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(54) **A process for preparing (branched-alkyl) arylsulphonates and a (branched-alkyl) arylsulphonate composition**

Verfahren zur Herstellung von Arylsulfonaten mit verzweigten Alkylgruppen und Arylsulfonat mit verzweigten Alkylgruppen enthaltende Zusammensetzung

Procede de preparation d'arylsulfonate a ramification alkyle et composition correspondante

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WO-A-01/05733 **WO-A-01/05755**
WO-A-99/05242 **US-A- 6 111 158**

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EP 1 698 680 B1

Description

FIELD OF THE INVENTION

[0001] This invention relates to a process for preparing (branched-alkyl)arylsulphonates and to compositions of the (branched-alkyl)arylsulphonates per se. This invention also relates to a process for preparing intermediate branched alkyl aromatic hydrocarbons and to compositions of the branched alkyl aromatic hydrocarbons per se.

BACKGROUND OF THE INVENTION

[0002] WO-A-99/05244, WO-A-99/05082 and US-A-6111158 relate to alkylarylsulphonate surfactants of which the alkyl groups are branched. Sources of the alkyl groups are for example paraffins with limited branching obtained by delinearisation of linear paraffins.

[0003] US-A-611158 relates to a process for producing phenyl-alkanes having lightly branched aliphatic alkyl groups, where the process comprises contacting monoolefin molecules with an aryl compound at alkylation conditions with a zeolite having an NES zeolite structure type, such as NU-87. The phenyl-alkanes produced have lightly branched aliphatic alkyl groups which are used to produce modified alkylbenzene sulfonates.

[0004] US-A-5849960 relates to surfactant sulphates based on branched alcohols. The branched alcohols in question have an average number of branches per molecule chain of at least 0.5. The branching comprises not only methyl branching but also ethyl branches, whilst the occurrence of longer branching is not excluded. The branched alcohols are made from branched olefins, which are made by skeletally isomerising linear olefins.

[0005] The market always asks for improvements in the performance of existing detergent formulations, inter alia by improving the surfactants present in the detergent formulations. For example, the laundry market asks for improvements in the surfactants' biodegradability, their cold water solubility and their cold water detergency. At least an improvement is sought in the balance of the properties. By the terminology "an improvement in the balance of the properties" it is meant that at least one property is improved, whilst at least one of the other properties is not deteriorated.

[0006] The present invention seeks to provide improvements in the performance of the known alkylarylsulphonate surfactants, or at least in an improvement in the balance of their performance properties. Relevant performance properties are biodegradability, cold water solubility and cold water detergency, for example cold water detergency in water of low hardness and in water of high hardness. Other relevant performance properties are the compatibility of the alkylarylsulphonate surfactants with other components present in detergent formulations, as described hereinafter, in particular, the compatibility with enzymes, i.e. the inability of the alkylarylsulphonate surfactants to denature enzymes during storage in an aqueous medium. Again other relevant performance properties, in particular for personal care applications, are mildness to the skin and to the eyes and the ability of high foaming, preferably providing foam with a fine structure of the foam cells. Further, an improved performance is sought as a chemical for enhanced oil recovery applications and for the removal of oil spillage, viz. an improved ability to emulsify oil/water and oil/brine systems and to stabilise emulsions of oil and water or brine, in particular at high temperature. Independently, the present invention seeks to provide a method for the manufacture of alkylarylsulphonate surfactants which is more versatile and economically more attractive than the known methods.

SUMMARY OF THE INVENTION

[0007] In accordance with this invention alkylarylsulphonate surfactants are prepared by dehydrogenating selected branched paraffins to produce branched olefins. These branched olefins can be converted into branched alkyl aromatics and subsequently into alkylarylsulphonate surfactants. It is an advantage of this invention that surfactants and intermediates can be made with a very low content of molecules which have a linear carbon chain. It is another advantage of the invention that products can be made of which the molecules have a low content of branches having three or more carbon atoms. It is also an advantage of the invention that products can be made of which the molecules have a low content of quaternary aliphatic carbon atoms. Without wishing to be bound by theory, it is believed that the presence of quaternary aliphatic carbon atoms in the molecules of the (branched-alkyl)arylsulphonate surfactants prevents to some extent their biodegradation and the presence of quaternary aliphatic carbon atoms in the isoparaffinic composition is therefore preferably avoided. In fact, it has been determined that the presence of 0.5% or less quaternary aliphatic carbon atoms in the molecules of the surfactants renders the surfactants substantially more biodegradable.

[0008] Accordingly, the present invention provides a process for preparing branched olefins, which process comprises dehydrogenating an isoparaffinic composition comprising 0.5% or less quaternary aliphatic carbon atoms over a suitable catalyst which isoparaffinic composition has been obtained by hydroisomerisation of a paraffinic wax and which isoparaffinic composition comprises paraffins having a carbon number in the range of from 7 to 18, of which paraffins at least a portion of the molecules is branched, the average number of branches per paraffin molecule being 0.5 to 2.5 and the

branching comprising methyl and optionally ethyl branches, said branched olefins comprising 0.5% or less quaternary aliphatic hydrocarbons, wherein said paraffinic wax is obtained in a Fischer Trapsch synthesis.

[0009] The present invention provides a process for preparing branched alkyl aromatic hydrocarbons, which process comprises contacting branched olefins with an aromatic hydrocarbon under alkylating conditions, which branched olefins have been obtained by a process which comprises dehydrogenating an isoparaffinic composition comprising 0.5% or less quaternary aliphatic carbon atoms over a suitable catalyst, which isoparaffinic composition has been obtained by hydroisomerisation of a paraffinic wax and which isoparaffinic composition comprises paraffins having a carbon number in the range of from 7 to 35, of which paraffins at least a portion of the molecules is branched, the average number of branches per paraffin molecule being 0.5 to 2.5 and the branching comprising methyl and optionally ethyl branches, said branched olefins comprising 0.5% or less quaternary aliphatic hydrocarbons, wherein said paraffinic wax is obtained in a Fischer-Trapsch synthesis.

[0010] The invention also provides a process for preparing (branched-alkyl)arylsulphonates, comprising sulphonating branched alkyl aromatic hydrocarbons which branched alkyl aromatic hydrocarbons have been prepared by the process for preparing branched alkyl aromatic hydrocarbons in accordance with the present invention.

