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(54) HYDROPHOBING AND FORMALDEHYDE SCAVENGING COMPOSITIONS COMPRISING WAX EMULSIONS AND RESORCINOL AND THEIR USE FOR INCREASING THE HYDROPHOBICITY OF WOOD COMPOSITE BOARDS AND FIBREGLASS OR ROCK WOOL INSULATIONS

WACHSEMULSIONEN MIT RESORCIN UND DEREN VERWENDUNG BEI DER HERSTELLUNG VON HOLZWERKSTOFFPLATTEN, GLASFASER UND STEINWOLLE

ÉMULSIONS DE CIRE COMPRENANT DU RÉSORCINOL ET LEUR UTILISATION DANS LA FABRICATION DE PANNEAUX DÉRIVÉS DU BOIS, FIBRE DE VERRE ET DE LAINE DE ROCHE

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Description

FIELD OF THE INVENTION

[0001] The present invention relates to compositions comprising O/W wax emulsions, including petroleum derived and vegetable derived wax emulsions, and resorcinol. The compositions according to the invention are useful for preparing hidrofugant formulations, i.e. waterproofing formulations; they may be used in the manufacture of several materials, for example of wood composite boards, such as wood derived boards, fibreboards, particleboards, chip boards, oriented strand boards, plywood and paperboards, but also of fibreglass or rock wool insulations. The formulations according to the invention are also useful for favouring the release of the materials manufactured therewith from molds and machinery used during manufacture, for reducing the formaldehyde emission, if formaldehyde is used during the manufacture of the materials, and allowing for lower press temperature and press factor during the manufacture of boards.

BACKGROUND OF THE INVENTION

Manufacture of wood composite boards

[0002] The manufacture of wood composite boards such as particleboard, fibreboard (MDF and HDF), chip boards, oriented strand boards and the like generally first comprises combining wood chips, fibres or particles and an adhesive. The mixture is then heated under pressure to cure the adhesive and to form the desired board. Formaldehyde based resins, such as phenol-formaldehyde (PF), are typical adhesives used in the manufacture of such panels.

[0003] In order to impart hydrophobing characteristics to wood composite boards, it is known in the State of the Art to include a wax emulsion into the board manufacturing process. Thus, once the board is made, the wax provides hydrophobic properties thereto and serves to repel water from being absorbed, thereby preventing deterioration of the board.

[0004] Wood composite boards, as well as fibreglass or rock wool insulations, manufactured with formaldehyde based adhesives, are known to result in formaldehyde emissions, both during their manufacture and also later, over time, during their storage or use. It is generally known that formaldehyde is a strong irritant and an allergenic agent, and it is also classified as a carcinogen.

Manufacture of fiberglass insulations and rock wool insulations

[0005] The manufacture of fiberglass and rock wool insulation products generally comprises a step of manufacture of the rock wool and fiberglass themselves, which can be performed by different procedures, for example according to the techniques known in the state of the art as rotary process (internal centrifuge), cascade process (external centrifuge), and flame attenuation process (pot & marble).

[0006] To ensure the assembly and adhesion of the fibers, an adhesive resin, generally a thermosetting resin, is projected onto the fibers (glass fiber or rock wool), or mixed with the fibers. The mixture of fibers and resin is subjected to a thermal treatment, at a temperature generally higher than 100 °C, in order to effect the polycondensation of the resin and thus obtain a thermal and/or acoustic insulation product. Commonly used adhesive compositions are resins derived from formaldehyde, similar to those used in the manufacture of wood derived boards or wood composite boards. During the manufacture further additives may be added to the mixture of fibers and adhesive, such as for example catalysts for crosslinking the resin or waterproofing emulsions (typically paraffin-based).

[0007] That is, the manufacture of fiberglass insulations and rock wool insulations has many similarities to the manufacture of wood derived boards or wood composite boards.

Formaldehyde

[0008] Formaldehyde is a monomer, which is used to polymerize with urea, melamine, phenol to form aminoplast resins. Formaldehyde is under discussion as an indoor air pollutant since the 1960s(O. Wittmann (1962), Holz Roh-Werkst., 20, 221 - 224), when the release of formaldehyde from particleboard during use was documented. Adverse health effects from indoor exposure to formaldehyde, especially irritation of the eyes and upper airways, were first reported in the mid-1960s. Formaldehyde emissions from materials bonded with urea formaldehyde resin were soon identified as the cause of the complaints. As a consequence, a guideline value of 0,1 ppm was already proposed in 1977 by the former German Federal Agency of Health to limit human exposure in dwellings. Criteria for the limitation and regulation of formaldehyde emissions from wood-based materials were established in 1981 in Germany and Denmark. Other countries followed and issued regulations in the mid 1980ies. Formaldehyde was identified as one of the priority indoor air pollutants *(*Spengler J.D. et al. (1983). Science, 221(4605), 9-17). In parallel, the first studies on the carcinogenicity of formaldehyde triggered an avalanche of scientific work.

