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(54) HOT ADHESIVE FORMULATION FOR ADHERING PLASTIC MATERIALS

(57) The invention describes an adhesive formulation specially designed to bond and stick plastic materials with no surface polarity and porosity such as polypropylene and the like, with no need for prior treatment of the surface to be bonded. The formulation essentially consists of a combination based on: amorphous polyolefins; other polymers to give the formulation properties of viscosity, flexibility, cohesion and tensile strength; tackifying resins which provide stickiness; waxes which allow regulation of the solidification speed of the adhesive, and other additives such as plasticisers and antioxidants, together with an adhesion promoting additive of the malonic acid type.

EP 2 586 841 A9

Description

Object of the Invention

[0001] The present invention refers to a hot melt formulation for sticking plastic materials, which provides an excellent combination of adhesive and mechanical properties. The invention's adhesive formulation provides an effective solution for creating joins between plastic substrates such as polyethylene, polypropylene and others, for which up until now it has been necessary to carry out costly surface treatments prior to the sticking process. Additionally, the adhesive formulation of the invention exhibits characteristics which allow it to be applied in industries as diverse as packaging and packing, labelling, textiles, automotive and other industrial assemblies. Another object of the invention consists of providing an adhesive formulation which has excellent adhesive properties at both high temperatures and low temperatures. This formulation consists essentially of a combination of components such as polyolefins, other polymers, tackifying resins and waxes, combined in proportions within specific ranges which allow a formulation with the abovementioned properties to be obtained.

Background to the invention

[0002] Hot melt adhesives are mainly used in industrial fields as varied as those of packaging and packing, textiles, manufacture of labels and adhesive tapes, disposable products (such as babies' nappies, for example), health products, bookbinding, industrial processes for assembling products such as wooden furniture, etc.

[0003] Hot melt adhesives have a wide application and perform particularly well when sticking porous substrates and those with surface polarity, as in the case of the different papers used in cardboard packaging. However, a hot melt adhesive is not in itself able to create a join when sticking substrates with no porosity and no polarity. In this case, prior surface treatments must be applied.

[0004] Plastic materials such as polypropylene constitute substrates which are more complicated to join because of the absence of porosity on their surface, which prevents the adhesive penetrating and developing physical anchor points on the substrate and, in particular, because of their absence of polarity. Polarity in a chemical bond means that the shared electrons in a chemical bond are attracted by one of the two atoms with the most force, creating a partially negative charge on this atom and a partially positive charge on the other. This generates a dipole between the two bodies, which is particularly predisposed to creating a bond with other chemical species by electrostatic attraction between the bonding electrons.

[0005] Polypropylene is a material which is formed of long saturated chains of carbon atoms in such a way that it has no polar groups like halogens, carbonyls, amino groups or unsaturations. This prevents the establishment of covalent or partially ionic bonding forces between the adherent and the substrate because there are no distributions of charge (dipoles). At most, Van der Waals type bonding forces, which are weak, may be established.

[0006] For these reasons, in order to create strong and lasting bonds between two substrates of polypropylene, it is necessary to carry out a surface treatment prior to the sticking process. This consists of degrading or eroding the surface to create irregularities on it, thereby promoting the appearance of physical anchor points, or generating the appearance of functional groups and charge distributions to create the appearance of chemical anchor points.

[0007] In the case of polypropylene, the surface treatments usually used are exposing it to:

- Corona discharge
- UV treatments (exposure to ultraviolet radiation using lamps)
- Ultrasound treatments
- Flame treatment

[0008] Surface treatments present obvious drawbacks, such as low production yields, high costs (particularly in the case of corona discharges and exposure to UV radiation) and the health and safety risks inherent in flame treatment.

