

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
25 January 2001 (25.01.2001)

PCT

(10) International Publication Number
WO 01/05733 A1

(51) International Patent Classification⁷: C07C 2/66,
5/22, 15/107, 5/333

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(21) International Application Number: PCT/US00/16336

(22) International Filing Date: 19 July 2000 (19.07.2000)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
09/356,574 19 July 1999 (19.07.1999) US

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(81) Designated States (national): AE, AL, AM, AT, AU, AZ,
BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK,
DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL,
IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU,
LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT,
RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA,
UG, US, UZ, VN, YU, ZA, ZW.

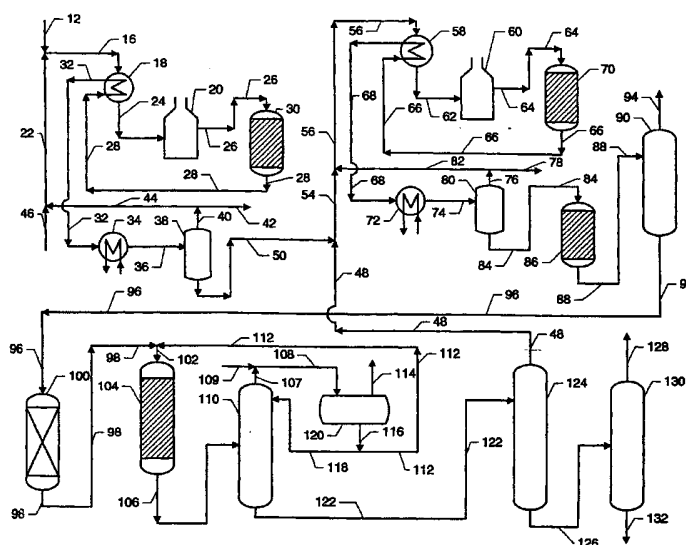
(84) Designated States (regional): ARIPO patent (GH, GM,
KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian
patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European
patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE,
IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG,
CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published:

— With international search report.

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: PROCESS FOR PRODUCING PHENYL-ALKANES COMPOSITIONS PRODUCED THEREFROM, AND USES THEREOF



(57) Abstract: The present invention is a process for producing phenyl-alkanes by paraffin isomerization (30) followed by paraffin dehydrogenation (70) and then by alkylation (104) of a phenyl-compound by a lightly branched olefin. The effluent (106) of the alkylation zone comprises paraffins that are recycled to the isomerization step (30) or to the dehydrogenation step (70). In addition, this invention is the compositions produced by these processes, and the use of compositions produced by these processes.



WO 01/05733 A1

“PROCESS FOR PRODUCING PHENYL-ALKANES
COMPOSITIONS PRODUCED THEREFROM, AND USES THEREOF”

FIELD

5 The invention relates to a process for the selective production of phenyl-alkane compositions, to the particular phenyl-alkane compositions produced therefrom, and to uses of those compositions.

BACKGROUND

10 More than thirty years ago, many household laundry detergents were made of branched alkylbenzene sulfonates (BABS). BABS are manufactured from a type of alkylbenzenes called branched alkylbenzenes (BAB). Alkylbenzenes (phenyl-alkanes) refers to a general category of compounds having an aliphatic alkyl group bound to a phenyl group and having the general formula of $(m_i\text{-alkyl})_i\text{-n-phenyl-alkane}$. The aliphatic alkyl group consists of an aliphatic alkyl chain, which is referred to by “alkane” in
15 the $(m_i\text{-alkyl})_i\text{-n-phenyl-alkane}$ formula. Of the chains of the aliphatic alkyl group, the aliphatic alkyl chain is the longest straight chain that has a carbon bound to the phenyl group. The aliphatic alkyl group may also consist of one or more alkyl group branches, each of which is attached to the aliphatic alkyl chain and is designated by a corresponding “ $(m_i\text{-alkyl})_i$ ” in the $(m_i\text{-alkyl})_i\text{-n-phenyl-alkane}$ formula. If it is possible to select two or more chains of equal lengths as the aliphatic alkyl chain, the choice goes to the chain carrying the greatest number of alkyl group branches. The subscript counter “i” thus has a value of from 1 to the number of alkyl group branches, and for each value
20 of i, the corresponding alkyl group branch is attached to carbon number m_i of the aliphatic alkyl chain. The phenyl group is attached to the aliphatic alkyl group, specifically to carbon number n of the aliphatic alkyl chain. The aliphatic alkylation chain is numbered from one end to the other, the direction being chosen so as to give the lowest number possible to the position of the
25 phenyl group.
30

The standard process used by the petrochemical industry for producing BAB consists of oligomerizing light olefins, particularly propylene, to branched olefins having 10 to 14 carbon atoms and then alkylating benzene with the branched olefins in the presence of a catalyst such as HF.

5 Although the product BAB comprises a large number of alkyl-phenyl-alkanes having the general formula $(m_i\text{-alkyl}_i)_i\text{-n-phenyl-alkane}$, for the purpose of illustrating three important characteristics of BAB it is sufficient to point out only two examples of BAB: $m\text{-alkyl-}m\text{-alkyl-n-phenyl-alkanes}$ where $m \neq n$, and $m\text{-alkyl-}m\text{-phenyl-alkanes}$ where $m \geq 2$.

10 The most prominent characteristic of BAB is that, for a large proportion of BAB, there is attached to the aliphatic alkyl chain of BAB generally at least one alkyl group branch, and more commonly three or more alkyl group branches. BAB thus has a relatively large number of primary carbon atoms per aliphatic alkyl group, since the number of primary carbon
15 atoms per aliphatic alkyl group in BAB equals the number of alkyl group branches per aliphatic alkyl group plus either one if $n = 1$, or two if $n \geq 2$, provided that the alkyl group branches themselves are unbranched. If any alkyl group branch itself is branched, then the aliphatic alkyl group in BAB has even more primary carbon atoms. Thus the aliphatic alkyl group in BAB
20 usually has three, four, or more primary carbon atoms. As for the alkyl group branches of the aliphatic alkylation group in BAB, each alkyl group branch is usually a methyl group branch, although ethyl, propyl, or higher alkyl group branches are possible.

Another characteristic of BAB is that the phenyl group in BAB can be
25 attached to any non-primary carbon atom of the aliphatic alkyl chain. This is typical of BAB that is produced from the standard BAB process used by the petrochemical industry. Except for 1-phenyl-alkanes whose formation is known to be disfavored due to the relative instability of the primary carbenium ion and neglecting the relatively minor effect of the branches of
30 the branched paraffins, the oligomerization step produces a carbon-carbon double bond that is randomly distributed along the length of the aliphatic

alkyl chain, and the alkylation step nearly randomly attaches the phenyl group to a carbon along the aliphatic alkyl chain. Thus, for example, for a phenyl-alkane which has an aliphatic alkyl chain having 10 carbon atoms and which was produced by the standard BAB process, the phenyl-alkane product would be expected to be an approximately random distribution of 2-, 3-, 4-, and 5-phenyl-alkanes, and the selectivity of the process to a phenyl-alkane like 2-phenyl alkane would be 25 if the distribution was perfectly random, but is typically between about 10 and about 40.

A third characteristic of BAB is the relatively high probability that one of the carbons of the aliphatic alkyl group is a quaternary carbon. In BAB, the quaternary carbon may be, as illustrated by the first BAB example, a carbon in the aliphatic alkyl group other than the carbon that is bonded by a carbon-carbon bond to a carbon in the phenyl group. However, as is illustrated by the BAB second example, the quaternary carbon may also be the carbon that is bonded by a carbon-carbon bond to a carbon in the phenyl group. When a carbon atom on the alkyl side chain not only is attached to two other carbons on the alkyl side chain and to a carbon atom of an alkyl group branch but also is attached to a carbon atom of the phenyl group, the resulting alkyl-phenyl-alkane is referred to as a "quaternary alkyl-phenyl-alkane" or simply a "quat." Thus, quats comprise alkyl-phenyl-alkanes having the general formula m-alkyl-m-phenyl-alkane. If the quaternary carbon is the second carbon atom numbered from an end of the alkyl side chain, the resulting 2-alkyl-2-phenyl-alkane is referred to as an "end quat." If the quaternary carbon is any other carbon atom of the alkyl side chain, as in the second BAB example, then the resulting alkyl-phenyl-alkane is referred to as an "internal quat." In known processes for producing BAB, a relatively high proportion, typically greater than 10 mol-%, of the BAB is internal quats.

About thirty years ago it became apparent that household laundry detergents made of BABS were gradually polluting rivers and lakes. Investigation into the problem led to the recognition that BABS were slow to biodegrade. Solution of the problem led to the manufacture of detergents

made of linear alkylbenzene sulfonates (LABS), which were found to biodegrade more rapidly than BABS. Today, detergents made of LABS are manufactured worldwide. LABS are manufactured from another type of alkylbenzenes called linear alkylbenzenes (LAB). The standard process used by the petrochemical industry for producing LAB consists of dehydrogenating linear paraffins to linear olefins and then alkylating benzene with the linear olefins in the presence of a catalyst such as HF or a solid catalyst. LAB are phenyl-alkanes comprising a linear aliphatic alkyl group and a phenyl group and have the general formula n-phenyl-alkane. LAB has no alkyl group branches, and consequently the linear aliphatic alkyl group normally has two primary carbon atoms (i.e., $n \geq 2$). Another characteristic of LAB that is produced by the standard LAB process is that the phenyl group in LAB is usually attached to any secondary carbon atom of the linear aliphatic alkyl group. In LAB produced using HF catalyst the phenyl group is slightly more likely to attach to a secondary carbon near the center as opposed to near the end of the linear aliphatic alkyl group, while in LAB produced by the Detal™ process approximately 25-35 mol-% of n-phenyl-alkanes are 2-phenyl-alkanes.

Over the last few years, other research has identified certain modified alkylbenzene sulfonates, which are referred to herein as MABS, which are different in composition from all alkylbenzene sulfonates used currently in commerce, including BABS and LABS, and from all alkylbenzene sulfonates produced by prior alkylbenzene processes, including those which alkylate aromatics using catalysts such as HF, aluminum chloride, silica-alumina, fluorided silica-alumina, zeolites, and fluorided zeolites. MABS also differ from these other alkylbenzene sulfonates by having improved laundry cleaning performance, hard surface cleaning performance, and excellent efficiency in hard and/or cold water, while also having biodegradability comparable to that of LABS.

MABS can be produced by sulfonating a third type of alkylbenzenes called modified alkylbenzenes (MAB), and the desired characteristics of MAB

are determined by the desired solubility, surfactancy, and biodegradability properties of MABS. MAB is a phenyl-alkane comprising a lightly branched aliphatic alkyl group and a phenyl group and has the general formula $(m_i\text{-alkyl}_i)_i\text{-n-phenyl-alkane}$. MAB usually has only one alkyl group branch, and the alkyl group branch is a methyl group, which is preferred, an ethyl group, or an n-propyl group, so that, where there is only one alkyl group branch and $n \neq 1$, the aliphatic alkyl group in MAB has three primary carbons. However, the aliphatic alkyl group in MAB may have two primary carbon atoms if there is only one alkyl group branch and $n = 1$, or, if there are two alkyl group branches and $n \neq 1$, four primary carbons. Thus, the first characteristic of MAB is that the number of primary carbons in the aliphatic alkyl group in MAB is intermediate between that in BAB and that in LAB. Another characteristic of MAB is that it contains a high proportion of 2-phenyl-alkanes, namely that from about 40 to about 100% of phenyl groups are attached selectively to the second carbon atom as numbered from an end of the alkyl side chain.

A final characteristic of the MAB alkylate is that the MAB has a relatively low proportion of internal quats. Some internal quats such as 5-methyl-5-phenyl-undecane produce MABS that has shown slower biodegradation, but end quats such as 2-methyl-2-phenyl-undecane produce MABS that show biodegradation similar to that of LABS. For example, biodegradation experiments show that in a porous pot activated sludge treatment, the ultimate biodegradation was greater for sodium 2-methyl-2-undecyl [C^{14}] benzenesulfonate than for sodium 5-methyl-5-undecyl [C^{14}] benzenesulfonate. See the article entitled "Biodegradation of Coproducts of Commercial Linear Alkylbenzene Sulfonate," by A. M. Nielsen et al., in Environmental Science and Technology, Vol. 31, No. 12, 3397-3404 (1997). A relatively low proportion, typically less than 10 mol-%, of MAB is internal quats.

Because of the advantages of MABS over other alkylbenzene sulfonates, catalysts and processes are sought that selectively produce

MAB. As suggested by the foregoing, two of the chief criteria for an alkylation process for the production of MAB are selectivity to 2-phenyl-alkanes and selectivity away from internal quaternary phenyl-alkanes. Prior art alkylation processes for the production of LAB using catalysts such as aluminum chloride or HF are incapable of producing MAB having the desired 2-phenyl-alkane selectivity and internal quat selectivity. In these prior art processes, when lightly branched olefins (i.e., olefins that have essentially the same light branching as that of the aliphatic alkyl group of MAB) react with benzene, quaternary phenyl-alkanes selectively form. One reaction mechanism that accounts for such selective quaternary phenyl-alkane formation is that the delinearized olefins convert, to various extents, into primary, secondary, and tertiary carbenium ion intermediates. Of these three carbenium ions, tertiary carbenium ions are the most stable, and because of their stability, are the most likely to form and react with benzene, thus forming a quaternary phenyl-alkane.

