

No 8066-8
IPDS

☒ Description : paged to paged
☒ Claim(s) : paged to paged
☐ Drawing(s) : paged to paged
 DATE OF RECEIPT

Mixtures of isomeric decyl alcohols, phthalates obtainable
therefrom, and their use as plasticizers

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

Esters of phthalic acid are used in large amounts as plasticizers, in particular for polyvinyl chloride. The alcohol component used is predominantly primary alcohols
 10 having 8 to 10 carbon atoms, 2-ethylhexanol currently being the most important of such alcohols. Phthalates formed from shorter-chain alcohols provide plasticizers having a good gelling strength. However, a disadvantage compared to longer-chained compounds is their greater
 15 volatility. Longer-chain esters on the other hand gel more slowly and have a lower low-temperature resistance.

The properties of phthalate plasticizers are influenced by the size of the alcohol molecule and also by the branching of the carbon chain. For example, alcohols with
 20 few branches produce ester plasticizers that are particularly valued despite their high low-temperature flexibility. Predominantly linear alcohols having 9 to 10 carbon atoms in the molecule are therefore becoming increasingly important as alcohol component. A precondition for their use is that they are available in large
 25 amounts and are relatively inexpensive.

According to German Patent 2 855 421, the plasticizers used are phthalates of C₈-alcohols, which are obtained by oxo reaction of C₈-olefins, hydrogenation of the reaction
 30 product and esterification of the C₈-alcohols with phthalic anhydride. From 3 to 20 % by weight of the starting olefins should have an isobutane skeleton in each molecular chain, less than 3 % by weight of the olefins contain quaternary carbon, and more than 90 % by
 35 weight of the total amount of the olefins are present as n-octenes, monomethylheptenes and dimethylhexenes.



This Sheet Has Been Replaced



- 2 -

Furthermore, the weight ratio of the total amount of n-octenes and monomethylheptenes to the dimethylhexenes should be more than 0.8.

5 Phthalates based on C_{10} -alcohols are the subject of European Patent Application 0 366 089. The C_{10} -alcohols are used in the form of a mixture that is obtained by hydroformylation of a butene fraction, aldol condensation of the resultant aldehyde mixture, and subsequent hydrogenation.

10 Another route for obtaining di-decyl phthalate mixtures is described in European Patent Application 0 424 767. The esters are prepared by a multistage process involving dimerization of butene mixtures, hydroformylation and hydrogenation of the resulting octene mixture to form a
15 nonanol mixture, dehydration of the nonanol mixture with the formation of a nonene mixture, and hydroformylation and hydrogenation of the nonene mixture with the formation of a decanol mixture.

20 The known processes still do not satisfy, as regards economic and technical aspects, all requirements that are placed on a process employed on a large scale, whether it is the fact that the starting substances are not available in sufficient amounts and/or not inexpensively, or that the conversion of the starting materials into the
25 alcohols involves processes that are too complicated.

The object was therefore to develop a process that starts from raw materials that are available at a reasonable price and that can be converted into the desired alcohols in a technically simple manner.

30 The invention consists in mixtures of isomeric decyl alcohols. These decyl alcohols are obtained by oligomerization of propylene in the presence of deactivated zeolites as catalysts, separation of the

This Sheet Has Been Replaced



- 3 -

C₉-olefins from the oligomer mixture, hydroformylation of the C₉-olefins to C₁₀-aldehydes, and hydrogenation of the C₁₀-aldehydes.

5 The C₉-olefins used as starting material for the preparation of the novel mixtures of isomeric decyl alcohols are contained in the product of the oligomerization of propylene in the presence of deactivated zeolites. The oligomerization of low molecular weight olefins such as propylene, n-butene, i-butene, n-pentene under the action
10 of special zeolites is a known reaction, and is described for example in US Patent 4 982 031. The catalytically active zeolites are preferably of the ZSM-5 type, whose surface has been deactivated with a sterically hindered base, e.g. a trialkylated pyridine. Propylene as the
15 olefin produces, for example, an oligomer mixture essentially comprising monoolefins having 6, 9, 12, 15, 18 and 21 carbon atoms. It is particularly significant that these olefins are largely unbranched. Based on the compounds of different molecular size in the oligomer
20 mixture, there are only about one to two methyl branches for every 15 carbon atoms arranged in an unbranched chain. Due to the low degree of branching, the C₉-olefins obtained as described hereinbefore differ recognizably from the propylene oligomer termed tripropylene, which is
25 prepared from propylene in the presence of acid catalysts, in particular phosphoric acid or sulfuric acid, and which comprises a mixture of highly branched nonenes.