[0009] REACH (Registration, Evaluation, Authorization and Restriction of Chemicals) entered into force in 2007. It is the main framework for chemical regulation in the European Union and adopted to improve the protection of human health and the environment from the risks that can be posed by chemicals. REACH not only applies to those chemicals used in industrial processes but also to chemicals in products for intended use at the customers site, for example building materials, textiles, consumer products and other appliances.

[0010] The European Chemicals Agency requests the provision of a Chemical Safety Report (CSR) for products manufactured using formaldehyde, following the "DECISION ON SUBSTANCE EVALUATION PURSUANT TO ARTICLE 46(1) OF REGULATION (EC) NO 1907/2006 for formaldehyde, CAS No 50-00-0 (EC No 200-001-8)".

[0011] The International Agency for Research on Cancer (IARC) classified formaldehyde as a human carcinogen (Group 1) in 2004. The definition of a Group 1 carcinogen according to IARC is as follows: *"There is enough evidence to conclude that it can cause cancer in humans".* The evaluation is based on information regarding the relationship between nasopharyngeal cancer and leukaemia related to the exposure to formaldehyde *(International Agency for Research on Cancer (IARC), 2006).* The European Commission classified formaldehyde as a 1B carcinogen and mutagen 2 on June 5th, 2014 in the ordinance EU 605/2014. Category 1B states that the carcinogenic effect has been demonstrated in animal trials and is probable for humans. The reclassification results in a series of consequences depending on national legislation.

[0012] For the workplace area the *Scientific Committee on Occupational Exposure Limits (SCOEL)* recommended an 8-hour TWA (time-weighted average) of 0,3 ppm and a STEL (Short Term Exposure Limit) of 0,6 ppm *(Scientific Committee on Occupational Exposure Limits (SCOEL), 2015).* SCOEL considers formaldehyde as a carcinogen Group C (genotoxic carcinogen with a mode-of-action-based threshold). The German MAK Commission *(Deutsche Forschungsgemeinschaft (DFG), 2016)* also defines a maximum workplace concentration of 0,3 ppm and classifies formaldehyde as a Group 4 carcinogen (substances that cause cancer in humans or animals or that are considered to be carcinogenic for humans and for which a MAK value can be derived). The *German Federal Institute for Occupational Health and Safety (BAuA)* argues that current literature indicates formaldehyde exposure concentrations without adverse effects, which supports the assumption of a threshold concentration and allows the derivation of an occupational limit value *(Bundesanstalt für Arbeitsschutz und Arbeitsmedizin (BAuA), 2015).*

[0013] The WHO confirmed their indoor guideline value for formaldehyde as 0,1 mg/m^3 in the year 2010 *(World Health Organization, 2010).* The WHO assessment was studied thoroughly in a further study and an air quality formaldehyde guideline of 0,1 mg/m^3 was considered to be protective against both acute and chronic sensory irritation in the airways in the general population *(*Nielsen GD et al. (2010), Arch Toxicol., 84, 423-446). Moreover, the same authors state that the formaldehyde WHO guideline value is also considered defendable for prevention of all types of cancer, including lymphohema-topoietic malignancies.

[0014] In 2016 Germany has adopted the WHO guideline value. The Committee on Indoor Guide Values has outlined the following: *"Based on a NOAEC (no observed adverse effect concentration) of 0,63 mg/m^3 for sensory irritation in humans, a factor of 1 for time extrapolation and a factor of 5 for inter human variability the Committee derives a precautionary indoor air guide value (RW I) of 0,1 mg formaldehyde per cubic meter...In conclusion, the indoor air guide value for formaldehyde is also protective against cancer risk of inhaled formaldehyde" (Ausschuss für Innenraumrichtwerte,* 2016a). The same committee stated that on the basis of the current data there is no clear association between formaldehyde exposure in the indoor environment and asthma in children *(Ausschuss für Innenraumrichtwerte, 2016b).*

