferably C_3-C_4 and/or C_{15}-C_{16} mono olefins. Random internal n-olefins as well as alpha olefins have been found to produce high quality linear dialkyl aromatic synthetic lubricants and base stock additives.

The dialkylaromatics can be prepared by alkylating benzene with a long chain C_{14} to C_{18} linear mono-olefin and then alkylating this mono-alkylate with a C_2 to C_4 linear mono-olefin, or vise-versa; or by alkylating a short chain monoalkylbenzene (eg ethyl benzene) with a linear C_{14} to C_{18} olefin or by alkylating a long chain (C_{14}-C_{18}) monoalkylbenzene with a C_2-C_4 olefin.

The preferred dialkyl aromatic hydrocarbon which is useful as synthetic specialty oil and lubricant base stock or base stock additive is ethyl hexadecylbenzene made by alkylating ethyl benzene with n-hexadecene or by mono alkylating benzene with the C_{16} olefin followed by alkylating this alkylate with ethylene. The long chain olefin can be either an alpha or random internal olefin, preferably the alpha or beta olefin, or mixtures thereof.

Alkylation is performed under typical Friedel Crafts conditions, employing typical Friedel Crafts catalyst, such as $AlCl_3$, HBr, HF, etc., or by using a zeolite or, preferably, a heterogeneous acidic catalyst such as an acidic amorphous wide pore silica alumina catalyst. The use of such an acidic amorphous wide pore silica alumina catalyst as an alkylation catalyst is disclosed and claimed in co-pending application OP-2955, U. S. Serial No. 603,034, filed even date herewith in the name of Heather Boucher. Alternatively, a collapsed zeolite of reduced crystallinity can be used as an aromatic alkylation catalyst and such use is disclosed and claimed in co-pending application, OP-2956, U. S. Serial No. 603,033, filed even date herewith in the names of Heather Boucher and Ian Cody.

The relationships between the structure and the physical properties of a dialkylbenzene are very subtle. It is well known that a long straight alkyl side chain promotes a high viscosity index. However, if this side chain is too long, the oil will have an undesirably high pour point. As well, it is believed that a di-n-alkylbenzene will have a lower viscosity index than a mono-n-alkylbenzene because it possesses more branched carbon atoms. It has been found in the present work that these traditionally accepted generalizations are not entirely correct. It has been found unexpectedly that the properties of di-n-alkylbenzenes which contain one short, 2 to 4 carbon side chain and one long, linear side chain are as good or better than those of linear mono-n-alkylbenzenes of the same molecular weight. That is, these di-n-alkylbenzenes possess the high viscosity indices, low viscosities and low volatilities of their linear mono-n-alkylbenzene isomers.

Many isomeric di-n-alkylbenzenes can be prepared where the total number of alkyl side chain carbon atoms can be distributed in different ways between the two linear side chains.

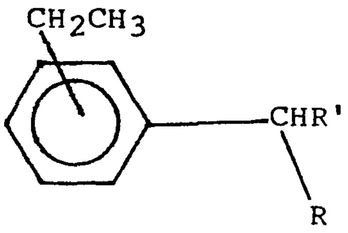
A di-n-alkylbenzene molecule containing 24 carbon atoms possesses 18 carbon atoms in its side chains. One isomeric possibility would have one carbon atom in one side chain and 17 in the other; a second isomeric possibility would have 2 carbon atoms in one side chain and 16 in the other, etc. It has been found that the most desirable properties of di-n-alkylbenzene isomers deteriorate as the lengths of the alkyl side chains become more equal. For example, it is seen in Table 1 that n-butyltetradecylbenzene (Example 3) has greater low temperature viscosity and a lower viscosity index than ethylhexadecylbenzene (Examples 1 and 2). Thus, the oil of Examples 1 and 2 are preferred. The lengths of the alkyl side chains are more equal in n-butyltetradecylbenzene than they are in ethylhexadecylbenzene.

The monoalkylbenzene isomer containing 24 carbons (Table 1, Example 4) is seen to have a relatively high pour point of -18°C, so that it was impossible to measure its viscosity at -25°C. This illustrates the advantage of di-alkylbenzene isomers as synthetic lubricating oils.

A tri-alkylbenzene isomer containing 24 carbons, ortho dimethyl hexadecylbenzene (Table 1, Example 5) is seen to have high viscosity, low viscosity index and a higher pour point than either of the dialkylbenzene isomers containing 24 carbons. This also illustrates the superiority of the dialkylbenzene isomers as lubricants. Thus, di-n-alkylbenzenes containing one very short alkyl side chain, and one very long alkyl side chain have the optimum structure for the oil to possess excellent physical properties as a lubricating oil basestock.

