

Air drying resin and composition

Citation for published version (APA):

B.V., DSM. IP., & B.V., DSM. IP. (2007). Air drying resin and composition. (Patent No. WO/2007/147559). DSM IP Assets B.V.

Document status and date:

Published: 27/12/2007

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
- The final author version and the galley proof are versions of the publication after peer review.
- The final published version features the final layout of the paper including the volume, issue and page numbers.

[Link to publication](#)

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license above, please follow below link for the End User Agreement:

www.tue.nl/taverne

Take down policy

If you believe that this document breaches copyright please contact us at:

openaccess@tue.nl

providing details and we will investigate your claim.

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
27 December 2007 (27.12.2007)

PCT

(10) International Publication Number
WO 2007/147559 A1

(51) International Patent Classification:
C09D 177/12 (2006.01) C08G 63/685 (2006.01)
C08G 69/44 (2006.01)

(21) International Application Number:
PCT/EP2007/005385

(22) International Filing Date: 19 June 2007 (19.06.2007)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
06012508.5 19 June 2006 (19.06.2006) EP

(71) Applicant (for all designated States except US): DSM IP ASSETS B.V. [NL/NL]; Het Overloon 1, NL-16411 TE Heerlen (NL).

(72) Inventors; and

(75) Inventors/Applicants (for US only): FRIEDERICHS, Joseph, Petronella [NL/NL]; Hofstraat 20, NL-6019 CC Wessem (NL). VAN BENTHEM, Rudolfus, Antonius, Theodorus, Maria [NL/NL]; Sportlaan 9, NL-6141 BR Limbricht (NL).

(74) Agent: JESPER, Hansen; DSM Intellectual Property, P.O. Box 9, NL-6160 MA Geleen (NL).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, MT, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— with international search report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: AIR DRYING RESIN AND COMPOSITION

(57) Abstract: The invention relates to an air-drying resin suitable for a coating composition characterized in that the resin is a polyesteramide prepared from: A) at least one anhydride chosen from the list containing succinic, glutaric, citraconic, itaconic or maleic anhydride or a combination of any of them, and B) at least one alkanol-amine, and C) at least one fatty acid, wherein the fatty acid is incorporated in the resin in an amount equivalent to an oil-length between 15 and 40%. This air-drying resin is both water- and solvent-soluble, having a combination of properties desirable for different types of applications. The invention relates also to a method for preparing such a polyesteramide resin, to a composition comprising at least one polyesteramide resin and a method for preparing such a composition, to a substrate fully or partially coated with this composition, a method for curing the coated substrate, the cured and coated substrate and the use of resin in various applications.



WO 2007/147559 A1

5

AIR DRYING RESIN AND COMPOSITION

The invention relates to an airdrying polyesteramide resin functionalized with unsaturated fatty acid groups; it also relates to a method for preparing such a resin, to a composition comprising at least one polyesteramide resin and a method for preparing such a composition, to a substrate fully or partially coated with this composition, a method for curing the coated substrate, the cured and coated substrate and the use of resin in various applications.

A composition containing such a resin is known from WO 00/32708. In WO 00/32708 an airdrying coating composition is disclosed, which coating composition comprises a polyesteramide containing at least two carboxyalkylamide groups derived from an unsaturated acid with between 10 and 28 carbon atoms.

WO 00/32708 has the disadvantage that the airdrying coating composition can only be made either water- or solvent-soluble. The same coating composition cannot therefore be used for both kinds of systems.

In general, paint manufacturers produce paints by adding their choice of additional components to a coating composition, comprising a binder. Paint manufacturers choose in general different components and binders when producing water-borne paints and others when producing solvent-borne paints. Thus a paint manufacturer who produces both types of paints, water-borne and solvent-borne, needs a large variety of components and binders as each component or binder is suitable for only one kind of paint, either water- or solvent-borne. This is due to various reasons, for example different pigments or other additives that are needed for solvents of different nature. It would be very advantageous, for paint manufacturers as well as for the end-users, when one resin would be available for compositions that can be dissolved both in water and solvent, while keeping its airdrying property.