[0011] Without wishing to be bound by theory, it is believed that any improvement in the performance properties of the (branched-alkyl)arylsulphonates prepared in accordance with this invention, compared with the known (branched-alkyl)arylsulphonates, resides in a difference in the distribution of branching along the respective paraffinic chains. Such differences in the distribution of branching are truly unexpected in view of the prior art and, therefore, they are inventive.

DETAILED DESCRIPTION OF THE INVENTION

[0012] As described herein, the isoparaffinic composition and the compositions of branched olefins, branched alkyl aromatic compounds and (branched-alkyl)arylsulphonates derived therefrom are generally mixtures comprising molecules with different, consecutive carbon numbers. Typically at least 75 %w, more typically at least 90 %w, of these compositions represent a range of molecules of which the heaviest molecules comprises at most 6 carbon atoms more than the lightest molecules.

[0013] The isoparaffinic composition comprises paraffins having a carbon number in the range of from 7 to 35, of which paraffins at least a portion of the molecules is branched. Preferably, the isoparaffinic composition comprises paraffins having a carbon number in the range of from 7 to 18, more preferably from 10 to 18. Preferably at least 75%w, more preferably at least 90%w, of the isoparaffinic composition consists of paraffins having a carbon number in the range of from 10 to 18. In practice, frequently at most 99.99%w, more frequently at most 99.9%w, of the isoparaffinic composition consists of paraffins having a carbon number in the range of from 10 to 18. It is most preferred that the isoparaffinic composition comprises paraffins having a carbon number in the range of from 11 to 14, in which case preferably at least 75%w, more preferably at least 90%w, of the isoparaffinic composition consists of paraffins having a carbon number in the range of from 11 to 14. In practice, frequently at most 99.99%w, more frequently at most 99.9%w, of the isoparaffinic composition consists of paraffins having a carbon number in the range of from 11 to 14. These selections are based on the effects that the paraffins of a lower carbon number ultimately yield surfactants, which are more volatile, and that the paraffins of a higher carbon number ultimately yield surfactants with less water solubility.

[0014] The average number of branches per paraffin molecule present in the isoparaffinic composition is at least 0.5, calculated over the total of the branched paraffins and, if present, the linear paraffins. Suitably the average number of branches is at least 0.7, and more suitably at least 0.8, for example 1.0. Suitably the average number of branches is at most 2.0, preferably at most 1.8, and in particular at most 1.4.

[0015] The number of methyl branches present in the isoparaffinic composition is suitably at least 20%, more suitably at least 40%, preferably at least 50% of the total number of branches. In practice the number of methyl branches is frequently at most 99%, more frequently at most 98% of the total number of branches. If present, the number of ethyl branches is suitably at least 0.1%, in particular at least 1%, more in particular at least 2% of the total number of branches. Suitably, the number of ethyl branches is at most 20%, in particular at most 15%, more in particular at most 10% of the total number of branches. The number of any branches, if present, other than methyl and ethyl branches, may be less than 10%, in particular less than 5% of the total number of branches. The number of any branches, if present, other than methyl and ethyl branches, may be more than 0.1%, typically more than 1% of the total number of branches.

[0016] For any application, and particularly for applications where biodegradability is important, the number of quaternary aliphatic carbon atoms is 0.5 % or less, most preferably less than 0.5 %, and in particular less than 0.3%. In practice the number of quaternary aliphatic carbon atoms present in the isoparaffinic composition is frequently more than 0.01% of the aliphatic carbon atoms present, more frequently more than 0.02%.

[0017] The content of branched paraffins of the isoparaffinic composition is typically at least 50%w, more typically at least 70%w, most typically at least 90%w, preferably at least 95%w, more preferably at least 99%w, in particular at least 99.9%w, relative to the weight of the isoparaffinic composition. In practice the content of branched paraffins is frequently at most 99.99 %w, more frequently at most 99.95%w, relative to the weight of the isoparaffinic composition. The content

of linear paraffins of the isoparaffinic composition is typically at most 50%w, more typically at most 30%w, most typically at most 10%w, preferably at most 5%w, more preferably at most 1%w, in particular at most 0.1%w, relative to the weight of the isoparaffinic composition. In practice the content of linear paraffins is frequently at least 0.01%w, more frequently at least 0.02%w, relative to the weight of the isoparaffinic composition.

[0018] >

[0019] The isoparaffinic composition is obtained by hydroisomerisation of a paraffinic composition, i.e. a composition which comprises predominantly linear paraffins, obtained from a Fischer Tropsch process Fischer Tropsch products are generally very low in their content of sulphur and nitrogen and they are cost effective. The Fischer Tropsch products may or may not comprise oxygenates. The product obtained in the hydroisomerisation process may be fractionated, for example, by distillation or otherwise, in order to isolate an isoparaffinic product of the desired composition. Such a hydroisomerisation process and subsequent fractionation is known, for example from US-A-5866748.

[0020] The isoparaffinic composition may be treated to lower the content of linear paraffins, in order to favourably adjust the average number of branches in the isoparaffinic composition. Such separation may be accomplished by separation using a molecular sieve as absorbent. The molecular sieve may be, for example, a zeolite 4A, a zeolite 5A, a zeolite X or a zeolite Y. Reference may be made to "Kirk-Othmer Encyclopedia of Chemical Technology", 4th edition, Volume 1, pp. 589-590, and Volume 16, pp. 911-916; and "Handbook of Petroleum Refining Processes" (R A Meyers, Ed.), 2nd edition, pp. 10.45-10.51, 10.75-10.77.

[0021] Catalysts suitable for the dehydrogenation of the isoparaffinic composition may be selected from a wide range. For example, they may be based on a metal or metal compound deposited on a porous support, the metal or metal compound being one or more selected for example from chrome oxide, iron oxide and, preferably, the noble metals. The noble metals are understood to be the metals of the group formed by platinum, palladium, iridium, ruthenium, osmium and rhodium. Preferred noble metals are palladium and, in particular, platinum.

[0022] Suitable porous supports may be supports of a carbon nature such as activated carbon, coke and charcoal; silica or silica gel, or other natural or synthetic clays or silicates, for example hydrotalcites; ceramics; refractory inorganic oxides such as alumina, titania or magnesia; naturally or synthetic crystalline aluminosilicates such as mordenite or faujasite; and combinations of two or more elements selected from these groups. The porous support is preferably an alumina, in particular gamma alumina or eta alumina.

[0023] The quantity of the metal or metal compound deposited on the porous support is not material to this invention. The quantity may suitably be selected in the range of from 0.01 to 5%w, preferably from 0.02 to 2%w, based on the weight of the catalyst.

