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(54) Title: COMPOSITIONS CONTAINING FATTY ACID ESTERS OF VEGETABLE ORIGIN AS SOLVENTS

(57) Abstract: The invention relates to bases for paints whose formulation is: - a resin belonging either to the family of MODIFIED ROSIN ESTER RESINS or to the family of MALEIC RESINS; - a solvent consisting of a C9 fatty acid (pelargonic acid) with a purity of 75-95%, esterified with C1 -C10 linear and branched alcohols; - an antioxidant (BHT).



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## Compositions containing fatty acid esters of vegetable origin as solvents

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### Technical Field of the Invention

The present invention relates to compositions comprising fatty acid esters of vegetable origin as solvents, more in particular the invention relates to the formulation of bases for resin-based paints belonging either to the family of ROSIN MODIFIED ESTER RESINS or to the family of MALEIC RESINS, and containing a solvent consisting of a C9 fatty acid (pelargonic acid) esterified with C1-C10 linear and branched alcohols with a degree of purity (75-95%) by mass, and methylpelargonate or pelargonic acid to complement to 100.

Within the scope of the present invention, the term "base(s) for paints" means the base(s) for coating materials, where coating materials are chosen among: paints, inks, varnishes, lacquers, enamels and coatings in general to protect, decorate and impregnate surfaces.

In the following, the term base(s) for paints and base(s) for coating materials are to be regarded as synonyms for the purposes of the present invention.

### Prior Art

The scope of the invention concerns the formulation of bases for paints containing generally: a solvent, and a resin derived from rosin and selected from those most widely used for paint-based printing inks (ROSIN MODIFIED ESTER RESINS or MALEIC RESINS). The above-mentioned bases for paints can be used for the formulation of paints useful for the protection of surfaces, preferably of wood and ceramics, as protective paints of printed matter, preferably in paper and cardboard, and as a base in the composition of printing inks.

The paints used as protection of surfaces and printed matter can be either transparent or coloured with dyes soluble in the used solvent, which is subsequently added to the dissolution of the resin in the chosen solvent.

The paint may be used for the preparation of printing inks with the addition of a pigment.

The term resin is used to describe a solid or liquid non-crystalline material of a species with a high molecular weight. Such materials often don't have a precise melting point. The resins used in paints for surface treatment and printing inks

contribute to the properties of hardness, brightness, adhesion and flexibility in an ink. They also represent the binder for the pigment.

The general process of the production of paint involves grinding the resin, that is provided solid in flakes in presence of the solvent, to obtain a fine particle size with a Cowles-type propeller for a time of 15 minutes at room temperature. The medium thus obtained is heated up to 120-150 °C for at least one hour, and then cooled to 80-90 °C. At this temperature, an antioxidant (generally BHT) is added up to 1% w/w. Then, the fluid is filtered three times through gauze filters (100 µm, 50 µm, and 25 µm).

The resins are divided into two categories: natural and synthetic. In the field of natural resins, most of commercially available materials are represented by rosin or *colofonia*, that derives directly from the drying of the resins engraved from the bark of pine trees.

Such resin is obtained tapping the living trees, sometimes with the help of an artificial extractor to accelerate the flow of material coming out of the engravings on the bark of the tree. Its price has increased slightly over the last ten years, even if there has been a small drop of its use. The production of rosin from living organisms proves to be an ecological process, differently from those exploiting raw fossils and entire tree trunks, because the rosin resin is a renewable starting material, and then it regenerates in times compatible for the production of printing inks.

The rosin tends to crystallize in a solution of mineral oils. Also, the paints made with this resin do not dry very well and require a long time for their superficial drying.

Thus, its main use is as a raw material to produce chemically modified derivatives, such as dimerized and polymerized rosin, *limited rosin* (rosin soaps or resinate metals), rosin esters, including maleic adducts, fumaric adducts or even modified resin in phenolic and alkyd resins.

The modified phenolic resins are also called "Rosin Modified Ester Resin", CAS: 68152-70-5. These resins have a widespread use in all types of carrier systems for printing inks and comprise many different qualities. Generally, they provide glossy finishes with a good chemical resistance, and are compatible with alkyd species and other resins to give high gloss printing inks with good properties of seizure resistance.

The process for obtaining the "Rosin Modified Ester" phenolic resins provides the reaction between rosin (approximately 85%) and a phenolic resin (about 15%) at 150 °C. Subsequently, the temperature is increased up to 250°C with the addition of glycerol or other polyalcohols in order to esterify the rosin acid. The functional properties of these resins depend on many factors, such as the chemical nature of the phenolic substituent, the used alcohol and the operating conditions of the plant.

"Rosin Modified Ester" phenolic resins are resins soluble in mineral oils and aromatic hydrocarbons, and generally require high temperatures (about 120 °C or higher) to solubilize. Some commercially available resins of this type are: YSER K16, YSER K4, BREMAPAL 2080, TERGRAF 940, TERGRAF 908, SYLVALITE RE100.

In recent years, vegetable-based esters capable of solubilizing the "Rosin Modified Ester Resins" have been developed. Such solvents derive from the esterification of fatty acids with a C16/C18/C18:1 chain with C1-C10[1] linear and branched alcohols. The dissolution of the "Rosin Modified Ester" phenolic resins using these solvents provides times longer than 45' at a temperature of 150 °C. The contents of resin that could be dissolved in these conditions do not exceed 45% by mass[2].

As an alternative, triglycerides obtained by esterification of glycerol and C5-C22 fatty acids (WO 2008/024968) have been proposed. However, the costs of these solvents are high (about 4 times than a fatty acid ester with monohydric alcohol) and often, despite having high performance in the solubilisation, they are not competitive against mineral solvents or fatty acid esters commercially available up to now.

Another class of synthetic resins widely used in printing inks is that of maleic or modified maleic resins, CAS: 8050-28-0 (Maleic Resin) especially in the field of printing of magazines (heatset) and newspapers (coldset). The maleic anhydride reacts by means of a Diels-Alder reaction with the natural rosin to give the desired maleic resin.

The rosin-based resins in formulations of inks and paints have the function of giving all the physical and rheological properties to the final product, i.e. sliding properties, surface resistance, superficial drying, elasticity of the final product, and in the case of inks, of allowing the pigment transfer, by means of its dispersion, from the spreading equipment (for example, a printer) to the medium to be decorated or protected. There are commercially available bases for paints consisting of solvent

and resin, which are used to disperse pigments, grinding varnish, or to act as overprint varnish. One of these bases for paints is the Setalin P7000 rosin compound dissolved in suitable solvents.