While it is desirable that the di-n-alkylbenzene possess one very long and one very short linear alkyl side chain, it has been found that the preferred structure is that in which the short alkyl side chain is ethyl, that is, a two carbon chain. The physical properties of this isomer are preferred over those exhibited by the isomer where the short carbon side chain is methyl, that is, a one carbon chain. It is not known why the ethyl isomer exhibits better physical properties than the methyl isomer. In Table 2, the physical properties of the methyl and ethyl isomers of C_{23} di-n-alkylbenzenes are listed. The oil of Example 12, the ethyl isomer, exhibits lower viscosity, a higher viscosity index and a lower pour point than the oil of Example 11, the methyl isomer. The oil of Example 12 is thus preferred.

The preferred structure of a di-n-alkylbenzene to be used as a lubricating basestock is represented by the following formula: (1):



(1)

In (1), R and R' are hydrogen or straight chain alkyl groups and the sum of the carbon atoms in the groups R and R^1 is 14 or 15. Thus, the total number of carbon atoms in the long, linear side chain is 15 or 16. The two alkyl groups can occupy any position relative to each other on the aromatic ring, that is, ortho, meta or para. It is expected that a mixture of these will result from most methods of preparing the di-n-alkylbenzenes. Using the preferred heterogenous acidic amorphous wide pore silica alumina catalyst of OP-2955 (Serial No. __________) yields a product possessing a very high concentration of long straight chain alkylate with minimum branching and minimum coproduction of undesirable polyalkylated aromatics and polymeric olefins with good activity maintenance. Coproduction of some minor quantity of polyalkylated aromatic has been found to be non-detrimental to the overall performance of the dialkyl aromatic hydrocarbon as a synthetic lube base stock or additive.

Synthetic lube oils having less than about 4 cSt viscosity at 100°C are used primarily as light blending stocks in, for example, part synthetic multigrade engine oils. Few hydrocarbon synthetic oils of less than about 4 cSt viscosity at 100°C are commercially available. Polyalphaolefins (primarily isoparaffins) having viscosities of 2-4 cSt/100°C and alkylbenzenes having viscosities of 1.8 and 5.1 cSt/100°C are commercially available; however, the lighter grade in each case is too volatile (100 LV% off at 375°C) for use as an engine oil blending stock.

A valuable material for many applications would have a viscosity of less than about 4 cSt/100°C but more than 2 cSt/100°C, for example, in the range of about 2.2 to 3.7 cSt/100°C. Such a material could be used at a lower treat rate than a conventional 4 cSt/100°C PAO in a many applications, resulting in a cost saving.

Dialkylaromatics can be prepared having any viscosity desired between about 2.2 and 4 cSt/100°C. The lightest alkylbenzene suitable as a blending stock would be that which just met volatility and low temperature specifications. This point is illustrated in Figure 1, which shows the boiling point curves of two di-alkylbenzenes, ethylpentadecylbenzene and ethylhexadecylbenzene and those of two PAO's (2 cSt/100°C and 4 cSt/100°C). The alkylbenzenes, having discrete molecular weights, have very narrow boiling ranges, while the PAO's, in contrast, contain several species each with distinct molecular weights and boiling ranges. The low boiling 2 cSt/100°C PAO fails volatility specifications in many applications, while the 4 cSt PAO is too viscous for certain applications.

Traditionally, alkylaromatics have been produced using Friedel-Crafts catalysts, such as HF and $AlCl_3$. HF is still extensively used in the production of detergent alkylates. While these processes have proven to be commercial, and can be used to produce the dialkylaromatic materials of the present invention useful as synthetic lubricants or base stock additives, they are not very desirable since to meet product quality standards extensive product processing and clean-up procedures will be required. The presence of chemicals such as $AlCl_3$, HF and the acid residues they leave behind, even after the product has been intensely and extensively washed, can have a dramatic adverse effect on oil stability.

Alkylating procedures also involve the use of acidic zeolites as alkylating catalysts. Typical zeolites, however, produce a mixture of mono-, di-, tri-, and polyalkylaromatic material.