It is an object of the invention to overcome one or more of the above-mentioned and other disadvantages and to provide an airdrying resin suitable for a coating composition. Surprisingly it was found that the desired resin properties were realized for a polyesteramide resin prepared from:

A) at least one anhydride chosen from the list containing succinic, glutaric,

citraconic, itaconic or maleic anhydride or a combination of any of them,
B) at least one alkanol-amine, and
at least one fatty acid, wherein that the fatty acid is incorporated in the resin in an amount equivalent to an oil-length between 15 and 40%.

5 This airdrying resin is both water- and solvent-soluble, having a combination of properties desirable for different types of applications.

A polyesteramide resin is a polymer having branched structure with a high functionality obtained by the polycondensation of for example anhydride with an alkanol-amine. Functionality is understood to be the average number of reactive groups
10 of a certain type per molecule in the resin composition. For details regarding the compounds and the processes used to produce polyesteramide in general, patent WO 99/16810 can be consulted as reference. In the present invention, to obtain the required properties, the branched polyesteramide resin was chosen such as to have three principle building blocks: alkanol-amine, anhydride and fatty acid groups.

15 Surprisingly it was found that such a resin has airdrying properties and it is both water- and solvent-soluble. Especially, no airdrying hyperbranched resin was found until now that is water-soluble. Another advantage is that the resin is transparent and additionally a composition containing the polyesteramide resin is quickly hardened by curing.

20 The three components from which the polyesteramide resin is generally prepared are: A) at least one anhydride, B) at least one alkanol-amine and C) at least one fatty acid. Preferably, unsaturated fatty acids or mixtures of fatty acids that contain also unsaturated fatty acids can be used, in order to achieve the airdrying property of the polyesteramide resin determined by the presence of the double bonds
25 within the fatty acid chains.

The anhydride used in the preparation of the polyesteramide according to the invention is: succinic, glutaric, citraconic, itaconic or maleic anhydride, or a combination of any of them. Preferably succinic or maleic anhydride is used, and more preferably a combination of succinic anhydride and maleic anhydride is used. A
30 mole ratio of between about 1:1 and 1:10 maleic anhydride to the succinic anhydride assures a better water solubility. The additional advantage of the combination of maleic and succinic anhydride is that it also boosts the airdrying. Only maleic anhydride or a too high percentage of it can induce discoloration and side-reactions, possibly making the resin less suitable for certain coating compositions.

35 The alkanol-amine may be a monoalkanol-amine, a dialkanol-amine,

a trialkanol-amine or a mixture of any of them. The degree of branching can be set via the alkanol-amines chosen. Highly branched structures with high functionality use as starting compounds di- and trialkanol-amines. Examples of suitable alkanol-amines are described in, for example, WO 00/32708. By preference, a dialkanol and more
5 preferred diisopropanolamine (DIPA) is chosen.

The fatty acid used in the preparation of the polyesteramide according to the invention will generally be a fatty acid having between 12 to 22 carbon atoms, preferably between 16 and 18 carbon atoms. Examples of suitable saturated aliphatic acids are for example 2-ethyl hexanoic acid, lauric acid, versatic acid and
10 stearic acid. Examples of suitable unsaturated fatty acids include dehydrated castor oil fatty acid, linoleic acid and/or linolenic acid. Examples of useful natural oil fatty acids are tall oil fatty acid, sunflower oil fatty acid, corn oil fatty acid, cottonseed oil fatty acid, peanut oil fatty acid, linseed oil fatty acid, soybean oil fatty acid, rapeseed oil fatty acid, rice bran oil fatty acid, safflower oil fatty acid and/or sesame oil fatty acid. In general,
15 both saturated and unsaturated fatty acid groups may be used, however unsaturated groups are preferred due to their role in the airdrying. Mixtures of all kinds of fatty acids may be used, however it is preferred when using a mixture to use a mixture of unsaturated fatty acids.

