

Mixtures of isomeric nonanols and decanols,
their preparation, phthalic esters obtained therefrom
and the use of these esters as plasticizers

5 The invention relates to mixtures of isomeric nonanols and decanols, a process for their preparation, the phthalic esters obtained from these alcohol mixtures and the use of these esters as plasticizers.

10 Esters of phthalic acid have wide application as plasticizers, in particular for polyvinyl chloride. The alcohol components used are mainly primary alcohols having from 8 to 10 carbon atoms, most important among them presently being 2-ethylhexanol. Phthalic esters of short-chain alcohols give plasticizers with good gelling power. A disadvantage however is their higher volatility. In
15 comparison, long-chain esters gel more slowly and have a poorer cold resistance.

20 The properties of the phthalic ester plasticizers are affected not only by the size of the alcohol molecule but also by the branching of the hydrocarbon chain. Thus alcohols with little branching give ester plasticizers of high cold flexibility. Largely linear alcohols having from 9 to 10 carbon atoms in the molecule are therefore becoming increasingly important as alcohol components. A prerequisite for their use is that they are available in
25 large quantities and at advantageous prices.

30 In German Patent 2 855 421, the plasticizers used are phthalates of C₉-alcohols which are obtained by the oxo-reaction of C₉-olefins, hydrogenation of the reaction product and esterification of the C₉-alcohols with phthalic anhydride. From 3 to 20% by weight of the starting olefins are said to have an isobutane skeleton in each molecular chain, less than 3% by weight of the olefins should contain quaternary carbon and more than 90% by weight of the total amount of olefins are said to
35 be present as n-octenes, monomethylheptenes and dimethylhexenes. Furthermore, the weight ratio of the



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total amount of the n-octenes and monomethylheptenes to the dimethylhexenes is said to be more than 0.8.

Phthalic esters based on C₁₀-alcohols are the subject of the European Patent Application 03 66 089. The C₁₀-alcohols are used in the form of a mixture which is obtained by hydroformylation of a butene fraction, aldol condensation of the aldehyde mixture thus obtained and subsequent hydrogenation. According to the process description the hydroformylation step is not subject to any limitations. Catalysts used may be cobalt as well as rhodium; the addition of an organic compound of trivalent phosphorus is not excluded.

Another route to obtaining didecylphthalate mixtures is described in European Patent Application 04 24 767. The preparation of the esters is carried out in a multistage process by dimerization of butene mixtures, hydroformylation and hydrogenation of the resulting octene mixture to give a nonanol mixture, dehydration of the nonanol mixture to form a nonene mixture and hydroformylation and hydrogenation of the nonene mixture to form a decanol mixture.

According to EP-B-0 052 999, plasticizer alcohols are prepared from a mixture of propylene and butenes in a molar ratio of from 2:1 to 1:3. The olefins are together converted by oxo reaction into a mixture of butyl and amyl aldehydes which is subjected to an aldol condensation. The resulting condensation products are subsequently hydrogenated to saturated alcohols.

The known alcohols or alcohol mixtures used for the preparation of plasticizers do not meet all economic and technical requirements which are demanded of products produced on an industrial scale, whether because the starting materials are not available in sufficient quantity and/or not at advantageous prices, or because the conversion of the starting materials into the

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alcohols necessitates extremely costly processes or because the quality of the plasticizers prepared from the alcohols leaves much to be desired.

5 It is therefore an object of the present invention to develop suitable alcohol or alcohol mixtures for the preparation of high-quality plasticizers. They should be obtained from economically available raw materials in a technically simple manner.

10 This object is achieved by mixtures of isomeric nonanols and decanols which are obtained by joint aldol condensation of n-butanal and pentanals in a molar ratio of from 1:2 to 1:10, the pentanal mixtures comprising from 60 to 90% by weight of n-pentanal, from 10 to 40% by weight of 2-methylbutanal and up to 1% by weight of
15 3-methylbutanal, hydrogenation of the aldol condensation product to the saturated alcohols and removal from the reaction mixture of the components boiling at lower temperatures than the nonanols and decanols.