5 The properties of these resins vary with the amount of existing rosin and maleic anhydride, and are divided into three main classes, which, according to the monomer composition and the degree of polymerization, result:

- 1) soluble in ethyl alcohol
- 2) soluble in glycols
- 3) soluble in mineral oils.

10 The present invention regards Category 3, since these resins are the only compatible with the solvents which are the subject of this invention, proposed for replacing the existing mineral oils. Some resins of this type and commercially available are: PERSEUS I, ERKAMAR VP 5089, SYLVAPRINT MM 4617. The other two types of resins are not compatible with the family of solvents mentioned in this  
15 invention. Mineral-based solvents of type D120/D140 (where 120 and 140 are the respective flash points in °C) and vegetable solvents (2-ethylhexyl palmitate, rapeseed biodiesel) commercially available are able to dissolve these resins in long times at 120°C[2].

As it can be seen from the description of the prior art, the preparation of paint  
20 bases using synthetic resins of the Rosin Modified Ester Resin or Maleic Resin type derived from the modification of natural resins, and which are the most used in the formulation of printing inks, has many drawbacks:

- 1) the need of using long times and high temperatures for the dissolution;
- 2) in some cases, the impossibility of avoiding the use of mineral-origin  
25 solvents due to the insolubility of resins;
- 3) the need to maintain the resin concentration in the solvents below 45% in order to ensure a complete dissolution.

#### Summary of invention

30 The present invention relates to the formulation of the bases for resin-based coating materials that are synthetic derivatives of rosin and belong either to the family of ROSIN MODIFIED ESTER RESINS or to the family of MALEIC RESINS. Such formulations of bases for coating materials are liquid and contain, as a solvent, one

or more esters according to the general formula (I), obtained by the combination of pelargonic acid (a C9 saturated fatty acid, preferably of vegetable origin) with ROH alcohols, in which the group R may be linear or branched with carbon atoms comprised between 1 and 10. This solvent resulted surprisingly effective regarding  
5 the above mentioned resins, allowing dissolutions up to 60% w/w or more in mass of resin, contrary to values not higher than 45% of the conventional mineral-origin D100/D120/D140 (where 100, 120 and 140 are the respective flash points in °C) or vegetable-origin (C12-C18 fatty acids esters)solvents.

Another subject of the invention is a process for obtaining the formulation of a  
10 base for coating materials, comprising the steps of mixing the resin (up to 60% w/w or more) in the solvent containing the compounds of general formula (I) at a temperature <100 °C for a time sufficient to solubilize the resin, typically a time shorter than 2 hours, preferably about 15-60 minutes.

Another subject is the use of the esters of general formula (I) in combination  
15 with the rosin-derived resins in quantities exceeding 45% w/w of resin for the preparation of a formulation of bases for coating materials, where the coating materials are chosen among: paints, inks, varnishes, lacquers, enamels and coatings in general to protect, decorate and impregnate surfaces; in particular, the use is destined to the field of printing inks and paints. Still a further subject of the invention  
20 is the use of the base for coating materials, where coating materials are chosen among: paints, inks, varnishes, lacquers, enamels and coatings in general to protect, decorate and impregnate surfaces. The base for coating materials can be used as such or mixed with other components, for example selected from: 2-3% w/w anti-oxidants, 4-5% w/w desiccants, 1-2% w/w rheology modifiers, 10-15% w/w pigments,  
25 6-8% w/w alkyd resins, 2-4% w/w polyethylene waxes, to prepare paints and inks. The base for the coating materials, paints and inks of the invention containing it may be applied to substrates as coating or can be used to impregnate said articles.

Yet another subject of the invention are formulations chosen among: paints, inks, varnishes, lacquers, enamels and coatings in general to protect, decorate and  
30 impregnate surfaces; said formulations comprising the base for coating materials of the invention in which the amount of the resin with respect to the solvent is higher than 45% by weight.

The solvents of general formula (I) according to the present invention schematically solve the following problems:

1) they represent a unique solvent for resins derived from rosin, in particular for both ROSIN MODIFIED ESTER RESINS and MALEIC RESINS.

5 Currently there is no category of commercially available solvents capable of dissolving both types of resins at temperatures lower than 120 °C, or even lower than 100 °C with resin:solvent ratios of about 45-70:65-30% w/w;

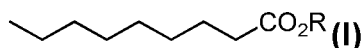
2) they guarantee a higher mass percentage of the resin in the paint, lower production times and temperatures of the above-mentioned resins;

10 3) they are in accordance with the current rules which require the replacement of fossil origin chemical products with those deriving from natural renewable sources, since they significantly reduce the environmental impact related to the use of the mineral solvents in the production of paints, which are the subject of this invention.

15 Further subjects of the invention will be apparent from the detailed description of the invention.

#### Detailed Description of The Invention

20 The compounds to be used as solvents according to the present invention have the following general formula:



and are obtained by reaction of a C9 saturated fatty acid with a ROH alcohol.

25 The solvents of general formula (I) are typically esters of pelargonic acid, a C9 saturated fatty acid of possible vegetable origin, in which the group R is a straight or branched carbon chain, preferably with carbon atoms comprised between 3 and 8 (examples of synthesized esters in the present invention are: isopropyl pelargonate, *n*-butyl pelargonate, *n*-hexyl pelargonate, *sec*-octyl pelargonate, 2-ethylhexyl pelargonate).

30 The solvents described in this invention can be obtained by an esterification reaction of pelargonic acid with a (C1-C10), preferably (C3, C8) linear or branched alcohol according to known methods [3]. The synthesis of esters of general formula (I) can be of two types: direct esterification and trans-esterification. In the first case the pelargonic acid is reacted with the desired alcohol, in a ratio of 1:1.5 by

weight, for 2 hours in the appropriate solvent (generally toluene) at the reflux temperature of the same solvent, and sulphuric acid is added as catalyst at 1% by weight. In the second case (trans-esterification), the methylpelargonate and the desired alcohol are reacted, in a ratio of 1:1.5 by weight, for 2 hours in the appropriate solvent (generally toluene) at the reflux temperature of the same solvent, and sulphuric acid is added as catalyst at 1%w/w.

Pelargonic acid can also be obtained from a renewable raw material such as oleic acid. In fact, it is a by-product of the synthesis of azelaic acid from oleic acid by oxidation with ozone or hydrogen peroxide [4].

It has been surprisingly found that the esters of pelargonic acid described above are excellent solvents for the resins derived from rosin described in the present invention, in particular those belonging both to the family of ROSIN MODIFIED ESTER RESINS (for example, K16 supplied by the company Yser) and to the family of MALEIC RESINS (for example Perseus 1 supplied by the company Yser).