[0015] Over the years, a number of national authorities also reassessed their indoor air guideline values *(*Salthammer et al. (2011), Chemosphere, 82(11), 1507-17*)* and subsequently intend to agree with the WHO recommendation of 0,1 mg/m^3. This harmonization is a pragmatic step as the WHO value is very well assessed and justified. Moreover, the guideline value is also not normally restrictive as formaldehyde conditions in normal living conditions tend to average between 0,02 and 0,04 mg/m^3 *(*Salthammer T et al. (2010), Chem Rev. 110, 2536-2572). According to the currently available state-of-the-art, an orientation to the WHO guideline value of 0,1 mg/m^3 would seem sensible, practicable and toxicologically defendable *(*Salthammer et al (2015), Int J Hyg Environ Health., 218(4),433-6). The argument is supported by Nielsen et al.(2013), Arch Toxicol., 87, 73-98. These authors have evaluated current guideline approaches and come to the conclusion that the WHO guideline has been strengthened.

[0016] It is therefore a continuous goal to absorb or "scavenge" the formaldehyde contained in wood composite boards and/or generated during the manufacture of such boards or other materials, such as rock wool or fibreglass insulations.

Formaldehyde emissions: test methods

[0017] Many organizations have defined the test methods with which the level of formaldehyde emissions has to be determined:
UNE-EN ISO 12460-3:2016: gas analysis method, which is an updated version from Wood-based panels - Determination of formaldehyde release - Part 3: Gas analysis method (ISO 12460-3:2015).

[0018] TSCA Title VI provides for quarterly and quality control testing for hardwood plywood, particleboard, and MDF

using specified methods developed by ASTM International, among them it is worth noting:
ASTM D5582-00 (Reapproved 2006), Standard Test Method for Determining Formaldehyde Levels from Wood Products Using a Desiccator. This test method describes a small-scale procedure for measuring formaldehyde emissions potential from wood products. The formaldehyde level is determined by collecting airborne formaldehyde in a small distilled water reservoir within a closed desiccator. The quantity of formaldehyde is determined by a chromotropic acid test procedure.

[0019] ASTM D6007-02, Standard Test Method for Determining Formaldehyde Concentrations in Air from Wood Products Using a Small-Scale Chamber. This test method measures the formaldehyde concentrations in air from wood products under defined test conditions of temperature and relative humidity. Results obtained from this small-scale chamber test method are intended to be comparable to results obtained testing larger product samples by the large chamber test method for wood products, Test Method E 1333.

[0020] ASTM E1333-10, Standard Test Method for Determining Formaldehyde Concentrations in Air and Emission Rates from Wood Products Using a Large Chamber. This test method measures the formaldehyde concentration in air and emission rate from wood products containing formaldehyde under conditions designed to simulate product use. The concentration in air and emission rate is determined in a large chamber under specific test conditions of temperature and relative humidity. The general procedures are also intended for testing product combinations at product-loading ratios and at air-exchange rates typical of the indoor environment.

[0021] BS EN 120:1992, Wood based panels. Determination of formaldehyde content-Extraction method called the perforator method, English Version. This European standard describes an extraction method, known as the perforator method, for determining the formaldehyde content of unlaminated and uncoated wood-based panels.

[0022] BS EN 717-2:1995, Wood-based panels-Determination of formaldehyde release-Part 2: Formaldehyde release by the gas analysis method, English Version. This European standard describes a procedure for determination of accelerated formaldehyde release from wood-based panels.

[0023] JIS A 1460:2001 Building boards-Determination of formaldehyde emission-Desiccator method: This method describes a method for testing formaldehyde emissions from construction boards by measuring the concentration of formaldehyde absorbed in distilled or deionized water from samples of a specified surface area placed in a glass desiccator for 24 hours.

Formaldehyde scavengers

[0024] Several compounds useful as formaldehyde scavengers are known in the State of the Art, such as, for example, urea, urea derivatives, urea resins, sodium metabisulphite, ammonium bisulphite.

[0025] Document WO 2010/054467 A1 describes emulsions having a high wax content, comprising formaldehyde scavengers; the formaldehyde scavengers are preferably selected from urea, a urea derivative, a urea resin, a urea-formaldehyde resin, a melamine- urea-formaldehyde resin, an ethylene urea compound, carbohydrazide, a natural polyphenol, tannin, lignin, lignosulphonate, or a combination thereof.

[0026] Another work (Costa et al. (2013), Wood Sci Technol (2013) 47: 1261-127) studies present the performance of sodium and ammonium bisulphite as formaldehyde scavengers in particleboard and MDF production; however, the use of these type of scavengers causes an excessive loss of mechanical properties in the final product that does not support the current market.