As a measure of the amount of fatty acid incorporated into the resin
20 composition, the oil length is used. The oil length (OL) is here and hereinafter defined as the weight ratio of oil (fatty acids calculated as triglyceride equivalent) to the total resin composition. In traditional alkyd resins, a resin with an oil length of less than 40% oil is generally referred to as "short oil resin", from 40-60% oil is called medium oil resin, from 60-70% is called long oil resin and from 70-85% is called very long oil resin.
25 For the polyesteramide resin according to the present invention, the oil length ranges between 15 and 40%. Below 15% OL airdrying was found to be difficult, while above 40% OL the resin was found to be no longer water-soluble.

The process for the preparation of the polyesteramide according to the invention is characterized in that the polyesteramide is obtained by reacting an anhydride, an
30 alkanol-amine and a fatty acid wherein the equivalent ratio alkanol-amine : anhydride (D:A) ranges between 1.0 : 1.0 and 2.5 : 1.0. The part of the range with lower amounts of alkanol-amine (D:A between 1.0 : 1.0 and 1.5 : 1.0) is particularly advantageous when the alkanol-amine is a dialkanol-amine and the anhydride does not contain any reactive double bonds, such
35 as for example succinic anhydride. The part of the range with higher amounts of

alkanol-amine (D:A between 1.5 : 1.0 and 2.5 : 1.0) is particularly advantageous when the alkanol-amine is a dialkanol-amine and the anhydride does contain reactive double bonds, such as for example maleic anhydride. The middle of the range is particularly advantageous when a mixture of anhydrides with and without reactive double bonds is used.

When the anhydride has substantially no reactive double bonds and the alkanol-amine is a dialkanol-amine, then the ratio $F : (3D - 2A)$ preferably ranges between 0.05 : 1.00 and 0.35 : 1.00 wherein

F = the molar amount of fatty acid
D = the molar amount of alkanol-amine
A = the molar amount of anhydride and
(3D-2A) = the molar amount of available hydroxyl groups on the polyesteramide backbone.

According to a preferred embodiment of the invention the ratio D : A ranges between 1.20 : 1.00 and 1.40 : 1.00 and the ratio $F : (3D-2A)$ is between 0.10 : 1.00 and 0.25 : 1.00.

In another embodiment encompassing for example also when the anhydride has reactive double bonds the amount of fatty acid is defined by the oil length, and it is highly preferred that the amount of fatty acid in the method according to the invention is adjusted relative to the amount of alkanol-amine and the anhydride to ensure that the oil length of the resulting resin ranges between 15 and 40%.

The process for the preparation may take place as a one step or as a two-step process.

The two-step process may take place by a process wherein in the first step the anhydride is reacted with alkanol-amine in an equivalent ratio alkanol-amine: anhydride between 1.0:1.0 and 1.5 : 1.0 at a temperature between 20°C and 150°C, to form a β -hydroxyalkyl-amide, after which, at a temperature between 120°C and 180°C, a polyesteramide resin is obtained through polycondensation with water being removed through distillation and in the second step the fatty acid is added in such amount that the ratio $F : (3D - 2A)$ ranges between 0.05 and 0.25 after which esterification with the β -hydroxyalkylamide groups of the polyesteramide resin takes place with water being removed through distillation.

The two-step process may also take place by a process wherein the anhydride is reacted with alkanol-amine in an equivalent ratio alkanol-amine: anhydride

between 1.0 : 1.0 and 1.5 : 1.0 at a temperature between 20°C and 150°C, to form a β -hydroxyalkyl-amide, after which, at a temperature between 120°C and 180°C, a polyesteramide is obtained through polycondensation with reaction water being removed and wherein the fatty acid is added before the polycondensation is completed.

5 Preferably the fatty acid is added between 0.5 and 4 hours before the polycondensation is completed.

The one step process takes place by a process wherein the anhydride, alkanol-amine and fatty acid are reacted at a temperature between 120°C and 180°C, reaction water being removed and wherein the equivalent ratio alkanol-amine: anhydride ranges between 1.0 : 1.0 and 1.5 : 1.0 and the ratio
10 F : (3D - 2A) ranges between 0.05 and 0.25. The reaction water can be removed by methods known to the person skilled in the art, for example distillation, azeotropic distillation, etc. Preferably distillation is used.