20 Preference is given to mixtures of isomeric nonanols and decanols which are prepared from n-butanal and pentanals which contain from 65 to 80% by weight of n-pentanal, from 20 to 35% by weight of 2-methylbutanal and up to 1% by weight of 3-methylbutanal. The alcohol mixtures are obtained by aldol condensation of mixtures containing
25 n-butanal and pentanals in a molar ratio of from 1:2 to 1:10, subsequent hydrogenation of the aldol condensation product and removal of the 2-ethylhexanol formed. The source of the aldehydes is immaterial; the criterion is chiefly economic. To promote the formation of alcohols
30 with little branching they must nevertheless meet the condition that the carbonyl group is on the terminal carbon atom and, in the case of the pentanals, that they are at least substantially unbranched. Therefore the pentanals used are mixtures containing from 60 to 90% by
35 weight of n-pentanal, from 10 to 40% by weight of 2-methylbutanal and up to 1% by weight of 3-methylbutanal.

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Preferred starting materials are aldehydes prepared by hydroformylation (oxo process) of propylene or butenes. The required olefins are available in industrial quantities. Propylene is obtained as byproduct in ethylene production by pyrolysis of hydrocarbon mixtures in the presence of water vapor and also in some refinery processes, particularly the catalytic cracking of petroleum fractions.

Mixtures containing but-1-ene and but-2-ene are also necessarily obtained in considerable quantities as refinery byproducts in the production of automotive fuels and in the production of ethylene by thermal cracking of higher hydrocarbons. They are isolated from the C₄ cracking fractions of the pyrolysis product by extraction of the buta-1,3-diene with a selective solvent and subsequent removal of the isobutene preferably by conversion into methyl tert-butyl ether. Instead of extracting the buta-1,3-diene, it can also be partly hydrogenated to butenes in the C₄ cracking fraction. The pyrolysis product freed of buta-1,3-diene is described as raffinate I. If the isobutene has also been removed it is referred to as raffinate II. This but-1-ene/but-2-ene mixture is particularly suitable for further processing into C₁₀-alcohols.

Basically all current industrially practiced hydroformylation processes are suitable for converting the olefins into aldehydes. It can thus be carried out in the presence of cobalt or else rhodium catalysts at pressures of from 10 to 35 MPa and at temperatures of from 120 to 180°C as well as in the presence of cobalt/phosphine catalysts at pressures of from 5 to 10 MPa or in the presence of rhodium catalysts which are modified by phosphine at temperatures of from 60 to 150°C and pressures of from 1 to 8 MPa. In the last-described variant of the hydroformylation reaction the catalyst may be homogeneously dissolved in the reaction mixture or form a separate phase from the reaction mixture.



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To prepare the aldehydes, propylene and the butenes may be reacted together, but preferably separately. It has proven particularly valuable to carry out the hydroformylation as a heterogeneous reaction in a two-phase system, a reaction which is described, for example, in DE-C-26 27 354. This embodiment of the oxo process ensures that olefins having their double bond at a terminal carbon atom form largely n-aldehydes and that isomerization of the olefins by migration of the double bond during the reaction is essentially avoided.

The two-phase 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 and described, for example, in DE-PS 26 27 354 and DD-PS 259 194. The reaction of the olefins is carried out at temperatures of from 70 to 150°C, preferably from 100 to 130°C, and at pressures in the range of from 0.4 to 30, in particular from 1 to 10 MPa, with water gas which contains carbon monoxide and hydrogen in a volume ratio of from 1:10 to 10:1. The rhodium concentration is from 20 to 1000 ppm by weight, preferably from 50 to 500 ppm by weight, based on the aqueous catalyst solution, with from 4 to 100 mol of water-soluble phosphine being used per mole of rhodium. The volume ratio of aqueous to organic phase is from 0.1 to 10:1.

The conversion of the butenes is appreciably increased if a phase-transfer reagent (solubilizer) is added to the aqueous catalyst solution. Materials which have proven particularly valuable are cationic solubilizers of the general formula $[A-N(R^1R^2R^3)]^+E^-$, in which A is a

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straight-chain or branched alkyl radical having from 6 to 25 carbon atoms, R^1 , R^2 , R^3 are identical or different and are straight-chain or branched alkyl radicals having from 1 to 4 carbon atoms and E is, in particular, sulfate, tetrafluoroborate, acetate, methosulfate, benzene-sulfonate, alkylbenzenesulfonate, toluenesulfonate, lactate or citrate.

