AU9335453

(12) PATENT ABRIDGMENT (11) Document No. AU-B-35453/93
(19) AUSTRALIAN PATENT OFFICE (10) Acceptance No. 659293

(54) Title
DECYL ALCOHOL MIXTURES, PHTHALIC ESTERS OBTAINABLE THEREFROM

International Patent Classification(s)
(51)^5 **C07C 031/125 C07C 029/17 C07C 069/80 C08K 005/12**

(21) Application No. : **35453/93** (22) Application Date : **26.03.93**

(30) Priority Data

(31) Number **4210028** (32) Date **27.03.92** (33) Country **DE GERMANY**

(43) Publication Date : **30.09.93**

(44) Publication Date of Accepted Application : **11.05.95**

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(56) Prior Art Documents
EP 0094456

(57) Claim

1. A mixture of isomeric decyl alcohols obtained by hydroformylation of butadiene in the presence of cobalt catalysts or rhodium catalysts to give an aldehyde mixture, isolation of the resulting aldehyde mixture from the reaction product, condensation of the aldehyde mixture in the presence of basic catalysts with formation of an aldol mixture and isolation and hydrogenation of the aldol mixture to give a mixture of isomeric decyl alcohols.

P/00/011 28/5/91
Regulation 3.2(2)

AUSTRALIA

Patents Act 1990

659293

ORIGINAL
COMPLETE SPECIFICATION
STANDARD PATENT

Application Number:
Lodged:

Invention Title:	DECYL ALCOHOL MIXTURES, PHTHALIC ESTERS OBTAINABLE THEREFROM AND THEIR USE AS PLASTICIZERS

The following statement is a full description of this invention, including the best method of performing it known to :-US

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 short-chain alcohols lead to plasticizers having good gelling capacity. However, their higher volatility is disadvantageous, compared with longer-chain compounds. 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 which are particularly highly regarded because of their 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 C_9 alcohols are used as plasticizers which are obtained by oxoreaction of C_8 olefins, hydrogenation of the reaction product and esterification of the C_9 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 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.

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 economic and technical requirements 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.

The object was therefore to develop a process which starts from raw materials which are cheaply available and which can also be converted in an industrially simple manner into the desired alcohols.

The invention comprises mixtures of isomeric decyl alcohols, which are obtained by hydroformylation of butadiene to give an aldehyde mixture, isolation of the resulting aldehyde mixture from the reaction product, condensation of the aldehyde mixture with formation of an aldol mixture and isolation and hydrogenation of the aldol mixture to give a mixture of isomeric decyl alcohols.

The starting material butadiene for the preparation of the mixture of isomeric decyl alcohols according to the invention is not only easily accessible by dehydrogenation of butane or butene, but is also unavoidably produced in considerable amounts in the preparation of ethylene by thermal cracking of light petroleum or higher hydrocarbons. It is isolated from the C_4 cracking cuts of the pyrolysis product, for example, by liquid-liquid extraction using a selective solvent such as acetronitrile, dimethylformamide or N-methylpyrrolidone.

Butadiene is used for the hydroformylation in the current commercial form, i.e. in a purity of at least 99.5% by weight. The hydroformylation of the conjugated diolefin is a reaction known per se. It proceeds under the action of both cobalt catalysts and rhodium catalysts. The cobalt-catalyst reaction is described, for example, by Adkins and Williams (J.Org.Chem. 17, 980, (1952)). A mixture of n- and i- valeraldehyde in the molar ratio 1:1 is formed in moderate yield.

Considerably more favourable aldehyde yields are achieved when the hydroformylation of butadiene is carried out in the presence of rhodium catalysts. Complex compounds of rhodium with a multidentate ligand which contains trivalent phosphorous atoms have proved themselves. A process based on such catalysts is described, for example, in European Patent 33 554.

In the context of the present invention, preference is given to the hydroformylation of the butadiene in a heterogeneous two-phase system. It is described, for example, in German Patent 26 27 354. Such a process is distinguished by the occurrence of an organic phase, which contains the starting olefin and the reaction product, and an aqueous phase in which the catalyst is dissolved. Catalysts used are water-soluble rhodium complexes with water-soluble phosphines as ligands. The water-soluble phosphines include in particular triarylphosphines, trialkylphosphines and alkyl-, aryl- or alkylaryldiphosphines, 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 is carried out at temperatures of 60 to 150°C, preferably 90 to 120°C and at pressures in the range from 0.4 to 30, in particular 1 to 10, MPa. The rhodium concentration is 20 to 2000 ppm by weight, preferably 50 to 500 ppm by weight, based on the aqueous catalyst solution; 4 to 100 mol of water-soluble phosphine are used per mol of rhodium. The volume ratio of aqueous to organic phase is 0.1 to 10:1.