A resin according to the invention can for example be used as a
15 component in pigment pastes, as a sole binder or as an assisting binder.

The invention also relates to the use of the resin according to the invention in a pigment paste. Pigment pastes also have, between others, the problem of dual solubility, i.e. the ability to be soluble both in water and in solvent. The air-drying property is also for pigment pastes an important advantage due to the improved speed
20 in drying. Various solutions were proposed to solve the problem of solubility both in water and in solvent, which is desirable for coating compositions. US5723537 describes a mixture of a water-soluble polyacrylate and a solvent-soluble polyester resin along with the use of a large amount of co-solvent. US4410657 describes a copolymer from acrylic (solvent-soluble) and N-vinyl monomers (water-soluble), also
25 in the presence of a co-solvent. The disadvantage of both suggested solutions is that the presence of a co-solvent is necessary to homogenize mixtures of polymers and water; without the co-solvent the problem of dual solubility cannot be solved. The use of co-solvents in pigment pastes has several disadvantages. First of all, a large amount of co-solvent needs to be used to obtain a good viscosity range for a corresponding
30 coating composition. Besides the fact that it is costly and thus less economical, after applying a coating composition containing such co-solvents, evaporation of a large amount of co-solvent takes place and that may have undesirable environmental and health effects. Also the levels of co-solvents that increase the VOC (volatile organic compound) level are more and more regulated by law. All the above-mentioned issues

would certainly be disadvantages also from the point of view of the consumer.

EP0507202A1 relates to a dye paste suitable for a mixture with dye and binding agent systems, where the mixture contains water-soluble and solvent-soluble or emulsifiable organic polymeric binding agents. However, this mixture does not have the airdrying property, which property is necessary because airdrying coatings can be slowed down in the drying process by dilution of the binder with the non-airdrying pigment paste binder.

An embodiment of the invention is related to the use of the polyesteramide resin in a pigment paste further comprising at least one binder, at least one pigment and at least one component chosen from water or an organic solvent or a mixture of any of them.

The resin according to the invention can for example be used as additive. Examples of use of such additives may be as: dispersant for pigments, hardness modifier, in water and solvent-based paint compositions or as surfactant. As an additive, it can be used both in airdrying and non-airdrying systems. It can be also an open time improver or a rheology modifier. Here and hereinafter, with "open time" is meant the time window wherein it is still possible to make readjustments to a wet paint layer without causing a damaged appearance.

The invention also relates to a composition comprising at least one polyesteramide resin and at least one component chosen from water or an organic solvent or a mixture of any of them.

The invention also relates to a coating composition comprising at least one polyesteramide resin and at least one crosslinker.

The coating composition according to the invention may be used in all kinds of coatings, for example: water-borne or solvent-borne coatings, powder coatings or radiation curable coating compositions.

The invention also relates to a substrate, fully or partially coated with a coating obtainable by using a pigment paste prepared in the process described above.

30

Examples

Preparation of fatty acid modified hyper branched polyesteramide.

Diisopropanolamine (DIPA) was introduced in a double-walled glass reactor, which was heated by means of thermal oil, fitted with a mechanical stirrer, a

35

distillation head, nitrogen and vacuum connections. At 60°C the anhydride or the mixture of anhydrides was added to the vessel. The reaction mixture was continuously stirred and gradually heated to approx 150°C. After 30 minutes the fatty acid was added and vacuum was applied during heating. The vacuum in the reactor was

5 adjusted to the release of reaction water so that this could be removed by distillation. After a total reaction time of approx 10 hours the viscous polymer had an acid value of < 5 mg KOH/gram resin. The resin was cooled to 95 °C and water of 95 °C was added under stirring in order to get a solid content appropriate for the application. After preparation of the polyesteramide, the solubility in water and white spirit was

10 established by visual inspection (presence of phase separation) following mixing of resin with water or white spirit. In Table 1, the experimental data for examples 1-7 is presented.

