

REPLACED SHEETS		SG
☒	Description : paged ...1... to paged ...7...	
☒	Claim(s) : paged ...2... to paged ...3...	
☐	Drawing(s) : paged ... to paged ...	
☒	Abstract : paged ...4... to paged ...	
DATE OF RECEIPT		

Decyl alcohol mixtures, phthalic esters
therefrom and their use as plasticizers

The invention relates to mixtures of isomeric decyl alcohols, a process for the preparation thereof, the phthalic esters obtained from these alcohols and their use as plasticizers.

Esters of phthalic acid are used to a great extent as plasticizers, in particular for polyvinyl chloride. The alcohol components chiefly used are primary alcohols having 8 to 10 carbon atoms; the most important of these is currently 2-ethylhexanol. Phthalic esters of shorter-chain alcohols lead to plasticizers having good gelling capacity. However, their higher volatility is disadvantageous. Longer-chain esters on the other hand gel more slowly and have a poorer cold resistance.

The properties of the phthalic ester plasticizers are influenced not only by the size of the alcohol molecule but also by the branching of the carbon chain. Thus alcohols having little branching give ester plasticizers having high cold flexibility. Substantially linear alcohols having 8 to 10 carbon atoms in the molecule are thus increasing in importance as alcohol component. A precondition for their use is that they are available in large amounts and at favorable cost.

According to German Patent 2 855 421, phthalates of C₈ alcohols are used as plasticizers which are obtained by oxoreaction of C₈ olefins, hydrogenation of the reaction product and esterification of the C₈ alcohols using phthalic anhydride. 3 to 20% by weight of the starting olefins are to have an isobutane skeleton in each molecule chain, less than 3% by weight of the olefins are to have quaternary carbon and more than 90% by weight of the total amount of the olefins are to be present as n-octenes, monomethylheptenes and dimethylhexenes. In addition, the weight ratio of the total amount of the n-octenes and monomethylheptenes to the dimethylhexenes



- 2 -

is to be more than 0.8.

Phthalic esters based on C_{10} alcohols are an object of European Patent Application 03 66 089. The C_{10} alcohols are used in the form of a mixture which is obtained by hydroformylation of a butene fraction, aldol condensation of the resulting aldehyde mixture and subsequent hydrogenation. The hydroformylation step is not subject to any restrictions according to the process description. Thus both cobalt and rhodium can be used as catalyst and the addition of an organic compound of trivalent phosphorus is not excluded.

Another route to obtain didecyl phthalate mixtures is described in European Patent Application 04 24 767. The preparation of the esters is carried out by a multi-stage process by dimerization of butene mixtures, hydroformylation and hydrogenation of the resulting octene mixture to give a nonanol mixture, dehydration of the nonanol mixture with formation of a nonene mixture and hydroformylation and hydrogenation of the nonene mixture with formation of a decanol mixture.

The known processes do not yet fulfil all the requirements from the economic and industrial aspect made of a process carried out on an industrial scale, whether it be that the starting materials are not available in sufficient quantity and/or are not available at favorable costs or that the conversion of the starting materials into the alcohols is associated with processes which are too expensive. In processes which start from butenes which are hydroformylated, the n-valeraldehyde content of the hydroformylation product should, in particular, be as high as possible, in order to promote the formation of straight-chain or only slightly branched alcohols.

The object was therefore to develop a process which starts not only from raw materials which are cheaply

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- 3 -

available but which can also be converted in an industrially simple manner into the desired straight-chain or slightly branched alcohols.

5 The invention comprises mixtures of isomeric decyl alcohols, which are obtained by hydroformylation of 1-butene- and 2-butene-containing mixtures in two stages, the reaction in the first stage being carried out in a heterogeneous reaction system with the use of rhodium compounds containing complexed water-soluble phosphines
10 as catalysts at temperatures of 70 to 150°C and pressures of 0.4 to 30 MPa and the reaction in the second stage being carried out in homogeneous phase in the presence of rhodium compounds as catalysts at temperatures of 90 to 180°C and pressures of 10 to 35 MPa to give aldehyde
15 mixtures, isolation and combination of the resulting aldehyde mixtures from the hydroformylation stages, condensation of the combined aldehyde mixture with formation of an aldol mixture and isolation and hydrogenation of the aldol mixture to give a mixture of
20 isomeric decyl alcohols.