In the described process propylene is up to 99% converted, the butanal mixture obtained comprising over 95% by weight of the n-compound. When but-1-ene/but-2-ene mixtures are used, it is preferably the but-1-ene which reacts. Depending on the selected reaction parameters, more than 95% of but-1-ene or but-2-ene is converted. From 60 to 90% by weight of n-pentanal are formed, the remainder comprising 2-methylbutanal with or without 3-methylbutanal.

After completion of the separate or joint hydroformylation, the aldehydes are separated from the catalyst, from the unreacted reaction components and from the other reaction products. In the case of the heterogeneous reaction this is by simple phase separation. For reaction in the homogeneous phase distillation is the usual separation process.

In the subsequent aldol condensation mixtures are used which contain, per mole of n-butanal, from 2 to 10 mol, in particular from 7 to 10 mol, of pentanals. The reaction of the aldehyde mixture is carried out in the conventional way using basic catalysts. Pretreatment of the aldehydes, for example a special purification, is not necessary. It is however advisable in the case of the butanals to remove i-butanal from the C_4 -aldehyde mixture by distillation, if the proportion thereof in the mixture exceeds approximately 2% by weight. Suitable catalysts are alkali metal carbonates or alkali metal hydroxides, in particular compounds of sodium or potassium and amines, preferably tertiary amines, such as

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triethylamine, tri-n-propylamine and tri-n-butylamine. The reaction is carried out at temperatures of from 60 to 160°C, in particular from 80 to 130°C and at atmospheric pressure or at a superatmospheric pressure of up to 1 MPa. The reaction time is from a few minutes to several hours and is in particular dependent on catalyst type and reaction temperature. Because of their higher reactivity the straight-chain aldehydes react preferentially. Self-condensation of n-butanal or n-pentanal forms C₈ or C₁₀-enals and the mixed condensation of n-butanal and n-pentanal gives C₉-enals. The reactions between n-butanal or n-pentanal and branched-chain pentanals proceed at appreciably lower rates, the reaction between branched-chain pentanals is largely insignificant.

The mixture of unsaturated aldehydes obtained by condensation is subsequently hydrogenated to a mixture containing nonyl and decyl alcohols together with 2-ethylhexanol and any butanols and pentanols arising from C₄- and C₅-aldehydes which may not have been converted by aldol condensation. The addition of hydrogen is carried out 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 usually between 100 and 180°C and the pressure between 1 and 10 MPa. According to the invention, the alcohol mixture obtained is subjected to distillation at from 100 to 125°C and at a pressure of from 1 to 4 kPa (from 10 to 40 mbar) to remove 2-ethylhexanol and further alcohols and also impurities which boil at lower temperatures than the nonanols and decanols.

The remaining mixture of nonanols and decanols is especially suitable as the alcohol component in phthalic esters which are to be used as plasticizers. The preparation of phthalic esters is known [cf. Ullmann, Encyclopädie der Technischen Chemie (1979), Vol. 18, page 536 ff]. Phthalic anhydride is advantageously reacted with the C₉-, C₁₀-alcohol mixture in a molar ratio of from

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1:2 to 1:3 in a single stage. The reaction rate can be increased by catalysts and/or by raising the reaction temperature. To shift the equilibrium in the direction of ester formation it is necessary to remove the water of reaction from the reaction mixture.

The phthalates obtained from the nonanol/decanol mixture of the invention are remarkable for their low volatility and good gelling ability.

Example 1

980.0 g of 2.5% strength NaOH (0.61 mol) are heated to 60°C under nitrogen and a mixture of 272.8 g (3.17 mol) of n-valeraldehyde, 181.8 g (2.11 mol) of 2-methylbutanal and 45.5 g (0.63 mol) of n-butyraldehyde is added over a period of 20 min. The mixture is heated to from 88 to 90°C under reflux for one hour. After cooling to 30°C the organic and aqueous phases separate.