One process that has been proposed for producing MAB comprises a three-step process. First, a feedstock comprising paraffins is passed to an isomerization zone to isomerize the paraffins and to produce an isomerized product stream comprising lightly branched paraffins (i.e., paraffins that have essentially the same light branching as that of the aliphatic alkyl group of MAB). Next, the isomerized product stream passes to a dehydrogenation zone where the lightly branched paraffins are dehydrogenated to produce a dehydrogenated product stream comprising lightly branched monoolefins (i.e., monoolefins that have essentially the same light branching as that of the lightly branched paraffins, and, consequently, that of the aliphatic alkyl group of MAB). Finally, the dehydrogenated product stream passes to an alkylation zone where the lightly branched monoolefins in the dehydrogenated product stream react with benzene to form MAB.

One of the problems with this proposed process is that conventional dehydrogenation reaction zones typically convert only about 10 wt-% of the entering paraffins to olefins, so that usually about 90 wt-% of the product

stream from the dehydrogenation zone comprises paraffins, including both linear and nonlinear paraffins. Because the product stream from the dehydrogenation zone enters the alkylation zone, these paraffins all enter the alkylation zone as well. Although it would be desirable to remove the paraffins prior to entering the alkylation zone, the difficulty of separating these paraffins from the monoolefins all of the same carbon number precludes such an arrangement. In the alkylation zone, typically more than 90 wt-% of the entering monoolefins are converted to phenyl-alkanes while the entering paraffins are essentially inert or unreactive. Thus, the alkylation effluent contains not only the desired product MAB but also these paraffins. Accordingly, processes for the production of MAB are sought that efficiently recover and utilize paraffins in the alkylation effluent.

SUMMARY

In one aspect, this invention is a process for the production of phenyl-alkanes, in particular modified alkylbenzenes (MAB), by the steps of paraffin isomerization, paraffin dehydrogenation, and alkylation of a phenyl compound, in which paraffins in the alkylation effluent are recycled to the isomerization step and/or the dehydrogenation step. The paraffins that are recycled may be linear or nonlinear paraffins, including lightly branched paraffins. Because the recycled paraffins can be converted into lightly branched olefins, this invention efficiently recovers paraffins in the alkylation effluent and uses them to produce valuable phenyl-alkane products. This aspect of the invention thus increases the yield of valuable products for a given amount of paraffinic feedstock charged to the process while avoiding the difficulty of separating the paraffins from the monoolefins after the paraffin dehydrogenation step and prior to the alkylation step.

The process aspect of this invention has several objectives. The primary objective of this invention is to produce phenyl-alkanes, in particular modified alkylbenzenes (MAB) by paraffin isomerization followed by paraffin dehydrogenation to olefins and then by alkylation of aromatics by olefins. An

additional objective of this invention is to increase the yield of phenyl-alkane in such a process and thereby to decrease the amount of paraffin feedstock, which is required for the process. Yet another objective is to remove unreacted paraffins from the phenyl-alkane product without the need for a
5 difficult and/or costly separation of paraffins from olefins after the dehydrogenation step and prior to the alkylation step.

This invention, when used for detergent alkylation, produces phenyl-alkanes that meet the increasingly stringent requirements of 2-phenyl-alkanes selectivity and internal quaternary phenyl-alkane selectivity for the
10 production of modified alkylbenzenes (MAB). The MAB, in turn, can be sulfonated to produce modified linear alkylbenzene sulfonates (MABS), which have improved cleaning effectiveness in hard and/or cold water while also having biodegradability comparable to that of linear alkylbenzene sulfonates.

15 In another aspect, this invention is the MAB compositions produced by the processes of this invention. It is believed that the MAB produced by the processes of this invention are not necessarily the products that would be produced by the prior art processes that do not recycle paraffins. Without being bound to any particular theory, it is believed that in the
20 dehydrogenation zone the extent of conversion of branched paraffins can be greater than that of normal (linear) paraffins, and/or that the extent of conversion of heavier paraffins can be greater than that of lighter paraffins. In these cases, the concentration of linear paraffins and/or lighter paraffins in the recycle paraffin stream could increase. This, in turn, could increase the
25 concentration and ultimately the conversion of linear and/or lighter paraffins in the dehydrogenation zone until the rate of removal from the process of linear and/or lighter paraffins via dehydrogenation and subsequent alkylation equals the rate of introduction into the dehydrogenation zone of those paraffins from the paraffin isomerization zone. Accordingly, for a given
30 extent of olefin conversion in the alkylation zone, the aliphatic alkyl chain of the MAB product of the present invention can be less branched and/or

shorter than that of the prior art processes. On sulfonation, the resulting MABS could likewise tend to have a less branched and/or shorter aliphatic alkyl chain than that of the prior art processes. Thus, for a given combination of feedstocks, the processes of this invention could produce particular MAB products having aliphatic alkyl chain with specially tailored extents of branching that are not necessarily the same as those of the prior art processes. This invention is, in another of its aspects, the use of MAB produced by the process of this invention as a lubricant.

DETAILED DESCRIPTION

The paraffinic feedstock preferably comprises nonbranched (linear) or normal paraffin molecules having generally from 8 to 28, preferably from 8 to 15, and more preferably from 10 to 15 carbon atoms. Two carbon atoms per nonbranched paraffin molecule are primary carbon atoms and the remaining carbon atoms are secondary carbon atoms.

The paraffinic feedstock may also contain a lightly branched paraffin, which is a paraffin having a total number of carbon atoms of from 8 to 28, of which three or four of the carbon atoms are primary carbon atoms and none of the remaining carbon atoms are quaternary carbon atoms. Preferably, the lightly branched paraffin from 8 to 15, and more preferably from 10 to 15, carbon atoms. The lightly branched paraffin generally comprises an aliphatic alkane having the general formula of $(p_i\text{-alkyl})_i\text{-alkane}$ and consists of an aliphatic alkyl chain and one or more alkyl group branches. If it is possible to select two or more chains of equal lengths as the aliphatic alkyl chain, the choice goes to the chain carrying the greatest number of alkyl group branches. The subscript counter "i" thus has a value of from 1 to the number of alkyl group branches, and for each value of i, the corresponding alkyl group branch is attached to carbon number p_i of the aliphatic alkyl chain. The aliphatic alkyl chain is numbered from one end to the other, the direction being chosen so as to give the lowest numbers possible to the carbon atoms having alkyl group branches.

The alkyl group branch or branches are generally selected from methyl, ethyl, and propyl groups, with shorter and normal branches being preferred. Preferably, the lightly branched paraffin has only one alkyl group branch, but two alkyl group branches are also possible. Lightly branched paraffins having two alkyl group branches or four primary carbon atoms comprise generally less than 40 mol-%, and preferably less than about 25 mol-%, of the total lightly branched paraffins. Lightly branched paraffins having one alkyl group branch or three primary carbon atoms comprise preferably more than 70 mol-% of the total lightly branched paraffins.

The paraffinic feedstock may also contain paraffins that are more highly branched than the lightly branched paraffins. The quantity of these highly branched paraffins charged to the process is preferably minimized. Paraffin molecules consisting of at least one quaternary carbon atom generally comprise less than 10 mol-%, preferably less than 5 mol-%, more preferably less than 2 mol-%, and most preferably less than 1 mol-%, of the paraffinic feedstock.

The paraffinic feedstock is normally a mixture of linear and lightly branched paraffins having different carbon numbers. Any suitable method for producing the paraffinic feedstock may be used. A preferred method is the separation of nonbranched (linear) hydrocarbons or lightly branched hydrocarbons from a kerosene boiling range petroleum fraction. The UOP Molex™ process is an established, commercially proven method for the liquid-phase adsorption separation of normal paraffins from isoparaffins and cycloparaffins using the UOP Sorbex separation technology. Other suitable processes are the UOP Kerosene Isosiv™ Process, and an Exxon vapor-phase adsorption process which uses ammonia as the desorbent. The feed streams to these adsorption processes, can be obtained by extraction or by suitable oligomerization processes. Reference may be made to the Handbook of Petroleum Refining Process, by Robert A. Meyers, McGraw-Hill, New York, 1997 for additional information on the UOP Molex™ and Kerosene Isosiv™ processes.

The composition of the paraffinic feedstock can be determined by gas chromatography according to the article by H. Schulz, et al., *Chromatographia* 1, 1968, 315.

5 The phenyl feedstock comprises a phenyl compound, which may be alkylated or otherwise substituted derivatives of or a higher molecular weight than benzene, including toluene, ethylbenzene, xylene, phenol, naphthalene, etc. Preferably, the phenyl compound is benzene.

For purposes of discussion, the subject process may be divided into an isomerization section, a dehydrogenation section, and an alkylation
10 section. In the isomerization section, the paraffinic feedstock is passed to a skeletal isomerization zone, which decreases the linearity and increases the number of primary carbon atoms of the paraffin molecules in the paraffinic feedstock. The number of methyl group branches of the aliphatic alkyl chain increases preferably by 2 or more preferably by 1. The total number of
15 carbon atoms of the paraffin molecule remains the same.

In the isomerization section a feedstream containing paraffins combines with recycled hydrogen. This forms an isomerization reactant stream which is heated and passed through a bed of a suitable catalyst maintained at the proper isomerization conditions of temperature, pressure,
20 etc. The effluent of this catalyst bed, or isomerization reactor effluent stream, is cooled, partially condensed, and passed to a vapor-liquid, or product, separator. The condensed material withdrawn from the product separator may be passed to a stripping separation zone which includes a stripping column that removes all compounds which are more volatile than
25 the lightest aliphatic hydrocarbon which is desired to charge to the dehydrogenation section of the process. Alternatively, the condensed material may be passed without stripping and with its more volatile aliphatic hydrocarbons to the dehydrogenation section and the dehydrogenated product stream is stripped in order to remove all compounds which are more
30 volatile than the lightest aliphatic hydrocarbon which it is desired to charge to

the alkylation section of the process. The paraffin-containing net stream that passes from the isomerization section to the dehydrogenation section is the isomerized product stream.

Skeletal isomerization of the paraffinic feedstock can be accomplished in any known manner known or by using any suitable known catalyst. Suitable catalysts comprise a metal of Group VIII (IUPAC 8-10) of the Periodic Table and a support material. Suitable Group VIII metals include platinum and palladium, each of which may be used alone or in combination. The support material may be amorphous or crystalline. Suitable support materials include amorphous alumina, amorphous silica-alumina, ferrierite, ALPO-31, SAPO-11, SAPO-31, SAPO-37, SAPO-41, SM-3, and MgAPSO-31, each of which may be used alone or in combination. ALPO-31 is described in US-A- 4,310,440. SAPO-11, SAPO-31, SAPO-37, and SAPO-41 are described in US-A- 4,440,871. SM-3 is described in US-A-4,943,424; US-A-5,087,347; US-A-5,158,665; and US-A-5,208,005. MgAPSO is a MeAPSO, which is an acronym for a metal aluminumsilicophosphate molecular sieve, where the metal Me is magnesium (Mg). MeAPSOs are described in US-A-4,793,984, and MgAPSOs are described in US-A-4,758,419. MgAPSO-31 is a preferred MgAPSO, where 31 means a MgAPSO having structure type 31. The isomerization catalyst may also comprise a modifier selected from the group consisting of lanthanum, cerium, praseodymium, neodymium, samarium, gadolinium, terbium, and mixtures thereof, as described in US-A-5,716,897 and US-A-5,851,949. It is believed that other suitable support materials include ZSM-22, ZSM-23, and ZSM-35, which are described for use in dewaxing in US-A-5,246,566 and in the article by S. J. Miller, in *Microporous Materials* 2 (1994) 439-449.

Operating conditions for skeletal isomerization of the paraffinic feedstock include vapor phase, liquid phase, and a combination of vapor and liquid phases. The hydrocarbons are preferably in the liquid phase. Hydrogen in excess of that soluble in the liquid hydrocarbons may be present. The paraffinic feedstock trickle as a liquid through a fixed bed of

solid catalyst in the presence of hydrogen vapor. The isomerization temperature is generally from 122 to 752°C. The isomerization pressure is generally from atmospheric pressure to 13790 kPa(g), but usually the pressure is maintained as low as practicable, to minimize capital and operating costs. The molar ratio of hydrogen per hydrocarbon is generally greater than 0.01:1, but is usually not more than 10:1.

The isomerized product stream comprises paraffins having a total number of carbon atoms per paraffin molecule of generally from 8 to 28, preferably from 8 to 15, and more preferably from 10 to 15 carbon atoms.