[0027] Another way known to reduce formaldehyde emission of boards is the reduction in Formaldehyde/Urea molar ratio; in fact, this has been a strategy adopted in the last decades to decrease formaldehyde emission (Myers GE et al. (1984), For Prod J 34(5):35-41). However, this reduction reduces the reactivity of Urea-Formaldehyde (UF) resins. Currently, reactivity of industrial UF adhesives is near the minimum limit accepted for industrial panel production (urea, a urea derivative, a urea resin, a urea-formaldehyde resin, a melamine- urea-formaldehyde resin, an ethylene urea compound, carbohydrazide, a natural polyphenol^, tannin, lignin, lignosulphonate, or a combination thereof.).

[0028] Substitution of UF resins by other formaldehyde-free adhesives does not convince industrial producers, due to their higher price or lower reactivity (Amazio P et al. (2011), J Appl Polym Sci 122(4):2779-2788); Despres A et al. (2010), Eur J Wood Prod 68(1):13-20; Tang L et al. (2011), Int J Adhes Adhes 31(6):507-512). In order to increase the degree of cure and reduce free formaldehyde at the end off cure, new catalysts were studied, but reactivity is still too low (Costa et al. (2012), Int Wood Prod J. 4(4), 242-247; Gunnells D et al. (1998), Catalyst systems. In: Bradfield J (ed) Resin and blending seminarproceedings, Portland, Oregon and Charlotte, North Carolina. For Prod Soc, p 176).

[0029] The use of scavengers, for example natural or bio-based scavengers (Eom Y-G et al. (2006), Mokchae Konghak 34:29-41; Kim S et al. (2009); Constr Build Mater 23(6), 2319-2323; Kim S et al. (2006), Macromol Mater Eng 291(9), 1027-1034) or other compounds having a good affinity to capture formaldehyde (Boran S, et al. (2011), Int J Adhes 31 (7), 674-678; Costa et al. (2012), Journal International Wood Products Journal, Volume 4, Issue 4, Pages 242-247; Park et al. (2008), J Appl Polym Sci 110(3): 1573 - 1580), in order to reduce formaldehyde emission from wood-based boards, is commonly adopted.

[0030] "Sodium metabisulphite as a scavenger of air pollutants for wood-based building materials", N A Costa et al., International Wood Products Journal, Volume 4 (2013), Issue 4, pages 242-247, studies the different applications of sodium metabisulphite as a formaldehyde scavenger, but it does not provide an in-depth analysis of the loss of mechanical properties and water resistance of the board, which means that this option is not feasible at an industrial level. Also, from the point of view of REACH, ammonium bisulphate is a hazardous substance; the handling of this substance involves significant measures to prevent workers from breathing sulphur oxides in the air.

[0031] "Formaldehyde emission in wood based panels: effect of curing reactions", N. A. Costa et al., International Wood Products Journal, Volume 5 (2014), Issue 3, pages 146-150, studies the effect of hexamine as a formaldehyde catalyst-scavenger, the use of acid catalysts versus latent catalysts, and their pros and cons. It establishes that the combination of citric and oxalic acids in solid form with latent ammonium sulphate catalysts is the best solution, combined with a low molar ratio resin, to obtain values of less than 4 mg of formaldehyde per 100 g of dry board, applying the EN120 perforator method.

[0032] The molar ratio of the resins used is too low: 0,90 moles of formaldehyde per mole of urea. In the article, the tensile mechanical properties are very low for the industrial quality standards accepted by the EPF (European Panel Federation).

[0033] In the conclusions of the article itself, it justifies the need to find new formaldehyde catalyst-scavenger systems that fulfil the requirements in terms of mechanical properties and formaldehyde emission of the board, which confirms that achieving a solution that fulfils these requirements is currently an industrial challenge.

[0034] "Scavengers for achieving zero formaldehyde emission of wood-based panels", Nuno A. Costa et al., Wood Science and Technology (2013), 47, pages 1261-1272, examined the performance of three formaldehyde scavengers known in the manufacture of boards: sodium metabisulphite, ammonium bisulphite, and urea. To obtain low formaldehyde emission values by the dessicator method (JIS method), more than 5% of the catalyst must be added in the resin, even up to 15%; this causes the tensile properties to drastically decrease; the boards presented as conclusions of this study were found to fail to comply with the minimum quality standards for the market, so this option is not feasible at the industrial level.