The 1-butene and 2-butene-containing mixtures used for the preparation of the mixture of isomeric decyl alcohols according to the invention are unavoidably produced in considerable amounts as refinery by-products in the
25 production of automobile fuels and in the preparation of ethylene by thermal cracking of higher hydrocarbons. They are obtained from the C₄ cracking cuts of the pyrolysis product by extraction of the butadiene using a selective solvent and subsequent isolation of the isobutene,
30 preferably by conversion into methyl tert-butyl ether. The pyrolysis product freed from butadiene is termed raffinate I; if, moreover, the isobutene is also isolated, one speaks of raffinate II. Instead of the butadiene being extracted, it can also be partially
35 hydrogenated in the C₄ cracking cut to give butenes. After isolation of the isobutene, a 1-butene/2-butene mixture

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- 4 -

is obtained which is particularly suitable for further processing to C₁₀ alcohols. Finally, there has recently been a move to hydrogenating the isolated butadiene to give butane and returning it to the cracking in order to increase the ethylene and propylene yield.

According to the invention, 1-butene- and 2-butene-containing mixtures, for example in the form of raffinate II, but also of other origin and composition, are hydroformylated in two stages. In the first stage 1-butene is preferably reacted to form a mixture which is predominantly composed of n-valeraldehyde and, in a subsidiary amount, of i-valeraldehyde. The reaction proceeds under conditions which substantially exclude isomerization of 1-butene to give 2-butene. In the second stage, the 2-butene is hydroformylated to give a mixture of n-valeraldehyde and i-valeraldehyde.

The first stage of the hydroformylation is carried out as a heterogeneous reaction in a two-phase system, a reaction which is described, for example, in German Patent 26 27 354. This process is characterized by the presence of an organic phase, which contains the starting olefins and the reaction product, and an aqueous phase in which the catalyst is dissolved. Catalysts used are water-soluble rhodium complexes which contain water-soluble phosphines as ligands. The phosphines include in particular triarylphosphines, trialkylphosphines and arylated or alkylated diphosphines, the organic radicals of which are substituted by sulfonic acid groups or carboxyl groups. Their preparation is known, cf., for example, German Patent 26 27 354 and German Democratic Republic Patent 259 194. The reaction of the butenes is carried out at temperatures of 70 to 150°C, preferably 100 to 130°C, and at pressures in the range from 0.4 to 30, in particular 1 to 10, MPa with water gas which contains carbon monoxide and hydrogen in the volume ratio 1:10 to 10:1. The rhodium concentration is 20 to 1000 ppm by

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- 5 -

weight, preferably 50 to 500 ppm by weight, based on the aqueous catalyst solution, and 4 to 100 mol of water-soluble phosphine are used per mole of rhodium. The volume ratio of aqueous to organic phase is 0.1 to 10:1.

5. The butene conversion is markedly increased if a phase transfer reagent (solubilizer) is added to the aqueous catalyst solution. In particular, cationic solubilizers of the formula $[A-N(R^1R^2R^3)]^+E^-$ have proved themselves, in which A is a straight-chain or branched alkyl radical having 6 to 25 carbon atoms, R^1 , R^2 , R^3 are identical or different and are straight-chain or branched alkyl radicals having 1 to 4 carbon atoms and E is in particular sulfate, tetrafluoroborate, acetate, methosulfate, benzenesulfonate, alkylbenzenesulfonate, toluenesulfonate, lactate or citrate.

In the case of a conversion of 1-butene of up to 95%, depending on the reaction parameters selected, the aldehyde mixture contains 90% or more of n-valeraldehyde; the remainder is i-valeraldehyde.

- 20 Olefin unreacted in the first stage, predominantly 2-butene, is hydroformylated in a second reaction stage in homogeneous phase and in the presence of rhodium as catalyst. Reaction temperatures which have proved themselves are 90 to 180°C and preferably 130 to 150°C and pressures of 10 to 35 MPa, in particular 20 to 30 MPa. Rhodium is supplied to the reaction mixture as a metal, expediently in finely divided form or, better, as a compound soluble in organic media, for example as carbonyl compound or as the salt of a carboxylic acid.
- 25 The rhodium concentration is 2 to 100 ppm by weight, preferably 5 to 30 ppm by weight, based on the butenes introduced into the second reaction stage. The presence of a solvent such as toluene, xylene or tetrahydrofuran is not necessarily required, since its function can be
- 30 taken over by the starting material and the reaction
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- 6 -

product. The water gas has the same composition as in the first reaction step. Depending on the reaction conditions, up to 99% of the olefin used is converted into n- and i-valeraldehyde.