[0009] The adhesive formulations currently existing on the market for sticking polypropylene and polyethylene-based substrates form weak adhesive bonds which lose their adhesion over time and with the process of crystal rearrangement; in other words, when the molecules forming the adhesive layer are reordered as a result of crystallisation through cooling, the adhesive/substrate interface becomes very weak and the bonding forces are so weak that a false sticking effect is produced. For these reasons it will be understood that there is a need in the current state of the art, which the invention is designed to meet by providing an adhesive capable of creating strong and lasting bonds between substrates of polypropylene with no need for prior treatment. This supposes great progress in plastic materials technology and makes it possible to develop other industrial applications in which the difficulty of creating bonds between apolar plastic materials constitutes a brake on the development of the sector. The adhesive formulation developed by this invention is designed to be extended to other sectors, like the automotive industry, for example, in which the current trend is to replace metal

with other plastic components, such as polypropylene, because they are much lighter and can be moulded into complex shapes.

[0010] To this effect, the adhesive formulation which is the subject of this invention develops bonding forces in such a way that the bond between the substrates remains long-lasting. The adhesive formulation of this invention has a low viscosity and short open time, which makes it applicable on packaging production lines, providing strong and lasting bonds with no need for prior surface treatments on the polypropylene substrates to be bonded. Another of the objectives of this invention consists of making the formulation as inexpensive as possible, to facilitate its commercialisation. In addition, another of the purposes of the invention is to ensure that the adhesive joins have the best heat resistance and good flexibility at low temperatures, so that the joins do not become brittle at low temperatures.

[0011] Document ES-2084346 refers to hot melt adhesives which include especially co-polymers of ethylene/α-olefin in which the α-olefin can have from 3 to 20 carbon atoms, and co-polymers of ethylene/butene-1, ethylene/ hexane-1/ ethylene/ octene-1, and ethylene/ octet-1 and ethylene/propylene. These co-polymers of ethylene with prescribed intervals of co-monomer can be prepared using polymerisation of the appropriate olefins in the presence of supported or unsupported catalyst systems containing metallocene.

[0012] Document ES-2179232 refers to an SIS-based adhesive formulation which can only be applied to labelling.

[0013] Document ES-2096346 refers to adhesives comprising two or more copolymers of ethylene-α-olefin with 3-20 carbon atoms, such as copolymers of ethylene/butene-1, ethylene/hexene-1, ethylene/octene-1 and ethylene/4-methylpentene-1. These ethylene copolymers with prescribed co-monomer range levels can be prepared by polymerisation of the appropriate olefins in the presence of cyclopentadienyl-transition metal compounds, supported or unsupported, and reactive organoaluminium or non-coordinating anion catalyst systems.

[0014] Document 742254 refers to the preparation of a certain class of polymers of poly(ester-amides)which are particularly suitable as hot melt adhesive compositions which are particularly advantageous for bonding plastics, such as polyester or polycarbonate polymers.

[0015] In document 5747573, on the formation of plastic containers, formulations with amorphous polyalphaolefins and a solid plasticiser like benzoates are used to improve their heat resistance.

[0016] Document 5512625 refers to the use of mixtures of amorphous and crystalline polyalphaolefins to improve the heat resistance.

[0017] In document 5041492, mixtures of amorphous polyalphaolefins, waxes and plasticisers are used to try and obtain a good adhesion in substrates of polypropylene for the automotive industry.

[0018] In document US-20080264562, mixtures of metallocene polypropylenes, resins and waxes are used with a semicrystalline polymer as an additive to promote adhesion.

[0019] In document ES-2162210, mixtures of amorphous polyalphaolefins and copolymers of ethylene/n-butyl acrylate are used to obtain adhesives particularly suitable for the wood sector.

Summary of the Invention

[0020] As stated in the present description, the objective of this invention consists of developing a formulation which can solve the problems existing in the current state of the art, related to sticking plastic materials, by providing a hot melt adhesive capable of forming strong bonds between apolar plastic substrates. Another objective of this invention is for these bonds to have good resistance to both high and low temperatures, while at the same time maintaining good flexibility. In addition, another purpose of this invention is to make the adhesive as inexpensive as possible and perfectly applicable to industrial production lines. Finally, the last objective of this invention is to obtain a type adhesive formulation which can be modified in terms of the additives used, to obtain hot melt adhesives with the physical characteristics required for each application, but always creating a strong bond.