Resorcinol

[0035] Resorcinol, also called m-dihydroxybenzene or 1,3-dihydroxybenzene, is a phenolic compound used in the manufacture of resins, plastics, dyes, medicine, and numerous other organic chemical compounds. It is produced in large quantities by sulfonating benzene with fuming sulfuric acid and fusing the resulting benzenedisulfonic acid with caustic soda. Reaction with formaldehyde produces resins used to make rayon and nylon amenable to impregnation with rubber, and as adhesives. As a chemical intermediate, resorcinol is converted to dyes, explosives, and pharmaceuticals; it is also employed in photographic developers and cosmetics. In medicine it is used externally in ointments and lotions as an antifungal.

[0036] By incorporating resorcinol during the synthesis of phenol-formaldehyde (PF) resins or by replacing phenol with resorcinol altogether, phenolic resins can be made with significant decreases in cure time compared with PF resin adhesives. The chemistry associated with the formation and curing of phenol-resorcinol-formaldehyde (PRF) and resorcinol-formaldehyde (RF) resins, is similar to that for PF resins. However, PRF and RF prepolymers are made at a low formaldehyde molar ratio and thus are essentially novolac resins. The prepolymers, which are stable, are cured by the addition of a hardener (e.g., paraformaldehyde or a formaldehyde solution). The PRF and RF resin adhesives are used in situations where fast or room temperature curing is required (e.g., finger jointed structures) or where the wooden assembly that is being bonded is too thick to allow that sufficient heat is transferred to the inside of said assembly (e.g., laminated timbers), so that the resin is cured at the bond lines. The main disadvantage of these resins is the much higher cost of resorcinol compared with that of phenol.

[0037] Resorcinol has been used in the production of rubber coated fabrics, particularly for increasing the adhesiveness of the fabrics with respect to rubber. GB1259470 discloses an emulsion comprising paraffin hydrocarbons and resorcinol as monomers and/or precondensates of thermosetting plastics, among other components.

[0038] GB2136008 discloses a formaldehyde binder composition, which comprises at least one organic hydroxy compound and at least one amide, in water. Glycerine as the organic hydroxy compound and urea as the amide compound are shown in the Examples to present a synergistic behaviour. Resorcinol as a further organic hydroxy compound is compared to monoethyleneglycol, dextrin and phenol, the composition comprising resorcinol showing the smallest reduction in formaldehyde.

SUMMARY OF THE INVENTION

[0039] The present invention provides hydrophobing and formaldehyde scavenging compositions, comprising and O/W suspension or emulsion, comprising at least one petroleum derived or at least one vegetable derived wax or oil, or a mixture thereof, and resorcinol, the compositions being useful for increasing the hydrophobicity of wood composite boards (including wood derived boards, fibreboards, particleboards, chip boards, oriented strand boards, plywood and paperboards), as well as of fibreglass or rock wool insulations, when used during their manufacture. The use of the compositions of the invention allows to obtain boards or insulations not only having good hydrofugant properties, but also having a formaldehyde emission of 0,005 mg of formaldehyde per square meter and hour or below, as measured by gas analysis method UNE-EN ISO 12460-3:2016.

[0040] Therefore, a first object of the invention is a hydrophobing and formaldehyde scavenging composition, which comprises:

- an O/W suspension or emulsion, which as the non-aqueous phase comprises at least one petroleum derived or at least one vegetable derived wax or oil, or a mixture of at least one petroleum derived and at least one vegetable derived wax or oil; and

- an aqueous resorcinol solution, containing from 35 to 45 wt. % resorcinol;

wherein the weight ratio of wax or oil with regard to resorcinol in the composition is between 4:1 and 1:4, the weight of wax or oil and resorcinol together being between 45 wt.% and 70 wt.% of the composition.

[0041] A further object of the invention is the use of the composition of the invention for increasing the hydrophobicity of hydrophilic materials (such as wood composite boards (including wood derived boards, fibreboards, particleboards, chip boards, oriented strand boards, plywood and paperboards) as well as fibreglass or rock wool insulations).

[0042] Further objects are wood composite boards and fibreglass or rock wool insulations, comprising a formaldehyde derived resin or adhesive and the composition of the invention, having a formaldehyde emission of 0,005 mg of formaldehyde per square meter and hour, or below, as measured by gas analysis method UNE-EN ISO 12460-3:2016.

DETAILED DESCRIPTION OF THE INVENTION

[0043] The compositions of the invention comprise an O/W suspension or emulsion comprising at least one at least one petroleum derived or at least one vegetable derived wax or oil.