5 After the hydroformylation is completed, the aldehyde mixture of both reaction steps is isolated from the catalyst, from the unreacted reactants and from the other reaction products. In the case of the heterogeneous reaction (first stage) this is achieved by simple phase
10 separation. When the reaction takes place in homogeneous phase, i.e. in the second stage of the novel process, distillation is the conventional separation process.

The aldol condensation of the aldehydes present as a mixture is carried out by a conventional route with the
15 action of basic catalysts. A pretreatment of the aldehydes, for example a special purification, is not required. The catalysts used are alkali metal carbonates or alkali metal hydroxides, in particular compounds of sodium or potassium and amines, preferably tertiary
20 amines, such as triethylamine, tri-n-propylamine and tri-n-butylamine. Temperatures of 60 to 160°C are employed, in particular 80 to 130°C, and atmospheric pressure or elevated pressure up to about 1 MPa is employed. The reaction time is a few minutes up to several hours and is
25 dependent, in particular, on the type of catalyst and reaction temperature. Because of its higher reaction rate, n-valeraldehyde principally dimerizes with itself or with isomeric valeraldehydes to give decenals; in contrast, condensation of the branched C₅ aldehydes
30 between themselves occurs completely in the background.

The aldehyde mixture obtained by condensation is then hydrogenated to give a decyl alcohol mixture. The hydrogen addition takes place in a known manner in the presence of catalysts. Suitable catalysts are, for
35 example, hydrogenation catalysts based on nickel,

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- 7 -

chromium or copper. The hydrogenation temperature is conventionally between 100 and 180°C and the pressure between 1 and 10 MPa. The decyl alcohol mixture is distilled for purification. It is especially suitable as alcohol component in phthalic esters which are to be used as plasticizers. The preparation of the phthalic esters is known [cf. Ullmann, Encyclopädie der Technischen Chemie [Encyclopedia of Industrial Chemistry] (1979), volume 18, page 536 ff]. Phthalic anhydride is expediently reacted with the decyl alcohol mixture in the molar ratio 1:2 in one stage. The reaction rate can be increased by catalysts and/or by increasing the reaction temperature. In order to displace the equilibrium in the direction of ester formation, it is necessary to eliminate the water formed from the reaction mixture.

The phthalates obtained from the decyl alcohol mixture according to the invention are distinguished as plasticizers by excellent cold properties.

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Patent claims

1. A mixture of isomeric decyl alcohols, obtained by hydroformylation of 1-butene- and 2-butene-containing mixtures in two stages, the reaction in the first stage being carried out in a heterogeneous reaction system with the use of rhodium compounds containing complexed water-soluble phosphines as catalysts at temperatures of 20. to 150°C and pressures of 0.1 to 20 MPa and the reaction in the second stage being carried out in homogeneous phase in the presence of rhodium compounds as catalysts at temperatures of 90 to 180°C and pressures of 10 to 35 MPa to give aldehyde mixtures, isolation and combination of the resulting aldehyde mixtures from the hydroformylation stages, condensation of the combined aldehyde mixture with formation of an aldol mixture and isolation and hydrogenation of the aldol mixture to give a mixture of isomeric decyl alcohols.
2. The mixture of isomeric decyl alcohols as claimed in claim 1, wherein the reaction in the first hydroformylation stage is carried out at temperatures of 100 to 130°C and at pressures of 1 to 10 MPa.
3. The mixture of isomeric decyl alcohols as claimed in claim 1 or 2, wherein the reaction in the first hydroformylation stage is carried out at a rhodium concentration of 20 to 1000 ppm by weight, preferably 50 to 500 ppm by weight, based on the aqueous catalyst solution.
4. The mixture of isomeric decyl alcohols as claimed in one or more of claims 1 to 3, wherein, in the first hydroformylation stage, 4 to 100 mol of water-soluble phosphine are used per mole of rhodium.