The aldol condensation product is hydrogenated in the presence of a nickel catalyst at a pressure of 10 MPa and 140°C. After filtering off the catalyst, a crude alcohol mixture is obtained which has the following composition (% by weight) determined by gas chromatography:

	First fraction	0.2
	2-methylbutanol	30.2
	n-pentanol	0.3
25	2-ethylhexanol	1.6
	2-ethyl-4-methylhexanol	2.1
	2-propylhexanol	6.4
	2-ethylheptanol	6.2
	2-propyl-4-methylhexanol	14.7
30	2-propylheptanol	35.4
	Final fraction	2.9

The distillative removal of the pentanols and 2-ethylhexanol gives an alcohol mixture with the following composition (% by weight):

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	2-ethyl-4-methylhexanol	3.2
	2-propylhexanol	9.9
	2-ethylheptanol	9.6
	2-propyl-4-methylhexanol	22.6
5	2-propylheptanol	54.7

10 The esterification with phthalic anhydride is carried out in the presence of sulfuric acid as catalyst and of cyclohexane for the azeotropic removal of the water of reaction. Neutralization, alcohol removal and drying results in a mixture of phthalic esters of isomeric nonanols and decanols which has a density of 0.967 g/ml at 20°C and a viscosity of 138 mPa.s.

Example 2

15 980.0 g of 2.5% strength NaOH (0.61 mol) are heated to 60°C under nitrogen and a mixture of 214.3 g (2.49 mol) of n-valeraldehyde, 143.0 g (1.66 mol) of 2-methylbutanal and 142.8 g (1.98 mol) of n-butyraldehyde is added dropwise over a period of 20 min. The mixture is heated to from 89 to 92°C under reflux for one hour. After
20 cooling to 30°C the organic and aqueous phases separate.

Hydrogenation as in Example 1 of the condensation product gives a crude alcohol mixture with the following composition (% by weight) determined by gas chromatography:

	First fraction	0.2
25	2-methylbutanol	20.9
	n-pentanol	0.2
	2-ethylhexanol	10.9
	2-ethyl-4-methylhexanol	5.2
	2-propylhexanol	13.9
30	2-ethylheptanol	13.5
	2-propyl-4-methylhexanol	10.0
	2-propylheptanol	22.3
	Final fraction	2.9

The distillative removal of the pentanols and

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2-ethylhexanol gives an alcohol mixture with the following composition (% by weight):

	2-ethyl-4-methylhexanol	8.0
	2-propylhexanol	21.4
5	2-ethylheptanol	20.8
	2-propyl-4-methylhexanol	15.4
	2-propylheptanol	34.4

10 Esterification with phthalic anhydride as in Example 1 results in an ester mixture which has a viscosity of 118 mPa.s and a density of 0.969 g/ml.

Example 3

15 A mixture of 280.0 g (3.25 mol) of n-valeraldehyde, 120.0 g (1.39 mol) of 2-methylbutanal and 120.0 g (1.66 mol) of n-butyraldehyde was converted to aldols in the presence of 1016 g of 2.5% strength NaOH (0.63 mol) as in Example 1.

Hydrogenation as in Example 1 of the condensation product gives a crude alcohol mixture with the following composition (% by weight):

20	First fraction	0.7
	2-methylbutanol	17.9
	n-pentanol	0.3
	2-ethylhexanol	7.0
	2-ethyl-4-methylhexanol	3.6
25	2-propylhexanol	13.8
	2-ethylheptanol	13.5
	2-propyl-4-methylhexanol	9.5
	2-propylheptanol	31.7
	Final fraction	2.0

30 The distillative workup gives an alcohol mixture with the following composition (% by weight):

2-ethyl-4-methylhexanol	5.1
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2-propylhexanol	19.2
2-ethylheptanol	18.7
2-propyl-4-methylhexanol	13.1
2-propylheptanol	43.9

- 5 Esterification with phthalic anhydride as in Example 1 results in an ester mixture which has a viscosity of 123 mPa.s and a density of 0.969 g/ml.

Examples 4 to 7

- 10 The Examples 4 to 7 are carried out similarly to Example 1; data relating to the composition of the starting mixture, the crude alcohol mixture and the alcohol mixture suitable for plasticizer production are shown in the table below.