The butadiene 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.

The hydroformylation of butadiene using rhodium as catalyst gives, both in the single-phase and in the two-phase reaction stsyem, in high yield, a mixture of predomin-antly saturated aldehydes. The ratio of saturated to unsaturated aldehyde can be varied within broad limits by variation of the hydrogen component in the synthesis gas. An increased hydrogen partial pressure favours the formation of saturated aldehydes.

The aldehyde mixture contains 90 percent or more of n-valeraldehyde and, only in subsidiary amounts, other aldehydes, including i-valeraldehyde, dialdehydes and other bi-products. The composition of the aldehyde mixture can be varied by selection of the phosphine ligands. Particularly high n/i ratios are attained using water-soluble rhodium catalysts which contain water-soluble alkylphosphines or alkyl- or aryldiphosphines as ligands.

After the hydroformylation is completed, the aldehyde mixture is isolated from the catalyst, from the unreacted reactants and from the other reaction products. When the reaction takes place in homogenous phase, distillation is the conventional separation process. If the hydroformylation was carried out in a two-phase system, product and catalyst can be separated from each other by a simple phase separation. In the industrial implementation, this process is considerably simpler and, because of the absent thermal stress, is also considerably gentler than the isolation of the aldehyde mixture by distillation. The hydroformylation of the butadiene can be carried out discontinuously or continuously independently of the procces used. A high selectivity to give n-valeraldehyde is achieved if only part of the butadiene used is converted into aldehyde and the remainder is recycled.

The aldol condensation of the aldehydes present as a mixture is carried out by a conventional route with the 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 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 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 C_5 aldehydes between themselves disappears completely.

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

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A mixture of isomeric decyl alcohols obtained by hydroformylation of butadiene in the presence of cobalt catalysts or rhodium catalysts to give an aldehyde mixture, isolation of the resulting aldehyde mixture from the reaction product, condensation of the aldehyde mixture in the presence of basic catalysts 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 hydroformylation of the butadiene is carried out in the presence of rhodium catalysts.

3. The mixture of isomeric decyl alcohols as claimed in claim 1 or 2, wherein the hydroformylation of the butadiene is carried out in the presence of water and water-soluble rhodium-phosphine complexes as catalyst.

4. The mixture of isomeric decyl alcohols as claimed in claim 3, wherein the hydroformylation of the butadiene is carried out in the presence of water-soluble rhodium complexes as catalyst which contain sulfonated phosphines as ligands.

5. The mixture of isomeric decyl alcohols as claimed in claim 3 or 4, wherein the hydroformylation of the butadiene is carried out in the presence of water-soluble rhodium complexes which contain sulfonated alkyl- or arylphosphines as ligands.

6. The mixture of isomeric decyl alcohols as claimed in claim 3 or 4, wherein the hydroformylation of the butadiene is carried out in the presence of water-soluble rhodium complexes as catalyst which contain sulfonated aryl, alkyl- or alkylaryldiphosphines as ligands.

7. The mixture of isomeric decyl alcohols as claimed in one or more of claims 3 to 6, wherein the hydroformylation of the butadiene is carried out in the presence of water and water-soluble rhodium-phosphine complexes as catalyst at temperatures of 70 to 150°C and at pressures of 0.4 to 30 MPa, the volume ratio of aqueous to organic phase is 0.1 to 10:1, the rhodium concentration in the aqueous catalyst solution is 20 to 2000 ppm and 4 to 100 mol of phosphine are used per mol of rhodium.

8. The mixture of isomeric decyl alcohols as claimed in one or more of claims 3 to 7, wherein the aqueous catalyst solution contains a phase transfer reagent.

9. 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 8.

10. A method of plasticizing whereby the mixture of isomeric didecyl phthalates as claimed in claim 9 are used.

DATED this 25th day of January, 1995
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Abstract of the disclosure

Mixtures of isomeric decyl alcohols are obtained by hydroformylation of butadiene to give aldehyde mixtures, condensation of the aldehyde mixtures isolated from the reaction product 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.