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- 9 -



5. The mixture of isomeric decyl alcohols as claimed in one or more of claims 1 to 4, wherein, in the first hydroformylation stage, a phase transfer reagent is added to the aqueous catalyst solution.
- 5 6. The mixture of isomeric decyl alcohols as claimed in one or more of claims 1 to 5, wherein the reaction in the second hydroformylation stage is carried out at 130 to 150°C and pressures of 20 to 30 MPa.
- 10 7. The mixture of isomeric decyl alcohols as claimed in one or more of claims 1 to 6, wherein the reaction in the second hydroformylation stage is carried out at a rhodium concentration of 2 to 100 ppm by weight, preferably 5 to 30 ppm by weight, based on the butenes introduced into the second hydroformylation stage.
- 15 8. A mixture of isomeric didecyl phthalates obtained by esterification of phthalic acid or phthalic anhydride with a mixture of isomeric decyl alcohols as claimed in one or more of claims 1 to 7.
- 20 9. Use of the mixture of isomeric didecyl phthalates as claimed in claim 8 as plasticizer.

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Frankfurt, 26.03.1992
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Abstract of the disclosure

Mixtures of isomeric decyl alcohols are obtained by hydroformylation of 1-butene- and 2-butene-containing mixtures in two stages to give aldehyde mixtures, condensation of the isolated and combined aldehyde mixtures with formation of an aldol mixture and isolation and hydrogenation of the aldol mixture. The mixture of isomeric decyl alcohols, esterified using phthalic acid, gives a mixture of isomeric decyl phthalates which are used as plasticizers.

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- ☒ Description : paged 1.1 to paged 7.1
☒ Claim(s) : paged 2.1 to paged 3.1
☐ Drawing(s) : paged 4.1 to paged 5.1
☒ Abstract : paged 6.1 to paged 7.1

1

DATE OF RECEIPT 25/2/97

Decyl alcohol mixtures, phthalic esters obtainable
therefrom and their use as plasticizers

The invention relates to mixtures of isomeric decyl alcohols, a process for the preparation thereof, the phthalic esters obtained from these alcohols and their use as plasticizers.

Esters of phthalic acid are used to a great extent as plasticizers, in particular for polyvinyl chloride. The alcohol components chiefly used are primary alcohols having 8 to 10 carbon atoms; the most important of these is currently 2-ethylhexanol. Phthalic esters of shorter-chain alcohols lead to plasticizers having good gelling capacity. However, their higher volatility is disadvantageous. Longer-chain esters on the other hand gel more slowly and have a poorer cold resistance.

The properties of the phthalic ester plasticizers are influenced not only by the size of the alcohol molecule but also by the branching of the carbon chain. Thus alcohols having little branching give ester plasticizers having high cold flexibility. Substantially linear alcohols having 8 to 10 carbon atoms in the molecule are thus increasing in importance as alcohol component. A precondition for their use is that they are available in large amounts and at favorable cost.

According to German Patent 2 855 421, phthalates of C₈ alcohols are used as plasticizers which are obtained by oxoreaction of C₈ olefins, hydrogenation of the reaction product and esterification of the C₈ alcohols using phthalic anhydride. 3 to 20% by weight of the starting olefins are to have an isobutane skeleton in each molecule chain, less than 3% by weight of the olefins are to have quaternary carbon and more than 90% by weight of the total amount of the olefins are to be present as n-octenes, monomethylheptenes and dimethylhexenes. In addition, the weight ratio of the total amount of the n-octenes and monomethylheptenes to the dimethylhexenes

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25 FEB 1997

25 FEB 1997

is to be more than 0.8.

Phthalic esters based on C_{10} alcohols are an object of European Patent Application 03 66 089. The C_{10} alcohols are used in the form of a mixture which is obtained by hydroformylation of a butene fraction, aldol condensation of the resulting aldehyde mixture and subsequent hydrogenation. The hydroformylation step is not subject to any restrictions according to the process description. Thus both cobalt and rhodium can be used as catalyst and the addition of an organic compound of trivalent phosphorus is not excluded.

Another route to obtain didecyl phthalate mixtures is described in European Patent Application 04 24 767. The preparation of the esters is carried out by a multi-stage process by dimerization of butene mixtures, hydroformylation and hydrogenation of the resulting octene mixture to give a nonanol mixture, dehydration of the nonanol mixture with formation of a nonene mixture and hydroformylation and hydrogenation of the nonene mixture with formation of a decanol mixture.