[0021] To meet the objectives described above, this invention has developed an adhesive formulation with excellent adhesion at room temperature, excellent heat resistance at high temperatures, and good flexibility at low temperatures so that it does not become brittle. The adhesive formulation of the invention uses the following combination:

- 10-70% of amorphous polyalphaolefins;
- 5-30% of another polymer;
- 10-55% of a tackifying resin or a mixture of tackifying resins;
- 0-20% of waxes;
- 0-30% of other additives such as plasticisers and/or antioxidants, and
- 0-5% of an additive to promote adhesion, such as malonic acid.

[0022] The formulations according to the invention have the following properties:

a) They can be applied using conventional application methods between 150-200 °C;

b) They have an open time of between 5-35 seconds:
c) They maintain acceptable bond strengths, preferably in the 0°-75 °C temperature range;
d) They have a ring and ball softening point of between 100-140 °C, and
e) They have a viscosity preferably between 6000 - 15000 cP at 190 °C, measured with a Brookfield viscometer with the 27 ring.

Detailed description of the invention

[0023] The adhesive formulation developed by the invention has between 10-70% of an amorphous polyalphaolefin, preferably between 20-70% of this amorphous polyalphaolefin. The amorphous polyalphaolefins, commonly called APAO, come from low pressure polymerisation of ethene, propene and 1-butene as monomers, using a Ziegler process. These polymers are predominantly amorphous, which is why they are known as APAO amorphous polyalphaolefins. Polyalphaolefins are the most suitable polymers for bonding apolar substrates like polypropylene substrates, but their disadvantage is their high degree of crystallinity, which makes the bonds very rigid and fragile, particularly at low temperatures. There is also increased slow cohesion, which is negative for industrial assembly processes which require short set-times. Amongst the commercially available references, the most favourable are Vestoplast®, made by Evonik. Within these, the most recommended are those with molecular weights by mass M_w between 34000 and 118000, or molecular weights by M_n number between 7300-23800 g/mol.

[0024] The adhesive formulation of the invention includes between 5-30% of another hot melt polymer or copolymer, which should preferably be chosen from amongst the group consisting of:

- Ethylene/vinyl/acetate
- ethylene/methyl/acrylate
- Styrene/isoprene/styrene
- Styrene/butene/isoprene
- Isotactic polypropylene, sindiotactic polypropylene
- polypropylene and amorphous polyethylenes.

[0025] The polymers are the skeleton of the adhesive and give it its properties of viscosity, flexibility, cohesion and its tensile strength. Of all these polymers, the most widely used for hot melt adhesive formulations is ethylene/vinyl/acetate. Ethylene/vinyl/acetate (commercially known as EVA), is a copolymer formed by monomer units of ethylene, vinyl and acetate. The acetate group provides the polymer with polarity, which is a positive feature for applications in which the substrates to be joined have a polarity, like paper or cardboard, but has a counter-productive effect when the substrates to be joined are not polar, like polypropylene. In addition, adhesives formulated with EVA have a low heat resistance. Examples of commercial products are Elvax®, distributed by Dupont, Evatanne® distributed by Arkema, and Alcudia® products distributed by Repsol.

[0026] Rubbers like SIS and SBS are elastomers and are characterised by their low glass transition temperature, which gives them flexibility at low temperatures. For this reason they are used for the formulation of pressure sensitive adhesives which develop weak bonding forces, and which have their greatest application in the labelling industry. These polymers are interesting as a second polymer to modify properties in case of applications requiring good flexibility at low temperatures, but they do not offer good cohesive strength as the service temperature increases. Commercial examples of these are Dynasol rubbers, commercialised under the names Calprene® and Solprene®.

[0027] The ethylene/acrylates are polymers with properties similar to those of the EVAs but with much lower glass transition temperatures; for this reason they are especially recommended for applications requiring flexibility of the adhesive bond at low temperatures. The drawback of these polymers is essentially the same as in the case of EVAs, i.e. the negative effect of the polarity when it comes to creating adhesive bonds on materials with no surface polarity. Commercial examples of these polymers are the Elvaloy® range by Dupont and the Lotryl® range by Arkema.

[0028] On the basis of the above, it can be understood that it is necessary to mix polymers, in percentages such as those described above and exemplified later, as required to create a good balance of properties between adhesion, flexibility at low temperatures and open time.