[0024] Further metals may be present in the catalyst used for the dehydrogenation of the isoparaffinic composition, in particular in the catalysts which comprise a noble metal. Such further metals may suitably be selected from Group 3a, Group 4a and Group 5a of the Periodic Table of Elements (cf. R C Weast (Ed,) "Handbook of Chemistry and Physics", 54th edition, CRC Press, inside cover). In particular, indium may be selected from Group 3a, tin may be selected from Group 4a or bismuth may be selected from Group 5a. Especially suitable further metals are alkali and alkaline earth metals. Preferred alkali metals are potassium, and in particular lithium.

[0025] Further elements which may be present in the catalyst used for the dehydrogenation of the isoparaffinic composition are halogens, in particular in combination with a metal of Group 4a, more in particular in combination with tin. Chlorine is a preferred halogen.

[0026] The quantity of such further metals or halogens may independently be in the range of from 0.01 to 5%w, preferably from 0.02 to 2%w, based on the weight of the catalyst.

[0027] Suitable catalysts for the dehydrogenation of the isoparaffinic composition are, for example, chrome oxide on gamma alumina, platinum on gamma alumina, palladium on gamma alumina, platinum/lithium on gamma alumina, platinum/potassium on gamma alumina, platinum/tin on gamma alumina, platinum/tin on hydrotalcite, platinum/indium on gamma alumina and platinum/bismuth on gamma alumina.

[0028] The dehydrogenation may be operated at a wide range of conditions. Suitably the temperature is in the range of from 300°C to 700 °C, more suitably in the range of from 400°C to 600 °C, in particular in the range of from 450°C to 550 °C. The total pressure may be an elevated pressure, such as in the range of from 110 to 1500 kPa a (1.1 to 15 bara) (i.e. kPa or bar absolute), preferably in the range of from 130 to 1000 kPa a (1.3 to 10 bara), in particular in the range of from 150 to 500 kPa a (1.5 to 5 bara). In order to prevent coking, hydrogen may be fed together with the isoparaffinic composition. Suitably, hydrogen and paraffins present in the isoparaffinic composition are fed at a molar ratio in the range of from 0.1 to 20, more suitably this molar ratio is in the range of from 0.5 to 15, in particular this molar ratio is in the range of from 1 to 10.

[0029] The residence time in the dehydrogenation is typically selected such that conversion level of the isoparaffinic composition is kept below 50 mole%, preferably in the range of from 5 to 30 mole%, in particular in the range of from 10 to 20 mole%. By keeping the conversion level low, side reactions may to some extent be prevented, such as diene formation and cyclisation reactions. Non-converted paraffins and dehydrogenated compounds may be separated from the dehydrogenation product and, if desired, non-converted paraffins may be recycled to the dehydrogenation step.

Such separation may be accomplished by extraction, by extractive distillation or, preferably, by using a molecular sieve as absorbent. The molecular sieve may be, for example, a zeolite 4A, a zeolite 5A, a zeolite X or a zeolite Y. If desired, linear olefins may be separated at least to some extent from branched olefin so that the content of branched olefin in the product as obtained from the dehydrogenation is increased further, but this option is generally not preferred.

[0030] The skilled person is aware of the techniques of preparing the catalysts, performing the dehydrogenation step and performing associated separation steps, for use in this invention. For example, suitable procedures for preparing catalysts and performing the dehydrogenation are known from US-A-5012021, US-A-3274287, US-A-3315007, US-A-3315008, US-A-3745112, US-A-4430517. For techniques suitable for the separation of branched olefins from linear olefins, reference may be made to "Kirk-Othmer Encyclopedia of Chemical Technology", 4th edition, Volume 1, pp. 589-591, and Volume 16, pp. 911-916; and "Handbook of Petroleum Refining Processes" (R A Meyers, Ed.), 2nd edition, pp. 10.45-10.51, 10.79-10.81.

[0031] The dehydrogenation in accordance with this invention yields typically a branched olefin composition comprising olefins having a carbon number in the range of from 7 to 35, of which olefins at least a portion of the molecules is branched, the average number of branches per molecule being at least 0.5 and the branching comprising methyl and optionally ethyl branches. Preferably, the branched olefin composition comprises olefins having a carbon number in the range of from 7 to 18, more preferably from 10 to 18. Preferably at least 75%w, more preferably at least 90%w, of the branched olefin composition consists of olefins having a carbon number in the range of from 10 to 18. In practice, frequently at most 99.99%w, more frequently at most 99.9%w, of the branched olefin composition consists of olefins having a carbon number in the range of from 10 to 18. It is most preferred that the branched olefin composition comprises olefins having a carbon number in the range of from 11 to 14, in which case preferably at least 75%w, more preferably at least 90%w, of the branched olefin composition consists of olefins having a carbon number in the range of from 11 to 14. In practice, frequently at most 99.99%w, more frequently at most 99.9%w, of the branched olefin composition consists of olefins having a carbon number in the range of from 11 to 14.

[0032] Suitably the average number of branches per olefin molecule present in the branched olefin composition is at least 0.7, and more suitably at least 0.8, for example 1.0. Suitably the average number of branches is at most 2.0, preferably at most 1.8, and in particular at most 1.4. The number of methyl branches is suitably at least 20%, more suitably at least 40%, preferably at least 50% of the total number of branches. In practice the number of methyl branches is frequently at most 99%, more frequently at most 98% of the total number of branches. If present, the number of ethyl branches is suitably at least 0.1%, in particular at least 1%, more in particular at least 2% of the total number of branches. Suitably, the number of ethyl branches is at most 20%, in particular at most 15%, more in particular at most 10% of the total number of branches. The number of any branches, if present, other than methyl and ethyl branches, may be less than 10%, in particular less than 5% of the total number of branches. The number of any branches, if present, other than methyl and ethyl branches, may be more than 0.1%, typically more than 1% of the total number of branches.

[0033] For any application, and particularly for applications where biodegradability is important, the number of quaternary aliphatic carbon atoms is 0.5 % or less, most preferably less than 0.5 %, and in particular less than 0.3%. In practice the number of quaternary aliphatic carbon atoms present in the branched olefins is frequently more than 0.01% of the aliphatic carbon atoms present, more frequently more than 0.02%.