The isomerized product stream generally contains a higher concentration of lightly branched paraffins, based on the total paraffins in the isomerized product stream, than the concentration of lightly branched paraffins in the paraffinic feedstock, based on the total paraffins in the paraffinic feedstock. The lightly branched paraffins having either two alkyl group branches or four primary carbon atoms comprise preferably less than 40 mol-%, and more preferably less than 30 mol-%, of the total lightly branched paraffins in the isomerized product stream. The lightly branched paraffins having either one alkyl group branch or three primary carbon atoms comprise preferably more than 70 mol-% of the total lightly branched paraffins in the isomerized product stream. The lightly branched paraffins having 3 or 4 primary carbon atoms and no quaternary carbon atoms comprise preferably more than 25 mol-%, and more preferably more than 60 mol-%, of the isomerized product stream. Monomethyl-alkanes are a preferred lightly branched paraffin of the isomerized product stream. When present in the isomerized product stream with the lightly branched paraffins, the linear paraffin content may be as high as 75 mol-%, but is generally less than about 40 mol-%, of the total paraffins in the isomerized product stream. Paraffin molecules consisting of at least one quaternary carbon atom generally comprise less than 10 mol-%, preferably less than 5 mol-%, more preferably less than 2 mol-%, and most preferably less than 1 mol-%, of the isomerized product stream.

In the dehydrogenation section, a stream containing paraffins combines with recycled hydrogen to form a dehydrogenation reactant stream that is heated and contacted with a dehydrogenation catalyst in a fixed bed maintained at dehydrogenation conditions. The effluent of the fixed catalyst bed, or the dehydrogenation reactor effluent stream, is cooled, partially condensed, and passed to a vapor-liquid separator. The vapor-liquid separator produces a hydrogen-rich vapor phase and a hydrocarbon-rich liquid phase. The condensed liquid phase recovered from the separator passes to a stripping column, which removes all compounds which are more volatile than the lightest hydrocarbon which is desired to be passed to the alkylation section. The olefin-containing net stream that passes from the dehydrogenation section to the alkylation section is the dehydrogenated product stream. Reference may be made to pages 1.53 to 1.66 and 5.11 to 5.19, which are incorporated herein by reference, of the previously-cited book by Meyers for additional information on LAB processes in general and paraffin dehydrogenation processes in particular.

The dehydrogenation catalyst may be in a moving catalyst bed or a fluidized bed. The dehydrogenation zone may comprise one or more catalyst-containing reaction zones with heat exchangers there between to ensure that the desired reaction temperature is maintained at the entrance to each reaction zone. Hot hydrogen-rich gas streams may be introduced between reaction zones to heat a stream passing between the reaction zones. Reference may be made to US-A-5,491,275 and US-A-5,689,029 for additional information. Each reaction zone may be operated in a continuous-type or batch-type manner. Each reaction zone may contain one or more catalyst beds. Hydrocarbons may contact any catalyst bed in an upward-, downward-, or radial-flow fashion, or may occur in a heat exchanging reactor. Reference may be made to US-A-5,405,586 and US-A-5,525,311, which are incorporated herein by reference, for additional information on heat exchanging reactors.

Dehydrogenation catalysts are well known in the prior art as exemplified by US-A-3,274,287; US-A-3,315,007; US-A-3,315,008; US-A-3,745,112; US-A-4,430,517; US-A-4,716,143; US-A-4,762,960; US-A-4,786,625; and US-A-4,827,072. However, a preferred catalyst is a layered composition comprising an inner core and an outer layer bonded to the inner core, where the outer layer comprises a refractory inorganic oxide having uniformly dispersed thereon at least one platinum group (Group VIII (IUPAC 8-10)) metal and at least one promoter metal, and where at least one modifier metal is dispersed on the catalyst composition. Preferably, the outer layer is bonded to the inner core to the extent that the attrition loss is less than 10 wt-% based on the weight of the outer layer. Reference may be made to U.S. application No. 09/185,189 filed November 3, 1998, which is incorporated herein by reference, for more information on this layered catalyst composition.

The dehydrogenation conditions are selected to minimize cracking, isomerizing, and polyolefin by-products. The hydrocarbon may be in the liquid phase or in a mixed vapor-liquid phase, but preferably it is in the vapor phase. Dehydrogenation conditions include a temperature of generally from 400°C to 900°C and preferably from 400°C to 525°C, a pressure of generally from 1 kPa(g) to 1013 kPa(g), and a LHSV of from 0.1 to 100 hr⁻¹. The pressure is maintained as low as practicable, usually less than 345 kPa(g), consistent with equipment limitations, to maximize chemical equilibrium advantages.

The isomerized product stream may be admixed with a diluent material such as hydrogen, before, while, or after passing to the dehydrogenation zone at a hydrogen to hydrocarbon mole ratio of 0.1:1 to 40:1, and preferably from 1:1 to 10:1. The diluent hydrogen stream passed to the dehydrogenation zone will typically be recycled hydrogen separated from the effluent from the dehydrogenation zone.

Water or a material which decomposes at dehydrogenation conditions to form water such as an alcohol, aldehyde, ether, or ketone, for example, may be added to the dehydrogenation zone, either continuously or intermittently, in an amount to provide, calculated on the basis of equivalent
5 water, from 1 to 20,000 weight ppm of the hydrocarbon feed stream. From 1 to 10,000 weight ppm of water addition gives best results when dehydrogenating paraffins having from 2 to 30 or more carbon atoms.

The monoolefin-containing dehydrogenated product stream from the paraffin dehydrogenation process is typically a mixture of unreacted
10 paraffins, linear (unbranched) olefins, and branched monoolefins including lightly branched monoolefins. Typically, from 25 to 75 vol-% of the olefins in the monoolefin-containing stream from the paraffin dehydrogenation process are linear (unbranched) olefins.

The dehydrogenated product stream may comprise a highly branched
15 monoolefin or a linear (unbranched) olefin, but the monoolefin is preferably a lightly branched monoolefin. A lightly branched monoolefin is a monoolefin having a total number of carbon atoms of from 8 to 28, of which three or four of the carbon atoms are primary carbon atoms and none of the remaining carbon atoms are quaternary carbon atoms. Preferably, the lightly branched
20 monoolefin has a total number of from 8 to 15, and more preferably from 10 to 15, carbon atoms.

The lightly branched monoolefin generally comprises an aliphatic alkene having the general formula of $(p_i\text{-alkyl})_i\text{-q-alkene}$. The lightly branched monoolefin consists of an aliphatic alkenyl chain, which is the
25 longest straight chain containing the carbon-carbon double bond of the lightly branched monoolefin, and one or more alkyl group branches, each of which is attached to the aliphatic alkenyl chain. If it is possible to select two or more chains of equal lengths as the aliphatic alkenyl chain, the choice goes to the chain carrying the greatest number of alkyl group branches. The
30 subscript counter "i" thus has a value of from 1 to the number of alkyl group

branches, and for each value of i , the corresponding alkyl group branch is attached to carbon number p_i of the aliphatic alkenyl chain. The double bond is between carbon number q and carbon number $(q + 1)$ of the aliphatic alkenyl chain. The aliphatic alkenyl chain is numbered from one end to the other, the direction being chosen so as to give the lowest number possible to the carbon atoms bearing the double bond.

The lightly branched monoolefin may be an alpha monoolefin or a vinylidene monoolefin, but is preferably an internal monoolefin. The term "internal olefins," as used herein, includes di-substituted internal olefins having the chemical formula $R-CH=CH-R$; tri-substituted internal olefins having the chemical formula $R-C(R)=CH-R$; and tetra-substituted olefins having the chemical formula $R-C(R)=C(R)-R$. The di-substituted internal olefins include beta internal olefins having the chemical formula $R-CH=CH-CH_3$. In each of the preceding chemical formulas in this paragraph, R is an alkyl group that may be identical to or different from other alkyl group(s), if any, in each formula.

For lightly branched monoolefins other than vinylidene olefins, the alkyl group branch or branches of the lightly branched monoolefin are generally selected from methyl, ethyl, and propyl groups, with shorter and normal branches being preferred. By contrast, for lightly branched monoolefins that are vinylidene olefins, the alkyl group branch attached to carbon number 2 of the aliphatic alkenyl chain may be selected not only from methyl, ethyl, and propyl groups but also from alkyl groups up to and including tetradecyl (C_{14}) groups, while any other alkyl group branch(es) of the vinylidene olefin is (are) generally selected from methyl, ethyl, and propyl groups with shorter and normal branches being preferred. For all lightly branched monoolefins, preferably the lightly branched monoolefin has only one alkyl group branch, but two alkyl group branches are also possible. Lightly branched monoolefins having either two alkyl group branches or four primary carbon atoms comprise generally less than 40 mol-%, and preferably less than about 30 mol-%, of the total lightly branched monoolefins, with the

remainder of the lightly branched monoolefins having one alkyl group branch. Lightly branched monoolefins having either one alkyl group branch or three primary carbon atoms comprise preferably more than 70 mol-% of the total lightly branched monoolefins. Monomethyl-alkenes are a preferred lightly
5 branched monoolefin of the dehydrogenated product stream.

Vinylidene monoolefins are normally a minor component and have a concentration of usually less than 0.5 mol-%, and more commonly less than 0.1 mol-%, of the olefins in the dehydrogenated product stream. Therefore, all references hereinafter to the lightly branched monoolefins and to the
10 dehydrogenated product stream will assume that no vinylidene monoolefins are present.

The composition of a mixture of lightly branched monoolefins can be determined by gas chromatography according to the previously mentioned article by Schulz et al. and using an injector with a hydrogenator insert tube
15 in order to hydrogenate monoolefins to paraffins.

In addition to the lightly branched monoolefin, other acyclic compounds may be in the dehydrogenated product stream. One of the advantages of this invention is that the dehydrogenated product stream can be passed directly to the alkylation reaction section despite the fact that that
20 stream also contains paraffins having the same number of carbon atoms as the lightly branched monoolefins. Thus, this invention avoids the need to separate the paraffins from the monoolefins prior to passing to the alkylation section. Other acyclic compounds include nonbranched (linear) olefins and monoolefins. Nonbranched (linear) olefins which may be charged have a
25 total number of carbon atoms per paraffin molecule of generally from about 8 to about 28, preferably from 8 to 15, and more preferably from 10 to 14 carbon atoms. Two carbon atoms per nonbranched olefin molecule are primary carbon atoms and the remaining carbon atoms are secondary carbon atoms. The nonbranched olefin may be an alpha monoolefin but is
30 preferably an internal monoolefin. The linear olefin content may be as high

as 75 mol-%, but is generally less than about 40 mol-%, of the total monoolefins in the dehydrogenated product stream.

The dehydrogenated product stream may contain, on average, fewer than 3, or from 2.25 to 4, or between 3 and 4, primary carbon atoms per monoolefin molecule in the dehydrogenated product stream.

Linear and/or nonlinear paraffins in the dehydrogenated product stream, have a total number of carbon atoms per paraffin molecule of generally from 8 to 28, preferably from 8 to 15, and more preferably from 10 to 14 carbon atoms. The nonlinear paraffins in the dehydrogenated product stream may include lightly branched paraffins and paraffins having at least one quaternary carbon atom. Such linear and nonlinear paraffins are expected to act as a diluent in the alkylation step and not to materially interfere with the alkylation step. However, the presence of such diluents in the alkylation reactor generally results in higher volumetric flow rates of process streams.

Monoolefins that are more highly branched than the lightly branched monoolefins are preferably minimized in the dehydrogenated product stream. Monoolefin molecules consisting of at least one quaternary carbon atom generally comprise less than 10 mol-%, preferably less than 5 mol-%, more preferably less than 2 mol-%, and most preferably less than 1 mol-% of the dehydrogenated product stream.

The lightly branched monoolefins are reacted with a phenyl compound. In the general case, the lightly branched monoolefins could be reacted with other phenyl compounds besides benzene, such as alkylated or otherwise substituted derivatives of benzene including toluene and ethylbenzene, but the preferred phenyl compound is benzene. Although the stoichiometry of the alkylation reaction requires only 1 molar proportion of phenyl compound per mole of total monoolefins, the use of a 1:1 mole proportion results in excessive olefin polymerization and polyalkylation. On the other hand, it is desired to have the phenyl compound:monoolefin molar

ratio as close to 1:1 as possible to maximize utilization of the phenyl compound and to minimize the recycle of unreacted phenyl compound. The actual molar proportion of phenyl compound to total monoolefin will have an important effect on both conversion and, selectivity of the alkylation reaction.

- 5 The total phenyl compound: monoolefin molar ratio may be generally from 2.5:1 up to 50:1 and normally from 8:1 to 35:1.

The phenyl compound and the lightly branched monoolefin are reacted under alkylation conditions in the presence of a solid alkylation catalyst. These alkylation conditions include a temperature in the range
10 between 80°C and 200°C, usually not exceeding 175°C. Since the alkylation is conducted in at least partial liquid phase, and preferably in either an all-liquid phase or at supercritical conditions, pressures for this embodiment must be sufficient to maintain reactants in the liquid phase. The requisite pressure necessarily depends upon the olefin, the phenyl
15 compound, and temperature, but normally is in the range of 1379-6895 kPa(g), and most usually 2069-3448 kPa(g).