[0029] Another of the elements involved in the adhesive formulation of this invention is constituted by the tackifying resins which provide stickiness when hot, reduce the viscosity and, consequently, improve the wettability of the adhesive on the substrate and increase the softening of the adhesive, improving its properties at high temperature. The preferred resins used are:

- Derivatives of colophony such as esters of colophony.
  Resins of linear and aromatic hydrocarbons, either pure or a mixture of the two.
- Terpenic or terpenophenolic resins.

- Phenolic resins.
- Coumarone-indene resins.

[0030] The problems which may arise with resins are problems of compatibility with the existing polymers in the formulation, which produces a separation of phases in the formulation and, consequently, a considerable reduction in the mechanical properties of the adhesive. Another of the aspects to be monitored when selecting the resins and their quantities is that they increase the glass transition temperature of the adhesive formulation, thereby increasing the degree of crystallinity, which may create brittle and fragile bonds which are not very strong. Finally, the high degree of polarity of the resins must be considered, as this may create a negative effect when forming bonds with non-polar substrates. The usual percentages of the resins in hot melt adhesive formulations vary between 10-55%. The resins currently on the market include colophonies like Silvatac® and the Silvalyte® range made by Arkema, and the Recmol® range made by Remsa. Amongst the hydrocarbon-derivative partially or totally hydrogenated synthetic resins are the Arkon® resins made by Arakawa and the Kristalex® resins by Eastman.

[0031] Another of the elements of the invention's adhesive formulation are the waxes, the percentage of which varies between 0-20% in the formulations. Waxes regulate the adhesive open time, i.e. they control the solidification speed of the adhesive. This means that the type and quantity of wax in the adhesive is fundamental for controlling the applicability on an industrial level on production lines with a fast rhythm. Waxes also reduce the viscosity and increase the softening of the adhesive depending on the melting point of the waxes used in the formulation and the quantity. The preferred types of waxes for the formulation of hot melt adhesives are:

- Paraffin waxes
- Microcrystalline waxes
- Polyethylene waxes
- Fischer-Tropsch type waxes

[0032] The problems associated with waxes are the high degree of crystallinity they bring to the adhesive formulation and, consequently, they can cause the adhesive layer to be fragile and brittle, creating weak bonds. Another problem associated with the correct choice of wax is the compromise between appropriate regulation of the open time so that the adhesive formulation can be adapted to the industry's automated production lines, and a suitable heat resistance which does not lead to the fragility effect described above.

[0033] In addition, in the adhesive formulation of the invention there are other components to be taken into account, such as:

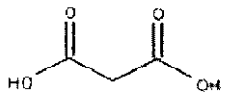
Antioxidant Additives:

Antioxidants are necessary in the adhesive formulation of the invention because they prevent heat degradation of the adhesive, something which is especially important given that the application temperatures are 160-190 °C and the long time spent by the hot melt adhesive in the heated application tank accelerates thermal decomposition.

Plasticising additives, rheology modifiers, etc.

[0034] In the additives category, both liquid and solid plasticisers are particularly useful additives for making the adhesive flexible and improving its performance at low temperatures. Plasticisers are molecules which prevent the polymer chains from moving closer during the crystallisation process of the adhesive: this distance between molecules minimises the adhesive's internal attraction properties and makes it possible for the adhesive to deform rather than breaking when effort is applied. Some of the most commonly used plasticisers are derivatives of polybutylene.

[0035] Another of the components of this adhesive formulation of the invention is malonic acid. Malonic acid is a dicarboxylic acid with the formula:



used in the adhesive formulation as an additive, in the 0-5% range, to carry out a surface treatment on the surface of the substrate to be joined, creating the anchor points necessary for good bonding. Adhesion is based on 2 types of forces: van der Waals forces and chemical bonds. Van der Waals forces are the basis of adhesion. These forces of

attraction act between the adhesive and the substrate. Meanwhile, chemical bonds produce the strongest type of adhesion. These forces are developed when the substrate has chemical groups which react with the adhesive, which is not the case for the plastic substrates covered by this invention.