Such solvents allow resin dissolutions even of 60% or more by mass of resin, contrary to values not higher than 45% of the conventional solvents of mineral origin D100/D120/D140, mixtures of C12-C20 linear and branched alkanes supplied by Exxon (where 100, 120 and 140 are the respective flash point in °C) or of vegetable origin 2-ethylhexyl esters of C12-C18 fatty acids, RADIA 7129 supplied by OLEOGEN.

Mineral spirits, soybean oil, rapeseed oil, linseed oil, methyl ester of lauric acid, ester compounds of fatty acids with chains different from C9 (as, for example, C12) or esters obtained by the combination of fatty acids with polyhydric alcohols (differently from those of the present invention, that are monohydric alcohols, are much less solving with respect to the compounds of general formula (I), since they involve dissolution temperatures of about 180-200 °C.

Contrary to the teachings of the prior art, it is possible to obtain the formulation of a base for coating materials according to the invention with a process that comprises the steps of: mixing the resin in an amount greater than 45% or more, preferably between 45 and 75%, more preferably 55-70%, in a solvent obtained by the reaction of an ROH alcohol with an C9 chain acid, typically pelargonic acid, at a temperature lower than 100 °C, and preferably between 80-90 °C, for a time



sufficient to solubilize the resin, typically a time shorter than 2 hours, preferably of about 15-60 minutes. Preferably, the solvent is of general formula (I).

The base for coating materials obtained is a clear solution consisting of one or more products obtained from the reaction of a C9 acid, typically pelargonic acid, and a ROH alcohol, in a quantity lower than 55% w/w, preferably between 55 and 35%, more preferably between 40 and 30% or lower, and rosin in a quantity higher than 45% w/w or more, preferably between >45 and 75%, more preferably 55-65% and 60-70%. Typically, the product of the reaction of the C9 acid and of the ROH alcohol consists of one or more compounds of general formula (I), optionally also in the presence of corresponding reagents.

The resin is a resin derived from rosin, in particular a resin belonging to the family of ROSIN MODIFIED ESTER RESINS and/or to the family of MALEIC RESINS.

The base for coating materials can be used as such as a surface protective coating or can be used for preparing inks, with the addition of a pigment (and other additives), which may contain other components in addition to esters of general formula (I); examples of other components have been mentioned previously, and anyway they are known by a person skilled in the art.

The base for coating materials as such, or mixed with other components, may be used for preparing products for surface coating and for inks. The base for coating materials of the invention, paints and inks containing it can be applied with known methods, for example by a process of offset printing, gravure printing, silk screening, coldset, pad printing on paper, cardboard, ceramics, wood, tinplate, plastic film substrates, or coatings materials can be used to protect said articles by applying them by impregnation, roller, brush, spray application.

The invention described herein offers four fundamental advantages compared to the state of the art:

1. shorter dissolution times due to the higher solvent power of the solvents prepared by us: up to 4 hours for known solvents and up to 30 minutes for solvents proposed in this invention,
2. lower working temperatures, up to 120 °C for traditional solvents and up to 80 °C for solvents proposed in this invention, which together with the advantages of

point 1 determine a lower waste of energy for the production of paints based on modified rosin ester resins and maleic resins,

3. paints with a higher percentage of resin (even up to 70% w/w or higher).

This aspect offers applications in fields not yet considered, as for example the production of paints for the sector of wood, ceramics, tinsplate, fiberglass, metal surface coating,

4. improvement of the eco-toxicological profile compared to solvents derived from mineral oils.

The following examples are given by way of illustration of the invention only and are not to be considered as limiting the scope thereof.

### Examples

#### Example 1. Synthesis of methyl pelargonate by direct esterification of pelargonic acid

The esterification procedure involves the reaction between a R-COOH acid and a R-OH alcohol, (C9) pelargonic acid was used as acidic moiety and methanol was used as alcohol with the following molar ratio 1:1.2 referred to the acid used.

As a catalyst to perform the reaction, 95-98% sulphuric acid H<sub>2</sub>SO<sub>4</sub> was used in a ratio of 1:100 by volume relative to the alcohol used.

The reaction mixture is reacted at reflux in toluene for 2 hrs.

The final product is a liquid and does not require any further purification prior to use.

#### Example 2. Synthesis of esters with C2-C8 alcohols for trans-esterification by methylpelargonate

The procedure of trans-esterification involves the reaction between an R-COOR acid ester and a R-OH alcohol, methyl ester of pelargonic acid (C9OMe) was used as starting ester, the following were used as alcohol:

- |   |             |               |                               |
|---|-------------|---------------|-------------------------------|
| - | 2-propanol  | CAS: 67-63-0  | reflux temperature 82 °C      |
| - | 1-n-butanol | CAS: 71-36-3  | reflux temperature 116-118 °C |
| - | 1-n-hexanol | CAS: 111-27-3 | reflux temperature 156-157 °C |
| - | 2-n-octanol | CAS: 123-96-6 | reflux temperature 174-181 °C |

- 2-ethylhexanol CAS: 104-76-7 reflux temperature 183-186°C

The alcohol was added to the starting ester in a molar ratio of 1:1, the catalyst was added in a ratio of 1:100 by volume relative to the alcohol used.

The reaction mixture is reacted at the reflux temperature of the alcohol used for 4 hrs for the 2-propanol and 1-*n*-butanol alcohols, other alcohols having a greater molecular weight for 24 hrs.

The products obtained are:

PAOiPrisopropyl pelargonate  $\text{CH}_3(\text{CH}_2)_7\text{C}(\text{O})\text{OCH}(\text{CH}_3)_2$

PAOBu butyl pelargonate  $\text{CH}_3(\text{CH}_2)_7\text{C}(\text{O})\text{O}(\text{CH}_2)_3\text{CH}_3$

10 PAOEshexyl pelargonate  $\text{CH}_3(\text{CH}_2)_7\text{C}(\text{O})\text{O}(\text{CH}_2)_5\text{CH}_3$

PAOOctyl pelargonate  $\text{CH}_3(\text{CH}_2)_7\text{C}(\text{O})\text{O}(\text{CH}_2)_7\text{CH}_3$

PAOEth 2-ethyl-hexyl pelargonate  $\text{CH}_3(\text{CH}_2)_7\text{C}(\text{O})\text{OCH}(\text{CH}_2)_2(\text{CH}_2)_2\text{CH}_3$

15 Example 3. Synthesis of esters with C2-C8 alcohols for esterification of hexanoic acid (C6, caproic acid)

The esterification procedure involves the reaction of caproic acid ( $\text{CH}_3(\text{CH}_2)_4\text{C}(\text{O})\text{OH}$ ) and a R-OH alcohol, as alcohols the following were used:

- 2-propanol CAS: 67-63-0 reflux temperature 82 °C
- 1-*n*-butanol CAS: 71-36-3 reflux temperature 116-118 °C
- 20 - 1-*n*-hexanol CAS: 111-27-3 reflux temperature 156-157 °C
- 2-*n*-octanol CAS: 123-96-6 reflux temperature 174-181 °C
- 2-ethylhexanol CAS: 104-76-7 reflux temperature 183-186°C

The esterification procedure involves the reaction of hexanoic acid and R-OH alcohol, chosen among the foregoing ones, with the following in a molar ratio of 1:1.2 relative to the acid used.