[0044] An emulsion, according to the IUPAC, is a "fluid colloidal system in which liquid droplets and/or liquid crystals are dispersed in a liquid. The droplets often exceed the usual limits for colloids in size. An emulsion is denoted by the symbol O/W if the continuous phase is an aqueous solution and by W/O if the continuous phase is an organic liquid (an 'oil'). More complicated emulsions such as O/W/O (i.e. oil droplets contained within aqueous droplets dispersed in a continuous oil phase) are also possible."

[0045] On the other hand, a suspension, according to the IUPAC, is "a liquid in which solid particles are dispersed".

[0046] Although paraffin suspensions are often named as paraffin emulsions, in fact they are suspensions, as the droplets of oil in the water phase, at normal temperature and pressure conditions, are in solid state. Therefore, the suspension and emulsion will be used indistinctively throughout the present description. The formulations as such are liquid in order to allow an easy application.

[0047] Emulsifiers are a group of substances of different origin and properties that will contribute to a greater stabilization of the emulsions or suspensions; this is due mainly to its amphiphilic or double affinity character, which, from the physicochemical point of view, is defined as a double polar and apolar property. Within this large group of compounds we can find e.g. surfactants.

Definitions

[0048] In the frame of the present invention, the following terms have the meanings indicated:
"Formaldehyde scavenger" in the frame of the present invention refers to any compound that allows to reduce the content of free formaldehyde in any product or composition. Any formaldehyde scavenger known in the State of the Art may be used. For example, the formaldehyde scavenger may be selected from, but is not limited to, urea, urea derivatives, hexamine, amino group containing compounds, hexamine, sulphite salts and metabisulphite salts.

[0049] "Non-ionic surfactants" are surfactants that do not bear an electrical charge. Although they do not contain an ionic group as their hydrophilic component, hydrophilic properties are conferred on them by the presence of a number of oxygen atoms in one part of the molecule which are capable of forming hydrogen bonds with molecules of water. For example, many long chain alcohols exhibit some surfactant properties, such as fatty alcohols, cetyl alcohol, stearyl alcohol, and cetostearyl alcohol, and oleyl alcohol. Other non-ionic surfactants are alcohol ethoxylates, polyglycol ethers, polyoxyethylene alkyl ethers, secondary alcohol ethoxylates, polyoxyethylene alkyl ethers, polyalkyl glycol alkyl ethers (e.g. polyethylene and polypropylene glycol alkyl ethers), glucoside alkyl ethers, polyethylene glycol alkylphenyl ethers or glycerol alkyl esters.

[0050] "Anionic surfactants" are surfactants that contain anionic functional groups at their head, such as sulfate, sulfonate, phosphate, and carboxylates. Prominent alkyl sulfates include ammonium lauryl sulfate, sodium lauryl sulfate (sodium dodecyl sulfate, SLS, or SDS), and the related alkyl-ether sulfates sodium laureth sulfate (sodium lauryl ether sulfate or SLES), and sodium myreth sulfate. Also docusate (dioctyl sodium sulfosuccinate), perfluorooctanesulfonate (PFOS), perfluorobutanesulfonate, alkyl-aryl ether phosphates and alkyl ether phosphates are anionic surfactants.

[0051] "Sauter mean diameter", also designated as D(3,2), D32 or D(32) is the mean diameter with the same ratio of volume to surface area as the entire ensemble It was originally developed by German scientist Josef Sauter in the late 1920s. The size of drops is determined based on the absorption/scattering of light. The technique depends on the fact that absorption/scattering is proportional to the surface area of the drops.

[0052] "Normal temperature and pressure conditions" refers to a temperature of 20 °C and an absolute pressure of 1 atm.

[0053] "O/W emulsion" refers to an oil in water emulsion.

[0054] "O/W suspension" refers to a suspension comprising solid particles of hydrogenated oil (wax) suspended in water; the terms suspension and emulsion are used indistinctively along the present description.

[0055] "Formaldehyde based resins" or "formaldehyde derived resins", as used in the frame of the present invention, refers to any resin or plastic which is produced from formaldehyde with other reactants, such as urea, phenol, or melamine. For example, urea-formaldehyde resin is a non-transparent thermosetting resin or plastic, produced from urea and formaldehyde. They are used in adhesives, finishes, particleboard, MDF, and molded objects. Phenol formaldehyde resins (PF) or phenolic resins are synthetic polymers obtained by the reaction of phenol or substituted phenol with formaldehyde. They have been widely used for the production of molded products including billiard balls, laboratory countertops, and as coatings and adhesives. Melamine formaldehyde resin is a hard, thermosetting plastic material made from melamine and formaldehyde by polymerization. In its butylated form, it is dissolved in n-butanol and xylene. It is then used to cross-link with alkyd, epoxy, acrylic, and polyester resins, used in surface coatings. There are many types, varying from very slow to very fast curing.

