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(54) Title: PROCESS FOR PREPARING AQUEOUS POLYURETHANE DISPERSIONS

(57) Abstract: The invention relates to a process for preparing water-based polyurethane dispersions. The process, or individual steps thereof, is or are carried out in static mixers.

Process for preparing aqueous polyurethane dispersions

The invention relates to a process for preparing aqueous polyurethane dispersions. The process, or individual steps thereof, is or are carried out in static mixers.

Stable aqueous polyurethane dispersions are used for example for one-component, isocyanate-free coating materials, coatings, sealants, adhesives and membranes. Their significance has been increasing continually for years for reasons of ecology (environmental compatibility, workplace safety) and economics. The viscosity and the rheology are independent of the molar mass, which can be adjusted over a wide range. In addition to these advantages these low-solvent or solvent-free products already correspond in terms of their application opportunities largely to their solventborne counterparts.

Aqueous polyurethane dispersions are composed of polyurethane polymers or polyurethane-polyurea polymers, which contain not only urethane groups but also urea groups and are obtainable by polyaddition reactions from polyols, polyisocyanates and polyamines. First, from the polyols and the polyisocyanates, polyurethane prepolymers are prepared which are then dispersed in the aqueous phase and chain-extended with polyamines to build the polyurethane-polyurea polymers. A distinction is made between anionic, cationic and nonionic polyurethane dispersions, according to the type of hydrophilic group which ensures the stabilization of the polyurethane prepolymer in the aqueous phase. These hydrophilic groups are incorporated into the prepolymer by way of suitable, modified polyols.

The preparation of aqueous polyurethane dispersions has been known for many years and is described in detail in a large number of publications (Houben-Weyl, Methoden der organischen Chemie, Volume E 20, Part I; Ullmann's Encyclopedia of Industrial Chemistry, Release 2003, 7th Edition, Wiley-VCH; Adv. Urethane Sci. Technol. 10 (1987), 121-187; DE 198 12 751; DE 199 57 604; WO 96/40811; US 2002/0028877 etc.). Within the art the Acetone Process, the Prepolymer Mixing Process and the Melt Emulsification Process have acquired the greatest significance. Generally speaking, the dispersions are prepared batchwise in stirred tanks. In that case the prepolymer is prepared in one tank and where appropriate the neutralization, the

dispersing and the chain extension are carried out in the same tank or in a second tank. A disadvantage of these batchwise operations is that for industrial production large stirred tanks with powerful stirrer mechanisms are required in order to apply the high shearing forces that are needed for dispersing and chain extension. A further problem is the reproducible preparation of the dispersions, since because of the complex chemical reactions the properties vary within a certain limits from one batch to the next. This problem also occurs during scale-up from laboratory to production. Continuous operations for preparing polyurethane dispersions are known (e.g., GB 14 14 930; DE 22 60 870; DE 23 11 635; DE 23 47 299; US 4,742,095; M. Keyvani, Advances in Polymer Technology, 22 (2003), 218-224). All of these operations require either powerful stirrer units or rotor-stator mixing elements, which entail high capital costs, energy costs and/or operating costs.

The use of static mixers for dispersing and chain extending is known in principle for the preparation of polyisocyanate dispersions in situ (US 5,221,710). The polyurethane prepolymers used for dispersing are adducts having an isocyanate content of at least 12% by mass. To date it has not been possible to carry out continuous dispersion of polyurethane prepolymers having an isocyanate content lower than 12% by mass and preparable by reacting isocyanates with polyols, owing to their high viscosities.

Surprisingly it has now been found that aqueous polyurethane dispersions can also be prepared by dispersing polyurethane prepolymers having an isocyanate content of < 12% by mass in static mixers. The viscosities required are set by appropriate temperature adjustment and/or by the use of an auxiliary solvent.