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		Ex. 4	Ex. 5	Ex. 6	Ex. 7
	Starting mixture				
	n-valeraldehyde				
	(g)	156.7	208.9	139.3	234.8
	(mol)	1.62	2.43	1.62	2.73
5	2-methylbutanal				
	(g)	17.4	52.0	34.8	26.1
	(mol)	0.20	0.60	0.40	0.30
	n-butyraldehyde				
	(g)	74.3	22.3	74.3	22.3
10	(mol)	1.03	0.31	1.03	0.31
	2.5% strength NaOH				
	(g)	480.5	528.0	480.0	528.5
	(mol)	0.30	0.33	0.30	0.33
	Crude alcohol mixture				
15	(in % by weight):				
	First fraction	0.2	0.2	0.2	0.2
	2-methylbutanol	4.6	13.1	9.9	6.5
	n-pentanol	0.3	0.3	0.2	0.3
	2-ethylhexanol	10.2	0.9	10.9	0.9
20	2-ethyl-4-methylhexanol	1.4	0.9	2.8	0.5
	2-propylheptanol	19.0	6.6	17.6	7.0
	2-ethylheptanol	18.5	6.4	16.9	6.7
	2-propyl-4-methylhexanol	3.3	10.1	6.2	6.1
	2-propylheptanol	40.6	59.6	33.2	69.8
25	Final fraction	1.9	1.9	2.1	2.0
	Alcohol mixture for				
	plasticizer				
	(in % by weight):				
	2-ethyl-4-methylhexanol	1.8	1.0	3.6	0.6
30	2-propylhexanol	22.9	7.9	23.0	7.8
	2-ethylheptanol	22.3	7.6	22.0	7.4
	2-propyl-4-methylhexanol	4.0	12.1	8.2	6.8
	2-propylheptanol	49.0	71.4	43.2	77.4

35 The excellent gelling ability of the phthalic-ester plasticizers produced from the alcohol mixture of the invention is shown by comparison with the established di(isodecyl) phthalate (DIDP) plasticizers.

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For assessment of the gelling ability the critical solubility temperature was determined in accordance with DIN 53 408.

Phthalic esters using alcohol DIDP
mixtures according to

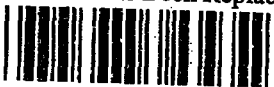
Example 1 Example 2 Example 3

critical solubility	139	133	135	140
temperature (°C)				

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The outstanding gelling ability of the phthalic esters obtained from the novel alcohol mixtures is shown by the critical solubility temperature, which is lower than for DIDP.

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What is claimed is:

1. A mixture of isomeric nonanols and decanols obtained by joint aldol condensation of n-butanal and pentanals in a molar ratio of from 1:2 to 1:10, in which the pentanal mixtures comprising from 60 to 90% by weight of n-pentanal, from 10 to 40% by weight of 2-methylbutanal and up to 1% by weight of 3-methylbutanal, hydrogenation of the aldol condensation product to the saturated alcohols and removal from the reaction mixture of the components boiling at lower temperatures than the nonanols and decanols.
2. A mixture of isomeric nonanols and decanols as claimed in claim 1, wherein the pentanals comprise mixtures of from 65 to 80% by weight of n-pentanal, from 20 to 35% by weight of 2-methylbutanal and up to 1% by weight of 3-methylbutanal.
3. A process for preparing mixtures of isomeric nonanols and decanols as claimed in claim 1 or 2, wherein propylene and the butenes are separately hydroformylated, mixtures of the butanals and pentanals obtained are condensed in the presence of basic catalysts, the condensation product is hydrogenated to saturated alcohols and the components boiling at lower temperatures than the nonanols and decanols are removed from the reaction mixture.
4. The process as claimed in claim 3, wherein the olefins are hydroformylated in the presence of an aqueous solution of rhodium-phosphine complexes as catalyst at from 70 to 150°C and a pressure of from 0.4 to 30 MPa.
5. The process as claimed in claims 3 or 4, wherein mixtures of butanals and pentanals are condensed at from 60 to 160°C in the presence of tertiary amines.

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6. The process as claimed in one or more of claims 3 to 5, wherein the condensation product is hydrogenated in the presence of nickel catalysts at from 100 to 180°C and a pressure of from 1 to 10 MPa.
- 5 7. The process as claimed in one or more of claims 3 to 6, wherein the components of the hydrogenation product boiling at lower temperatures than the nonanols and the decanols are removed from the hydrogenation product by distillation at from 100 to 125°C and at a pressure of from 1 to 4 kPa (from 10 to 40 mbar).
- 10 8. A plasticizer obtained by esterification of alcohol mixtures as claimed in claim 1 or 2 with phthalic acid or phthalic anhydride.