[0056] "Wood composite boards" in the frame of the present invention refers to boards obtained by binding and compressing natural fibres, optionally in combination with synthetic fibres, Examples thereof, but not limited to, are particleboard, fibreboard (MDF and HDF), chip boards, oriented strand boards and plywood.

[0057] "Synthetic fibres" in the frame of the present invention refers to fibres from polyester, polyethylene or polypropylene.

[0058] "Natural fibres" in the frame of the present invention refers to wood fibres, chips, particles, flakes or strands, and/or other natural fibres like flax, hemp, rye straw, wheat straw, rice straw, hemp stalks, kenaf stalks or sugar cane residues.

[0059] "Catalyst for curing formaldehyde based resins", in the frame of the present invention, is meant to be any substance suitable to be used to cure formaldehyde based resins. It may be selected from the group comprising ammonium bisulfite, ammonium nitrate, and ammonium sulfate, but is not limited to said catalysts. Said catalysts are needed to cure resins based on formaldehyde, which are generally used in the manufacture of all kinds of wood derived boards, fibreboards, particleboards, chipboards, oriented strand boards, and similar. If the formulations of the invention contain one or more catalysts, no further catalysts or formulations containing catalysts need to be used during the curing process.

Compositions of the invention

[0060] In a first aspect, the present invention is related to a hydrophobing and formaldehyde scavenging composition, comprising:

- an O/W suspension or emulsion, which as the non-aqueous phase comprises at least one petroleum derived or at least one vegetable derived wax or oil, or a mixture of at least one petroleum derived and at least one vegetable derived wax or oil; and

- an aqueous resorcinol solution, containing from 35 to 45 wt. % resorcinol;

wherein the weight ratio of pure wax with regard to pure resorcinol is between 4:1 and 1:4, the weight of wax or oil and resorcinol together being between 45 wt.% and 70 wt.% of the composition.

[0061] That is, in the above indicated weight ratio, the weight of wax or oil in the O/W suspension or emulsion is considered, with regard to the weight of resorcinol in the aqueous resorcinol solution.

[0062] The ratio of wax with respect to resorcinol may be, for example, between 3:1 and 1:3, or between 2,5:1 and 1:4, or between 2,5:1 and 1:3, or between 2,5:1 and 1:2,5, or between 3:1 and 1:4, or between 4:1 and 3:1, or between 1,5:1 and 1:1,5, or about 1:1.

[0063] "The weight of wax or oil and resorcinol together" means the sum of the weight of wax or oil and the weight of resorcinol; such a weight is defined as being between 45 wt.% and 70 wt.% of the composition, but preferably is between

45 wt.% and 65 wt.%, or between 50 wt.% and 65 wt. %, or between 55 wt.% and 65 wt.%.

[0064] As noted above, the terms "suspension" and "emulsion" throughout the present patent application are used indistinctly, as the oily particles in the aqueous phase of the O/W suspension, at normal temperature and pressure conditions, are often in the solid state.

[0065] The non-aqueous phase may comprise at least one petroleum derived wax or oil, such as paraffin wax, for example paraffin corresponding to CAS No. 8002-74-2, or slack wax (petroleum), for example as corresponding to CAS No. 64742-61-6. The non-aqueous phase may consist only of one petroleum derived wax or oil, or a mixture of one or more thereof. As examples of an O/W suspension or emulsion that may be comprised in the composition of the invention, commercial resins known as FORESA WAX (available to the public from the Spanish company FORESA, S:A: (http://www.foresa.com/en), followed by a four-digit number, may be used, for example, but not limited to, FORESA WAX 2102 (the European UFI (https://poisoncentres.echa.europa.eu/es/ufi-generator) for this suspension nowadays is 30001013/1). FORESA WAX 2102 contains a combination of two types of paraffin, namely about 45 wt% of a paraffin with a low oil content (oil content below 6 wt%, melting point 49-58 °C), and about 11 wt.% of a paraffin with high oil content (oil content maximum 12 wt%, melting point 42-53°C), has a solids content of 58-62 wt.% and a pH at 25°C between 8,5 and 10,5.