Surprisingly it has been found that static mixers are very efficient for the continuous preparation of aqueous polyurethane dispersions having < 12% by mass NCO content. One reason for the improved reproducibility and/or compliance with tighter specification limits as compared with conventional preparation in a stirred tank is the short and precisely adjustable residence time in static mixers. In the course of the preparation of polyurethane dispersions in batch operations, the metering and complete mixing/dispersing of the polyurethane prepolymer in water or of water in the polyurethane prepolymer takes a certain time, normally of the order

of several minutes. This time varies within certain limits from one batch to the next and, in comparison with the mixing and residence time in static mixers according to the present process, is very long and is a disadvantage, since in the course of dispersing, the isocyanate groups of the polyurethane prepolymer may react with the water and hence are no longer available for chain extension. As a result there is also variation from one batch to the next in the free isocyanate group content, which makes precise metering of the chain extender component more difficult and also makes it more difficult to adjust the specification. These unwanted side reactions can be reduced to a minimum in static mixers owing to the shorter residence time, since there the volume flows can always be metered and mixed directly in the correct proportion. This is manifested in particular in connection with the use of inexpensive aromatic polyisocyanates which are of high reactivity with water, whose aqueous dispersions are difficult to obtain by batch operations and may require additional process steps (blocking of the isocyanate groups). A further advantage of the process of the invention is the fact that in the course of ongoing production of the polyurethane dispersions it is still possible to make corrections to the reaction conditions and so to effect fine tuning or else a change of product (adjustment of particle size, for example, through the degree of neutralization or solids content), which in the case of batchwise production is possible only from one batch to the next.

The invention provides a process for preparing aqueous polyurethane dispersions which comprises dispersing polyurethane prepolymers having an isocyanate content of < 12% by mass in water in a static mixer.

In the process a polyurethane prepolymer having an isocyanate content of < 12% by mass is dispersed with an aqueous component in a static mixer.

As the polyurethane prepolymer it is preferred to use an anionic (a) or cationic (b) hydrophilically modified and neutralized polyurethane prepolymer or a polyurethane prepolymer which has been hydrophilically modified by way of nonionic (c) groups. It is also possible to use mixtures of these prepolymers a) to c).

The polyurethane prepolymers a) to c) can be prepared by any desired methods.

Likewise possible is the preparation of the polyurethane prepolymers a) and b) in a separate static mixer prior to dispersing with the aqueous component. In that case a suitable anionically (a) or cationically (b) modifiable polyurethane prepolymer is reacted with a neutralizing component, prior to dispersing in a static mixer, for partial or complete neutralization, to form the dispersible polyurethane prepolymer, which is said to have been modified.

It is also possible to carry out simultaneous partial or complete neutralization and dispersing of a suitable anionically or cationically modifiable polyurethane prepolymer in one step in a single static mixer using a water/neutralizing agent mixture.

The dispersed polyurethane prepolymer obtained in accordance with the invention is subsequently, if desired, reacted with a chain extender component, likewise in a static mixer or conventionally, by a prior art method, to form the finished polyurethane dispersion.

If desired, in the process of the invention an auxiliary solvent is added for adjusting the viscosity of the polyurethane prepolymer.

Anionically or cationically modifiable (i.e., non-neutralized) or nonionically modified polyurethane prepolymers suitable for the process of the invention are known from the literature (see above) and are prepared by polyaddition reactions of polyols and polyisocyanate components and, if desired, auxiliary solvents and/or catalysts. Polymeric and/or monomeric polyols are used which have two or more polyisocyanate-reactive hydroxyl groups, such as polyester polyols, polyether polyols, polyhydroxy polycarbonates, polyhydroxy polyacetals, polyhydroxy polyacrylates, polyhydroxy polyesteramides, polyhydroxy polythioethers, polyalkylene polyols, polyhydroxy polycaprolactones, vinyl-modified polyether polyols, macromonomeric polyols, techelenes or polyhydroxy epoxy resins or mixtures thereof and/or all low molecular mass polyols such as 1,2-ethanediol, 1,2-propanediol, 1,2-propylene glycol, 1,3-propanediol, 1,3-propylene glycol, 1,4-butanediol, 1,4-butylene glycol, 1,6-hexanediol, 2-methyl-1,3-propanediol, 2,2-dimethylol-1,3-propanediol, 1,4-bis(hydroxymethyl)-cyclohexane, 1,2,3-propanetriol, 2-hydroxymethyl-2-methyl-1,3-propanol, 2-ethyl-2-