Table 1

Resin example	DIPA (g)	Anhydride		DIPA/Anhydride Mole Ratio	Fatty acid Soya (g)	Oil length (%)	solubility	
		Succinic Anhydride (g)	Maleic Anhydride (g)				Water	White spirit
Unit								
1	584.07	158.84	153.7	1.4	105.40	11	+	-
2	540.40	145.11	142.21	1.4	172.28	18	+	+
3	510.53	137.09	134.35	1.4	218.03	23	+	+
4	482.38	129.53	126.94	1.4	261.14	28	+	+
4a	481.14	258.40	-	1.4	260.47	28	+	+
5	449.76	120.77	118.36	1.4	311.11	33	+	+
6	421.27	113.12	110.86	1.4	354.75	38	+	+
6a	420.32	225.73	-	1.4	353.95	38	+	+
7	353.99	95.06	93.16	1.4	457.80	49	-	+

From Table 1 it is found that the resins with oil length between 15-40% are soluble in both water and oil.

Preparation of pigment pasta

5 Resin No 3 as described above was then used as a dispersant in a pigment paste with the following formulation:

- 62% pigment Bayferrox 130 M.
- 1% Bentone SD-2.
- 10 - 10% Resin No 3.
- 27% water.

The paste was milled in the standard way using glass beads resulting in a stable homogeneous pigment paste

15

Optical properties

A coating composition was prepared by mixing by standard means 3 grams of the above prepared pigment paste based on Resin No 3 with 20 grams WB alkyd emulsion based on Uradil 554 leading to a homogeneous coating composition denoted
20 Formulation a. Thereafter Formulation a was applied to a contrast card (100 μm film) by standard means and the coating composition was allowed to cure at room temperature to form a dry film. The optical properties were established by a standard lab-tester for the dried film of the coating composition as indicated below.

25	*L	-0.29
	*a	-0.07
	*b	-0.39
	Delta E	0.47
	Color strength	100%

30

Based on these data it may be concluded that the resulting dry film showed a good optical appearance on the level of what is required by a coating composition. The polyester amide pigment base was found to be compatible with both Alkyd resin Uralac AD44 in white spirit (60%) and water born Alkyd resin Uradil 554.

35

Hardness

For comparison, hardness data of the white paint base based on WB alkyd emulsion Uradil 554 without pigment paste were collected (formulation b). A comparative coating sample (Formulation c) was also prepared similar as described for the sample with
5 pigment paste and Resin No. 3, but with a commercially available pigment concentrate based on Disperbyk 185 replacing Resin No. 3.

The König hardness development in dry films of the coatings based on formulation a, b
10 and c was measured after 3 days. König hardness was measured according to ASTM D 4366. The results of the hardness measurements are shown in Table 2.

Table 2

System	Pendulum hardness after 3 days
	König (s)
Formulation a (with pigment paste according to invention)	18
Formulation b (without pigment paste)	18
Formulation c (with pigment paste Comparative example)	9

From this table, it is observed that the König hardness values are similar for the
15 formulations with and without pigment paste according to the invention (Formulation a and b, respectively), and that the formulation with pigment paste according to the invention (Formulation a) provides superior hardness as compared to the formulation with a standard pigment paste (Formulation c)