While the alkylation conditions are sufficient to alkylate the phenyl compound with the lightly branched monoolefin, it is believed that under alkylation conditions only minimal skeletal isomerization of the lightly
20 branched monoolefin occurs. Skeletal isomerization of an olefin under alkylation conditions means isomerization that occurs during alkylation and which changes the number of carbon atoms in the aliphatic alkenyl chain of the olefin, in the aliphatic alkyl chain of the phenyl-alkane product, or in any reaction intermediate that is formed or derived from the lightly branched
25 monoolefin prior to the withdrawal of the phenyl-alkane product from the alkylation conditions. Generally less than 15 mol-%, and preferably less than 10 mol-%, of the olefin, the aliphatic alkyl chain, and any reaction intermediate undergoes skeletal isomerization. It is further believed that under alkylation conditions minimal skeletal isomerization occurs for any
30 other olefins in the olefinic feedstock. Thus, alkylation preferably occurs in the substantial absence of skeletal isomerization of the lightly branched

monoolefin, and the extent of light branching of the lightly branched monoolefin is identical to the extent of light branching in the aliphatic alkyl chain in the phenyl-alkane product molecule. Accordingly, the number of primary carbon atoms in the lightly branched monoolefin is preferably the same as the number of primary carbon atoms per phenyl-alkane molecule. However, the number of primary carbon atoms in the phenyl-alkane product may be slightly higher than or slightly less than the number of primary carbon atoms in the lightly branched monoolefin.

The alkylation of the phenyl compound with the lightly branched monoolefins produces $(m_i\text{-alkyl})_i\text{-n-phenyl-alkanes}$, where the aliphatic alkyl group has two, three, or four primary carbon atoms per phenyl-alkane molecule. Preferably, the aliphatic alkyl group has three primary carbon atoms per phenyl-alkane molecule, and more preferably one of the three primary carbon atoms is in a methyl group at one end of the aliphatic alkyl chain, the second primary carbon atom is in a methyl group at the other end of the chain, and the third primary carbon atom is in a single methyl group branch attached to the chain. Generally from 0 mol-% to 75 mol-%, and preferably from 0 mol-% to 40 mol-%, of the $(m_i\text{-alkyl})_i\text{-n-phenyl-alkanes}$ produced may have 2 primary carbon atoms per phenyl-alkane molecule. Generally, as many as possible, and typically from 25 mol-% to 100 mol-%, of the $(m_i\text{-alkyl})_i\text{-n-phenyl-alkanes}$ produced may have 3 primary carbon atoms per phenyl-alkane molecule. Generally from about 0 mol-% to 40 mol-% of the $(m_i\text{-alkyl})_i\text{-n-phenyl-alkanes}$ produced may have 4 primary carbon atoms. Monomethyl-phenyl-alkanes are preferred. The number of primary, secondary, and tertiary carbon atoms per product phenyl-alkane molecule can be determined by high resolution multipulse nuclear magnetic resonance (NMR) spectrum editing and distortionless enhancement by polarization transfer (DEPT). Reference may be made to the brochure entitled "High Resolution Multipulse NMR Spectrum Editing and DEPT," which is distributed by Bruker Instruments, Inc., Manning Park, Billerica, Massachusetts, USA, for additional information.

The alkylation of the phenyl compound with the lightly branched monoolefins has a selectivity of 2-phenyl-alkanes of generally from 40 to 100 and preferably from 60 to 100, and an internal quaternary phenyl-alkane selectivity of generally less than 10 and preferably less than 5. Quaternary phenyl-alkanes can form by alkylating the phenyl compound with a lightly branched monoolefin having at least one tertiary carbon atom. The resulting quaternary phenyl-alkane may be either an internal or an end quat.

Alkylation of the phenyl compound by the lightly branched monoolefins may be conducted either as a batch method or, preferably, in a continuous manner. The alkylation catalyst may be used as a packed bed or a fluidized bed. The olefinic feedstock to the reaction zone may be passed either upflow or downflow, or even horizontally as in a radial bed reactor. The admixture of benzene and the olefinic feedstock containing the lightly branched monoolefins is introduced at a total phenyl compound:monoolefin molar ratio of between 2.5:1 and 50:1, although usually between 8:1 and 35:1. Olefin may be fed into several discrete points within the reaction zone, and at each zone the phenyl compound:monoolefin molar ratio may be greater than 50:1 while the total benzene:olefin ratio still will be within the stated range. The total feed mixture, that is, phenyl compound plus olefinic feedstock containing lightly branched monoolefins, is passed through the packed bed at a liquid hourly space velocity (LHSV) between 0.3 and 6 hr⁻¹ depending upon alkylation temperature, how long the catalyst has been used, and so on. Lower values of LHSV within this range are preferred. The temperature in the reaction zone will be maintained at between 80°C and 200°C, and pressures generally will vary between 1379 and 6895 kPa(g) to ensure a liquid phase or supercritical conditions. After passage of the phenyl compound and the olefinic feedstock through the reaction zone, the effluent is collected and separated into unreacted phenyl compound which is recycled to the feed end of the reaction zone, paraffin which is recycled to the dehydrogenation unit, and phenyl-alkanes. The phenyl-alkanes are usually further separated into the monoalkylbenzenes, used in subsequent

sulfonation to prepare alkylbenzene sulfonates, and the oligomers plus polyalkylbenzenes. Since the reaction usually goes to at least about 98% conversion based on the monoolefin, little unreacted monoolefin is recycled with paraffin.

5 Any suitable alkylation catalyst may be used in the present invention, provided that the requirements for conversion, selectivity, and activity are met. Preferred alkylation catalysts comprise zeolites having a zeolite structure type selected from the group consisting of BEA, MOR, MTW, and NES. Such zeolites include mordenite, ZSM-4, ZSM-12, ZSM-20, offretite,
10 gmelinite, beta, NU-87, and gottardiite. These zeolite structure types, the term "zeolite structure type," and the term "isotypic framework structure" are used herein as they are defined and used in the Atlas of Zeolite Structure Types, by W. M. Meier, et al., published on behalf of the Structure Commission of the International Zeolite Association by Elsevier, Boston,
15 Massachusetts, USA, Fourth Revised Edition, 1996. Alkylations using NU-87 and NU-85, which is an intergrowth of zeolites EU-1 and NU-87, are described in US-A-5,041,402 and US-A-5,446,234, respectively. Gottardiite, which has an isotypic framework structure of the NES zeolite structure type, is described in the articles by A. Alberti et al., in Eur. J. Mineral., 8, 69-75
20 (1996), and by E. Galli et al., in Eur. J. Mineral., 8, 687-693 (1996). Most preferably, the alkylation catalyst comprises mordenite.

Useful zeolites for the alkylation catalyst generally have at least 10 percent of the cationic sites thereof occupied by ions other than alkali or alkaline-earth metals. Such other ions include, but are not limited to
25 hydrogen, ammonium, rare earth, zinc, copper, and aluminum. Of this group, particular preference is accorded ammonium, hydrogen, rare earth, or combinations thereof. In a preferred embodiment, the zeolites 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.,
30 ammonium ions, which upon calcination yield the hydrogen form. This exchange is conveniently carried out by contact of the zeolite with an

ammonium salt solution, e.g., ammonium chloride, utilizing well known ion exchange techniques. In certain embodiments, the extent of replacement is such as to produce a zeolite material in which at least 50 percent of the cationic sites are occupied by hydrogen ions.

5 The zeolites may be subjected to various chemical treatments, including alumina extraction (dealumination) and combination with one or more metal components, such as the metals of Groups IIIB (IUPAC 3), IVB (IUPAC 4), VIB (IUPAC 6), VIIB (IUPAC 7), VIII (IUPAC 8-10), and IIB (IUPAC 12). It is also contemplated that the zeolites may, in some
10 instances, desirably be subjected to thermal treatment, including steaming or calcination in air, hydrogen, or an inert gas, e.g. nitrogen or helium. A suitable steaming treatment comprises contacting the zeolite with an atmosphere containing from 5 to 100% steam at a temperature of from 250°C to 1000°C. Steaming may last for a period of between 0.25 and 100
15 hours and may be conducted at pressures ranging from sub-atmospheric to several hundred atmospheres.

 It may be useful to incorporate the zeolites that are useful in this invention in another material, e.g., a matrix material or binder that is resistant to the temperature and other conditions used in the process. Suitable matrix
20 materials include synthetic substances, naturally occurring substances, and inorganic materials such as clay, silica, and/or metal oxides. Matrix materials can be in the form of gels including mixtures of silica and metal oxides. Gels including mixtures of silica and metal oxides may be either naturally occurring or in the form of gels or gelatinous precipitates. Naturally occurring
25 clays which can be composited with the zeolite used in this invention include those of the montmorillonite and kaolin families, which families include the sub-bentonites and the kaolins commonly known as Dixie, McNamee-Georgia, and Florida clays or others in which the main mineral constituent is halloysite, kaolinite, dickite, nacrite, or anauxite. Such clays can be used as
30 a matrix material in their raw states as originally mined, or can be subjected to calcination, acid treatment or chemical modification prior to their use as

matrix materials. In addition to the foregoing materials, the zeolite used in this invention may be compounded with a porous matrix material, such as alumina, silica-alumina, silica-magnesia, silica-zirconia, silica-thoria, silica-beryllia, silica-titania, and aluminum phosphate as well as ternary combinations, such as silica-alumina-thoria, silica-alumina-zirconia, silica-alumina-magnesia, and silica-magnesia-zirconia. The matrix material may be in the form of a cogel. The relative proportions of and matrix material may vary widely, with the zeolite content ranging generally from between 1 and 99% by weight, usually in the range of 5 to 80% by weight, and preferably in the range of 30 to 80% by weight, of the combined weight of zeolite and matrix material.

The zeolites that are useful in the alkylation catalyst generally have a framework silica:alumina molar ratio of from 5:1 to 100:1. When the zeolite of the alkylation catalyst is mordenite, the mordenite has a framework silica:alumina molar ratio generally of from 12:1 to 90:1, and preferably of from 12:1 to 25:1. The term "framework silica:alumina molar ratio" means the molar ratio of silica per alumina, that is the molar ratio of SiO_2 per Al_2O_3 , in the zeolite framework.

When zeolites have been prepared in the presence of organic cations they may not be sufficiently catalytically active for alkylation. Without being bound to any particular theory, it is believed that the insufficient catalytic activity is the result of the organic cations from the forming solution occupying the intracrystalline free space. Such catalysts may be activated, for example, by heating in an inert atmosphere at 540°C for one hour, ion exchanging with ammonium salts, and calcining at 540°C in air. The presence of organic cations in the forming solution may be essential to forming particular zeolites. Some natural zeolites may sometimes be converted to zeolites of the desired type by various activation procedures and other treatments such as ion exchange, steaming, alumina extraction, and calcination. When synthesized in the alkali metal form, the zeolite is conveniently converted to the hydrogen form, generally by intermediate

formation of the ammonium form as a result of ammonium ion exchange and calcination of the ammonium form to yield the hydrogen form. Although the hydrogen form of the zeolite catalyzes the reaction successfully, the zeolite may also be partly in the alkali metal form.

5 The selective alkylation zone produces a selective alkylation zone effluent that enters separation facilities for the recovery of products and recyclable feed compounds. The selective alkylation zone effluent stream passes into a benzene column which produces an overhead stream containing benzene and a bottoms stream containing the alkylate product.
10 This bottoms stream passes into a paraffin column which produces an overhead liquid stream containing unreacted paraffins and a bottoms stream containing the product alkylate and any higher molecular weight side product hydrocarbons formed in the selective alkylation zone. This paraffin column bottoms stream may pass to a rerun column which produces an overhead
15 alkylate product stream containing the detergent alkylate and a rerun column bottoms stream containing polymerized olefins and polyalkylated benzenes (heavy alkylate). Alternatively, if the heavy alkylate content of the paraffin column bottoms stream is sufficiently low, a rerun column is not necessary and the paraffin column bottoms stream may be recovered as the net
20 detergent alkylate stream from the process.

 In accord with this invention, at least a portion of the overhead liquid stream of the paraffin column is recycled to the isomerization zone, the dehydrogenation zone, or both zones. Preferably, the portion of the overhead liquid stream of the paraffin column that is recycled to the
25 isomerization zone or the dehydrogenation zone is an aliquot portion of the overhead liquid stream. An aliquot portion of the overhead liquid stream is a fraction of the overhead liquid stream that has essentially the same composition as the overhead liquid stream. The paraffin column overhead stream comprises paraffins having a total number of carbon atoms per
30 paraffin molecule of generally from 8 to 28, preferably from 8 to 15, and more preferably from 10 to 15 carbon atoms. Preferably, at least a portion of

the paraffin column overhead liquid stream is recycled to only the dehydrogenation zone. Generally, from 50 to 100 wt-% of the overhead liquid stream of the paraffin column is recycled to the isomerization zone and/or the dehydrogenation zone, and preferably all of the overhead liquid stream of the paraffin column is recycled to only the dehydrogenation zone.