30 In order to isolate the C₉-olefins that are intended to be processed further, the oligomerization product is separated in a conventional way by distillation into individual fractions. The nonene fraction that is obtained can be hydroformylated without additional purification stages.

35 The hydroformylation of the C₉-olefin mixture used as starting material according to the invention is carried

This Sheet Has Been Replaced



- 4 -

- out by the prior art processes customarily used for olefins. Cobalt as well as rhodium may be used in a manner known per se as catalysts. The reaction can be carried out in the homogeneous liquid phase, in other words with catalysts that are soluble in organic media, or can be carried out in heterogeneous reaction systems with catalysts that are dissolved in water. The last-mentioned reaction procedure has been found to be suitable particularly in conjunction with rhodium catalysts.
- 10 In the case of hydroformylation in homogeneous reaction systems, the conventional process with cobalt catalysts is used. Temperatures of from 90 to 150°C, pressures of from 10 to 30 MPa and catalyst concentrations of from 0.1 to 1.5 % by weight of cobalt, based on the olefin
- 15 employed, are the standard reaction conditions. Instead of cobalt, the hydroformylation catalyst may also be rhodium, which is substantially more active than cobalt and is therefore used in a lower concentration. The reaction is normally carried out at temperatures of from
- 20 80 to 200°C and pressures of from 10 to 60 MPa using from 0.1 to 50 mg, preferably from 2 to 10 mg, of rhodium per kg of olefin. An effective catalyst compound in both cases is the hydridocarbonyl $\text{HMe}(\text{CO})$, where $\text{Me} = \text{Co}, \text{Rh}$.
- 25 Instead of catalyzing the conversion of the olefin mixture to aldehydes using simple carbonyl compounds, modified carbonyl compounds of cobalt or rhodium may also be successfully used. Modified carbonyl compounds are taken to mean compounds of the aforementioned metals that also contain further complex ligands besides carbon
- 30 monoxide in the molecule. This variant of the hydroformylation reaction also belongs, when cobalt catalysts and also rhodium catalysts are used, to the prior art. Preferred complex ligands are organic compounds of trivalent phosphorus. Examples of such com-
- 35 pounds are triarylphosphines such as triphenylphosphine, trialkylphosphines such as tributylphosphine,

This Sheet Has Been Replaced



- 5 -

- tri(alkyl/aryl)phosphines such as diethylphenylphosphine, triaryl phosphites such as triphenyl phosphite, trialkyl phosphites such as triethyl phosphite, tri(alkyl/aryl) phosphites and phospholes. Also suitable are bidentate
- 5 ligands, for example diphosphines or diphosphites, which contain two phosphorus(III) atoms capable of participating in complex formation, preference being given among these compounds to those that form chelates with the metal atoms. Particularly suitable as ligands are
- 10 sterically hindered phosphites capable of participating in the chelate formation, which form, with the inclusion of the central metal atom, rings containing nine atoms. Such phosphites are described, for example, in EP 0 353 770 A2 and in EP 0 435 071 A2.
- 15 The ligands are normally used in excess, i.e. in an amount that is greater than that required for the complex formation. A ratio of metal atom to ligand molecule (in moles) of from 1 : 5 to 1 : 100 is chosen in practice. As is known, this ratio depends on, inter alia, the nature
- 20 of the ligand. Modified cobalt or rhodium catalysts permit the use of lower reaction pressures than unmodified catalysts, pressures of from 0.1 to 10 MPa, or from 0.5 to 6 MPa being usual. The reaction temperatures when modified cobalt catalysts are used are from 140 to 180°C
- 25 and are thus higher than in the case of the corresponding rhodium catalysts, which require temperatures of from 90 to 130°C. The synthesis gas used for the hydroformylation contains about equal volumes of hydrogen and carbon monoxide, though deviations from this composition in
- 30 either direction are not damaging.

Instead of being carried out in a homogeneous phase, the hydroformylation of the C₃-olefins can also be carried out in a heterogeneous two-phase system, an embodiment of the oxo synthesis, which is described, for example, in German

35 Patent 26 27 354. Such a process is notable for the existence of two liquid phases, namely an organic phase that

This Sheet Has Been Replaced



- 6 -

contains the starting olefin and the reaction product, and an aqueous phase in which the catalyst is dissolved. Suitable catalysts are water-soluble rhodium complex compounds with water-soluble phosphines as ligands.