The structures, and thus the properties, of alkylaromatics prepared using different catalysts differ. Early attempts to synthesize linear alkylbenzenes for biodegradable detergent manufacture, using heterogeneous acidic catalysts, were unsatisfactory due to the co-production of >10% non-linear (non-biodegradable) alkylate. This side product was the result of acid-catalyzed skeletal rearrangement of the linear alkylaromatics or, more likely, of the linear olefin reactant. This type of rearrangement has been reported in recent patents concerning the high temperature alkylation of aromatics with linear olefins using ZSM-5 catalyst. (See U. S. Patent No. 4,301,316 and U. S. Patent No. 4,301,317).

Preferred alkylation procedures involve the use of wide pore acidic amorphous silica-alumina materials as catalyst (disclosed and claimed in copending application OP-2955, U. S. Serial No. ________, filed even date herewith), and the use of low crystallinity, partially collapsed zeolites (disclosed and claimed in copending application OP-2956, U. S. Serial No. ________, filed even date herewith). Use of these two above-identified procedures produce alkylaromatic mixtures rich in monoalkylated aromatic product.

In OP-2955, U. S. Serial No. ________, it is disclosed that the reaction of aromatic compounds with relatively long-chain alkylating agents (eg olefins), when carried out in the presence of certain large pore, non-crystalline silica-alumina catalysts, will result in phenylalkanes. The major product of the reaction is that which results from mono-alkylation; very little polyalkylation or olefin polymerization occurs.

The non-crystalline silica alumina catalysts utilizable in the process, as disclosed in OP-2955, U. S. Serial No. ________, may be natural or synthetic and are characterized by channels or networks of pores, the radii of the openings to the channels ranging from about 20 Å to about 1,000 Å, and averaging from about 40 Å to about 500 Å.

The ratio of silica to alumina present in these catalysts is less important than the pore radii. The silica to alumina ratio can lie between about one and about 10, preferably between 2 and 7. Two examples of catalysts which fall under the above description are the High Alumina (Si/Al = 3) and Low Alumina (Si/Al = 6) amorphous catalysts manufactued by Armak. The average pore radius in the High Alumina catalyst is 100 Å, while that in the Low Alumina catalyst is 188 Å.

The catalysts useful in the conversion process have at least 10% of the cationic sites occupied by ions other than alkali or alkaline earth metals. Typical but non-limiting replacing ions include ammonium, hydrogen, rare earth, zinc, copper and aluminum. Of this group, particular preference is accorded ammonium, hydrogen, rare earth and combinations thereof. In a preferred embodiment, the catalysts are converted to the predominantly hydrogen form, generally by replacement of the alkali metal or other ion originally present with hydrogen ion precursors, e.g., ammonium ions, which upon calcination yield the hydrogen form.

The process is carried out by contacting the aromatic compound, which may be a substituted or unsubstituted benzene, with the alkylating agent in the presence of the non-crystalline silica-alumina catalyst under suitable alkylation conditions. Preferred conditions include a temperature of between about 25°C and 500°C and a pressure of at least about 150 psig, preferably at least about 180 psig a feed weight hourly space velocity (WHSV) of between about 0.1 and about 500 hr^{-1} and an alkylating agent to aromatic molar rates of 1:1 to 1:10. Preferred reaction conditions include a temperature with the range of about 70°C to 250°C at a WHSV of between about 0.5 and 100 hr^{-1} and a pressure of at least about 180 psig. The reactants may be in either the vapour phase or the liquid phase and may be neat, i.e., free from intentional admixture or dilution with other materials, or may be brought into contact with the catalyst with the aid of carrier gases or diluents such as, for example, hydrogen or nitrogen.

The alkylation process described herein may be carried out as a batch type, semi-continuous or continuous operation utilizing a fixed bed or moving bed catalyst system.

The preferred method of use is continuous operation.

In OP-2956, U. S. Serial No. ________, the alkylation process using the acidic low crystallinity partially collapsed zeolite, the alkylation conditions employed are as follows: a temperature of between about 50 to 200°C, preferably about 60 to 150°C, more preferably about 70 to 140°C; at a pressure of about 0 to 200 psig, preferably about 120 psig and greater, most preferably about 180 psig and greater using a dry gas atmosphere such as hydrogen or nitrogen at a space velocity (WHSV gm olefin:gm catalyst/hr) of about 0.1 to 10 hr^{-1}, preferably about 0.5 to 4 hr^{-1}, most preferably about 0.8 to 2 hr^{-1}. The ratio of aromatic to alkylating agent (preferably olefin) starting material is about 1:1 to 10:1, preferably about 2:1 to 8:1, most prefefably about 3:1 to 5:1.

The process of OP-2956, U. S. Serial No. 603,033, can be practiced in either a batch or continuous mode, the continuous mode being preferred.