As a catalyst to perform the reaction, 95-98% sulphuric acid  $\text{H}_2\text{SO}_4$  was used in a ratio of 1:100 by volume relative to the alcohol used.

The reaction mixture is reacted at reflux in toluene for 2 hrs.

At the end of the reaction, toluene is removed by distillation.

30 The products obtained are:

CAOiPrisopropyl caproate  $\text{CH}_3(\text{CH}_2)_4\text{C}(\text{O})\text{OCH}(\text{CH}_3)_2$

CAOBu butyl caproate  $\text{CH}_3(\text{CH}_2)_4\text{C}(\text{O})\text{O}(\text{CH}_2)_3\text{CH}_3$

CAOEshexyl caproate  $\text{CH}_3(\text{CH}_2)_4\text{C}(\text{O})\text{O}(\text{CH}_2)_5\text{CH}_3$

CAOOctyl caproate  $\text{CH}_3(\text{CH}_2)_4\text{C}(\text{O})\text{O}(\text{CH}_2)_7\text{CH}_3$

CAOEtEs 2-ethyl-hexyl caproate  $\text{CH}_3(\text{CH}_2)_4\text{C}(\text{O})\text{OCH}(\text{CH}_2)_2(\text{CH}_2)_2\text{CH}_3$

The final products are liquid and do not require any further purification prior to use.

5

Example 4. Synthesis of esters with C2-C8 alcohols for esterification of dodecanoic acid (C12, lauric acid)

The esterification procedure involves the reaction of lauric acid ( $\text{CH}_3(\text{CH}_2)_{10}\text{C}(\text{O})\text{OH}$ ) and a R-OH alcohol, the following were used as alcohols:

- |    |   |                |               |                               |
|----|---|----------------|---------------|-------------------------------|
| 10 | - | 2-propanol     | CAS: 67-63-0  | reflux temperature 82 °C      |
|    | - | 1-n-butanol    | CAS: 71-36-3  | reflux temperature 116-118 °C |
|    | - | 1-n-hexanol    | CAS: 111-27-3 | reflux temperature 156-157 °C |
|    | - | 2-n-octanol    | CAS: 123-96-6 | reflux temperature 174-181 °C |
|    | - | 2-ethylhexanol | CAS: 104-76-7 | reflux temperature 183-186 °C |

15 The esterification procedure involves the reaction of dodecanoic acid and R-OH alcohol, chosen among the foregoing ones, with the following in a molar ratio of 1:1.2 relative to the acid used.

As a catalyst to perform the reaction, 95-98% sulphuric acid  $\text{H}_2\text{SO}_4$  was used in a ratio of 1:100 by volume relative to the alcohol used.

20 The reaction mixture is reacted at reflux in toluene for 2 hrs.

At the end of the reaction, toluene is removed by distillation.

The products obtained are:

LAOiPrisopropyl laurate  $\text{CH}_3(\text{CH}_2)_{10}\text{C}(\text{O})\text{OCH}(\text{CH}_3)_2$

LAOBubutyl laurate  $\text{CH}_3(\text{CH}_2)_{10}\text{C}(\text{O})\text{O}(\text{CH}_2)_3\text{CH}_3$

25 LAOEs hexyl laurate  $\text{CH}_3(\text{CH}_2)_{10}\text{C}(\text{O})\text{O}(\text{CH}_2)_5\text{CH}_3$

LAOOctyl laurate  $\text{CH}_3(\text{CH}_2)_{10}\text{C}(\text{O})\text{O}(\text{CH}_2)_7\text{CH}_3$

LAOEtEs 2-ethyl-hexyl laurate  $\text{CH}_3(\text{CH}_2)_{10}\text{C}(\text{O})\text{OCH}(\text{CH}_2)_2(\text{CH}_2)_2\text{CH}_3$

The final products are liquid and do not require any further purification prior to use.

30

Example 5. Preparation of the base for coating materials.

The formulation of the base for coating materials was: 50/55% w/w commercial resin, modified rosin phenolic or maleic resin dissolved in a 45/50% solvent.

5 Three commercial solvents (D100, mineral oil; 7129, 2-ethylhexyl palmitate; PARYOL TMC 810T, caprylic/capric triglyceride) and the solvents described in examples 1-4 were used. The resins of Example 1 and the chosen solvent were placed on a heating plate under magnetic stirring at 80 °C for one hour, and then allowed to cool to ambient temperature for 24 hrs. Tables 1 and 2 show the times when the solution becomes clear and no deposit is found.

10

**Table 1. ROSIN MODIFIED ESTER RESIN BASED PAINTS**

Solvent	Origin	45% resin (dissolution time at 80 °C, min)	55% resin (dissolution time at 80 °C, min)
D100Mineral Oil CAS: Reg. No. 64742-47-8	Commercial	>60	A clear solution is not obtained after 2 hrs
CAOiPrisopropylcaproate $\text{CH}_3(\text{CH}_2)_4\text{C}(\text{O})\text{OCH}(\text{CH}_3)_2$	Example 3	>60	A clear solution is not obtained after 2 hrs
CAOBubutylcaproate $\text{CH}_3(\text{CH}_2)_4\text{C}(\text{O})\text{O}(\text{CH}_2)_3\text{CH}_3$	Example 3	>60	A clear solution is not obtained after 2 hrs
CAOEshexylcaproate $\text{CH}_3(\text{CH}_2)_4\text{C}(\text{O})\text{O}(\text{CH}_2)_5\text{CH}_3$	Example 3	>60	A clear solution is not obtained after 2 hrs
CAOOctylcaproate $\text{CH}_3(\text{CH}_2)_4\text{C}(\text{O})\text{O}(\text{CH}_2)_7\text{CH}_3$	Example 3	>60	A clear solution is not obtained after 2 hrs
CAOEtEs2-ethyl-hexyl caproate $\text{CH}_3(\text{CH}_2)_4\text{C}(\text{O})\text{OCH}(\text{CH}_2)_2(\text{CH}_2)_2\text{CH}_3$	Example 3	>60	A clear solution is not obtained after 2 hrs
PAOMemethylpelargonate $\text{CH}_3(\text{CH}_2)_7\text{C}(\text{O})\text{OCH}_3$	Example 1	15	16
PAOiPrisopropylpelargonate $\text{CH}_3(\text{CH}_2)_7\text{C}(\text{O})\text{OCH}(\text{CH}_3)_2$	Example 2	13	15
PAOBun-butylpelargonate $\text{CH}_3(\text{CH}_2)_7\text{C}(\text{O})\text{O}(\text{CH}_2)_3\text{CH}_3$	Example 2	13	14