Regardless of whether recycling is to the isomerization zone or the dehydrogenation zone, the overhead stream of the paraffin column may contain both nonbranched (linear) paraffins and lightly branched paraffins, even if only nonbranched paraffins are charged to the process. This is because the skeletal isomerization zone typically converts from 60 wt-% to 80 wt-% of the entering nonbranched paraffins to lightly branched paraffins, the dehydrogenation zone typically converts from 10 wt-% to 15 wt-% of the entering paraffins to olefins, and the fraction of olefins in the dehydrogenated product stream that are lightly branched olefins is approximately the same as the fraction of paraffins in the isomerized product stream that are lightly branched paraffins. Thus, since the conversion of olefins in the alkylation zone is generally greater than 90 wt-% of the entering olefins, and more typically greater than 98 wt-%, and since the conversion of paraffins in the alkylation zone is essentially nil, the alkylation zone effluent will contain lightly branched paraffins. To illustrate this in operation, it is helpful to consider the initial operation of the subject process where only linear paraffins are charged to the isomerization zone and the isomerization zone converts x wt-%, of the entering nonbranched paraffins to lightly branched paraffins. Lightly branched paraffins will begin to appear in the overhead stream of the paraffin column. As these lightly branched paraffins are recycled to the isomerization zone, the mixture of paraffins charged to the isomerization zone will gradually shift from a mixture of only nonbranched paraffins to a mixture of nonbranched and lightly branched paraffins. Accordingly, the isomerization zone may then be operated at conditions so that the nonlinear paraffin conversion is less than x wt-%. Over time, the degree of isomerization conversion can be further adjusted until a steady state is established at which the rate of conversion of

nonbranched paraffins to lightly branched paraffins in moles per unit time in the isomerization zone is approximately equal to the net rate at which MAB phenyl-alkanes are recovered from the process.

The concentration of monoolefins in the paraffin column overhead liquid stream is generally less than 0.3 wt-%. Monoolefins in the paraffin column overhead liquid stream may be recycled to the isomerization zone and/or the dehydrogenation zone. The concentration of paraffins having at least one quaternary carbon atom in the paraffin column overhead liquid stream is preferably minimized.

One variant of the process of this invention includes the selective hydrogenation of diolefins in the dehydrogenated product stream, since diolefins may be formed during the catalytic dehydrogenation of paraffins. Selective diolefin hydrogenation converts the diolefins to monoolefins, and produces a selective diolefin hydrogenation product stream that has a lower concentration of diolefins than the dehydrogenated product stream.

Another variant of the process of the instant invention includes selective removal of aromatic by-products in the dehydrogenated product stream. Aromatic by-products may be formed during the catalytic dehydrogenation of paraffins, and these by-products may cause a number of deleterious effects in the process. Suitable aromatics removal zones include sorptive separation zones containing a sorbent such as a molecular sieve and in particular 13X zeolite (sodium zeolite X), and liquid-liquid extraction zones. The aromatic by-products may be selectively removed from the dehydrogenated product stream, but also, or instead, the isomerized product stream and/or the overhead liquid stream of the paraffin column that is recycled to the isomerization zone or the dehydrogenation zone. Where the subject process includes a selective diolefin hydrogenation zone the aromatic byproducts may be selectively removed from the selective diolefin hydrogenation product stream. Although the selective removal of these aromatic by-products is preferably accomplished on a continuous basis,

selective removal may also be done intermittently or on a batch-wise basis. Detailed information on selective removal of aromatic by-products from an alkylaromatic process for the production of LAB is disclosed in US-A-5,276,231, which is incorporated herein by reference and may be referred to
5 for additional information. It is believed that a person of ordinary skill in the art is capable of modifying the teachings of US-A-5,276,231 with respect to aromatic by-products removal, so as to successfully remove aromatic by-products from a process for the production of MAB.

10 In another aspect of the present invention, this invention is the MAB compositions produced by the processes disclosed herein.

In yet another aspect of the present invention, this invention is the use of the MAB compositions produced by the processes disclosed herein as lubricants. These phenyl-alkanes are believed to have properties of viscosity, temperature-dependence of viscosity, and density that make them
15 advantageous for use as petroleum lubricants. The use of phenyl-alkanes as lubricants is described, for example, in the article by E. R. Booser in Kirk-Othmer Encyclopedia of Chemical Technology, Fourth Edition, Volume 15, John Wiley and Sons, New York, New York, USA, 1995, pp. 463-517, to which reference may be made for a description of such lubricants and their
20 use.

The drawing shows a preferred arrangement for an integrated isomerization-dehydrogenation-alkylation scheme of this invention.

A paraffin feed comprising an admixture of C₁₀-C₁₃ normal paraffins is charged to a line 12. The normal paraffins in line 12 are admixed with a
25 hydrogen-containing stream from line 22 and the admixture passes through line 16. A mixture of paraffins and hydrogen flowing through line 16 is first heated in the indirect heat exchanger 18 and is then passed through a line 24 into a fired heater 20. Alternatively, instead of admixing the hydrogen-containing stream in line 22 with the normal paraffins upstream of both
30 exchanger 18 and heater 20 as shown in the drawing, the stream in line 22

may be admixed with the normal paraffins between the exchanger 18 and the heater 20 or between the heater 20 and the reactor 30. The resultant mixture of hydrogen and liquid paraffins passes through line 26 into an isomerization reactor 30. Inside the reactor 30, the paraffins are contacted in the presence of an isomerization catalyst at conditions which effect the conversion of a significant amount of the normal paraffins to lightly branched paraffins. There is thus produced an isomerization reactor effluent stream carried by line 28 which comprises a mixture of hydrogen, normal paraffins, and lightly branched paraffins. This isomerization reactor effluent stream is first cooled by indirect heat exchanger in the heat exchanger 18 and after passing through a line 32 is then further cooled in an indirect heat exchanger 34. This cooling is sufficient to condense substantially all of the C₁₀-plus hydrocarbons into a liquid phase stream and to separate the liquid phase stream from the remaining vapor, which is rich in hydrogen. This isomerization reactor effluent stream then passes through a line 36 and enters the vapor-liquid separation vessel 38, wherein it is divided into a hydrogen-rich vapor phase stream removed through line 40 and an isomerized product stream removed through line 50. The vapor phase stream is divided into a net purge stream to remove C₁-C₇ light hydrocarbons through a line 42 and a hydrogen stream that is recycled by line 44. The hydrogen stream in line 44 is combined with a hydrogen make-up stream that is charged to line 46. The combination of the hydrogen stream in line 44 and the make-up stream in line 46 produces the recycle stream in line 22.

The isomerized product stream removed from the bottom of the separation vessel 38 contains normal paraffins, lightly branched paraffins, and some dissolved hydrogen. The isomerized product stream, which is the liquid phase portion of the effluent of the separation vessel 38, is then passed through line 50 to combine with recycle paraffins in a line 48. The combined stream of paraffins flows through a line 54 and is admixed with recycled hydrogen from a line 82 to form a mixture of paraffins and hydrogen that flows through a line 56. The mixture of paraffins and hydrogen flowing

through the line 56 is first heated in an indirect heat exchanger 58 and then passes through a line 62 to a fired heater 60. The two-phase mixture of hydrogen and liquid paraffins that is withdrawn from the fired heater 60 passes through a line 64 into a dehydrogenation reactor 70. Inside the dehydrogenation reactor 70, the paraffins contact a dehydrogenation catalyst at conditions which effect the conversion of a significant amount of the paraffins to the corresponding olefins. There is thus produced a dehydrogenation reactor effluent stream carried by line 66 which comprises a mixture of hydrogen, paraffins, monoolefins including lightly branched monoolefins, diolefins, C₉-minus hydrocarbons, and aromatic hydrocarbons. This dehydrogenation reactor effluent stream is first cooled by indirect heat exchange in the heat exchanger 58, passes through a line 68, and is then further cooled in an indirect heat exchanger 72. This cooling is sufficient to condense substantially all of the C₁₀-plus hydrocarbons into a liquid phase stream and separate the liquid phase stream from the remaining hydrogen-rich vapor. This dehydrogenation reactor effluent stream flows through a line 74 and enters the vapor-liquid separation vessel 80. In the separation vessel 80, the dehydrogenation reactor effluent stream is divided into a hydrogen-rich vapor phase stream removed through a line 76 and a dehydrogenation product stream removed through a line 84. The vapor phase stream is divided into a net hydrogen product stream removed through a line 78 and the hydrogen-containing stream that is recycled by the line 82.

The dehydrogenated product stream removed from the bottom of the separation vessel 80 contains normal paraffins, lightly branched paraffins, normal monoolefins, lightly branched monoolefins, C₉-minus hydrocarbons, diolefins, aromatic by-products, and some dissolved hydrogen. The dehydrogenated product stream, which is the liquid phase effluent of the separator vessel 80, is then passed through a line 84 to a selective hydrogenation reactor 86. Inside the selective hydrogenation reactor 86, the dehydrogenated product stream is contacted in the presence of a selective hydrogenation catalyst at conditions which effect the conversion of a

significant amount of the diolefins to the corresponding monoolefins. This conversion by hydrogenation can be effected using the dissolved hydrogen in the dehydrogenated product stream and/or additional make-up hydrogen (not shown) charged to the selective hydrogenation reactor. There is thus
5 produced a selective hydrogenation reactor effluent stream carried by a line 88, which comprises a mixture of hydrogen, normal paraffins, lightly branched paraffins, normal monoolefins, lightly branched monoolefins, C₉-minus hydrocarbons, and aromatic by-product hydrocarbons. This selective hydrogenation reactor effluent is then passed through the line 88 to a
10 stripping column 90. In this stripping column, the C₉-minus hydrocarbons produced in the dehydrogenation reactor as by-products and any remaining dissolved hydrogen are separated from the C₁₀-plus hydrocarbons and concentrated into a net overhead stream removed from the process through a line 94.

15 The remainder of the hydrocarbons entering the stripping column 90 are concentrated into a stripping effluent stream carried by a line 96. The stripping effluent stream is then passed into an aromatics removal zone 100. In this zone, the stripping effluent stream is contacted with an adsorbent under conditions which promote the removal of the aromatic by-products.
20 The effluent from the aromatics removal zone 100 is transferred via a line 98. This stream comprises an admixture of the normal paraffins, lightly branched paraffins, normal monoolefins, and lightly branched monoolefins, and has a greatly reduced concentration of aromatic by-products compared to the stripping effluent stream. This admixture is combined with benzene from a
25 line 112 and passed via a line 102 into an alkylation reactor 104. In the alkylation reactor, benzene and the monoolefins are contacted with an alkylation catalyst at alkylation-promoting conditions to produce phenyl-alkanes.

The alkylation reactor effluent stream is carried by a line 106 and
30 passes into a benzene fractionation column 110 by a line 106. This stream comprises an admixture of benzene, normal paraffins, lightly branched

paraffins, phenyl-alkanes comprising one phenyl portion and one aliphatic alkyl portion having 1 or 2 primary carbon atoms, and phenyl-alkanes comprising one aliphatic alkyl portion and one phenyl portion where the aliphatic alkyl portion has 2, 3, or 4 primary carbon atoms and has no quaternary carbon atoms except for any quaternary carbon atom bonded to the phenyl portion. In other words, this stream comprises an admixture of benzene, normal paraffins, lightly branched paraffins, LAB, and MAB. This stream is separated in benzene fractionation column 110 into a bottom stream and an overhead stream comprising benzene and possibly light gases. The overhead stream is carried by a line 107 and combines with make-up benzene charged to a line 109. The combined stream flows through a line 108 to a separator drum 120 from which noncondensed light gases, if any, are removed via a line 114 and condensed liquid is withdrawn by a line 116 to supply reflux to column 110 via a line 118 and benzene for recycle by a line 112. A line 122 carries the remainder of the alkylation effluent stream from column 110 to a paraffin column 124 from which a bottom stream containing the phenyl-alkanes and heavy alkylate by-products is taken by a line 126. The contents of line 126 are separated in a rerun column 130 into a bottom stream 132 comprising heavy alkylate and an overhead alkylate product stream 128 containing the phenyl-alkane compounds. The overhead stream from the paraffin column 124 is a recycle stream that contains a mixture of paraffins that are recycled to the dehydrogenation zone via the line 48. Although not shown in the drawing, some of the overhead stream from the paraffin column 124 may be passed to the isomerization zone rather than to the dehydrogenation zone.

As alternatives to the process flow shown in the drawing, the overhead stream in line 48 may be introduced into the dehydrogenation zone at other locations, such as into line 62, line 64, or reactor 70. In the case where the location is the dehydrogenation reactor 70, the overhead stream may be introduced at an intermediate point between the inlet of line 64 and the outlet of line 66, so that the overhead stream might contact only a portion

of the catalyst in the dehydrogenation reactor 70. Another way of contacting the overhead stream with some but not all of the dehydrogenation catalyst is to divide the dehydrogenation reactor 70 into two or more catalyst-containing subreactors connected in a series flow arrangement by one or more lines, and to introduce the overhead stream into a line between subreactors. Whether an intermediate introduction point in the dehydrogenation reactor 70 is preferred depends on factors including the olefin content of the overhead stream and the dehydrogenation reaction conditions including conversion. Similarly, in the embodiment where the overhead stream in line 48 is introduced to the isomerization zone, the point of introduction may be upstream of the inlet of line 26 to the isomerization reactor 30 so that the overhead stream might contact all of the catalyst in the isomerization reactor 30. However, depending on the isomerization reaction conversion, the degree of branching of the overhead stream in line 48, and other factors, the point of introduction may be an intermediate point between the inlet of line 26 and the outlet of line 28, thereby resulting in the overhead stream contacting only some of the catalyst in the isomerization reactor 30. The isomerization reactor 30 may be divided into two or more smaller reactors in series, so that the overhead stream may be introduced to pass through some but not all of the isomerization reactors. By analyzing the composition of the isomerized product, dehydrogenated product, and alkylate product streams, a person of ordinary skill in the art is able to select the preferred point of introduction for recycling the overhead stream into the process.