[0036] Some chemical groups are notable for their ability to form van der Waals bonds. These groups can improve adhesion when they are present in the adhesive or in the substrate. The following table includes these groups in approximate descending order of adhesion properties.

Group	Van der Waals attraction
Organic acid	High
Nitryl	High
Amide	High
Hydroxyl	Intermediate
Ester	Intermediate
Acetate	Intermediate
Chloride	Intermediate
Ether	Low
Ethylene	Low

[0037] Polymers which have low adhesion properties can be improved with the addition of a small percentage of an organic acid or acrylonitrile. In the case of the present invention, malonic acid is used to improve the adhesion of the formulations contained in it.

[0038] The components of the adhesive formulations are mixed in a double-walled stainless steel mixer, with a Cowles-type stirrer.

[0039] The applied test methods are:

Viscosity: Viscosity measured using a Brookfield-type RVT viscometer with the 27 ring at 190 °C.
Softening point: Softening point using the ring and ball method according to ASTM E28.
Adhesion: Adhesion was measured against time, i.e. counting the time taken until the false adhesion effect described above occurs, if it occurs at all. The specimens are polypropylene test tubes. The unsticking is carried out manually and the bond is considered poor if, an hour after sticking, there is an adhesion failure; it is considered fair if at least three hours elapse; and it is considered good if twelve hours elapse with no adhesion failure or if it cannot be unstuck. The tests were carried out in triplicate and the bonds were conditioned at 20 °C, 4 °C and -2 °C. In addition to subjecting the formulations which are the subject of this invention to test, comparative tests were carried out with two adhesives currently available on the market.

[0040] The practice of the invention is illustrated in the examples included in the following table.

Raw material	Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5	Ex. 6	Ex. 7	Ex. 8	Ex. 9	Ex. 10
Vestoplast 708	15	15	15	20	15	15	20	20	20	15
Vestoplast	15	15	15	0	15	10	5	5	5	10
Vestoplast	20	20	20	35	20	25	25	25	25	25
PA 446	13	13	-	-	-	-	-	-	-	-
PA 443	-	-	13	13	-	-	-	-	-	-
Elvax 410	-	-	-	-	13	13	18	15	12	15
Arkon M 100	21,5	21	21	26	21	21	21	21	21	21
Recmol 100E	10	10	10	-	10	10	5	5	5	5
LP 1040P	5	5	5	5	5	5	5	5	5	5
Daelim PB 450	-	-	-	-	-		-	3	6	3

(continued)

Raw material	Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5	Ex. 6	Ex. 7	Ex. 8	Ex. 9	Ex. 10
Malonic acid	-	0,5	0,5	0,5	0,5	0,5	0,5	0,5	0,5	0,5
BHT	0,5	0,5	0,5	0,5	0,5	0,5	0,5	0,5	0,5	0,5
Adhesion 20 °C	Poor	Good	Fair	Good	Good	Good	Good	Good	Good	Good
Adhesion: 4 °C	Poor	Poor	Poor	Poor	Poor	Poor	Poor	Good	Good	Good
Adhesion: -2 °C	Poor	Poor	Poor	Poor	Poor	Poor	Poor	Fair	Good	Good

[0041] The examples in the table above show how the addition of malonic acid improves the adhesion of the adhesive formulations. Meanwhile, it shows how a suitable combination of the APAOs and another thermoplastic polymer, in this case EVA, improves the adhesion and the cohesion of the adhesive. Finally, it can also be seen how the adhesion and the cohesion of the adhesive at low temperatures can be improved by adding the appropriate concentrations of plasticiser, in this case Daelim®.

Claims

1. A hot melt formulation for sticking plastic materials, in particular for sticking materials which have no porosity or polarity on their surface, such as polypropylene and the like, with no need to apply any type of prior surface treatment, and whose adhesive bond has characteristics of increased heat resistance and improved flexibility at low temperatures compared to the usual formulations currently in existence, **characterised in that** the formulation includes a combination composed of the following components:

    - 10-70% amorphous polyalphaolefins;
    - 5-30% of another polymer;
    - 10-55% of a tackifying resin or a mixture of tackifying resins;
    - 0-20% of waxes;
    - 0-30% of other additives such as plasticisers and antioxidants:
    - 0-5% of an adhesion promoting additive as malonic acid.