PAOEtEs2-ethylhexyl pelargonate CH <sub>3</sub> (CH <sub>2</sub> ) <sub>7</sub> C(O)OCH(CH <sub>2</sub> ) <sub>2</sub> (CH <sub>2</sub> ) <sub>2</sub> CH <sub>3</sub>	Example 2	50	Clear solution
LAOiPrisopropyllaurate CH <sub>3</sub> (CH <sub>2</sub> ) <sub>10</sub> C(O)OCH(CH <sub>3</sub> ) <sub>2</sub>	Example 4	>60	A clear solution is not obtained after 2 hrs
LAOBubutyllaurate CH <sub>3</sub> (CH <sub>2</sub> ) <sub>10</sub> C(O)O(CH <sub>2</sub> ) <sub>3</sub> CH <sub>3</sub>	Example 4	>60	A clear solution is not obtained after 2 hrs
LAOEsHexyllaurate CH <sub>3</sub> (CH <sub>2</sub> ) <sub>10</sub> C(O)O(CH <sub>2</sub> ) <sub>5</sub> CH <sub>3</sub>	Example 4	>60	A clear solution is not obtained after 2 hrs
LAOOctyllaurate CH <sub>3</sub> (CH <sub>2</sub> ) <sub>10</sub> C(O)O(CH <sub>2</sub> ) <sub>7</sub> CH <sub>3</sub>	Example 4	>60	A clear solution is not obtained after 2 hrs
LAOEtEs2-ethylhexyl laurate CH <sub>3</sub> (CH <sub>2</sub> ) <sub>10</sub> C(O)OCH(CH <sub>2</sub> ) <sub>2</sub> (CH <sub>2</sub> ) <sub>2</sub> CH <sub>3</sub>	Example 4	>60	A clear solution is not obtained after 2 hrs
71292ethylhexyl palmitate CH <sub>3</sub> (CH <sub>2</sub> ) <sub>12</sub> C(O)OCH(CH <sub>2</sub> ) <sub>2</sub> (CH <sub>2</sub> ) <sub>2</sub> CH <sub>3</sub> CAS: Reg. No. 29806-73-3	Commercial	>60	A clear solution is not obtained after 2 hrs
PARYOL TMC 810T caprylic/capric triglyceride CAS: Reg. No. 73398-61-5	Commercial	>60	A clear solution is not obtained after 2 hrs

Table 2. MALEIC RESIN BASED PAINTS

Solvent	Origin	45% resin (dissolution time at 80 °C, min)	55% resin (dissolution time at 80 °C, min)
D100 Mineral oil CAS: Reg. No. 64742-47-8	Mineral	>120	A clear solution is not obtained after 2 hrs
7129 2-ethylhexyl palmitate CAS: Reg. No. 29806-73-3	Vegetable	>240	A clear solution is not obtained after 4 hrs

CAOiPrisopropylcaproate $\text{CH}_3(\text{CH}_2)_4\text{C}(\text{O})\text{OCH}(\text{CH}_3)_2$	Example 3	>60	A clear solution is not obtained after 4 hrs
CAOBubutylcaproate $\text{CH}_3(\text{CH}_2)_4\text{C}(\text{O})\text{O}(\text{CH}_2)_3\text{CH}_3$	Example 3	>60	A clear solution is not obtained after 4 hrs
CAOEshexylcaproate $\text{CH}_3(\text{CH}_2)_4\text{C}(\text{O})\text{O}(\text{CH}_2)_5\text{CH}_3$	Example 3	>60	A clear solution is not obtained after 4 hrs
CAOOctylcaproate $\text{CH}_3(\text{CH}_2)_4\text{C}(\text{O})\text{O}(\text{CH}_2)_7\text{CH}_3$	Example 3	>60	A clear solution is not obtained after 4 hrs
LAOEts2-ethylhexyl caproate $\text{CH}_3(\text{CH}_2)_4\text{C}(\text{O})\text{OCH}(\text{CH}_2)_2(\text{CH}_2)_2\text{CH}_3$	Example 3	>60	A clear solution is not obtained after 4 hrs
PAOMemethylpelargonate $\text{CH}_3(\text{CH}_2)_7\text{C}(\text{O})\text{OCH}_3$	Vegetable (this invention)	10	15
PAOiPrisopropylpelargonate $\text{CH}_3(\text{CH}_2)_7\text{C}(\text{O})\text{OCH}(\text{CH}_3)_2$	Vegetable (this invention)	10	15
PAOBun-butylpelargonate $\text{CH}_3(\text{CH}_2)_7\text{C}(\text{O})\text{O}(\text{CH}_2)_3\text{CH}_3$	Vegetable (this invention)	15	20
PAOEts2-ethylhexyl pelargonate $\text{CH}_3(\text{CH}_2)_7\text{C}(\text{O})\text{OCH}(\text{CH}_2)_2(\text{CH}_2)_2\text{CH}_3$	Example 2	60	Clear solution
LAOiPrisopropyllaurate $\text{CH}_3(\text{CH}_2)_{10}\text{C}(\text{O})\text{OCH}(\text{CH}_3)_2$	Example 4	>60	A clear solution is not obtained after 2 hrs
LAOBubutyllaurate $\text{CH}_3(\text{CH}_2)_{10}\text{C}(\text{O})\text{O}(\text{CH}_2)_3\text{CH}_3$	Example 4	>60	A clear solution is not obtained after 2 hrs
LAOEshexyllaurate $\text{CH}_3(\text{CH}_2)_{10}\text{C}(\text{O})\text{O}(\text{CH}_2)_5\text{CH}_3$	Example 4	>60	A clear solution is not obtained after 2 hrs