In practicing the alkylation process of OP 2956, USSN 603,033, a metal free, acidic low crystallinity partially collapsed large pore zeolite is employed as the catalyst. The procedure employed to produce the low crystallinity, partially collapsed zeolite is described in detail in copending application U. S. Serial No. 416,092, filed September 8, 1982. In general the procedure involves deeply exchanging the cation sites of the zeolite, preferably a wide pore zeolite such as Zeolite Y or Zeolite X, with ions which can be thermally decomposed into hydroxyl group, such as NH_4^+ ions, drying the exchanged zeolite, then calcining the exchanged zeolite in a relatively dry atmosphere so as to reduce the crystallinity of the material as compared with the zeolite starting material. The degree of cation exchange is generally to a level of greater than about 50%, with exchanges to a level of greater than 70% being preferred. The exchanged zeolite is dried so as to preferably contain no more than an equilibrium amount of moisture. The calcination is conducted at a temperature of at least about 300°C (generally about 300 to 600°C) in a relatively dry atmosphere, e.g., an atmosphere which generally contains less than about 1 psi water vapor partial pressure at the conditions used. The calcined material may then be further treated by roasting in an inert-nonreactive or reducing atmosphere containing no more than trace amounts of mositure, or in a vacuum, at from 400 to 900°C.

The crystalline zeolite starting material is subjected to the above recited procedure so as to produce a low crystallinity partially collapsed zeolite product marked by having about 30-80% retained crystallinity as measured by XRD. Crystallinity losses of greater than about 70% are not desirable in the catalyst since such-a material has been found to be not as selective for the production of monoalkylation product. Crystallinity loss can be controlled by adjusting either or both of the amount of moisture present in the environment during the calcination step (the greater the moisture content the lower the loss of crystallinity) and/or the thickness of the bed of the cation exchanged material in the calcination oven (the thicker the bed of cation exchanged material, the lower the loss of crystallinity at a given calcination temperature). The low crystallinity, partially collapsed zeolite which is preferred for use therefore has about 30-80% retained crystallinity as determined by x-ray diffraction (XRD).

The percentage of retained crystallinity in a low crystallinity, partially collapsed zeolite sample is obtained by averaging the heights of five major peaks in the XRD pattern and comparing this value to the average of the height of these five peaks in the XRD pattern of the parent sodium zeolite. The five (major) peaks which are used in the calculation are those which occur at θ° values of 15.5, 20.2, 23.5, 26.9 and 31.3.

Samples of Zeolite Y which possess reduced crystallinity, as mentioned above, are active catalysts for the alkylation of aromatic hydrocarbons, such as benzene, toluene and ethylbenzene, with olefins. The activity and selectivity exhibited by the catalyst depends strongly on the degree of crystallinity retained by the catalyst. In particular, Zeolite Y which has been deeply exchanged with NH_4^+ ions, calcined at a temperature between about 350°C and 550°C, and then conditioned in a hydrogen atmosphere up to a temperature of 450°C, exhibits very high selectivity for monoalkylation of light aromatic molecules with linear olefins. XRD analyses showed that the catalytic material possessed a percentage of crystallinity greater than 50%, but less than 100%. Materials possessing a percentage of crystallinity less than about 50% are usable but exhibit inferior selectivity and activity and are not preferred for that reason.

Consequently, the catalyst preparation parameters employed are selected from the ranges recited above, but chosen employing the guidelines respecting mixture content, temperature and bed thickness previously recited so as to provide a material possessing about 50% retained crystallinity.

The selectivity for monoalkylation observed using these catalysts is very high, generally being greater than or equal to 90%, and at times greater than or equal to 96%. This high selectivity is not in general achievable with pure zeolitic catalysts or with homogeneous catalysts, such as hydrofluoric acid. In these cases, where a broader product distribution is obtained, fairly complicated separation schemes are required, and in the case of typical Friedel-Crafts catalysts (using, e.g., $AlCl_3$ or HF) purification procedures are also required if the product is to be acceptable for use as a synthetic lube oil basestock or basestock additive.

The alkylation product may be purified, if necessary, and/or recovered from the starting materials or coproduced by products, if desired, by standard separation techniques. For example, the presence of unsaturated olefinic dimer in the alkylation product may be undesirable in applications where good oxidative stability is required. In this case, hydrogenation, either with an olefin-specific hydrogenation catalyst or with a hydrogenation catalyst which will saturate the olefin dimer and convert the alkylaromatics to naphthenes, may be desirable. Alternatively, purification may be carried out by physical separation techniques such as by distillation, or selective permeation through a perm-selective membrane such as an asymmetric reverse osmosis polyimide membrane. Such a procedure for separating the alkylation product from the starting materials and byproducts and the simultaneous separation of the alkylate product into its isomers using membranes is described and claimed in copending application Attorney Docket No. 2903, U. S. Serial No. 603,028, filed even date herewith.