2. Formulation according to claim 1, wherein the amorphous polyolefin preferably having mass molecular weights Mw between 34000 and 118000.

3. Formulation according to claim 1, **characterized in that** the other polymers consist thermofusible polymers chosen in the group consisting of ethylene / vinyl / acetate, ethylene / methyl acrylate / styrene / isoprene / styrene, styrene /bute no / isoprene, isotactic polypropylene, syndiotactic polypropylene and amorphous polypropylene and polyethylene.

4. Formulation according to claim 1, **characterized in that** the tackifying resins are preferably selected in the group consisting of resin derivatives such as resin asters; linear resins and aromatic hydrocarbon, pure or mixtures of both; terpene or terpene resins, phenolic resins, and coumarone-indene resins.

5. Formulation according to claim 1, **characterized in that** the waxes involved in the composition are preferably chosen in the group consisting of paraffin waxes, microcrystalline waxes, polyethylene waxes and waxes Fischer-Tropsch type.

Amended claims in accordance with Rule 137(2) EPC.

1. A hot melt formulation for sticking plastic materials, in particular for sticking materials which have no porosity or polarity on their surface, such as polypropylene and the like, with no need to apply any type of prior surface treatment, and whose adhesive bond has characteristics of increased heat resistance and improved flexibility at low temperatures compared to the usual formulations currently in existence, **characterised in that** the formulation includes a combination composed of the following components:

- 20-70% amorphous polyalphaolefins, APAO.
- 5-30% of another polymer
- 20-60% of a tackifying resin
- 5-25% of waxes
- 0.1-15% of other additives such as plasticisers and stabilisers
- 0.1-5% of an adhesion promoting additive

2. A hot melt formulation according to claim 1, **characterised in that** the amorphous polyalphaolefins consist of copolymers and terpolymers of ethene, 1-butene and propene produced using a low pressure Ziegler polymerisation method, making them polymers with a low degree of crystallisation.

3. A hot melt formulation according to claim 1, **characterised in that** the said other polymer is a copolymer of ethylene/ vinyl acetate with an acetate percentage of 28% and a density comprised in the interval of 0.94-0.96 g/cc.

4. A hot melt formulation according to claim 1, **characterised in that** the said tackifying resin is a hydrogenated C9 hydrocarbon resin.

5. A hot melt formulation according to claim 1, **characterised in that** the waxes are selected from within the group of polyethylene waxes, of the Fischer-Tropsch type, which are microcrystalline and paraffin.

6. A hot melt formulation according to claim 1, **characterised in that** the said other additive is a plasticiser of the pulybutene type, which provides flexibility to the adhesive formulation if the final service conditions require it.

7. A hot melt formulation according to claim 1, **characterised in that** the adhesion-promoting additive is an adhesion promoter designed to increase the bonding forces, and consists particularly of malonic acid.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/ES2011/000214

A. CLASSIFICATION OF SUBJECT MATTER

C09J123/02 (2006.01)
C09J153/02 (2006.01)
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)
C09J

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 practicable, search terms used)

EPODOC, INVENES, WPI

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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X	WO 03033612 A1 (BOSTIK FINDLEY INC) 24/04/2003, page 10, line 8-page 11, line 3; page 14; page 13, lines 16-19; page 17, lines 1-10.	1-5
X	US 5080978 A (AMOCO CO.) 14/01/1992, column 4, lines 42- 49; column 6, lines 58-68; Table 6.	1-5

☒ 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
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"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

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"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 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	Date of mailing of the international search report
23/09/2011	**(24/11/2011)**
Name and mailing address of the ISA/ OFICINA ESPAÑOLA DE PATENTES Y MARCAS Paseo de la Castellana, 75 - 28071 Madrid (España) Facsimile No.: 91 349 53 04	Authorized officer M. Bautista Sanz Telephone No. 91 3498553

Form PCT/ISA/210 (second sheet) (July 2009)

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
PCT/ES2011/000214

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