LAOOctyllaurate $\text{CH}_3(\text{CH}_2)_{10}\text{C}(\text{O})\text{O}(\text{CH}_2)_7\text{CH}_3$	Example 4	>60	A clear solution is not obtained after 2 hrs
LAOEtEs2-ethylhexyl laurate $\text{CH}_3(\text{CH}_2)_{10}\text{C}(\text{O})\text{OCH}(\text{CH}_2)_2(\text{CH}_2)_2\text{CH}_3$	Example 4	>60	A clear solution is not obtained after 2 hrs
71292 ethylhexyl palmitate $\text{CH}_3(\text{CH}_2)_{12}\text{C}(\text{O})\text{OCH}(\text{CH}_2)_2(\text{CH}_2)_2\text{CH}_3$ CAS: Reg. No. 29806-73-3	Commercial	>60	A clear solution is not obtained after 2 hrs
PARYOL TMC 810T caprylic/capric triglyceride CAS: Reg. No. 73398-61-5	Commercial	80	Clear solution after 4 hrs

From the data of Tables 1 and 2, it can be seen that the solvents commercially available at present (mineral oil, palmitic acid ester, triglyceride) show low performance in the solubilization of resins. It is confirmed that the best commercial solvent is triglyceride, but with very long dissolution times. On the other hand, also esters of fatty acids other than palmitic acid, such as lauric acid (C12) or capric acid (C6) cannot be used. Surprisingly, the solvents related to the present invention, derived from pelargonic acid (C9), have shown immediately a very high solvent power. Actually, the resin dissolution using common commercially available mineral or vegetable solvents generally requires at least one hour under the same conditions. With the solvents of this invention, the complete dissolution is performed in just 15 minutes, thus a quarter of the time relative to the dissolution procedure with commercially available vegetable or mineral solvents.

The use of the solvents of the present invention allows the formulation of bases for coating materials with a high content of resin up to 55/60% w/w to allow their application as such not only in the field of paints and printing inks, but also in the field of surface coating of wood, ceramics and tinfoil, where better properties of gloss, drying and surface resistance are required.

#### Example 6. Solvent power of pelargonic acid esters

A first assessment of the higher solvent power of pelargonic acid esters with respect to the classical solvents can be performed by means of the analysis of the



data obtained with the dynamic light scattering technique (SMD 6000 Laser Quantum apparatus, 50 mW source of light beam at 532.5 nm) carried out on the solution at 5% by weight of modified phenolic (Table 3) and Maleic (Table 4) Resin, solubilized with traditional mineral solvents (base mineral oil D100), traditional vegetal oil (RADIA 7129) and the solvents of the present invention. The DLS technique (*Dynamic Light Scattering*) allows to monitor the intensity depending on time of the light scattered by an object into a solution. The speed of fluctuation of the light intensity depends on the speed with which the element capable of generating such scattering moves into a solution; the latter is described by the diffusion coefficient  $D$ , which is related to the size of the particles into the solution, in particular to the hydrodynamic radius  $R_i$  of a ball moving in a solvent having a viscosity  $\eta$ , according to the Stokes-Einstein equation:

$$D = \frac{kT}{6\pi\eta R_i}$$

where  $k$  is the Boltzmann constant and  $T$  is the temperature.

The measurements of the dynamic light scattering allowed to evaluate the capacity of different solvents, used to disperse the two resins, to generate sub-micrometric aggregates: K16 and a maleic resin. This dispersion capacity is linked to the solvent capacity of individual substances. The lower is the size of aggregates, the better is the solvent power for the solute concerned. In the case of the present invention, the solvent consists of the compounds of general formula (I) and solutes are modified PHENOLIC RESINS and MALEIC RESINS. In this case, the smaller is the hydrodynamic radius, better is the solvation degree of the resin by the solvent, which is therefore better than solvents giving a lower solvation degree, and therefore a larger hydrodynamic radius relative to the same resins. The hydrodynamic radii found by DLS for the solvents used by us are the lowest compared to the other commercially available solvents studied. The high solvent power, therefore confirmed by the hydrodynamic radius, has a huge impact on the paint final properties and on the production mode. The final properties are affected by the fact that the higher solvent power of our compounds allows to dissolve the rosin and maleic resins up to 70% by weight, and therefore allow to produce paints having a high degree of gloss and very high surface resistance, since these latter properties depend on the amount of resin that a solvent can dissolve to form a paint. In addition, the production mode

of the paint was performed at 80°C instead of 200°C because our compounds are more solvent with respect to the commercially available ones and need a lower operating temperature in order to dissolve completely and appropriately the resins concerned.

5 A first assessment was of visual type, where clear solutions were obtained after treatment, and after that a measurement of the DLS was carried out to assess their dispersion. Actually, in samples having a good resin dispersion, which are clear, particles with sub-micrometric size (2-300 nm) are obtained; sizes are associated with the presence of more or less large aggregates. In the extreme cases of  
10 precipitation phenomena (> 1000 nm), the sample appears cloudy, and this is associated with a very poor resin dispersion.

In our case, from the data shown in Tables 1 and 2 of Example 3 it can be clearly seen that the diffusion coefficient for the solvents of the invention, and therefore the size of the aggregates, is considerably lower than in solvents  
15 commercially available at present for dispersing modified phenolic resins and maleic resins. Actually, for D100 and RADIA 7129 solvents, aggregate sizes exceeding the limit of detectability by DLS are obtained, and therefore it can be deduced that they disperse in a poorer way such resins relative to solvents of the present invention. A  
20 5% w/w modified synthetic phenolic resin was used for the mixtures to be tested by DLS obtained industrially by esterification of rosin with pentaerythritol, and subsequent polymerization with phenol, trade name SIRIUS XVI, supplied by YSER. The Maleic Resin used is Perseus I supplied by Yser.

**Table 3. ROSIN MODIFIED ESTER RESIN**

Sample	Origin	Diffusion coefficient (cm <sup>2</sup> /sec)	Polydispersity index	Hydrodynamic radius (nm)
D100 mineral oil CAS: Reg. No. 64742-47-8	Commercial	-	-	-
7129 2-ethylhexyl palmitate CAS: Reg. No. 29806-73-3	Commercial	-	-	-
PAOMe methylpelargonate CH <sub>3</sub> (CH <sub>2</sub> ) <sub>7</sub> C(O)OCH <sub>3</sub>	Example 1	(2.4 ± 0.3) 10 <sup>-8</sup>	0.76±0.11	8.9 ± 0.9
PAOiPr isopropylpelargonate CH <sub>3</sub> (CH <sub>2</sub> ) <sub>7</sub> C(O)OCH(CH <sub>3</sub> ) <sub>2</sub>	Example 2	(2.4 ± 0.4) 10 <sup>-8</sup>	0.64±0.14	9.2 ± 1.3

PAOBu n-butylpelargonate $\text{CH}_3(\text{CH}_2)_7\text{C}(\text{O})\text{O}(\text{CH}_2)_3\text{CH}_3$	Example 2	$(1.69 \pm 0.11)10^{-8}$	0.71±0.06	12.9 ± 0.4
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**Table 4. MALEIC RESIN**