hydroxymethyl-1,3-propanediol, 2,2-bis(hydroxymethyl)-1,3-propanediol or mixtures thereof. Examples of preferred polyisocyanate components are polyisocyanates, polyisocyanate derivatives or polyisocyanate homologs containing two or more aliphatic, cycloaliphatic or aromatic isocyanate groups. Particularly suitable are the polyisocyanates which are adequately known in polyurethane chemistry, or combinations thereof, such as 1,4-diisocyanatobutane, 1,6-diisocyanatohexane (HDI), 1,12-diisocyanatododecane, 1,4-diisocyanatocyclohexane, 1-isocyanato-5-isocyanatomethyl-3,3,5-trimethylcyclohexane (IPDI), bis(4-isocyanatocyclohexyl)methane (H_{12}MDI), 1,3-bis(1-isocyanato-1-methyl)benzene (XDI), 1,3-bis(1-isocyanato-1-methylethyl)benzene (m-TMXDI), 2,4-diisocyanatotoluene (TDI), bis(4-isocyanatophenyl)-methane (MDI), 1,6-diisocyanato-2,2,4(2,4,4)-trimethylhexane (TMDI) and optionally isomers, higher homologs and/or technical-grade mixtures of the individual polyisocyanates. In addition it is also possible to use mixtures and derivatives of the abovementioned diisocyanates that contain allophanate, biuret, carbodiimide, isocyanurate, uretdione or urethane groups and if desired blocked polyisocyanates as well, as described in DE 196 26 886, for example.

Compounds which are used that have an anionically, cationically and/or nonionically dispersing action are those containing, for example, carboxylate, sulfonate, phosphonate, sulfonium, ammonium or phosphonium groups or groups which can be converted into the aforementioned groups by salt formation (referred to as anionically or cationically modifiable groups/compounds), and/or polyether groups (referred to as nonionically emulsifiable groups), and which can be incorporated into the prepolymers by means of existing isocyanate-reactive groups, and having two or more polyisocyanate-reactive groups, such as compounds containing OH and/or NH_2 groups, for example. Representatives of these compounds are, for example, 2-hydroxymethyl-3-hydroxypropanoic acid, 2-hydroxymethyl-2-methyl-3-hydroxypropanoic acid, 2-hydroxymethyl-2-ethyl-3-hydroxypropanoic acid, 2-hydroxymethyl-2-propyl-3-hydroxypropanoic acid, citric acid, tartaric acid, alanine, taurine, 2-amino-ethylaminoethanesulfonic acid, polyethylene glycols, polypropylene glycols and polybutylene glycols prepared starting from alcohols, the block copolymers and monomethyl ethers of these polyglycols, and all polymeric polyols modified accordingly.

Preferred auxiliary solvents are inert solvents which possess no miscibility gap with water over wide ranges, such as N-methylpyrrolidone, n-butyl glycol, di-n-butyl glycol, acetone, methyl ethyl ketone or tetrahydrofuran, for example.

The neutralizing component used for anionically modifiable polyurethane prepolymers comprises bases, examples being tertiary amines such as N,N-dimethylethanolamine, N-methyldiethanolamine, triethanolamine, N,N-dimethylisopropanolamine, N-methyldiisopropanolamine, triisopropylamine, N-methylmorpholine, N-ethylmorpholine, triethylamine or ammonia, for example, or alkali metal hydroxides such as lithium hydroxide, sodium hydroxide or potassium hydroxide, for example. For cationically modifiable polyurethane prepolymers use is made of corresponding acids, such as formic acid, acetic acid, propionic acid, sulfuric acid, dimethyl sulfate or succinic acid, for example. In the case of the nonionically modified polyurethane prepolymers there is no neutralization step.