The catalyst used in the examples reported herein manufactured by Armak and sold under the designation Ketjen HA1.5E, is a metal-free, wide pore amorphous silica-alumina the use of which is encompassed by OP-2955 USSN ________. Non-linear alkylate production is minimal ($\leq 2\%$). Non-linear material exhibits a lower VI and is more volatile than the linear product; its presence would be detrimental to the quality of any alkylaromatic used as a lube oil.

Light alkylbenzenes were alkylated with linear olefins to determine the suitability of the alkylated products as light lubricating oil stocks and lubricating oil blending stocks. Dialkylaromatic materials bearing the aromatic ring close to the ends of the long alkyl side chain are preferred since they have high VI, lower viscosity and lower volatility than the average structures. Ethylhexadecylbenzene has been found to be the preferred dialkylbenzene alkylate. Isolation of the monoalkylated aromatic from the total mixture is not required; the bulk reaction mixture exhibits excellent physical properties.

The alkylbenzenes reported in Tables 1 and 2 were prepared using the procedure of OP 2955, USSN ________ employing a heterogeneous amorphous, wide pore silica-alumina, a metal-free amorphous catalyst supplied by Armak Inc. (Ketjen HA1.5E). Alphaolefins (Gulf Chemical or Aldrich) were randomized by heating (200-210^{o}C) over alumina pellets, and were monitored using the α-olefin peak (1640 CM^{-1}) in the infrared spectrum. They were then distilled to recover olefin monomer and passed through a silica gel column to remove impurities (trace diolefins, which have been found to adversely affect catalyst life). Most of the alkylates were prepared by heating together (batch reaction) a 4:1 molar ratio of aromatic:randomized olefin, with the catalyst (0.4 g/g olefin) at 120^{o}C (or at the boiling point of the aromatic if that was lower) until reaction was complete.

The mono-alkylation product was generally produced with about 80-90% selectivity. The reaction mixtures were fractionally distilled under high vacuum to recover the products on mono-alkylation. Gas chromatographic analysis was used to monitor product purity. The properties of the linear alkylates prepared containing a total of 24, 25 and 26 carbons are reported in Table 1, and those of the alkylates containing 22 and 23 carbons are reported in Table 2.

Ethylhexadecylbenzene is seen to have the most desirable properties as a synthetic lube oil as it exhibits a number of excellent physical properties including low viscosity, high viscosity index, low pour point and low volatility ($\leq$ 10% at 375°C). It was hydrogenated to its cyclohexane analogue to determine whether the naphthenic oil offers any advantage over the alkylbenzene. Hydrogenation was carried out in a 1 liter autoclave at 200°C for 3 hours at 1500 psig H_2, using Harshaw Ni-0104T catalyst (1/8" pellets, 6.25 g/100 ml oil). The properties of ethylhexadecyclohexane are given in Table 3.

Table 1

Properties of (non-hydrogenated) C_{24}-C_{25} + C_{26} Linear Alkylbenzenes (a, b)

Formula	ΘEtC_{16}	ΘEtC_{16}	$\Theta(n\text{-}C4)C_{14}$	ΘC_{18}	$\Theta(O\text{-}Me_2)C_{16}$
Carbon Number	24	24	24	24	24
Example Number	1 (c)	2	3	4	5(e)
Physical Properties					
Viscosity, cSt, 40°C	10.40	10.55	10.61	10.22	13.93
100°C	2.77	2.76	2.73	2.77	3.17
-25°C	357	374	390	--	N/A
Viscosity Index	109	102	94	115	84
Bromine Number	N/A	--	2.21 (d)	0.05	N/A
Pour Point (°C)	-42	-51	<-54	-18	-39
Volatility, LV%, 375°C	7	10	28	3	5

(a) Me = Methyl, Et = Ethyl, n-C_4 = n-butyl, Θ = benzene.
(b) Olefins were bond randomized prior to alkylation reaction except where noted.
(c) Alpha Olefin was used in alkylation reaction.
(d) Olefin dimer co-distills with alkylate.
(e) Prepared using Union Carbide SK-500 catalyst and alpha olefin.