Sample	Origin	Diffusion coefficient (cm <sup>2</sup> /sec)	Polydispersity index	Hydrodynamic radius (nm)
D100 Mineral oil CAS: Reg. No. 64742-47-8	Commercial	-	-	-
7129 2-ethylhexyl palmitate CAS: Reg. No. 29806-73-3	Commercial	-	-	-
PAOMe methylpelargonate $\text{CH}_3(\text{CH}_2)_7\text{C}(\text{O})\text{OCH}_3$	Example 1	$(1.4 \pm 0.1)10^{-7}$	0.90±0.42	1.7±0.6
PAOiPr isopropylpelargonate $\text{CH}_3(\text{CH}_2)_7\text{C}(\text{O})\text{OCH}(\text{CH}_3)_2$	Example 2	$(7.95 \pm 0.17)10^{-8}$	1.0±0.3	2.74±0.11
PAOBu n-butylpelargonate $\text{CH}_3(\text{CH}_2)_7\text{C}(\text{O})\text{O}(\text{CH}_2)_3\text{CH}_3$	Example 2	$(9.3 \pm 0.3)10^{-8}$	0.70±0.06	2.34 ± 0.8

5 From a first analysis of Tables 3 and 4, it can be seen that in the case of the solvents commercially available at present in dissolution conditions (80 °C for 1 hour) neither a diffusion coefficient nor the hydrodynamic radius (measured by means of the laser light scattering technique, DLS) of the populations present in the dispersion cannot be defined. The impossibility to determine these parameters reflects the

10 absence of suitably solvated resin agglomerates, which indicates a precise and lower solvent power of products currently in use if compared with the solvents of the present invention. It follows that with the latter, production times and temperatures are reduced, and the product quality is improved because it has greater stability over time and a more effective application profile in printing and coating.

15

#### Example 7 Production of offset printing ink

10 kg, i.e. 2.5 kg for each colour in the YMCK four-colour standard (yellow, magenta, cyan, black) of offset printing ink were prepared using the paint of Example 5 described in our invention, according to the following formula:

20 Sunbrite Yellow 13 pigment for yellow;  
Sunbrite Red 57:1 pigment for magenta;

	Sunbrite Blue pigment 15:3 for cyan;	
	Sunbrite Black 7 pigment for black; Sunchemical	20%
	Example 5 paint base	60%
	WorleéKyd S23 alkyd resin	10%
5	Micro Powder Mp 22 vf hydrocarbon wax	5%
	Hydroquinone	1%
	Mn(octanoate) <sub>2</sub>	2%
	Soybean oil	2%

The mixture was stirred under a Cowles disperder for 30 minutes, thereafter it  
 10 was refined on three-cylinder machine until obtaining pigment particles smaller than  
 10 microns (assay carried out with BYK-Gardner grindometer).

The inks thus obtained were tested by analyses of viscosity, yield value,  
 tensile strength, surface resistance and setoff drying.

The results obtained are as follows:

15 Theoretical background

Viscosity, tensile strength and yield value (pour point) are important  
 parameters to understand the behaviour of the printing ink in the printing machine.  
 Typically (see Printing Ink Manual, Springer, 1988), ranges for inks suitable for  
 printing are:

20 viscosity: 200-350 poise (Laray viscometer, falling bar, processing with Casson  
 equation)

yield value: 10000-15000 dy/cm<sup>2</sup>(Laray viscometer, falling bar, processing with  
 Casson equation)

tensile strength: 13-18 (inkometer 1100, Rycobel Group).

25 Rub off is an important post printing test to perform always to assess the  
 adhesion properties of the ink to the substrate and the surface resistance to  
 scratches and cutting of the final printed matter. Printed ink undergoes rubbing with  
 a constant weight for a known time to check the surface resistance of the final  
 product. If the printed matter results scratched, then in test is positive, meaning that  
 30 rub off resulted, and thus the ink is not suitable for printing.

Setting is a further post-printing parameter of fundamental importance for  
 understanding the ink drying power on the substrate, in order to prevent the

phenomenon of setting off that could lead to a contamination of the entire pile of sheets output from the printer. Apart from contaminating the pile of sheets, it makes the final printing result graphically unacceptable, since part of the ink is transferred from the printed face to the non-printed face of the top sheet in the pile. Printed ink  
5 undergoes a constant pressure from a printing machine that carries a blank sheet that will be put in contact with the printed sheet (setting off test). This setting off test will assess the portion of ink that is transferred by pressure from the printed sheet on the blank sheet pressed against the printed sheet always with the same pressure, but at subsequent intervals (in our case, 10", 30", 60", 90", 120"). After 120", if setting off is  
10 still present, the ink is still drying, and the test is negative, i.e. ink does not dry superficially and may not be suitable for printing.

*Yellow ink:*

Viscosity:  $220 \pm 20$  poise (Laray viscometer, falling bar, processing with Casson equation).

15 Yield value:  $12200 \pm 1000$  dy/cm<sup>2</sup> (Laray viscometer, falling bar, processing with Casson equation).

Tensile strength: 15 (ink o meter 1100, Rycobel Group).

Rubbing off: negative, printed ink resists to rubbing test (Sutherland ink rub tester, weight: 2 lb, 30 cycles, 21 cycles per minute).

20 Setting off: positive after 2 minutes, ink dries superficially during the test, (IGT ink setting testing machine).

*Red ink:*

Viscosity:  $250 \pm 20$  poise (Laray viscometer, falling bar, processing with Casson equation).

25 Yield value:  $13300 \pm 15000$  dy/cm<sup>2</sup> (Laray viscometer, falling bar, processing with Casson equation).

Tensile strength: 16 (ink o meter 1100, Rycobel Group).

Rubbing off: negative, printed ink resists to rubbing test (Sutherland ink rub tester, weight: 2 lb, 30 cycles, 21 cycles per minute).

30 Setting off: positive after 2 minutes, ink dries superficially during the test, (IGT ink setting testing machine).

*Blue ink:*

Viscosity:  $260 \pm 20$  poise (Laray viscometer, falling bar, processing with Casson equation).

Yield value:  $13800 \pm 15000$  dy/cm<sup>2</sup> (Laray viscometer, falling bar, processing with Casson equation).

Tensile strength: 16 (ink o meter 1100, Rycobel Group).

5 Rubbing off: negative, the printed ink resists to rubbing test (Sutherland ink rub tester, weight: 2 lb, 30 cycles, 21 cycles per minute).

Setting off: positive after 2 minutes, ink dries superficially during the test, (IGT ink setting testing machine).