CLAIMS

1. Airdrying resin suitable for a coating composition characterized in that the resin is a polyesteramide prepared from:
 - 5 A) at least one anhydride chosen from the list containing succinic, glutaric, citraconic, itaconic or maleic anhydride or a combination of any of them, and
 - B) at least one alkanol-amine,
 - C) at least one fatty acid,
- 10 characterized in that the fatty acid is incorporated in the resin in an amount equivalent to an oil-length between 15 and 40%.
2. Resin according to claim 1 characterized in that the polyesteramide is prepared from only succinic and/or maleic anhydride as the anhydride, preferably the polyesteramide is prepared from a combination of succinic
15 anhydride and maleic anhydride and more preferably the mole ration between maleic anhydride to succinic anhydride is between 1 : 1 to 1 : 10.
3. Resin according to any one of the claims 1 to 2, wherein the fatty acid comprises an unsaturated fatty acid selected from the group of dehydrated
20 castor oil fatty acid, linoleic acid, linolenic acid, tall oil fatty acid, sunflower oil fatty acid, corn oil fatty acid, cottonseed oil fatty acid, peanut oil fatty acid, linseed oil fatty acid, soybean oil fatty acid, rapeseed oil fatty acid, rice bran oil fatty acid, safflower oil fatty acid, sesame oil fatty acid and a mixture of at least two of these fatty acids.
4. Resin according to any one of the claims 1 to 3, wherein the alkanol-amine is
25 a dialkanol, preferably the alkanol-amine is diisopropanolamine and/or diethanolamine, most preferably the alkanol-amine is diisopropanolamine.
5. Process for the preparation of a polyesteramide according to any one of the claims 1 to 4 in one step by reacting A, B, C, at a temperature between 120-
30 180°C while reaction water is removed and whereby the equivalent ratio alkanol-amine: anhydride ranges between 1.0 : 1.0 and 2.5 : 1.0.
6. Process for the preparation of a polyesteramide according to any one of the claims 1 to 4 in two steps comprising step 1 wherein the anhydride is reacted with alkanol-amine in an equivalent ratio alkanol-amine : anhydride between
35 1.0 : 1.0 and 1.5 : 1.0 at a temperature between 20°C and 150°C, to form a β -hydroxyalkyl-amide and step 2 wherein a polyesteramide is obtained at a

temperature between 120°C and 180°C through polycondensation, with reaction water being removed and wherein the fatty acid is added before the polycondensation is completed.

7. Process according to claim 5 or 6, wherein fatty acid is added in an amount to realize an oil length of the resulting resin in the range of 15 and 40%.
5
8. Composition comprising at least one resin according to anyone of claims 1 to 4 and at least one component chosen from water or an organic solvent or a mixture of any of them.
9. Coating composition comprising at least one resin according to anyone of claims 1 or 4 and at least one crosslinker.
10
10. Substrate, fully or partially coated with a composition according to claim 8 or 9.
11. Use of resin according to anyone of claims 1 or 4 in a pigment paste comprising at least one resin according to anyone of claims 1 or 4, at least one pigment and at least one component chosen from water or an organic solvent or a mixture of any of them.
15

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2007/005385

A. CLASSIFICATION OF SUBJECT MATTER
INV. C09D177/12 C08G69/44 C08G63/685

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)
C09G C09D

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 00/32708 A (DSM NV [NL]; BENTHEM RUDOLFUS ANTONIUS THEO [NL]; BEETSMA JOCHUM [NL];) 8 June 2000 (2000-06-08) cited in the application claims 1,9,10 page 1, line 23 - line 30 page 9, line 21 - page 13, line 2	1-11
A	US 2 638 449 A (WHITE RALPH V ET AL) 12 May 1953 (1953-05-12) examples 2,23	1-11
A	EP 0 326 356 A1 (NIPPON OILS & FATS CO LTD [JP]) 2 August 1989 (1989-08-02) page 6, column 61 - column 65	1-11

Further documents are listed in the continuation of Box C.

See patent family annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *&* document member of the same patent family

Date of the actual completion of the international search

13 September 2007

Date of mailing of the International search report

20/09/2007

Name and mailing address of the ISA/
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

Authorized officer

Bergmeier, Martin

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2007/005385

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 0032708	A	08-06-2000	AT 296867 T 15-06-2005
			AU 1585900 A 19-06-2000
			DE 69925634 D1 07-07-2005
			DE 69925634 T2 04-05-2006
			ES 2242434 T3 01-11-2005
US 2638449	A	12-05-1953	NONE
EP 0326356	A1	02-08-1989	AU 2872789 A 17-08-1989
			CA 1320166 C 13-07-1993
			CN 1036222 A 11-10-1989
			DE 68906555 D1 24-06-1993
			DE 68906555 T2 26-08-1993
			JP 1190791 A 31-07-1989
			JP 2508783 B2 19-06-1996
US 4885008 A 05-12-1989			