In the final reaction step, in which there is an increase in molar mass in the aqueous medium, the chain extender component used comprises polyamines containing two or more polyisocyanate-reactive amino groups. Examples of suitable polyamines include adipic dihydrazide, ethylenediamine, diethylenetriamine, triethylenetetramine, tetraethylenepentamine, pentaethylenehexamine, dipropylenetriamine, hexamethylenediamine, hydrazine, isophoronediamine, N-(2-aminoethyl)-2-aminoethanol, 1,3- and 1,4-phenylenediamine, 4,4'-diphenylmethanediamine, amino-functional polyethylene oxides and/or polypropylene oxides, adducts of salts of 2-acrylamido-2-methylpropane-1-sulfonic acid and ethylenediamine, or any desired combinations or polyamines.

In one preferred exemplary embodiment of the process of the invention all of the mass flows, reaction temperatures, residence times and the individual static mixers are harmonized with one another so as to ensure optimum commixing and reaction times. A non-neutralized anionically or cationically modifiable polyurethane prepolymer is pumped from a reservoir continuously into the static mixer. From a further reservoir a neutralizing agent is pumped, again continuously, into the static mixer, in which it is mixed with the prepolymer and at the same time neutralizes the anionically or cationically modifiable groups to form hydrophilic, ionic

groups. The resultant modified or neutralized polyurethane prepolymer is subsequently dispersed in a further static mixer in water, which is pumped continuously from a third reservoir again into the second static mixer. From the static mixer the polyurethane dispersion, with a free isocyanate group content required for the subsequent chain extension, passes into a third static mixer. Simultaneously, from a fourth reservoir, the chain extender, which if desired may be in the form of an aqueous solution, is metered continuously into the third static mixer. This is where chain extension takes place. The finished, stable polyurethane dispersion can be dispensed directly into reservoirs or processed further or applied. If a polyurethane prepolymer is used which is not hydrophilically modified by way of nonionic groups (i.e., a nonionically modified polyurethane prepolymer, as it is called), the neutralization step disappears. The same applies to an embodiment in which a non-neutralized, anionically or cationically modifiable polyurethane prepolymer is neutralized and dispersed with a neutralizing agent/water mixture in one step. For the process of the invention it is not essential that all of the steps of the process are carried out continuously in static mixers. It is also not essential whether all of the steps of the process are carried out in two or more mixers or in only one static mixer.

All that is essential to the invention is the dispersing of the polyurethane prepolymer in a static mixer, said prepolymer having an NCO content of < 12% by mass prior to dispersing.

In accordance with the invention polyurethane dispersions are prepared which have an NCO content of < 12% by mass, but preferably < 5% by mass, very preferably < 0.5% by mass.

The examples which follow serve to illustrate the process of the invention further, without said process being restricted to the examples.

Example 1

Preparation of an anionically modifiable polyurethane prepolymer

A stirred tank is charged with 2400 g of N-methylpyrrolidone, 500 g of dimethylolpropionic acid, 5500 g of Oxyester T 1136 (manufacturer: Degussa) and 135 g of trimethylolpropane and this initial charge is heated to 60°C. Subsequently a solution of 5 g of dibutyltin laurate in 3500 g of isophorone diisocyanate is added over a period of 1 h, after which the mixture is

heated to 80°C and reaction is continued until an isocyanate content of 3.8% by mass has been reached. The prepolymer thus prepared possesses a viscosity of 7100 mPas at 50°C and an acid number of 21.9 mg KOH/g.

Example 2

Batch preparation of an aqueous polyurethane dispersion

300 g of the prepolymer from Example 1 are neutralized in a stirred tank (toothed disk with a peripheral speed of approximately 10 m/s) at 50°C with 10 g of triethylamine (added over the course of 15 s, after-reaction time 15 s) and dispersed by adding 400 g of water (added over the course of 40 s, after-reaction time 15 s). This is followed by chain extension with 70 g of a 10% strength solution of ethylenediamine in water. The dispersion obtained has a pH of 8.0, a solids content of 32.2% (dried at 150°C for 1.5 h) and a viscosity of 33 mPas at 20°C.