Table 1 Continued

Properties of (non-hydrogenated) C_{24}-C_{25} + C_{26} Linear Alkylbenzenes (a, b)

Formula	ΘEt_2C_{14}	$\Theta(n\text{-}C_4)C_{15}$	$\Theta sec\text{-}C_4C_{15}$	ΘEt_2C_{16}	ΘnC_4C_{16}
Carbon Number	24	25	25	26	26
Example Number	6	7	8	9	10
<u>Physical Properties</u>					
Viscosity, cSt, 40°C	12.42	12.08	13.48	15.37	13.41
100°C	2.94	3.01	3.13	3.42	3.24
-25°C	584	432	634	767	504
Viscosity Index	79	103	87	93	108
Bromine Number	0.35	0.39	0.49 (d)	0.02	0.12
Pour Point (°C)	<-54	<-54	<-54	<-54	-51
Volatility, LV%, 375°C	56	1	4	3	2

(a) Me = Methyl, Et = Ethyl, n-C_4 = n-butyl, Θ = benzene.
(b) Olefins were bond randomized prior to alkylation reaction except where noted.
(c) Alpha Olefin was used in alkylation reaction.
(d) Olefin dimer co-distills with alkylate.
(e) Prepared using Union Carbide SK-500 catalyst and alpha olefin.

Table 2

PROPERTIES OF (NON-HYDROGENATED) C_{22}-C_{23} LINEAR ALKYL BENZENES (a, b)

Formula	ΘMeC_{16}	ΘEtC_{15}	ΘC_{16}
Carbon Number	23	23	22
Example Number	11	12	13
<u>Physical Properties</u>			
Viscosity, cSt, 40°C	10.21	9.21	7.90
100°C	2.62	2.52	2.27
Viscosity Index	83	99	94
Bromine Number	N/A	0.03	0.18
Pour Point (°C)	-48	<-54	-39
Volatility, LV%, 375°C	46	60	97

(a) Me = Methyl, Et = ethyl, Θ = benzene

(b) Olefins bond randomized prior to alkylation reaction.

Table 3

PROPERTIES OF ETHYLHEXADECYLBENZENE AND ITS HYDROGENATION PRODUCT, ETHYLHEXADECYLCYCLOHEXANE*

Compound:	Ethyl-Hexadecyl Cyclohexane	Ethylhexadecyl Benzene
		$\text{Et}\phi\text{C}_{16}$
~~Derivation (from)~~	~~2A~~	~~-~~
Refractive Index (75°C)	1.4437	1.4621
C_A	<1%	-
Viscosity, cSt, 40°C	13.34	10.55
100°C	3.17	2.76
-25°C	626	374
VI	99	102
Pour Point, °C	-42	-51
Volatility, LV%, 375°C	4	10
368°C	2	2
Boiling Point (°C) at	376; 5	372; 5
LV% off (GCD)	382; 20	377; 20
	389; 50	383; 50
	394; 80	389; 80
	398; 95	405; 95

*Hydrogenation catalyst Harshaw-Ni-0104T (1/8" pellets, 6.25 g/100 ml oil), 1500 psig H_2, 200°C, 3 hr.

As is seen, the properties of light alkylbenzenes depend strongly on their structure. Generally, for species of the same molecular weight, the more branched the structure, the greater the oil's viscosity, the lower its VI and the lower its boiling point.

A more subtle effect of molecular structure on physical properties can be observed among alkylbenzene isomers which differ solely in the point of attachment of the long alkyl side chain to the benzene ring. Isomers in which the aromatic nucleus is bonded to the alkyl side chain near its end have a more pronounced linear structure, and exhibit physical properties consistent with this. These isomers have higher VI's, lower viscosities, lower volatilities and higher pour points than those where ring attachment occurs more towards the middle of the alkyl side chain.

The above structure/physical property analyses are intended to illustrate basic trends, particularly among isomeric species, and are consistent with literature teaching. Minor, batch-to-batch variations in the physical properties of these compounds can be expected, which reflect the limitations of separation procedure. This would be expected to disappear if large scale continuous processing were in use whereby such differences would tend to be masked.

The study of the properties of light alkylbenzenes indicates that these compounds can exhibit properties desirable in a synthetic lube oil. As oxidation stability is an important feature of lubricating oils, hydrogenation of the dialkyl benzenes, either olefin selective or complete, may be desirable and possibly necessary. Any of the commercially available olefin selective hydrogenation catalyst could be used under typical, hydrogenation conditions.