The known processes do not yet fulfil all the requirements from the economic and industrial aspect made of a process carried out on an industrial scale, whether it be that the starting materials are not available in sufficient quantity and/or are not available at favorable costs or that the conversion of the starting materials into the alcohols is associated with processes which are too expensive. In processes which start from butenes which are hydroformylated, the n-valeraldehyde content of the hydroformylation product should, in particular, be as high as possible, in order to promote the formation of straight-chain or only slightly branched alcohols.

The object was therefore to develop a process which starts not only from raw materials which are cheaply

available but which can also be converted in an industrially simple manner into the desired straight-chain or slightly branched alcohols.

5 The invention comprises mixtures of isomeric decyl alcohols, which are obtained by hydroformylation of 1-butene- and 2-butene-containing mixtures in two stages, the reaction in the first stage being carried out in a heterogeneous reaction system with the use of rhodium compounds containing complexed water-soluble phosphines
10 as catalysts at temperatures of 70 to 150°C and pressures of 0.4 to 30 MPa and the reaction in the second stage being carried out in homogeneous phase in the presence of rhodium compounds as catalysts at temperatures of 90 to 180°C and pressures of 10 to 35 MPa to give aldehyde
15 mixtures, isolation and combination of the resulting aldehyde mixtures from the hydroformylation stages, condensation of the combined aldehyde mixture with formation of an aldol mixture and isolation and hydrogenation of the aldol mixture to give a mixture of
20 isomeric decyl alcohols.

The 1-butene and 2-butene-containing mixtures used for the preparation of the mixture of isomeric decyl alcohols according to the invention are unavoidably produced in considerable amounts as refinery by-products in the
25 production of automobile fuels and in the preparation of ethylene by thermal cracking of higher hydrocarbons. They are obtained from the C₄ cracking cuts of the pyrolysis product by extraction of the butadiene using a selective solvent and subsequent isolation of the isobutene,
30 preferably by conversion into methyl tert-butyl ether. The pyrolysis product freed from butadiene is termed raffinate I; if, moreover, the isobutene is also isolated, one speaks of raffinate II. Instead of the butadiene being extracted, it can also be partially
35 hydrogenated in the C₄ cracking cut to give butenes. After isolation of the isobutene, a 1-butene/2-butene mixture

REPLACEMENT SHEET

25 FEB 1997

25 FEB 1997

- 4 -

is obtained which is particularly suitable for further processing to C_{10} alcohols. Finally, there has recently been a move to hydrogenating the isolated butadiene to give butane and returning it to the cracking in order to increase the ethylene and propylene yield.

According to the invention, 1-butene- and 2-butene-containing mixtures, for example in the form of raffinate II, but also of other origin and composition, are hydroformylated in two stages. In the first stage 1-butene is preferably reacted to form a mixture which is predominantly composed of n-valeraldehyde and, in a subsidiary amount, of i-valeraldehyde. The reaction proceeds under conditions which substantially exclude isomerization of 1-butene to give 2-butene. In the second stage, the 2-butene is hydroformylated to give a mixture of n-valeraldehyde and i-valeraldehyde.

The first stage of the hydroformylation is carried out as a heterogeneous reaction in a two-phase system, a reaction which is described, for example, in German Patent 26 27 354. This process is characterized by the presence of an organic phase, which contains the starting olefins and the reaction product, and an aqueous phase in which the catalyst is dissolved. Catalysts used are water-soluble rhodium complexes which contain water-soluble phosphines as ligands. The phosphines include in particular triarylphosphines, trialkylphosphines and arylated or alkylated diphosphines, the organic radicals of which are substituted by sulfonic acid groups or carboxyl groups. Their preparation is known, cf., for example, German Patent 26 27 354 and German Democratic Republic Patent 259 194. The reaction of the butenes is carried out at temperatures of 70 to 150°C, preferably 100 to 130°C, and at pressures in the range from 0.4 to 30, in particular 1 to 10, MPa with water gas which contains carbon monoxide and hydrogen in the volume ratio 1:10 to 10:1. The rhodium concentration is 20 to 1000 ppm by

25 FEB 1997

- 5 -

weight, preferably 50 to 500 ppm by weight, based on the aqueous catalyst solution, and 4 to 100 mol of water-soluble phosphine are used per mole of rhodium. The volume ratio of aqueous to organic phase is 0.1 to 10:1.