[0034] The content of branched olefins of the branched olefin composition is typically at least 50%w, more typically at least 70%w, most typically at least 90%w, preferably at least 95%w, more preferably at least 99%w, in particular at least 99.9%w, relative to the weight of the branched olefin composition. In practice the content of branched olefins is frequently at most 99.99 %w, more frequently at most 99.95%w, relative to the weight of the branched olefin composition. The content of linear olefins of the branched olefin composition is typically at most 50%w, more typically at most 30%w, most typically at most 10%w, preferably at most 5%w, more preferably at most 1%w, in particular at most 0.1%w, relative to the weight of the branched olefin composition. In practice the content of linear olefins is frequently at least 0.01%w, more frequently at least 0.05%w, relative to the weight of the branched olefins composition.

[0035] The branched olefin composition may comprise paraffins, which were not converted in the dehydrogenation. Such non-converted paraffins may suitably be removed in a subsequent stage, in particular during the work-up of the alkylation reaction mixture, as described hereinafter, and recycled to the dehydrogenation step. If the branched olefin composition comprises paraffins, the specifications given in the three paragraphs preceding the present paragraph relate to the olefinic portion of the branched olefin composition. Typically quantity of the olefinic portion present in the branched olefin composition is in the range of from 1 to 50% mole relative to the total number of moles of olefins and paraffins present, more typically in the range of from 5 to 30% mole, in particular from 10 to 20% mole, on the same basis. Typically quantity of the paraffinic portion present in the branched olefin composition is in the range of from 50 to 99% mole relative to the total number of moles of olefins and paraffins present, more typically in the range of from 70 to 95% mole, in particular from 80 to 90% mole, on the same basis.

[0036] The preparation of branched alkyl aromatic hydrocarbons by contacting the branched olefins with the aromatic hydrocarbon may be performed under a large variety of alkylating conditions. Preferably, the said alkylation leads to monoalkylation, and only to a lesser degree to dialkylation or higher alkylation, if any.

[0037] The aromatic hydrocarbon applicable in the alkylation may be one or more of benzene; toluene; xylene, for example o-xylene or a mixture of xylenes; and naphthalene. Preferably, the aromatic hydrocarbon is benzene.

[0038] The molar ratio of the branched olefins to the aromatic hydrocarbons may be selected from a wide range. In order to favor monoalkylation, this molar ratio is suitably at least 0.5, preferably at least 1, in particular at least 1.5. In practice this molar ratio is frequently less than 1000, more frequently less than 100.

[0039] The said alkylation may or may not be carried out in the presence of a liquid diluent. Suitable diluents are, for example, paraffin mixtures of a suitable boiling range, such as the paraffins which were not converted in the dehydrogenation and which were not removed from the dehydrogenation product. An excess of the aromatic hydrocarbon may act as a diluent.

[0040] The alkylation catalyst, which may be applied, may be selected for example from a large range of zeolitic alkylation catalysts. In order to favour monoalkylation, it is preferred that the zeolitic alkylation catalysts have pore size dimensions in the range of from 4 to 9 Å, more preferably from 5 to 8 Å and most preferably from 5.5 to 7 Å, on the understanding that when the pores have an elliptical shape, the larger pore size dimension is the dimension to be considered. The pore size dimensions of zeolites has been specified in W M Meier and D H Olson, "Atlas of Zeolite Structure Types", 2nd revised edition (1987), published by the Structure Commission of the International Zeolite Association. Suitable zeolitic alkylation catalysts are zeolites in acidic form selected from zeolite Y and zeolites ZSM-5 and ZSM-11. Preferably the zeolitic alkylation catalysts are zeolites in acidic form selected from mordenite, ZSM-4, ZSM-12, ZSM-20, offretite, gemelinite and cancrinite. Particularly preferred zeolitic alkylation catalysts are the zeolites which have an NES zeolite structure type, including isotypic framework structures such as NU-87 and gottardiite, as disclosed in US-A-6111158. The zeolites which have an NES zeolite structure type give, advantageously, a high selectivity to 2-aryl-alkanes. Further examples of suitable zeolitic alkylation catalyst have been given in WO-A-99/05082.

[0041] Suitably, the zeolitic alkylation catalyst has a molar ratio of Si to Al of at least 5:1 and suitably at most 500:1, in particular at most 100:1. In particular when the zeolitic alkylation catalyst is of the NES zeolite structure type, the molar ratio of Si to Al is preferably in the range of from 5:1 to 25:1, more preferably from 10:1 to 20:1. The molar ratio of Si to Al of the zeolitic alkylation catalyst is meant to be the molar ratio of the SiO_4 tetrahedra to the AlO_4 tetrahedra, i.e. the framework Si/Al molar ratio.

[0042] The zeolitic alkylation catalyst has preferably at least a portion of the cationic sites occupied by ions other than alkali or alkaline earth metal ions. Such replacing ions could be one or more selected from the group of for example ammonium, hydrogen and rare earth. In a preferred embodiment the zeolitic alkylation catalyst is at least partly in the hydrogen form, i.e. acidic form, in particular completely in the hydrogen form. Suitably at least 10%, preferably at least 50%, more preferably at least 90% of the cationic sites is occupied by hydrogen ions. In practice, frequently at most 99%, more frequently at most 95% of the cationic sites is occupied by hydrogen ions. This is generally accomplished by exchange of the alkali metal ion or another ion for a hydrogen ion precursors, e.g. ammonium ions, which upon calcination yields the hydrogen form.

[0043] It is preferred that the zeolitic alkylation catalyst is used in pellet form comprising for example at least 1 %w, typically at least 50 %w, preferably at least 90 %w of the zeolitic alkylation catalyst. A conventional binder may be present in the pellets. Useful conventional binders may be inorganic materials, such as clay, silica and/or metal oxides. The zeolitic alkylation catalyst may be compounded with other materials, such as porous matrix materials, for example, alumina, silica/alumina, silica/magnesia, silica/zirconia and silica/titania, silica/alumina/thoria and silica/alumina/zirconia.

[0044] Processes for treatment of the zeolitic alkylation catalyst or of precursors thereof to prepare an active form of the zeolitic alkylation catalyst are given in WO-A-99/05082. Examples of such treatments are ion exchange reactions, dealumination, steaming, calcination in air, in hydrogen or in an inert gas, and activation.

[0045] The zeolitic alkylation catalyst is suitably applied in a quantity of from 0.5 to 100%w, preferably from 1 to 50 %w, relative to the weight of the branched olefins applied.

[0046] The preparation of branched alkyl aromatic hydrocarbons by contacting the branched olefins with the aromatic hydrocarbon may be performed under alkylating conditions involving reaction temperatures selected from a large range. The reaction temperature is suitably selected in the range of from 30°C to 300 C, more suitably in the range of from 100°C to 250°C.