The excellent viscometric properties of some of the bulk alkylates suggests that isolation of specific alkylates from the bulk alkylation products is probably not necessary: the bulk products stream would probably have properties similar to those of the corresponding specific alkylates. Thus, while hydrogenation to remove olefinic unsaturation would be desirable and possibly necessary, distillation or other separation procedures to recover specific alkylate products could be eliminated. Processing would simply involve alkylation (in a continuous reactor), stripping of excess light aromatic for recycle and hydrogenation.

Alkylcyclohexanes are not currently marketed as synthetic lubricating oils, although they might be expected to offer some of the more desirable properties of PAO's (in particular, excellent high temperature oxidation stability) with none of the disadvantages of the PAO processing scheme (BF_3 catalyzed oligomerization to yield a broad range of oligomers). One alkylbenzene - ethylhexadecylbenzene - was completely hydrogenated to its cyclohexane analogue. Conversion to the naphthene is accompanied by increases in viscosity and boiling point (5°C) and a minor decrease in VI (3 units, Table 3). These changes are consistent with literature teaching [~~(2,3)~~]. Naphthenic oils generally exhibit higher viscosities than iso-paraffins, presumably because of inter-annular interactions. Preliminary bench oxidation testing of this oil suggests its oxidation stability is superior to Gulf 4 cSt/100°C PAO.

The alkylaromatics discussed herein were prepared using randomized linear olefins representative of olefins obtained by n-paraffin dehydrogenation. In order to indicate the quality of alkylaromatics prepared from the readily available alpha olefins, compare the EtC_{16} prepared using alpha hexadecene with the EtC_{16} reaction product obtained using the randomized olefin (Examples 1 and 2). It is seen that the α-olefin product is marginally less viscous, and has a slightly higher VI. The major difference between the two samples is the higher pour point of the α-olefin product, which results from the longer average alkyl chain length in these molecules. It should be remembered, however, that some randomization of the alpha olefin prior to alkylation does occur over the alkylation catalyst.

In this patent specification, the following conversions are used :

Å = 1×10^{-10}m
psig = 6.895 kPa gauge
inch (") = 2.54 cm

The co-pending application U.S. Serial No. 416092 filed September 8, 1982 referred to herein corresponds to our European patent application No.83305166.7.

The co-pending application OP-2955, U.S. Serial No. 603034 referred to herein corresponds to our European patent application No.   filed on or about the same date as the present application and entitled : "Alkylation of Aromatic Molecules using Wide Pore, Amorphous Silica-Alumina Catalyst" (inventor : H. A. Boucher).

The co-pending application OP-2956, U.S. Serial No. 603033 referred to herein corresponds to our European patent application No.   filed on or about the same date as the present application and entitled : "Alkylation of Aromatic Molecules using a Silica-Alumina Catalyst Derived from Zeolite" (inventors: H. A. Boucher and I. A. Cody).

The co-pending application Attorney Docket No. 2903, U.S. Serial No. 603028 referred to herein corresponds to our European patent application No.   filed on or about the same date as the present application and entitled: "Process for Separating Alkylaromatics from Aromatic Solvents and the Separation of the Alkylaromatic Isomers using Membranes" (inventors: L. E. Black and H. A. Boucher).

CLAIMS:

1. A synthetic specialty oil or lubricating oil base stock or base stock additive comprising a dialkyl aromatic hydrocarbon processing two pendant alkyl side chain groups of significantly different lengths one alkyl group containing 2 to 4 carbons and the other alkyl group containing 14 to 18 carbons and the aromatic moiety being phenyl the dialkyl aromatic hydrocarbon containing a total of 23 to 28 carbons.

2. The synthetic specialty oil or lubricating oil base stock or base stock additive of Claim 1 wherein the dialkyl aromatic hydrocarbon possesses two pendant alky side chain groups of significantly different lengths, one alkyl group containing 2 to 4 carbons, and the other alkyl group containing 15 to 17 carbons and the aromatic moiety being phenyl, the dialkyl aromatic hydrocarbon containing a total of 23 to 28 carbons.

3. The synthetic specialty oil or lubricating oil base stock or base stock additive of claim 2 wherein the dialkyl aromatic hydrocarbon possesses two pendant alkyl side chains groups of significantly different lengths, one alkyl group containing 2 to 4 carbons and the other alkyl group containing 15 to 16 carbons and the aromatic moiety being phenyl, the dialkyl aromatic hydrocarbon containing a total of 23 to 28 carbons.

4. The synthetic specialty oil or lubricating oil base stock or base stock additive of claim 1, 2 or 3 wherein the dialkyl aromatic hydrocarbon contains a total of 23 to 26 carbons.