Sulfonation of the phenyl-alkane compounds in the overhead alkylate product stream 128 can be accomplished as hereinbefore described to produce phenyl-alkane sulfonic acids, which can be neutralized as hereinbefore described.

The following examples are presented to illustrate the benefit and advantages associated with the instant invention.

EXAMPLES

Examples 1 and 2 illustrate the use of preferred isomerization catalysts for this invention. The following procedure was employed in both Examples 1 and 2. A 20 cc sample of isomerization catalyst was placed in a tubular reactor having an inside diameter of 1.27 cm. The isomerization catalyst was pre-reduced by contact with 0.27 Nm³/h of hydrogen at 69 kPa(g) while the catalyst temperature was held at 110°C for 1 hour, increased from 110°C to 400°C over 3 hours, and then held at 400°C for 2 hours. After this pre-reduction, the isomerization catalyst was cooled to 150°C.

Next, the catalyst was tested for isomerization using a feed mixture of C₁₀-C₁₄ linear paraffins. The feed mixture ("feed") was passed over the isomerization catalyst at a LHSV of 5 hr⁻¹, at a molar ratio of hydrogen per hydrocarbon of 1.5:1, and at a pressure of 3447 kPa(g). The catalyst temperature was adjusted to achieve a desired conversion of the linear paraffins. The effluent of the tubular reactor was passed to a gas-liquid separator, and a liquid phase ("product") was collected from the separator. The product was analyzed by gas chromatography as already described herein.

The individual components determined by gas chromatograph of the feed and the product were grouped into five classifications for purposes of Examples 1 and 2: light products having 9 or less carbon atoms (C₉-); linear paraffins having 10 to 14 carbon atoms ("linear"); monomethyl-branched paraffins having 10 to 14 carbon atoms in the product ("mono"); dimethyl-branched paraffins and ethyl-branched paraffins having 10 to 14 carbon atoms in the product ("di"); and heavy products having 15 or more carbon atoms (C₁₅+). Based on these five groupings, the following performance measures were computed:

i. Conversion:

$$\text{Conversion} = 100 \times [1 - (\text{linears in product})/(\text{linears in feed})].$$

ii. Monomethyl selectivity:

Monomethyl selectivity = $100 \times [\text{mono}/(\text{mono} + \text{di})]$.

iii. Lights yield:

Lights yield = $100 \times [C_9-/ (C_9- + (\text{linears in product}) + \text{mono} + \text{di} + C_{15+})]$.

iv. Heavies yield:

5 Heavies yield = $100 \times [C_{15+}/ (C_9- + (\text{linears in product}) + \text{mono} + \text{di} + C_{15+})]$.

EXAMPLE 1

The catalyst for Example 1 was prepared by coextruding 0.39 wt-% Pt on a support comprising an extrudate of 60 wt-% SAPO-11 and 40 wt-% alumina. During isomerization, the conversion was 73.4 mol-%, the monomethyl selectivity was 55.5 mol-%, the lights yield was 7.9 mol-%, and the heavies yield was 0.01 mol-%.

EXAMPLE 2

15 The catalyst for Example 2 was prepared by impregnating 0.26 wt-% Pt with 50 wt-% MgAPSO-31 and 50 wt-% alumina. During isomerization, the conversion was 73.3 mol-%, the monomethyl selectivity was 69.6 mol-%, the lights yield was 13.5 mol-%, and the heavies yield was less than 0.01 mol-%.

20 Examples 1 and 2 show the good conversion and high selectivity to monomethyl paraffins that can be achieved with isomerization catalysts comprising SAPO-11 and MgAPSO-31.

EXAMPLE 3

Example 3 illustrates a preferred dehydrogenation catalyst for use in this invention, and a method of preparing the catalyst. Alumina spheres were prepared by the well known oil drop method which is described in US-
5 A- 2,620,314 which is incorporated by reference. This process involves forming an aluminum hydrosol by dissolving aluminum in hydrochloric acid. Hexamethylene tetraamine was added to the sol to gel the sol into spheres when dispersed as droplets into an oil bath maintained at 93°C. The droplets remained in the oil bath until they set and formed hydrogel
10 spheres. After the spheres were removed from the hot oil, they were pressure aged at 135°C and washed with dilute ammonium hydroxide solution, dried at 110°C, and calcined at 650°C for 2 hours to give gamma alumina spheres. The calcined alumina was crushed into a fine powder having a particle size of less than 200 microns (0.2 mm).

15 Next, a slurry was prepared by mixing 258 g of an aluminum sol (20 wt-% Al_2O_3) and 6.5 g of a 50% aqueous solution of tin chloride and 464 g of deionized water and agitated to uniformly distribute the tin component. To this mixture there were added 272 g of the above prepared alumina powder, and the slurry was ball milled for 2 hours thereby reducing the maximum
20 particle size to less than 40 microns (0.04 mm). This slurry (1000 g) was sprayed onto 1 kg of alpha alumina cores having an average diameter of about 1.05 mm by using a granulating and coating apparatus for 17 minutes to give an outer layer of about 74 microns (0.074 mm). At the end of the process, 463 g of slurry were left which did not coat the cores. This layered
25 spherical support was dried at 150°C for 2 hours and then calcined at 615°C for 4 hours in order to convert the pseudoboehmite in the outer layer into gamma alumina and convert the tin chloride to tin oxide.

The calcined layered support (1150 g) was impregnated with lithium using a rotary impregnator by contacting the support with an aqueous

solution (1:1 solution: support volume ratio) containing lithium nitrate and 2 wt-% nitric acid based on support weight. The impregnated catalyst was heated using the rotary impregnator until no solution remained, dried, and then calcined at 540°C for 2 hours.

5 The tin and lithium containing composite was now impregnated with platinum by contacting the above composite with an aqueous solution (1:1 solution: support volume ratio) containing chloroplatinic acid and 1.2 wt-% hydrochloric acid (based on support weight). The impregnated composite was heated using the rotary impregnator until no solution remained, dried,
10 calcined at 540°C for 2½ hours, and reduced in hydrogen at 500°C for 2 hours. Elemental analysis showed that this catalyst contained 0.093 wt-% platinum, 0.063 wt-% tin and 0.23 wt-% lithium with respect to the entire catalyst. The distribution of the platinum was determined by Electron Probe Micro Analysis (EPMA) using a Scanning Electron Microscope which showed
15 that the platinum was evenly distributed throughout the outer layer only.

EXAMPLE 4

 The catalyst of Example 3 was tested for dehydrogenation activity. In a 1.27 cm reactor, 10 cc of catalyst was placed and a hydrocarbon feed composed of 8.8 wt-% n-C₁₀, 40.0 wt-% n-C₁₁, 38.6 wt-% n-C₁₂, 10.8 wt-%
20 n-C₁₃, 0.8 wt-% n-C₁₄ and 1 vol-% non-normals was flowed over the catalyst under a pressure of 138 kPa(g), a hydrogen hydrocarbon molar ratio of 6:1, and a LHSV of 20 hr⁻¹. Water at a concentration of 2000 ppm based on hydrocarbon weight was injected. The total normal olefin concentration in the product (%TNO) was maintained at 15 wt-% by adjusting reactor
25 temperature.

 The results of the testing are as follows. Selectivity for TNO at 120 hours on stream, which is calculated by dividing %TNO by total conversion, is 94.6 wt-%. Non-TNO selectivity, which is calculated as 100% - %TNO, is 5.4 wt-%.

The results show that the layered catalyst useful in this invention has both low deactivation rate and high selectivity to normal olefins. Because the hydrocarbon feed in this example comprised mostly normal paraffins, the high selectivity for TNO indicates that relatively little skeletal isomerization of the hydrocarbon feed occurred during dehydrogenation.

EXAMPLE 5

Example 5 illustrates an alkylation catalyst for use in this invention that was formulated by a method consistent with that of an alkylation catalyst. The starting material was the hydrogen form of a mordenite having a $\text{SiO}_2/\text{Al}_2\text{O}_3$ of 18, hereinafter referred to as the starting mordenite. 90 parts by weight of the starting mordenite were mixed with 10 parts by weight of alumina powder. An acidified peptization solution was added to the mixture. The admixture was then extruded by means known in the art. After the extrusion process, the extrudate was dried and calcined. Following the drying and calcining steps, the extrudate was washed with an aqueous solution comprising 3 wt-% HCl for 2 hours at 66°C at a solution to extrudate volume ratio of about 6:1. After the wash step, the extrudate was rinsed for 1 hour with water at a solution to extrudate volume ratio of about 5:1, and then dried.

EXAMPLE 6

Example 6 illustrates the use of the alkylation catalyst in Example 5.

An olefinic feedstock comprising a blend of monomethyl C_{12} olefins and having the composition shown in Table 1 was used.

Table 1: Composition of Olefinic Feedstock

Olefin Component	Content (wt-%)
Lights ¹	0.64
Linear olefins ²	30.11
6-methyl undecene	7.66
5-methyl undecene	15.33
4-methyl undecene	11.82
3-methyl undecene	12.95
2-methyl undecene	8.87
Other alkyl olefins ³	9.05
Heavies ⁴	3.53
Total	99.96

¹ Lights include olefins having fewer than 12 carbon atoms.

² Linear olefins include C₁₂ linear olefins.

³ Other alkyl olefins include dimethyl, trimethyl, and other C₁₂ olefins

⁴ Heavies include C₁₂ olefin dimers and trimers.

The olefinic feedstock was mixed with benzene to produce a combined feedstock consisting of 93.3 wt-% benzene and 6.7 wt-% olefinic feedstock, which corresponds to a molar ratio of benzene per olefin of about 30:1. A cylindrical reactor, which has an inside diameter of 22.2 mm, was loaded with 75 cc (53.0 g) of the extrudate prepared in Example 5.

The combined feedstock was passed to the reactor and contacted the extrudate at a LHSV of 2.0 hr⁻¹, a total pressure of 3447 kPa(g), and a reactor inlet temperature of 125°C. At these conditions, the reactor lined out over a period of 24 hours and then a selective liquid product was collected over the period of the next 6 hours.

The selective liquid product was analyzed by ¹³C nuclear magnetic resonance (NMR) in order to determine the selectivity to 2-phenyl-alkanes and end quaternary phenyl-alkanes. The NMR analytical method typically consists of the following. A 0.5 g sample of phenyl-alkane mixture is diluted to 1.5 g with anhydrous deuterated chloroform. A 0.3 milliliter aliquot of the diluted phenyl-alkane mixture is mixed with 0.3 milliliter of 0.1 M chromium

(III) acetylacetonate in deuterated chloroform in a 5 mm NMR tube. A small amount of tetramethylsilane (TMS) is added to the mixture as a 0.0 ppm chemical shift reference. The spectrum is run on a Bruker ACP-300 FT-NMR spectrometer, which is available from Bruker Instruments, Inc.,
5 Billerica, Massachusetts, USA. The carbon spectrum is run at a field strength of 7.05 Tesla or 75.469 MHz in a 5 mm QNP probe with a sweep width of 22727 Hz (301.1 ppm) and about 65000 data points are collected. The quantitative carbon spectrum is obtained using gated on-acquisition ^1H decoupling (inverse gated decoupling). The quantitative ^{13}C spectrum is run
10 with 7.99 microsecond (90°) pulses, 1.442 second acquisition time, a 5 second delay between pulses, a decoupler power, using composite pulse decoupling (CPD), of 18H with a pulse width of 105 microseconds (90°) and at least 2880 scans. The number of scans used depends on whether benzene is stripped from the liquid product prior to taking the above-
15 mentioned 0.5 g sample. The data processing is done with the Bruker PC software WINNMR-1D, Version 6.0, which is also available from Bruker Instruments, Inc. During data processing a line broadening of 1Hz is applied to the data. Specific peaks are integrated in the region between 152 ppm and 142 ppm. The ^{13}C NMR peak identifications of the chemical shifts of the
20 benzylic carbon of the phenyl-alkane isomers is shown in Table 2. As used herein, the term "benzylic carbon" means the carbon in the ring of the phenyl group that is bound to the aliphatic alkyl group.

Table 2: ¹³C NMR Peak Identifications

CHEMICAL SHIFT OF THE BENZYLIC CARBON (PPM)	PHENYL-ALKANE ISOMER	TYPE OF QUAT ¹
149.6	2-methyl-2-phenyl	End
148.3	4-methyl-2-phenyl	NQ
	m-methyl-m-phenyl, m>3	Internal
148.0	5-methyl-2-phenyl	NQ
147.8	m-methyl-2-phenyl, m>5	NQ
	5-methyl-2-phenyl	NQ
	2-phenyl (linear)	NQ
	3-methyl-3-phenyl	Internal
147.6	4-methyl-2-phenyl	NQ
147.2	3-methyl-2-phenyl	NQ
146.6	3-methyl-2-phenyl	NQ
146.2 - 146.3	m-methyl-4-phenyl, m≠4	NQ
145.9 - 146.2	m-methyl-3-phenyl, m>5	NQ
145.9	3-phenyl (linear)	NQ

¹ NQ = Nonquat

The peak at 148.3 ppm is identified both with 4-methyl-2-phenyl-alkanes and with m-methyl-m-phenyl-alkanes (m>3). However, when the m-methyl-m-phenyl-alkanes (m>3) are present at more than 1%, they are seen as a distinct peak at 0.03 ppm upfield of the peak for the 4-methyl-2-phenyl-alkanes. The peak at 147.8 ppm is considered herein to be identified with the 2-phenyl-alkanes as shown in Table 2, with possible interference from 3-methyl-3-phenyl-alkanes.