[0047] Work-up of the alkylation reaction mixture may be accomplished by methods known in the art. For example, a solid catalyst may be removed from the reaction mixture by filtration or centrifugation. Unreacted hydrocarbons, for example branched olefins, any excess of intake aromatic hydrocarbons or paraffins, may be removed by distillation.

[0048] The general class of branched alkyl aromatic compounds which may be made in accordance with this invention can be characterised by the chemical formula R-A, wherein R represents a radical derived from the branched olefins according to this invention by the addition thereto of a hydrogen atom, which branched olefins have a carbon number in the range of from 7 to 35, in particular from 7 to 18, more in particular from 10 to 18, most in particular from 11 to 14; and A represents an aromatic hydrocarbyl radical, in particular a phenyl radical.

[0049] The branched alkyl aromatic compounds obtained with the process of this invention may be sulphonated by any method of sulphonation which is known in the art. Examples of such methods include sulphonation using sulphuric

acid, chlorosulphonic acid, oleum or sulphur trioxide. Details of a preferred sulphonation method, which involves using an air/sulphur trioxide mixture, are known from US-A-3427342.

[0050] Any convenient work-up method may be employed after the sulphonation. The sulphonation reaction mixture may be neutralised with a base to form the (branched-alkyl)arylsulphonate in the form of a salt. Suitable bases are the hydroxides of alkali metals and alkaline earth metals; and ammonium hydroxides, which provide the cation M of the salts as specified below.

[0051] The general class of (branched-alkyl)arylsulphonates which may be made in accordance with this invention can be characterised by the chemical formula $(R\text{-}A'\text{-}SO_3)_nM$, wherein R represents a radical derived from the branched olefins according to this invention by the addition thereto of a hydrogen atom, which branched olefins have a carbon number in the range of from 7 to 35, in particular from 7 to 18, more in particular from 10 to 18, most in particular from 11 to 14; A' represents a divalent aromatic hydrocarbyl radical, in particular a phenylene radical; M is a cation selected from an alkali metal ion, an alkaline earth metal ion, an ammonium ion, and mixtures thereof; and n is a number depending on the valency of the cation(s) M, such that the total electrical charge is zero. The ammonium ion may be derived from an organic amine having 1, 2 or 3 organic groups attached to the nitrogen atom. Suitable ammonium ions are derived from monoethanol amine, diethanol amine and triethanol amine. It is preferred that the ammonium ion is of the formula NH_4^+. In preferred embodiments M represents potassium or magnesium, as potassium ions can promote the water solubility of the (branched-alkyl)arylsulphonates and magnesium can promote their performance in soft water.

[0052] The (branched-alkyl)arylsulphonate surfactants which can be made in accordance with this invention may be used as surfactants in a wide variety of applications, including detergent formulations such as granular laundry detergent formulations, liquid laundry detergent formulations, liquid dishwashing detergent formulations; and in miscellaneous formulations such as general purpose cleaning agents, liquid soaps, shampoos and liquid scouring agents.

[0053] The (branched-alkyl)arylsulphonate surfactants find particular use in detergent formulations, specifically laundry detergent formulations. These formulations are generally comprised of a number of components, besides the (branched-alkyl)arylsulphonate surfactants themselves: other surfactants of the ionic, nonionic, amphoteric or cationic type, builders, cobuilders, bleaching agents and their activators, foam controlling agents, enzymes, anti-greying agents, optical brighteners, and stabilisers.

[0054] Liquid laundry detergent formulations may comprise the same components as the granular laundry detergent formulations, but they generally contain less of the inorganic builder component. Hydrotropes may be present in the liquid detergent formulations. General purpose cleaning agents may comprise other surfactants, builders, foam control agents, hydrotropes and solubiliser alcohols.

[0055] Formulations may contain a large amount of the builder and cobuilder components, in amounts up to 90w%, preferably between 5 and 35w%, based on the weight of the formulation, to intensify the cleaning action. Examples of common inorganic builders are phosphates, polyphosphates, alkali metal carbonates, silicates and sulphates. Examples of organic builders are polycarboxylates, aminocarboxylates such as ethylenediaminotetraacetates, nitrilotriacetates, hydroxycarboxylates, citrates, succinates and substituted and unsubstituted alkanedi- and polycarboxylic acids. Another type of builder, useful in granular laundry and built liquid laundry agents, includes various substantially water-insoluble materials which are capable of reducing the water hardness e.g. by ion exchange processes. In particular the complex sodium aluminosilicates, known as type A zeolites, are very useful for this purpose.

[0056] Formulations may also contain percompounds with a bleaching action, such as perborates, percarbonates, persulphates and organic peroxy acids. Formulations containing percompounds may also contain stabilising agents, such as magnesium silicate, sodium ethylenediaminetetraacetate or sodium salts of phosphonic acids. In addition, bleach activators may be used to increase the efficiency of the inorganic persalts at lower washing temperatures. Particularly useful for this purpose are substituted carboxylic acid amides, e.g. tetraacetylethylenediamine, substituted carboxylic acids, e.g. isononyloxybenzenesulphonate and sodiumcyanamide.

[0057] Examples of suitable hydrotropic substances are alkali metal salts of benzene, toluene and xylene sulphonic acids; alkali metal salts of formic acid, citric and succinic acid, alkali metal chlorides, urea, mono-, di-, and triethanolamine. Examples of solubiliser alcohols are ethanol, isopropanol, mono- or polyethylene glycols, monopropylene glycol and etheralcohols.

[0058] Examples of foam control agents are high molecular weight fatty acid soaps, paraffinic hydrocarbons, and silicon containing de-foamers. In particular hydrophobic silica particles are efficient foam control agents in these laundry detergent formulations.

[0059] Examples of known enzymes which are effective in the laundry detergent formulations are protease, amylase and lipase. Preference is given to the enzymes which have their optimum performance at the design conditions of the washing and cleaning agent.

[0060] A large number of fluorescent whiteners are described in the literature. For the laundry washing formulations, the derivatives of diaminostilbene disulphonates and substituted distyryibiphenyl are particularly suitable.

[0061] As antigreying agents, water soluble colloids of an organic nature are preferably used. Examples are water soluble polyanionic polymers such as polymers and copolymers of acrylic and maleic acid, cellulose derivatives such

as carboxymethyl cellulose methyl- and hydroxyethylcellulose.