5. The butene conversion is markedly increased if a phase transfer reagent (solubilizer) is added to the aqueous catalyst solution. In particular, cationic solubilizers of the formula $[A-N(R^1R^2R^3)]^+E^-$ have proved themselves, in which A is a straight-chain or branched alkyl radical having 6 to 25 carbon atoms, R^1 , R^2 , R^3 are identical or different and are straight-chain or branched alkyl radicals having 1 to 4 carbon atoms and E is in particular sulfate, tetrafluoroborate, acetate, methosulfate, benzenesulfonate, alkylbenzenesulfonate, toluenesulfonate, lactate or citrate.

In the case of a conversion of 1-butene of up to 95%, depending on the reaction parameters selected, the aldehyde mixture contains 90% or more of n-valeraldehyde; the remainder is i-valeraldehyde.

- 20 Olefin unreacted in the first stage, predominantly 2-butene, is hydroformylated in a second reaction stage in homogeneous phase and in the presence of rhodium as catalyst. Reaction temperatures which have proved themselves are 90 to 180°C and preferably 130 to 150°C and pressures of 10 to 35 MPa, in particular 20 to 30 MPa. Rhodium is supplied to the reaction mixture as a metal, expediently in finely divided form or, better, as a compound soluble in organic media, for example as carbonyl compound or as the salt of a carboxylic acid.
- 25
- 30 The rhodium concentration is 2 to 100 ppm by weight, preferably 5 to 30 ppm by weight, based on the butenes introduced into the second reaction stage. The presence of a solvent such as toluene, xylene or tetrahydrofuran is not necessarily required, since its function can be
- 35 taken over by the starting material and the reaction

25 FEB 1997

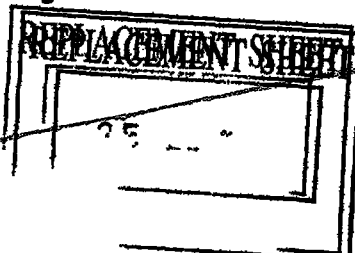
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product. The water gas has the same composition as in the first reaction step. Depending on the reaction conditions, up to 99% of the olefin used is converted into n- and i-valeraldehyde.

- 5 After the hydroformylation is completed, the aldehyde mixture of both reaction steps is isolated from the catalyst, from the unreacted reactants and from the other reaction products. In the case of the heterogeneous reaction (first stage) this is achieved by simple phase
10 separation. When the reaction takes place in homogeneous phase, i.e. in the second stage of the novel process, distillation is the conventional separation process.

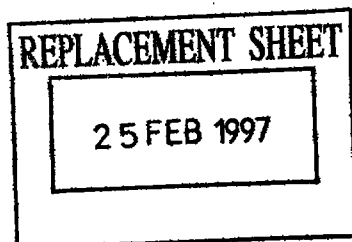
- The aldol condensation of the aldehydes present as a mixture is carried out by a conventional route with the
15 action of basic catalysts. A pretreatment of the aldehydes, for example a special purification, is not required. The catalysts used are alkali metal carbonates or alkali metal hydroxides, in particular compounds of sodium or potassium and amines, preferably tertiary
20 amines, such as triethylamine, tri-n-propylamine and tri-n-butylamine. Temperatures of 60 to 160°C are employed, in particular 80 to 130°C, and atmospheric pressure or elevated pressure up to about 1 MPa is employed. The reaction time is a few minutes up to several hours and is
25 dependent, in particular, on the type of catalyst and reaction temperature. Because of its higher reaction rate, n-valeraldehyde principally dimerizes with itself or with isomeric valeraldehydes to give decenals; in contrast, condensation of the branched C₅ aldehydes
30 between themselves occurs completely in the background.

- The aldehyde mixture obtained by condensation is then hydrogenated to give a decyl alcohol mixture. The hydrogen addition takes place in a known manner in the presence of catalysts. Suitable catalysts are, for
35 example, hydrogenation catalysts based on nickel,



chromium or copper. The hydrogenation temperature is conventionally between 100 and 180°C and the pressure between 1 and 10 MPa. The decyl alcohol mixture is distilled for purification. It is especially suitable as
5 alcohol component in phthalic esters which are to be used as plasticizers. The preparation of the phthalic esters is known [cf. Ullmann, Encyclopädie der Technischen Chemie [Encyclopedia of Industrial Chemistry] (1979), volume 18, page 536 ff]. Phthalic anhydride is
10 expediently reacted with the decyl alcohol mixture in the molar ratio 1:2 in one stage. The reaction rate can be increased by catalysts and/or by increasing the reaction temperature. In order to displace the equilibrium in the direction of ester formation, it is necessary to elimi-
15 nate the water formed from the reaction mixture.