The end quaternary phenyl-alkane selectivity is computed by dividing the integral of the peak at 149.6 ppm by the sum of the integrals of all of the peaks listed in Table 2, and multiplying by 100. The 2-phenyl-alkane

selectivity can be estimated if the amount of internal quaternary phenyl-alkanes contributing to the peaks at 148.3 ppm and 147.8 ppm is less than about 2%, as determined by the hereinafter-described gas chromatography/mass spectrometry method. As a first approximation, this condition is met when the sum of the integrals of the 4-phenyl-alkane and 3-phenyl-alkane peaks at 146.2 - 146.3 ppm and 145.9 - 146.2 ppm (respectively) is small relative to the sum of the integrals of all the peaks from 145.9 ppm to 149.6 ppm and the end quaternary phenyl-alkane selectivity is less than 10. When this is the case, the 2-phenyl-alkane selectivity is computed by dividing the sum of integrals of the peaks from 149.6 to 146.6 ppm by the sum of the integrals of all of the peaks listed in Table 2, and multiplying by 100.

The selective liquid product is also analyzed by gas chromatography/mass spectrometry in order to determine the selectivity to internal quaternary phenyl-alkanes. The gas chromatography/mass spectrometry analytical method typically consists of the following. The selective liquid product is analyzed by an HP 5890 Series II gas chromatograph (GC) equipped with an HP 7673 autosampler and an HP 5972 mass spectrometer (MS) detector. An HP Chemstation was used to control the data acquisition and analysis. The HP 5890 Series II, HP 7673, HP 5972, and HP Chemstation, or suitable equivalent hardware and software, are available from Hewlett Packard Company, Palo Alto, California, USA. The GC is equipped with a 30 meter x 0.25 mm DB1HT(df = 0.1 μ m) column or equivalent, which can be obtained from J&W Scientific Incorporated, Folsom, California, USA. Helium carrier gas at 103 kPa(g) and 70°C is used in constant pressure mode. The injector temperature is held at 275°C. The transfer line and MS source temperatures are held at 250°C. An oven temperature program of 70°C for 1 minute, then to 180°C at 1°C per minute, then to 275°C at 10°C per minute, then hold at 275°C for 5 minutes is used. The MS is tuned by the HP Chemstation software with the

software set to standard spectra autotune. The MS detector is scanned from 50-550 Da with a threshold = 50.

5 The concentrations of internal quaternary phenyl-alkanes in the selective liquid product are determined (i.e., the selective liquid product is quantitated) using the method of standard addition. Background information on standard addition methods can be found in Chapter 7 of the book entitled, Samples and Standards, by B. W. Woodget et al., published on behalf of ACOL, London by John Wiley and Sons, New York, in 1987.

10 First, a stock solution of internal quaternary phenyl-alkanes is prepared and quantitated. Benzene is alkylated with a monomethyl alkene using a nonselective catalyst such as aluminum chloride. The nonselective liquid product of this alkylation contains a blend of internal quaternary phenyl-alkanes and is referred to as the stock solution of internal quaternary phenyl-alkanes. Using standard GC methodology, the largest peaks
15 corresponding to internal quaternary phenyl-alkanes in the stock solution are identified, and the concentrations of the internal quaternary phenyl-alkanes in the stock solution are determined (i.e., the stock solution is quantitated) using a flame ionization detector (FID). The concentration of each internal quaternary phenyl-alkane is computed by dividing the area of the peak of
20 that internal quaternary phenyl-alkane by the sum of the areas of all of the peaks.

Next, a spiking solution of internal quaternary phenyl-alkanes is prepared. An aliquot portion of the stock solution is diluted with dichloromethane (methylene chloride) to attain a nominal concentration of
25 100 wppm of one particular internal quaternary phenyl-alkane of interest (e.g., 3-methyl-3-phenyl decane). The solution that results is referred to as the spiking solution of internal quaternary phenyl-alkanes. The concentration of any other particular internal quaternary phenyl-alkane in the spiking solution may be greater or less than 100 wppm, depending on the
30 concentration of that internal quaternary phenyl-alkane in the stock solution.

Third, a sample solution is prepared. A weight of 0.05 g of an aliquot portion of the selective liquid product is added to a 10 milliliter volumetric flask. Then the contents of the flask are diluted with dichloromethane by adding dichloromethane up to the 10 milliliter mark. The resulting contents
5 of the flask are referred to as the sample solution.

Fourth, a resultant solution is prepared. A weight of 0.05 g of an aliquot portion of the selective liquid product is added to a 10 milliliter volumetric flask. The spiking solution is then added to the flask up to the 10 milliliter mark to dilute the contents. The resulting contents of the flask are
10 referred to as the resultant solution.

Both the sample solution and the resultant solution are analyzed by GC/MS using the above-described conditions. Table 3 lists the ions that were extracted from the full MS scan, plotted, and integrated using the HP Chemstation software. The HP Chemstation software is used to determine
15 the individual extracted ion peak areas that correspond to the internal quats listed in Table 3.

TABLE 3:
RATIO OF MASS TO CHARGE OF ION FOR PEAKS OF EXTRACTED
IONS

INTERNAL QUATERNARY PHENYL- ALKANE	NUMBER OF CARBON ATOMS IN ALIPHATIC ALKYL GROUP OF THE INTERNAL QUATERNARY PHENYL-ALKANE	RATIO OF MASS TO CHARGE (M/Z) OF TWO EXTRACTED IONS CORRESPONDING TO INTERNAL QUATERNARY PHENYL-ALKANE
3-methyl-3-phenyl	11	133 and 203
	12	133 and 217
	13	133 and 231
4-methyl-4-phenyl	11	147 and 189
	12	147 and 203
	13	147 and 217
5-methyl-5-phenyl	11	161 and 175
	12	161 and 189
	13	161 and 203

The concentration of each internal quaternary phenyl-alkane in Table 3 is computed using the following formula:

$$C = S \left(\frac{A_1}{A_2 - A_1} \right)$$

where

5 C = concentration of internal quaternary phenyl-alkane in sample solution, wt-%

 S = concentration of internal quaternary phenyl-alkane in spiking solution, wt-%

10 A₁ = peak area of internal quaternary phenyl-alkane in sample solution, area units

 A₂ = peak area of internal quaternary phenyl-alkane in resultant solution, area units

15 The concentrations C and S have the same units, provided that the areas A₁ and A₂ have the same units. Then, the concentration of each internal quaternary phenyl-alkane in the selective liquid product is computed from the concentration of that internal quaternary phenyl-alkane in the sample solution by accounting for the dilution effect of the dichloromethane in the sample solution. In this manner, the concentration in the selective liquid
20 product of each of the internal quaternary phenyl-alkanes in Table 3 is computed. The total concentration of internal quaternary phenyl-alkanes in the selective liquid product, C_{IQPA}, is computed by summing the individual concentrations of each of the internal quaternary phenyl-alkanes in Table 3.

It should be pointed out that the selective liquid product may contain internal quaternary phenyl-alkanes other than those listed in Table 3, such as m-methyl-m-phenyl-alkanes where $m > 5$, depending on the number of carbon atoms in the aliphatic alkyl groups of the phenyl-alkanes. It is believed that, with the C_{12} olefinic feedstock and the conditions of this Example 6, the concentrations of such other internal quaternary phenyl-alkanes are relatively low compared to those of the internal quaternary phenyl-alkanes listed in Table 3. Therefore, for purposes of this Example 6, the total concentration of internal quaternary phenyl-alkanes in the selective liquid product, C_{IQPA} , is computed by summing only the individual concentrations of each of the internal quaternary phenyl-alkanes in Table 3. However, if the olefinic feedstock had comprised olefins having, say, up to 28 carbon atoms, then the total concentration of internal quaternary phenyl-alkanes in the selective liquid product, C_{IQPA} , would be computed by summing individual concentrations of m-methyl-m-phenyl-alkanes, where m is from 3 to 13. In more general terms, if the olefinic feedstock contains olefins having x carbon atoms, then the total concentration of internal quaternary phenyl-alkanes in the selective liquid product, C_{IPQA} , is computed by summing individual concentrations of m-methyl-m-phenyl-alkanes where m is from 3 to $x/2$. At least one peak with a ratio of mass to charge (m/z) of an extracted ion corresponding to each internal quaternary phenyl-alkane can be identified, so that the concentration of all internal quaternary phenyl-alkanes may be determined and then summed to arrive at C_{IQPA} .

The selectivity to internal quaternary phenyl-alkanes in the selective liquid product is computed using the following formula:

$$Q = 100 \left(\frac{C_{IQPA}}{C_{MAB}} \right)$$

where

Q = selectivity to internal quaternary phenyl-alkanes

C_{IQPA} = concentration of internal quaternary phenyl-alkanes in selective liquid product, wt-%

C_{MAB} = concentration of modified alkylbenzenes in selective liquid product, wt-%

5

The concentration of modified alkylbenzenes, C_{MAB} , in the selective liquid product is determined in the following manner. First, the concentration of impurities in the selective liquid product is determined by a gas chromatography method. As used in this context of determining C_{MAB} , the term "impurities" means components of the selective liquid product that lie outside a specific retention time range that is used in the gas chromatography method. "Impurities" generally includes benzene, some dialkylbenzenes, olefins, paraffins, etc.

To determine the amount of impurities from the selective liquid product, the following gas chromatography method is used. Equivalent equipment, equivalent sample preparation, and equivalent GC parameters that are different from those described below but that produce equivalent results to those described below may also be used to determine the amount of impurities in the selective liquid product.

Equipment:

- Hewlett Packard Gas Chromatograph HP 5890 Series II equipped with a split/splitless injector and flame-ionization detector (FID)
- J&W Scientific capillary column DB-1HT, 30 meter length, 0.25 mm inside diameter, 0.1 micro-meter film thickness.
- Restek Corporation (USA) Red lite Septa 11 mm.
- Restek 4 mm Gooseneck inlet sleeve with a carbofrit.
- O-ring for inlet liner Hewlett Packard.
- J. T. Baker Company (USA) HPLC grade methylene chloride or equivalent.

- 2 ml gas chromatograph autosampler vials with crimp tops, or equivalent.

Sample Preparation:

- Weigh 4-5 mg of sample into a 2 ml GC autosampler vial.
- Add 1 ml methylene chloride to the GC vial; seal with crimp vial Teflon lined closures (caps); and mix well.

GC Parameters:

- Carrier gas: hydrogen.
- Column head pressure: 62 kPa
- Flows: column flow, 1 ml/min; split vent, about 3 ml/min; septum purge, 1 ml/min.
- Injection: HP 7673 Autosampler, 10 microliter syringe, 1 microliter injection.
- Injector temperature: 350°C
- Detector temperature: 400°C
- Oven temperature program: initial hold at 70°C for 1 minute; heating rate of 1°C per minute; final hold at 180°C for 10 minutes.

Two standards that have been freshly distilled to a purity of more than 98 mol-% are required for this gas chromatography method. In general, each standard is a 2-phenyl-alkane. One of the 2-phenyl-alkane standards, which is referred to hereinafter as the light standard, has at least one fewer carbon atom in its aliphatic alkyl group than that of the olefin in the olefinic feedstock charged to the alkylation zone that has the fewest number of carbon atoms. The other 2-phenyl-alkane standard, which is referred to hereinafter as the heavy standard, has at least one more carbon atom in its aliphatic alkyl group than that of the olefin in the olefinic feedstock charged to the alkylation zone that has the most number of carbon atoms. For example, if the olefins in the olefinic feedstock that is charged to the alkylation zone have from 10 to 14 carbon atoms, then the suitable standards include 2-phenyl-octane as the light standard and 2-phenyl-pentadecane as the heavy standard.

Each standard is subjected to the gas chromatography method using the conditions specified above to determine its retention time, and the two standard retention times in turn define a retention time range. Then, an aliquot sample of the selective liquid product is analyzed by the gas chromatography method using the above conditions. If more than about 90% of the total GC area is within the retention time range, then the impurities in the selective liquid product are deemed to be not more than about 10 wt-% of the selective liquid product, and, for the sole purpose of computing the selectivity to internal quaternary phenyl-alkanes, C_{MAB} is assumed to be 100 wt-%.

On the other hand, if the percent of the total GC area within the retention time range is not more than about 90%, then the impurities in the selective liquid product are deemed to be more than about 10 wt-% of the selective liquid product. In this case, in order to determine C_{MAB} , impurities are removed from the selective liquid product, and the following distillation method is used. Equivalent equipment, equivalent procedures, and equivalent distillation conditions that are different from those described below but that produce equivalent results to those described below may also be used to remove impurities in the selective liquid product.