[0062] The (branched-alkyl)arylsulphonate surfactants which can be made in accordance with this invention may also advantageously be used in personal care products, in enhanced oil recovery applications and for the removal of oil spillage off-shore and on inland water-ways, canals and lakes.

[0063] The formulations obtainable according to the invention typically comprise one or more inert components. For instance, the balance of liquid detergent formulations is typically an inert solvent or diluent, most commonly water. Powdered or granular detergent formulations typically contain quantities of inert filler or carrier materials.

[0064] As used herein, the average number of branches per molecule, further particulars of the type and position of branching and the content of quaternary aliphatic carbon atoms are as defined in US-A-5849960 and they are determined by the methods as described in US-A-5849960. Also the further analytical methods and the test methods are as described in US-A-5849960.

[0065] Unless specified otherwise, the low-molecular weight organic compounds mentioned herein have typically at most 40 carbon atoms, more typically at most 20 carbon atoms, in particular at most 10 carbon atoms, more in particular at most 6 carbon atoms. Organic compounds are deemed to be compounds which comprise carbon atoms and hydrogen atoms in their molecules. The group of low-molecular weight organic compounds does not include polymers and enzymes.

[0066] As defined herein, ranges for numbers of carbon atoms (i.e. carbon number) include the numbers specified for the limits of the ranges. Number of carbon atoms as defined herein include the carbon atoms along the carbon backbones, as well as branching carbon atoms, if any.

[0067] The following example will illustrate the nature of the invention without its scope.

Example 1 (prophetic)

[0068] A Fischer Tropsch hydrocarbon mixture of linear paraffins having at least 5 carbon atoms, further comprising a minor quantity of oxygenates, is subjected to conditions of hydrocracking and hydroisomerisation by contacting the hydrocarbon mixture, in the presence of hydrogen, with a palladium on silica-alumina catalyst (0.5%w Pd, 55%w Al_2O_3, 45%w SiO_2 at a temperature of 350°C and at a pressure of 6000 kPa a (60 bara), applying a liquid hourly space velocity of 0.5 l/l/h and a hydrogen to wax feed ratio of 400 Nl/l (liquid volumes at 20°C, "Nl" refers to the gas volume at 0°C, 100 kPa (1 bar)).

[0069] The hydrocracking/hydroisomerisation product stream is fractionated by distillation and by separation over a molecular sieve zeolite 5A such that an isoparaffinic composition is obtained which consists of branched and linear paraffins having a carbon number in the range of from 10 to 15. The average number of branches is 1.9 per paraffin molecule. The number of methyl branches is 60% of the total number of branches. The number of ethyl branches is 15% of the total number of branches. The quantity of branched paraffins present in the isoparaffinic composition is more than 96%w, and the quantity of linear paraffins present in the isoparaffinic composition is less than 4%w, based on the weight of the isoparaffinic composition.

[0070] The isoparaffinic composition is subjected to conditions of dehydrogenation by contacting the isoparaffinic composition, in the presence of hydrogen, with a platinum on gamma alumina catalyst (0.5%w platinum) at a temperature of 490°C and at a pressure of 250 kPa a (2.5 bara), applying in the feed a hydrogen/paraffins molar ratio of 4. The residence time of the isoparaffinic composition is controlled such that the conversion is 15%.

[0071] The dehydrogenation product is fractionated by separation over a molecular sieve zeolite 5A to remove paraffins. A paraffin free olefin fraction is obtained.

[0072] The olefin fraction is reacted with benzene under alkylating conditions, at a molar ratio of benzene to the olefins of 20, at a temperature of 190°C and in the presence of an acidic mordenite catalyst in a quantity of 15%w relative to the weight of the olefin fraction.

[0073] The alkylation product is isolated and purified by filtration and removing the volatile components by distillation.

[0074] The isolated, purified alkylation product is then sulphonated by a known method.

Example 2 (prophetic)

[0075] The procedure of example 1 is repeated, except that the separation over a molecular sieve is omitted, and that the quantity of branched paraffins present in the isoparaffinic composition obtained is 70%w and the quantity of linear paraffins present in the isoparaffinic composition obtained is 30%w, based on the weight of the isoparaffinic composition, and in the isoparaffinic composition obtained the average number of branches is 1.3 per paraffin molecule. In other aspects the isoparaffinic composition is as indicated in example 1.

Example 3 (prophetic)

[0076] The procedure of example 1 is repeated, except that the Fischer Tropsch hydrocarbon mixture consists es-

sentially of a wax of linear paraffins having at least 30 carbon atoms. The isoparaffinic composition obtained is of a similar composition as specified in example 1.

Example 4 (prophetic)

[0077] The procedure of example 3 is repeated, except that the separation over a molecular sieve is omitted, and that the quantity of branched paraffins present in the isoparaffinic composition obtained is 90%w and the quantity of linear paraffins present in the isoparaffinic composition obtained is 10%w, based on the weight of the isoparaffinic composition, and in the isoparaffinic composition obtained the average number of branches is 1.7 per paraffin molecule. In other aspects the isoparaffinic composition is as indicated in example 1.

Examples 5-8 (prophetic)

[0078] The procedures of examples 1-4 are repeated except that in each case the isoparaffinic composition obtained consists of branched and linear paraffins having a carbon number in the range of from 10 to 14, instead of from 10 to 15. In other aspects the isoparaffinic compositions obtained are as indicated in the respective example of examples 1-4.

Examples 9-16 (prophetic)

[0079] The procedures of examples 1-8 are repeated except that in each procedure the removal of paraffins from the dehydrogenation product is omitted and that, instead, paraffins are removed from the alkylation products by distillation. In each procedure a paraffin free alkylation product is obtained and subsequently sulphonated.

Example 17

[0080] C_{9-22} branched paraffins produced by polymerisation using methane and syn gas (H_2 and CO)as starting materials were hydrocracked, producing branched paraffins, separated by distillation, and fractions were collected. The individual fractions were analysed for carbon number distribution. Based on the analyses, selected fractions were blended together to meet the specification on carbon number distribution as follows: <10% C_{10}; <2% C_{14}; balance C_{11}-C_{13} (hereinafter collectively "C_{11}-C_{13} paraffins.")

[0081] The following analytical data contain structural information about the resulting branched paraffin. Note: Samples A and B in the table below are the same sample, analysed at different times. Sample B should be more accurate, as it is the more recent and reflects some small improvements in the analytical method over time.