Example 3

Continuous preparation of an aqueous polyurethane dispersion

The prepolymer from Example 1 is pumped from a reservoir at 50°C with a volume flow of 150 g/min into a static mixer (SMX mixer from Sulzer; residence time 0.3 min) and mixed with 5 g/min of triethylamine from a second reservoir. The neutralized prepolymer is then dispersed in a further static mixer (SMX mixer from Sulzer; residence time 0.7 min) with a water stream of 200 g/min from a third reservoir, and then subjected to chain extension in a third static mixer (SMXL mixer from Sulzer; residence time 1.2 min) from a fourth reservoir with 35 g/min of a 10% strength solution of ethylenediamine in water. The dispersion obtained has a pH of 8.4, a solids content of 31.7% and a viscosity of 29 mPas at 20°C and is therefore comparable with the conventionally prepared dispersion from Example 2.

What is claimed is:

1. A process for preparing an aqueous polyurethane dispersion which comprises dispersing polyurethane prepolymers having an isocyanate content of < 12% by mass in water in a static mixer.

2. A process as claimed in claim 1, wherein
   a) neutralized, anionically modified,
   b) neutralized, cationically modified
   and/or
   c) nonionic
   dispersible polyurethane prepolymers are used.

3. A process as claimed in claim 2, wherein components a) and/or b) are prepared beforehand by fully or partly neutralizing an anionically or cationically modifiable polyurethane prepolymer with a neutralizing agent or neutralizing agent mixture in a static mixer.

4. A process as claimed in claim 1, wherein an anionically and/or cationically modifiable polyurethane prepolymer is neutralized and dispersed in a static mixer with a mixture of neutralizing component(s) and water in one step.

5. A process as claimed in at least one of the preceding claims, wherein a dispersed polyurethane prepolymer containing isocyanate groups is reacted with a chain extender component or with a mixture of chain extender components in a static mixer.

6. A process as claimed in at least one of the preceding claims, wherein an auxiliary solvent is added for adjusting the viscosity of the polyurethane prepolymer.

7. A process as claimed in at least one of the preceding claims, wherein polyols selected from the group consisting of polyester polyols, polyether polyols, polyhydroxy polycarbonates, polyhydroxy polyacetals, polyhydroxy polyacrylates, polyhydroxy polyesteramides,

polyhydroxy polythioethers, polyalkylene polyols, polyhydroxy polycaprolactones, vinyl-modified polyether polyols, macromonomeric polyols, techelenes or polyhydroxy epoxy resins or mixtures thereof are used as starting compounds for preparing the polyurethane prepolymers.

8. A process as claimed in at least one of the preceding claims, wherein low molecular mass polyols selected from 1,2-ethanediol, 1,2-propanediol, 1,2-propylene glycol, 1,3-propanediol, 1,3-propylene glycol, 1,4-butanediol, 1,4-butylene glycol, 1,6-hexanediol, 2-methyl-1,3-propanediol, 2,2-dimethylol-1,3-propanediol, 1,4-bis(hydroxymethyl)-cyclohexane, 1,2,3-propanetriol, 2-hydroxymethyl-2-methyl-1,3-propanol, 2-ethyl-2-hydroxymethyl-1,3-propanediol, 2,2-bis(hydroxymethyl)-1,3-propanediol or mixtures thereof are used as starting compounds for preparing the polyurethane prepolymers.

9. A process as claimed in at least one of the preceding claims, wherein polyisocyanates, polyisocyanate derivatives or polyisocyanate homologs are used as starting compounds for preparing the polyurethane prepolymers.

10. A process as claimed in at least one of the preceding claims, wherein polyisocyanate components containing allophanate, biuret, carbodiimide, isocyanurate, uretdione or urethane groups are used as starting compounds for preparing the polyurethane prepolymers.

11. A process as claimed in at least one of the preceding claims, wherein blocked polyisocyanates are used as starting compounds for preparing the polyurethane prepolymers.