5 Water-soluble phosphines include in particular triarylphosphines, trialkylphosphines and alkyl-, aryl- or alkylaryldiphosphines, whose organic radicals have been substituted by sulfonyl groups or carboxyl groups. The reaction is carried out at temperatures of from 60 to

10 150°C, preferably from 90 to 120°C, and under pressures in the range from 0.4 to 30 MPa, in particular from 1 to 10 MPa. The rhodium concentration is from 20 to 2000 ppm by weight, preferably from 50 to 500 ppm by weight, based on the aqueous catalyst solution, and from 4 to 100 mol

15 of water-soluble phosphine are used per mol of rhodium. The volume ratio of aqueous phase to organic phase is from 0.1 to 10 : 1.

The olefin conversion is significantly increased if a phase transfer reagent (solubilizer) is added to the

20 aqueous catalyst solution. Particularly suitable are cationic solubilizers of the formula $[A-N(R^1R^2R^3)]^+E^-$, 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

25 radicals having 1 to 4 carbon atoms, and E is in particular sulfate, tetrafluoroborate, acetate, methosulfate, benzenesulfonate, alkylbenzenesulfonate, toluenesulfonate, lactate or citrate.

The hydroformylation of the C_6 -olefins used according to

30 the invention with cobalt or rhodium as catalyst, which is carried out either in the one-phase or two-phase reaction system, yields a mixture of isomeric decanals in high yield. This mixture contains 80 percent or more of straight-chain C_{10} -aldehyde and only minor amounts of

35 methyl-branched and dimethyl-branched aldehydes. The composition of the aldehyde mixture can be influenced by

This Sheet Has Been Replaced



- 7 -

varying the reaction conditions and/or the catalyst, in particular by the choice of ligand when using modified carbonyls.

5 After completion of the hydroformylation, the aldehyde mixture is separated from the catalyst, from the unconverted reaction participants, and from the other reaction products. Distillation is the normal separation process when carrying out the reaction in a homogeneous phase. If
10 the hydroformylation was carried out in a two-phase system, the product and catalyst can be separated from one another by simple phase separation. This process is substantially simpler in its technical execution and, on account of the absence of high temperatures, is also
15 considerably more gentle than the distillative isolation of the aldehyde mixture. The hydroformylation of the C₈-olefin mixture may be carried out batchwise or continuously, irrespective of the process employed.

The isomeric decanals separated from the remaining constituents of the reaction mixture are then hydrogenated to a decyl alcohol mixture. The addition of
20 hydrogen is effected in a known manner in the presence of catalysts. Suitable catalysts are, for example, hydrogenation catalysts based on nickel, chromium or copper. The hydrogenation temperature is generally from 100 to
25 180°C and the pressure is from 1 to 10 MPa. The decyl alcohol mixture is purified by distillation. The mixture is highly suitable as alcohol component in phthalates that are to be used as plasticizers. The preparation of the phthalates is known [cf. Ullmann, Encyclopädie der
30 Technischen Chemie (1979), Vol. 18, p. 536 ff]. Phthalic anhydride is expediently reacted with the decyl alcohol mixture in one stage in a molar ratio of 1: 2. The reaction rate can be increased by using catalysts and/or raising the reaction temperature. In order to displace
35 the equilibrium in the direction of ester formation, the water formed must be removed from the reaction mixture.

This Sheet Has Been Replaced



- 8 -

The phthalates obtained from the decyl alcohol mixture according to the invention are distinguished as plasticizers by outstanding low-temperature properties.

5 The invention is illustrated in more detail in the following example, but is not restricted to this specific embodiment.

Example

1. Starting olefin

10 An oligomeric propylene is used that has been obtained by reacting propylene on a deactivated zeolite as catalyst and that comprises about 87.3 % by weight of tripropylene and 12.7 % by weight of tetrapropylene. A high proportion of the olefins is linear, a very small amount being slightly branched.

15 2. Hydroformylation

500 g of the olefin mixture are reacted in a 1 litre capacity autoclave with water gas ($H_2:CO = 1:1$) at $170^\circ C$ and 27 MPa for 4 hours, and in the presence of 10 g of $CoCO_3$ and 15 g of water. The autoclave contents are decompressed and cooled, and 52 g of water are added. The autoclave is re-closed and heated at $190^\circ C$ for 2 hours while stirring. The contents are cooled and the organic and aqueous phases are separated from one another. 549 g of crude aldehyde are obtained.