*Black ink:*

10 Viscosity:  $240 \pm 20$  poise (Laray viscometer, falling bar, processing with Casson equation).

Yield value:  $13500 \pm 15000$  dy/cm<sup>2</sup> (Laray viscometer, falling bar, processing with Casson equation).

Tensile strength: 16 (ink-o-meter 1100, Rycobel Group).

15 Rubbing off: negative, the printed ink resists to rubbing test (Sutherland ink rub tester, weight: 2 lb, 30 cycles, 21 cycles per minute).

Setting off: positive after 2 minutes, ink dries superficially during the test, (IGT Ink setting testing machine).

Inks thus obtained were printed on the industrial offset printing machine KBA Rapida 106, for a full cycle of printing of 8 hours at a speed of 10,000 sheets per  
20 hour. The ink did not show any printing problems at graphic level, nor any issues of emulsion properties with the wetting mixture present on the printing machine. Thus, the outcome of printing is positive. The final printed matter underwent rub off and setting tests with negative results for the first and positive for the second. Also, the post printing tests shall therefore be considered positive.

25 The goodness of the test print and post printing parameters of inks produced with the paint of Example 5 of our invention demonstrate that our solvents are applicable as products to be used for the formulation of rosin and maleic based paints and for the production of offset printing inks.

### 30 Bibliography

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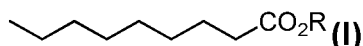
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## CLAIMS

1. Use as a solvent of a compound which is obtained by esterification reaction between a C9 fatty acid and C1-C10 straight or branched chain alcohols in formulations selected from paints, printing inks, surface coatings, varnishes, lacquers, enamels and coatings in general, wherein said formulations comprise a resin derived from rosin selected from those belonging either to the family of ROSIN MODIFIED ESTER RESINS or to the family of MALEIC RESINS and mixtures thereof, in an amount higher than 45% by weight.

2. Use according to the preceding claim, in which the compound to be used as solvent is selected from the compounds having the following general formula:



in which R is a linear or branched chain of carbon atoms, carbon atoms ranging between 1 and 10, preferably between 3 and 8, particularly preferred are: methyl pelargonate, isopropylpelargonate, *n*-butyl pelargonate, *n*-hexyl pelargonate, sec-octylpelargonate, 2-ethylhexyl pelargonate, and mixtures thereof.

3. Formulations for printing inks, paints, varnishes, lacquers, enamels, and coatings comprising a resin derived from rosin and a solvent that is obtained by esterification reaction between a C9 fatty acid and C1-C10 straight or branched chain alcohols in which the resin is contained in an amount higher than 45% w/w with respect to the solvent, preferably in an amount ranging between 45% and 70% w/w.

4. Formulations according to claim 3, wherein the printing inks are chosen between offset printing inks, either for application on a non-food packaging medium or for application on an absorbing - such as mono-coated cardboard - and non-absorbing food packaging - such as bi-coated cardboard - medium, heatset, coldset, paints and coatings, and are clear or coloured for natural or synthetic surfaces selected from wood, ceramics, paper, cardboard and tinplate.

5. Manufacturing process for printing inks, paints, lacquers, enamels, coatings and varnishes comprising the step of mixing at a temperature lower than



100 °C, preferably between 80 °C and 90 °C, for a time shorter than 1 hour, preferably between 30 and 45 minutes, a resin derived from rosin with a solvent obtained by esterification reaction between a C9 fatty acid and C1-C10 straight or branched chain alcohols, whose ratio resin/solvent is higher than 45% by weight.

5

6. Base for coating materials that is a clear solution consisting of:

(i) a solvent that is the reaction product between a C9 saturated fatty acid and ROH alcohols, wherein the group R is linear or branched with carbon atoms ranging between 1 and 10, and

10

(ii) a resin derived from rosin, selected from those belonging either to the family of ROSIN MODIFIED ESTER RESINS or to the family of MALEIC RESINS, and mixtures thereof,

15

wherein the amount of the resin (ii) relative to the solvent (i) is higher than 45% by weight, preferably between >45 and 75% by weight, more preferably 55-65% and 60-70% by weight.

7. Base for coating materials according to claim 6, wherein the ratio resin:solvent is 45-70:65-30% w/w.

20

8. Manufacturing process of the base for coating materials according to any one of claims 6-7, wherein the mixing of the resin (ii) with the solvent (i) is carried out at a temperature lower than 100 °C, preferably between 80 °C and 90 °C, for a time shorter than 1 hour, preferably between 15 and 60 minutes, more preferably between 30 and 45 minutes.

25

9. Use of the base for coating materials according to any one of claims 6-7, for the preparation of varnishes, paints, lacquers, enamels, coatings and printing inks.

30

10. Use of the base for coating materials according to any one of claims 6-7, as such or mixed with other components to prepare varnishes, paints, lacquers, enamels and inks to be applied on substrates such as coating, or as impregnating material for articles.

11. Formulations selected from inks, paints, lacquers, enamels, coatings and varnishes comprising the base according to any of the preceding claims 6-7, wherein the quantity of the resin (ii) relative to the solvent (i) is higher than 45% by weight.

5

12. Impregnated or superficially coated articles with the base for coating materials according to any one of claims 6-7 or with the formulations according to claim 11.

10

INTERNATIONAL SEARCH REPORT

International application No  
PCT/IB2018/050632

A. CLASSIFICATION OF SUBJECT MATTER  
INV. C09D11/00  
ADD.  
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)  
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 practicable, 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	EP 2 548 929 A1 (DAINIPPON INK & CHEMICALS [JP]) 23 January 2013 (2013-01-23) paragraphs [0021] - [0028] -----	1-12
A	US 2013/194362 A1 (SAO AKIHITO [JP] ET AL) 1 August 2013 (2013-08-01) paragraphs [0038] - [0043], [0096] -----	1-12
A	WO 2008/024968 A1 (SUN CHEMICAL CORP [US]; PULINA TILLMANN [DE]; JOHNKE CHRISTIAN [DE]) 28 February 2008 (2008-02-28) page 5, lines 3-8 page 7, lines 24-30; claim 6 -----	1-12
A	EP 2 208 763 A1 (COGNIS IP MAN GMBH [DE]) 21 July 2010 (2010-07-21) paragraph [0019]; claim 1 -----	1-12
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Further documents are listed in the continuation of Box C.

See patent family annex.

\* Special categories of cited documents :

<p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier application or patent but published on or after the international filing date</p> <p>"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)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p>	<p>"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</p> <p>"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</p> <p>"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</p> <p>"&amp;" document member of the same patent family</p>
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Date of the actual completion of the international search  19 April 2018	Date of mailing of the international search report  16/05/2018
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Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer  Zellner, Armin
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## INTERNATIONAL SEARCH REPORT

International application No  
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