12. A process as claimed in at least one of the preceding claims, wherein polyisocyanates selected from 1,4-diisocyanatobutane, 1,6-diisocyanatohexane (HDI), 1,12-diisocyanatododecane, 1,4-diisocyanatocyclohexane, 1-isocyanato-5-isocyanatomethyl-3,3,5-trimethylcyclohexane (IPDI), bis(4-isocyanatocyclohexyl)methane (H_{12}MDI), 1,3-bis(1-isocyanato-1-methyl)benzene (XDI), 1,3-bis(1-isocyanato-1-methylethyl)benzene

(m-TMXDI), 2,4-diisocyanatotoluene (TDI), bis(4-isocyanatophenyl)methane (MDI) and 1,6-diisocyanato-2,2,4(2,4,4)-trimethylhexane (TMDI) are used as starting compounds for preparing the polyurethane prepolymers.

13. A process as claimed in at least one of the preceding claims, wherein compounds containing carboxylate, sulfonate, phosphonate, sulfonium, ammonium or phosphonium groups or groups which can be converted into the aforementioned groups by salt formation are used for anionic and/or cationic modification.

14. A process as claimed in claim 13, wherein 2-hydroxymethyl-3-hydroxypropanoic acid, 2-hydroxymethyl-2-methyl-3-hydroxypropanoic acid, 2-hydroxymethyl-2-ethyl-3-hydroxypropanoic acid, 2-hydroxymethyl-2-propyl-3-hydroxypropanoic acid, citric acid, tartaric acid, alanine, taurine, 2-aminoethylaminoethanesulfonic acid are used.

15. A process as claimed in at least one of the preceding claims, wherein polyethylene glycols, polypropylene glycols or polybutylene glycols prepared starting from alcohols, block copolymers and monomethyl ethers of these polyglycols, and all polymeric polyols modified accordingly are used for nonionic modification.

16. A process as claimed in at least one of the preceding claims, wherein adipic dihydrazide, ethylenediamine, diethylenetriamine, triethylenetetramine, tetraethylenepentamine, pentaethylenehexamine, dipropylenetriamine, hexamethylenediamine, hydrazine, isophoronediamine, N-(2-aminoethyl)-2-aminoethanol, 1,3- and 1,4-phenylenediamine, 4,4'-diphenylmethanediamine, amino-functional polyethylene oxides and/or polypropylene oxides, adducts of salts of 2-acrylamido-2-methylpropane-1-sulfonic acid and ethylenediamine, or any desired combinations of polyamines, are used as chain extenders.

17. A process as claimed in at least one of the preceding claims, wherein a polyurethane dispersion having an NCO content of < 12% by mass, but preferably < 5% by mass, more preferably < 0.5% by mass, is prepared.

INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08G18/08 C08G18/10 B01F3/10 B01F5/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C08G B01F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 221 710 A (MARKUSCH ET AL) 22 June 1993 (1993-06-22) cited in the application column 1, line 65 - column 2, line 9 claims 1-6; example 1	1-17
A	US 4 742 095 A (MARKUSCH ET AL) 3 May 1988 (1988-05-03) cited in the application column 2, line 9 - column 4, line 36; claims 1-10; examples	1-17
A	EP 0 747 408 A (BAYER) 11 December 1996 (1996-12-11) page 2, line 37 - page 3, line 7 page 5, line 25 - line 51; claim 1; example 1	1

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

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Date of the actual completion of the international search	Date of mailing of the international search report
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Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340–2040, Tx. 31 651 epo nl, Fax: (+31–70) 340–3016	Bourgonje, A

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INTERNATIONAL SEARCH REPORT

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DE 16 45 656 A (WYANDOTTE CHEMICALS) 6 August 1970 (1970-08-06) page 3, line 8 - page 4, line 15 page 21, line 10 - page 22, line 19; claims 1,2; example 1 _____	1

INTERNATIONAL SEARCH REPORT

Information on patent family members

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PCT/EP2005/050504

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