The distillation method to remove impurities from the selective liquid product uses a 5-liter, 3-necked round bottom flask with a magnetic stir bar and a few boiling chips. A 24.1 cm long Vigreux condenser is placed in the center neck of the flask. A water cooled condenser is attached to the top of the Vigreux condenser which is fitted with a calibrated thermometer. A vacuum receiving flask is attached to the end of the condenser. A glass stopper is placed in one side arm of the 5-liter flask and a calibrated thermometer is placed in the other side arm. The flask and the Vigreux condenser are wrapped with aluminum foil. To the 5-liter flask is added a weight of 2200 to 2300 g of an aliquot portion of the selective liquid product which contains about 10 wt-% or more of impurities, as determined by the above gas chromatography method. A vacuum line leading from a vacuum

pump is attached to the receiving flask. The selective liquid product in the 5-liter flask is stirred, and vacuum is applied to the system. Once the maximum vacuum is reached (at least 25.4 mm Hg by gauge or less), the selective liquid product is heated by means of an electric heating mantle.

5 After the heating begins, the distillate is collected in two fractions. One fraction, which is referred to hereinafter as fraction A, is collected from 25°C to the temperature of the boiling point of the light standard. The other fraction, fraction B, is collected from the temperature of the boiling point of the light standard to the temperature of the boiling point of the heavy
10 standard. Low-boiling fraction A and high-boiling pot residues are discarded. Fraction B contains the modified alkylbenzenes of interest, and is weighed. This method can be scaled as needed. Vapor pressures for phenyl-alkanes at various temperatures can be determined from the article in Industrial and Engineering Chemistry, Vol. 38, 1946, starting at page 320.

15 Next, an aliquot sample of fraction B is analyzed by the gas chromatography method using the above conditions. If more than about 90% of the total GC area for fraction B is within the retention time range, then the impurities in fraction B are deemed to be not more than about 10 wt-% of the selective liquid product, and, for the sole purpose of computing the
20 selectivity to internal quaternary phenyl-alkanes, C_{MAB} is computed by dividing the weight of fraction B collected by the weight of the aliquot portion of the selective liquid product charged to the 5-liter flask in the above distillation method. On the other hand, if the percent of the total GC area for fraction B within the retention time range is not more than about 90%, then
25 the impurities in fraction B are deemed to be more than about 10 wt-% of fraction B. In this case, impurities are removed from fraction B by again using the above distillation method. Accordingly, a low-boiling fraction (which is referred to as fraction C), high-boiling pot residues are discarded, a fraction (which is referred to herein as fraction D) containing the modified
30 alkylbenzenes of interest is recovered and weighed, and an aliquot sample of fraction D is analyzed by the gas chromatography method. If more than

about 90% of the total GC area for fraction D is within the retention time range, then for the sole purpose of computing the selectivity to internal quaternary phenyl-alkanes, C_{MAB} is computed by dividing the weight of fraction D by the weight of the aliquot portion of the selective liquid product originally charged to the 5-liter flask. Otherwise, the distillation and gas chromatography methods are repeated for fraction D.

The above-described distillation and gas chromatography methods can be repeated until a fraction containing the modified alkylbenzenes of interest and having less than 10 wt-% impurities is collected, provided that sufficient quantity of material remains after each distillation for further testing by these methods. Then, once C_{MAB} is determined, the selectivity to internal quaternary phenyl-alkanes, Q , is computed using the above formula.

The results of these analyses are shown in the Table 4:

Table 4: Liquid Product Analysis

<u>2-Phenyl- Alkane Selectivity</u>	<u>End Quaternary Phenyl-Alkane Selectivity</u>	<u>Internal Quaternary Phenyl-Alkane Selectivity</u>
82.0%	6.98%	1.9%

In the absence of shape selectivity, such as if an alkylation catalyst such as aluminum chloride or HF were used, most of the 2-methyl undecene would be expected to form 2-methyl-2-phenyl undecane (that is, an end quat). Likewise, most of the 6-methyl undecene, 5-methyl undecene, 4-methyl undecene, and 3-methyl undecene would be expected to form internal quats. The linear olefins would be expected to produce a statistical distribution of 2-phenyl-dodecane, 3-phenyl-dodecane, 4-phenyl-dodecane, 5-phenyl-dodecane, and 6-phenyl-dodecane. Thus, if the lights, the heavies, and the other alkyl olefins listed in Table 1 are excluded from the computations, the 2-phenyl-alkane selectivity would be no greater than 17 and the internal quaternary phenyl-alkane selectivity would approach 55.

Table 4 shows that the 2-phenyl-alkane selectivity is significantly higher than expected in the absence of shape selectivity and that the internal quaternary alkylbenzene selectivity obtained using the mordenite catalyst is much less than the internal quaternary alkylbenzene selectivity that would be expected
5 in the absence of shape selectivity.

CLAIMS:

1. A process for producing phenyl-alkanes, the process comprising the steps of:

5 a) passing a feed stream containing C₈-C₂₈ paraffins to an isomerization zone, operating the isomerization zone at isomerization conditions sufficient to isomerize paraffins, and recovering from the isomerization zone an isomerized product stream comprising paraffins;

10 b) passing at least a portion of the isomerized product stream to a dehydrogenation zone, operating the dehydrogenation zone at dehydrogenation conditions sufficient to dehydrogenate paraffins, and recovering from the dehydrogenation zone a dehydrogenated product stream comprising monoolefins and paraffins, wherein the monoolefins in the dehydrogenated product stream have from about 8 to about 28 carbon atoms, and wherein at least a portion of the monoolefins in the dehydrogenated product stream have 3 or 4 primary carbon atoms and no quaternary carbon atoms;

15 c) passing a phenyl- compound and at least a portion of the dehydrogenated product stream comprising monoolefins to an alkylation zone, operating the alkylation zone at alkylation conditions sufficient to alkylate the phenyl compound with monoolefins in the presence of an alkylation catalyst to form phenyl-alkanes comprising molecules having one phenyl portion and one aliphatic alkyl portion containing from about 8 to about 28 carbon atoms; wherein at least a portion of the phenyl-alkanes formed in the alkylation zone have 2, 3, or 4 primary carbon atoms and no quaternary carbon atoms except for any quaternary carbon atom bonded by a carbon-carbon bond with a carbon atom of the phenyl portion; and wherein the alkylation has a selectivity to 2-phenyl-alkanes of from 40 to

100 and a selectivity to internal quaternary phenyl-alkanes of less than 10;

- d) recovering from the alkylation zone an alkylate product stream comprising phenyl-alkanes and a recycle stream comprising paraffins; and
- e) passing at least a portion of the recycle stream to the isomerization zone or the dehydrogenation zone.

2. The process of Claim 1 further characterized in that the at least a portion of the isomerized product stream has a concentration of paraffins having 3 or 4 primary carbon atoms and no quaternary carbon atoms of greater than about 25 mol-% of the at least a portion of the isomerized product stream.

3. The process of Claim 1 further characterized in that the at least a portion of the isomerized product stream has a concentration of paraffins having secondary carbon atoms and 2 primary carbon atoms of less than about 75 mol-% of the at least a portion of the isomerized product stream.

4. The process of Claim 1 further characterized in that the alkylation catalyst comprises a zeolite having a zeolite structure type selected from the group consisting of BEA, MOR, MTW, and NES.

5. The process of Claim 1 wherein the phenyl compound comprises a compound selected from the group consisting of benzene, toluene, and ethylbenzene.

6. The process of Claim 1 wherein the phenyl-alkanes comprise monomethyl-phenyl-alkanes.

7. The process of Claim 1 wherein at least a portion of the recycle stream passes to the isomerization zone, and further characterized in that the isomerization zone contains a first bed containing isomerization catalyst and a second bed containing isomerization catalyst, the feed stream passes to the first bed operating at first bed conditions to isomerize paraffins, a first bed effluent comprising

paraffins is withdrawn from the first bed, at least a portion of the first bed effluent and the at least a portion of the recycle stream passes to the second bed operating at second bed conditions to isomerize paraffins, and the isomerized product stream is recovered from the second bed.

5

8. The process of Claim 1 wherein at least a portion of the recycle stream passes to the dehydrogenation zone, and further characterized in that the dehydrogenation zone contains a first bed containing dehydrogenation catalyst and a second bed containing dehydrogenation catalyst, the at least a portion of the isomerized product stream passes to the first bed operating at first bed conditions to dehydrogenate paraffins, a first bed effluent comprising paraffins is withdrawn from the first bed, at least a portion of the first bed effluent and the at least a portion of the recycle stream passes to the second bed operating at second bed conditions to dehydrogenate paraffins, and the dehydrogenated product stream is recovered from the second bed.

10

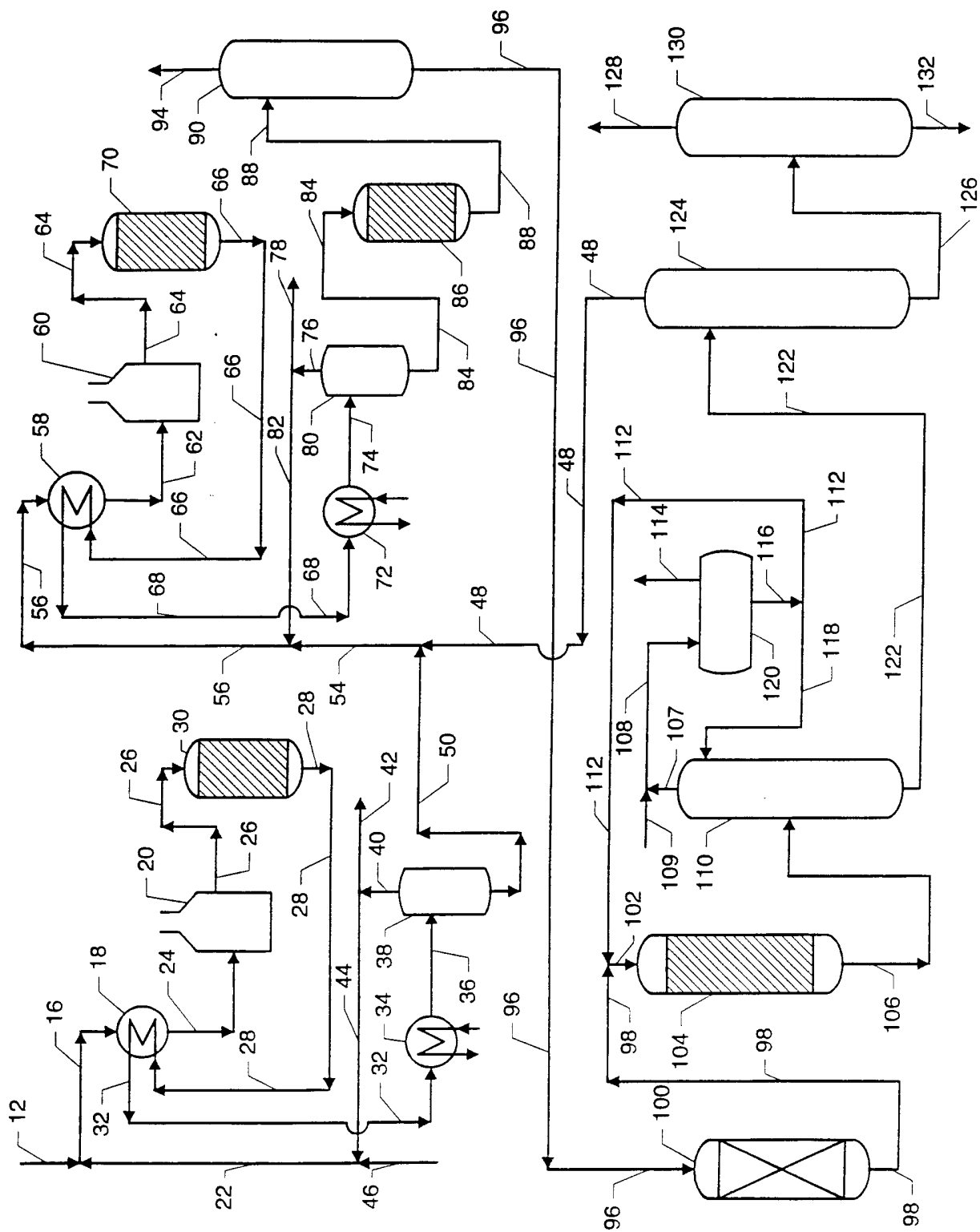
15

9. A modified alkylbenzene composition, wherein the modified alkylbenzene is produced by the process of Claim 1.

20

10. The use of the modified alkylbenzene composition according to Claim 9 as a lubricant.

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US00/16336

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) :C07C 2/66, 5/22, 15/107, 5/333

US CL :585/323, 448, 455, 660, 661, 740, 750, 751

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)

U.S. : 585/323, 448, 455, 660, 661, 740, 750, 751

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)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
E, Y	US 6,111,158 A (MARINANGELI et al) 29 August 2000, abstract, col. 8, lines 22-53, col. 18, lines 41 through col. 20, line 24.	1-10

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	"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
"A" document defining the general state of the art which is not considered to be of particular relevance	"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
"E" earlier document published on or after the international filing date	"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
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"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	

Date of the actual completion of the international search

27 SEPTEMBER 2000

Date of mailing of the international search report

17 OCT 2000

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