[0082] A sample of C_{11}-C_{13} paraffins was dehydrogenated essentially using known dehydrogenation techniques. In order to run NMR analysis and confirm that the dehydrogenation process does not cause any significant changes in the skeletal structure of the resulting olefin, the resulting product, was re-hydrogenated using a commercial platinum on carbon catalyst and, the resulting product, sample C in the table, was analysed using the same method as was used for samples A and B. The results are contained in column C of the first table and the first set of NMR data.

SAMPLE	**A**	**B**	**C**	**Control 1**	**Control 2**
Ratio branched paraffins to linear paraffins =	**1.9**	**1.8**	**1.8**	**2.6**	**2.6**
Ratio mmp paraffins to linear paraffins =	**0.9**	**0.9**	**0.9**	**2.4**	**2.5**
Ratio highly branched paraffins to linear paraffins =	**1.0**	**0.9**	**0.9**	**0.1**	**0.1**

[0083] The NMR data and chromatographic data gave information on carbon chain length distribution and structure:

NMR Branching Analysis of Dehydrogenated Paraffins

Number of carbons in alkane chain	12 (from GC data)
Branching Index	1.1
%Overall Type of Branching	
C1 (methyl)	79.3
C2 (ethyl)	19.4

(continued)

%Overall Type of Branching	
C3+ (propyl+)	1.3

NMR Branching Analysis of Rehydrogenated Paraffins	
Number of carbons in alkane chain	12 (from GC data)
Branching Index	1.1
%Overall Type of Branching	
C1 (methyl)	73.7
C2 (ethyl)	21.6
C3+ (propyl+)	4.6

[0084] The "Alcohol End Branching Analysis (C-1 refers to alcohol carbon)" box describes branching in the molecule as it pertains to the location of such branches relative to the alcohol end of the molecule. When branching is present next door to the alcohol carbon (C2 carbon), the NMR is able to actually differentiate between, methyl, ethyl and propyl or longer branch types. When branching is on the carbon two away from the alcohol carbon (C3), NMR can only tell that there is a branch but cannot tell if it is a methyl, an ethyl or a propyl or longer. By the time you are three bonds away from the alcohol carbon, the NMR cannot tell if there is any kind of branching. So, the entry "%no branching or branching at the C4+ position" coadds linear molecules as well as molecules that have branching 3+ bonds away from the alcohol carbon.

[0085] The "%Overall Type of Branching" box gives the amounts of C1 (methyl), C2 (ethyl) and C3+ (propyl or longer) branches in the molecule irrespective of where these branches might occur relative to the alcohol end.

[0086] NMR analysis of the candidate sample showed a quaternary carbon content below 0.5%. Molecules containing quaternary carbons are known to be difficult to biodegrade. Hence, a quaternary carbon content below 0.5% renders these materials very useful and quicker to biodegrade.

Example 18

[0087] Using the procedures described in Example 17, the quaternary carbon content of alcohol molecules found in a competitive product were measured. The competitive product was a highly methyl branched alcohol prepared by oligomerisation of propylene followed by hydroformylation, which converted the olefin into a highly methyl branched alcohol. The quaternary carbon content was approximately 0.6. US-A-5112519 describes this product as "a highly methyl branched tridecyl alcohol known for its use in lubricants and detergent formulations which does not require rapid biodegradation."

Example 19 (prophetic)

[0088] The C_{11}-C_{13} paraffins from Example 17 are subjected to the conditions outlined in Example 1 to produce a paraffin free olefin fraction.

[0089] The olefin fraction is reacted with benzene under alkylating conditions, at a molar ratio of benzene to the olefins of 20, at a temperature of 190°C and in the presence of an acidic mordenite catalyst in a quantity of 15%w relative to the weight of the olefin fraction.

[0090] The alkylation product is isolated and purified by filtration and removing the volatile components by distillation. The isolated, purified alkylation product is then sulphonated by a known method.

Claims

1. A process for preparing branched olefins, which process comprises dehydrogenating an isoparaffinic composition comprising 0.5% or less quaternary aliphatic carbon atoms over a suitable catalyst which isoparaffinic composition has been obtained by hydroisomerisation of a paraffinic composition and which isoparaffinic composition comprises paraffins having a carbon number in the range of from 7 to 18, of which paraffins at least a portion of the molecules is branched, the average number of branches per paraffin molecule being 0.5 to 2.5 and the branching comprising methyl and optionally ethyl branches, said branched olefins comprising 0.5% or less quaternary aliphatic hydrocarbons, wherein the paraffinic composition is obtained in a Fischer-Tropsch process.

2. A process as claimed in claim 1, wherein the content of branched paraffins of the isoparaffinic composition is at least 50 %w relative to the weight of the isoparaffinic composition.

3. A process as claimed in claim 1 or 2, wherein the number of methyl branches present in the isoparaffinic composition is at least 20% of the total number of branches.

4. A process for preparing branched alkyl aromatic hydrocarbons, which process comprises contacting branched olefins with an aromatic hydrocarbon under alkylating conditions, which branched olefins have been obtained by a process which comprises dehydrogenating an isoparaffinic composition comprising 0.5% or less quaternary aliphatic carbon atoms over a suitable catalyst, which isoparaffinic composition has been obtained by hydroisomerisation of a paraffinic composition and which isoparaffinic composition comprises paraffins having a carbon number in the range of from 7 to 35, of which paraffins at least a portion of the molecules is branched, the average number of branches per paraffin molecule being 0.5 to 2.5 and the branching comprising methyl and optionally ethyl branches, said branched olefins comprising 0.5% or less quaternary aliphatic hydrocarbons, wherein the paraffinic composition is obtained in a Fischer-Tropsch process.

5. A process as claimed in claim 4, wherein the aromatic hydrocarbon is benzene.

6. A process for preparing (branched-alkyl)arylsulphonates, comprising sulphonating branched alkyl aromatic hydrocarbons which branched alkyl aromatic hydrocarbons have been prepared by a process as claimed in claim 4 or 5.

7. The process of claim 4, 5 or 6, wherein at least 75%w of the isoparaffinic composition consists of paraffins having a carbon number in the range of from 11 to 14.