25 3. Hydrogenation of the crude aldehyde

The crude aldehyde is treated with hydrogen in a 2.8 l capacity autoclave at $150^\circ C$ and under a pressure of 10 MPa in the presence of a nickel catalyst (10 % by vol., based on the starting product). The contents are then cooled, the pressure is released, and the contents

30

This Sheet Has Been Replaced



- 9 -

are hydrogenated again under the same reaction conditions with the addition of a further 5 % by vol. of a nickel catalyst. The reactor is cooled, the pressure is released, and the product is separated from the nickel catalyst by filtration.

4. Distillation of the crude alcohol

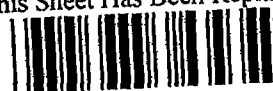
825.5 g of crude alcohol are then distilled in a 1 m column containing glass rings 5 mm in diameter. A first running is removed at an overhead temperature of 100°C and 13.3 kPa pressure, and an intermediate cut is removed at 135°C and 6.7 kPa pressure. The main fraction is obtained at an overhead temperature of 147°C and 6.7 kPa. Gas chromatography analysis shows an alcohol content of 95.7 % by weight. The yield of C₁₀-alcohol, based on the feedstock olefin, is 72 % of theory.

5. Esterification of the pure alcohol

380.4 g (2.3 mol) of C₁₀-alcohol and 148.1 g (1 mol) of phthalic anhydride are reacted in the presence of 0.59 g of concentrated sulfuric acid at 135°C, the water formed in the reaction being removed. The reaction is complete after 6 hours, and the reaction product is neutralized with 5 % strength sodium hydroxide solution. A steam distillation is then carried out at 135°C and 15 kPa. The distillate is washed with water and then dried for 5 hours in a stream of nitrogen at 135°C and 2 to 3 kPa. After filtration a clear liquid is obtained having the following characteristic data:

	Ester content	99.41 % by weight
	Alcohol content	0.22 % by weight
30	Pt/Co color index	5 - 10
	Density (g/ml; 20°C)	0.9655
	Viscosity (mPa.s; 20°C)	108
	Acid number (mg KOH/g)	0.06

This Sheet Has Been Replaced



- 10 -

The viscosity of the ester is considerably lower than the viscosity of currently available products based on conventional propylene polymers, which is 120 to 130 mPa.s/20°C. The ester is thus notable for its

5 outstanding processing properties.

- 11 -

Patent claims

1. A mixture of isomeric decyl alcohols obtained by oligomerization of propylene in the presence of deactivated zeolites as catalysts, separation of the C₈-olefins from the oligomer mixture, hydroformylation of the C₈-olefins to C₁₀-aldehydes, and hydrogenation of the C₁₀-aldehydes.
5
2. A mixture of isomeric decyl alcohols as claimed in claim 1, wherein the hydroformylation of the C₈-olefins is carried out in the presence of cobalt catalysts.
10
3. A mixture of isomeric decyl alcohols as claimed in claim 1, wherein the hydroformylation of the C₈-olefins is carried out in the presence of rhodium catalysts.
15
4. A mixture of isomeric decyl alcohols as claimed in claim 1 or 3, wherein the hydroformylation of the C₈-olefins is carried out in the presence of rhodium complex compounds as catalysts, which contain organic phosphines as ligands.
20
5. A mixture of isomeric decyl alcohols as claimed in one or more of claims 1, 3 and 4, wherein the hydroformylation is carried out in the presence of rhodium complex compounds as catalysts, which contain water-soluble organic phosphines as ligands.
25
6. A mixture of isomeric decyl alcohols as claimed in claim 1 or 3, wherein the hydroformylation of the C₈-olefins is carried out in the presence of rhodium complex compounds as catalysts, which contain organic phosphites as ligands.
30

This Sheet Has Been Replaced



- 12 -



7. A mixture of isomeric decyl alcohols as claimed in one or more of claims 1, 3 and 6, wherein the hydroformylation of the C_8 -olefins is carried out in the presence of rhodium complex compounds that contain sterically hindered organic phosphites as ligands.
- 5
8. A mixture of isomeric decyl phthalates obtained by esterifying phthalic acid or phthalic anhydride with mixtures of isomeric decyl alcohols as claimed in one or more of claims 1 to 7.
- 10 9. The use of the mixtures of isomeric di-decyl phthalates as claimed in claim 9 as plasticizers.

This Sheet Has Been Replaced