5. The synthetic speciality oil or lubricating oil base stock or base stock additive of claim 4 wherein the dialkyl aromatic hydrocarbon contains a total of 24 carbons.

6. The synthetic speciality oil or lubricating oil base stock or base stock additive of any one of claims 1 to 5 wherein the dialkyl aromatic hydrocarbon comprises ethyl hexadecylbenzene.

BOILING POINT CURVES OF SEVERAL LIGHT SYNTHETIC LUBE OILS

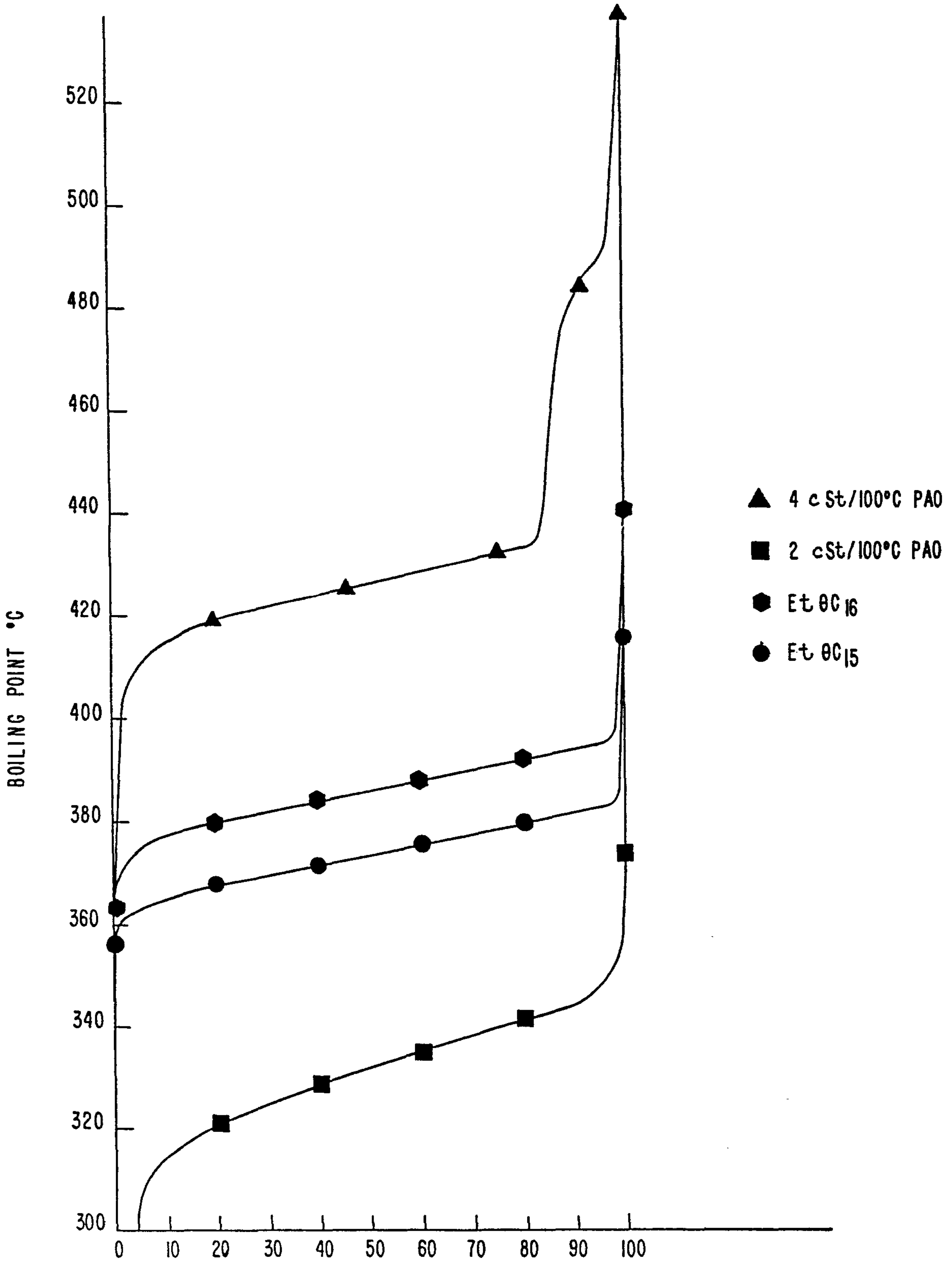


FIG. I