The phthalates obtained from the decyl alcohol mixture according to the invention are distinguished as plasticizers by excellent cold properties.



Patent claims



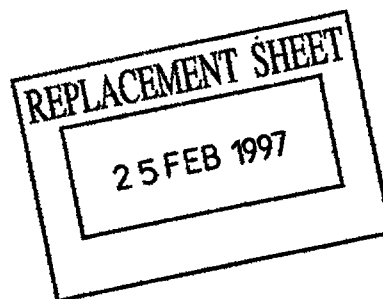
1. A mixture of isomeric decyl alcohols, obtained by hydroformylation of 1-butene- and 2-butene-containing mixtures in two stages, the reaction in the first stage being carried out in a heterogeneous reaction system with the use of rhodium compounds containing complexed water-soluble phosphines as catalysts at temperatures of 20 to 150°C and pressures of 0.1 to 20 MPa and the reaction in the second stage being carried out in homogeneous phase in the presence of rhodium compounds as catalysts at temperatures of 90 to 180°C and pressures of 10 to 35 MPa to give aldehyde mixtures, isolation and combination of the resulting aldehyde mixtures from the hydroformylation stages, condensation of the combined aldehyde mixture with formation of an aldol mixture and isolation and hydrogenation of the aldol mixture to give a mixture of isomeric decyl alcohols.
2. The mixture of isomeric decyl alcohols as claimed in claim 1, wherein the reaction in the first hydroformylation stage is carried out at temperatures of 100 to 130°C and at pressures of 1 to 10 MPa.
3. The mixture of isomeric decyl alcohols as claimed in claim 1 or 2, wherein the reaction in the first hydroformylation stage is carried out at a rhodium concentration of 20 to 1000 ppm by weight, preferably 50 to 500 ppm by weight, based on the aqueous catalyst solution.
4. The mixture of isomeric decyl alcohols as claimed in one or more of claims 1 to 3, wherein, in the first hydroformylation stage, 4 to 100 mol of water-soluble phosphine are used per mole of rhodium.

REPLACEMENT SHEET

25 FEB 1997



5. The mixture of isomeric decyl alcohols as claimed in one or more of claims 1 to 4, wherein, in the first hydroformylation stage, a phase transfer reagent is added to the aqueous catalyst solution.
- 5 6. The mixture of isomeric decyl alcohols as claimed in one or more of claims 1 to 5, wherein the reaction in the second hydroformylation stage is carried out at 130 to 150°C and pressures of 20 to 30 MPa.
- 10 7. The mixture of isomeric decyl alcohols as claimed in one or more of claims 1 to 6, wherein the reaction in the second hydroformylation stage is carried out at a rhodium concentration of 2 to 100 ppm by weight, preferably 5 to 30 ppm by weight, based on the butenes introduced into the second hydroformylation stage.
15
8. A mixture of isomeric didecyl phthalates obtained by esterification of phthalic acid or phthalic anhydride with a mixture of isomeric decyl alcohols as claimed in one or more of claims 1 to 7.
- 20 9. Use of the mixture of isomeric didecyl phthalates as claimed in claim 8 as plasticizer.



Abstract of the disclosure

**DECYL ALCOHOL MIXTURES, PHTHALIC ESTERS OBTAINABLE
THEREFROM AND THEIR USE AS PLASTICIZERS**

Mixtures of isomeric decyl alcohols are obtained by hydroformylation of 1-butene- and 2-butene-containing mixtures in two stages to give aldehyde mixtures, condensation of the isolated and combined aldehyde mixtures with formation of an aldol mixture and isolation and hydrogenation of the aldol mixture. The mixture of isomeric decyl alcohols, esterified using phthalic acid, gives a mixture of isomeric decyl phthalates which are used as plasticizers.

REPLACEMENT SHEET

25 FEB 1997