Patentansprüche

1. Verfahren zur Herstellung verzweigter Olefine, welches die Dehydrierung einer Isoparaffin-Zusammensetzung, die aus 0,5% oder weniger quaternären aliphatischen Kohlenstoffatomen besteht, mittels einem geeigneten Katalysator umfasst, und die Isoparaffin-Zusammensetzung durch Hydroisomerisierung einer Paraffin-Zusammensetzung gewonnen wird, und die Isoparaffin-Zusammensetzung Paraffine enthält, die eine Kohlenstoffzahl in einem Bereich von 7 bis 18 aufweisen, und zumindest ein Teil der Moleküle dieser Paraffine verzweigt sind, und die mittlere Anzahl an Verzweigungen pro Paraffinmolekül zwischen 0,5 und 2,5 liegt und die Verzweigung Methyl- und gegebenenfalls Ethylverzweigungen umfasst, wobei die verzweigten Olefine 0,5% oder weniger quaternäre aliphatische Kohlenwasserstoffe enthalten, wobei die Paraffin-Zusammensetzung in einem Fischer-Tropsch-Verfahren gewonnen wird.

2. Verfahren nach Anspruch 1, wobei der Anteil an verzweigten Paraffinen in der Isoparaffin-Zusammensetzung mindestens 50 Gew.-% bezogen auf das Gewicht der Isoparaffin-Zusammensetzung beträgt.

3. Verfahren nach Anspruch 1 oder 2, wobei die Anzahl der Methylverzweigungen, die in der Isoparaffin-Zusammensetzung vorhanden sind, mindestens 20% der Gesamtanzahl der Verzweigungen ausmacht.

4. Verfahren zur Herstellung verzweigter alkylaromatischer Kohlenwasserstoffe, welches das Inkontaktbringen der verzweigten Olefine mit einem aromatischen Kohlenwasserstoff unter Alkylierungsbedingungen umfasst, und die verzweigten Olefine durch ein Verfahren gewonnen werden, das die Dehydrierung einer Isoparaffin-Zusammensetzung, die 0,5% oder weniger quaternäre aliphatische Kohlenstoffatome enthält, mittels einem geeigneten Katalysator umfasst, und die Isoparaffin-Zusammensetzung durch Hydroisomerisierung einer Paraffin-Zusammensetzung gewonnen ist und die Isoparaffin-Zusammensetzung Paraffine enthält, die eine Kohlenstoffzahl in einem Bereich von 7 bis 35 aufweisen, und zumindest ein Teil der Moleküle dieser Paraffine verzweigt ist, und die mittlere Anzahl der Verzweigungen pro Paraffinmolekül zwischen 0,5 bis 2,5 liegt, und die Verzweigung Methyl- und gegebenenfalls Ethylverzweigungen umfasst, wobei die verzweigten Olefine 0,5% oder weniger quaternäre aliphatische Kohlenwasserstoffe enthalten, wobei die Paraffin-Zusammensetzung in einem Fischer-Tropsch-Verfahren gewonnen wird.

5. Verfahren nach Anspruch 4, wobei der aromatische Kohlenwasserstoff Benzol ist.

6. Verfahren zur Herstellung von (verzweigten Alkyl-)arylsulphonaten, umfassend die Sulfonierung verzweigter alkylaromatischer Kohlenwasserstoffe, wobei die verzweigten alkylaromatischen Kohlenwasserstoffe durch ein Verfahren nach einem der Ansprüche 4 oder 5 hergestellt werden.

7. Verfahren nach Anspruch 4, 5 oder 6, wobei zumindest 75 Gew.-% der Isoparaffin-Zusammensetzung aus Paraffinen bestehen, die eine Kohlenstoffzahl in einem Bereich von 11 bis 14 aufweisen.

Revendications

1. Procédé de préparation d'oléfines ramifiées, lequel procédé comprend la déshydrogénation d'une composition isoparaffinique comprenant 0,5 % ou moins d'atomes de carbone aliphatiques quaternaires sur un catalyseur approprié, laquelle composition isoparaffinique a été obtenue par hydroisomérisation d'une composition paraffinique et laquelle composition isoparaffinique comprend des paraffines ayant un nombre d'atomes de carbone dans la plage de 7 à 18, au moins une partie des molécules de ces paraffines étant ramifiées, le nombre moyen de ramures par molécule de paraffine étant de 0,5 à 2,5 et la ramification comprenant les ramures méthyle et facultativement éthyle, lesdites oléfines ramifiées comprenant 0,5 % au moins d'hydrocarbures aliphatiques quaternaires, dans lequel la composition paraffinique est obtenue dans un procédé Fischer-Tropsch.

2. Procédé selon la revendication 1, dans lequel la teneur en paraffines ramifiées de la composition isoparaffinique est d'au moins 50 % en poids par rapport au poids de la composition isoparaffinique.

3. Procédé selon la revendication 1 ou 2, dans lequel le nombre de ramures méthyle présentes dans la composition isoparaffinique est d'au moins 20 % du nombre total de ramures.

4. Procédé de préparation d'hydrocarbures aromatiques d'alkyle ramifié, lequel procédé comprend la mise en contact d'oléfines ramifiées avec un hydrocarbure aromatique dans des conditions d'alkylation, lesquelles oléfines ramifiées ont été obtenues par un procédé qui comprend la déshydrogénation d'une composition isoparaffinique comprenant 0,5 % ou moins d'atomes de carbone aliphatiques quaternaires sur un catalyseur approprié, laquelle composition isoparaffinique a été obtenue par hydroisomérisation d'une composition paraffinique et laquelle composition isoparaffinique comprend des paraffines ayant un nombre d'atomes de carbone dans la plage de 7 à 35, au moins une partie des molécules de ces paraffines étant ramifiées, le nombre moyen de ramures par molécule de paraffine étant de 0,5 à 2,5 et la ramification comprenant les ramures méthyle et facultativement éthyle, lesdites oléfines ramifiées comprenant 0,5 % au moins d'hydrocarbures aliphatiques quaternaires, dans lequel la composition paraffinique est obtenue dans un procédé Fischer-Tropsch.

5. Procédé selon la revendication 4, dans lequel l'hydrocarbure aromatique est le benzène.

6. Procédé de préparation d'arylsulfonates (d'alkyle ramifié) comprenant la sulfonation d'hydrocarbures aromatiques d'alkyle ramifié, lesquels hydrocarbures aromatiques d'alkyle ramifié ont été préparés par un procédé selon la revendication 4 ou 5.

7. Procédé selon la revendication 4, 5 ou 6, dans lequel au moins 75 % en poids de la composition isoparaffinique consiste en des paraffines ayant un nombre d'atomes de carbone dans la plage de 11 à 14.

REFERENCES CITED IN THE DESCRIPTION

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