[0066] The non-aqueous phase may comprise at least one vegetable derived wax or oil, for example palm oil, hydrogenated palm oil or soy oil. The non-aqueous phase may consist only of one oil, or of a mixture of 2 or more oils. The vegetable oil may be mixed with at least one petroleum derived wax or oil, as defined above.

[0067] The O/W suspension or emulsion comprised in the composition of the invention may comprise from about 1 wt% to 5 wt% of surfactant, the surfactant being one or more selected from anionic and non-ionic surfactants.

[0068] The composition according to the invention may comprise up to 25 wt. % of a catalyst for curing formaldehyde derived resins.

[0069] The composition according to the invention may comprise at least one formaldehyde scavenger. Such a formaldehyde scavenger may be selected from, but is not limited to, urea, urea derivatives, urea resins, sodium metabisulfite, ammonium bisulphite, monoethanolamine, and diethanolamine. The scavenger may be contained in concentrations, for example, between 0,5 and 20 wt.%, or 0,5 and 15 wt.%, or between 1 and 30 wt.%, or between 1 and 20 wt%, or between 1 and 15 wt.%, or between 2 and 20 wt.%, or between 5 and 20 wt.%, or between 5 and 15 wt.%, among others.

[0070] The O/W suspension or emulsion which is part of the composition of the invention, when the non-aqueous phase is at least one vegetable derived wax or oil, could be, for example, a formulation that comprises an O/W suspension, which comprises:

- from 1 wt% to 5 wt% of surfactant, the surfactant being one or more selected from anionic and non-ionic surfactants, the surfactant being added as such or obtained in situ by addition of between 1 and 2 wt% of an ethanolamine;

- 15 wt% to 50 wt% of hydrogenated or partially hydrogenated palm oil;

- from 0 to 25 wt% of paraffin;

- from 0 to 8 wt% of soy oil;

wherein the total amount of oil, being the sum of palm oil, paraffin and soy oil in the O/W suspension does not exceed 55 wt%; wherein, within the total amount of oils, from 2 to about 10 wt% is non hydrogenated oil, and the rest is hydrogenated and/or partially hydrogenated oil; and wherein the O/W suspension has a solids content of between 30 wt.% and 55 wt.%, and the rest of the suspension, until reaching 100 wt.%, is water, the solids content comprising all the compojnents which are different than water.

[0071] It has surprisingly been found that if the iodine value of the total amount of oils in the formulation is above 10 g of iodine per 100 g of the total amount of oils, the suspensions and thus the formulations therewith obtained are kinetically much more stable than if the iodine value is below 10

[0072] The surfactant of such a formulation may be a mixture of at least one non-ionic surfactant and at least one anionic surfactant.

[0073] Such a formulation may contain up to 25 wt.% of at least one further formaldehyde scavenger, in order to scavenge excess formaldehyde in the formaldehyde based resins, typically used formaldehyde scavengers are urea, monoethanolamine, and diethanolamine, but other formaldehyde scavengers may be used in the formulations of the invention, such as urea, urea derivatives, urea resins, sodium metabisulfite, ammonium bisulphite. The composition may contain one or more formaldehyde scavengers, the total amount thereof being up to 25 wt.%, with regard to the total weight of the composition.

[0074] Such a formulation may contain up to 25 wt. % of at least one catalyst for curing formaldehyde based resins; this catalyst, in the frame of the present invention, is meant to be any substance suitable to be used to cure formaldehyde based resins. It may be selected from the group comprising ammonium bisulphite, ammonium nitrate, and ammonium sulphate, but is not limited to said catalysts. Said catalysts are needed to cure resins based on formaldehyde, which are generally used in the manufacture of all kinds of wood derived boards, fibreboards, particleboards, chipboards, oriented strand boards, and similar. If the formulations of the invention contain one or more catalysts, no further catalysts or formulations containing catalysts need to be used during the curing process. The composition may contain one or more catalysts for curing formaldehyde based resins, the total amount thereof being up to 25 wt.%, with regard to the total weight of the composition.

[0075] The composition may simultaneously comprise up to 25 wt% of at least one formaldehyde scavenger and up to 25 wt. % of at least one catalyst for curing formaldehyde based resins.

[0076] The composition of the invention may be used to increase the hydrophobicity of hydrophilic materials. They may be used, for example, in the manufacture of wood derived boards, fibreboards, particleboards, chipboards, oriented strand boards, fibreglass or rock wool insulations, or combinations thereof, as well as in industrial refining processes of lignocellulosic material.

[0077] The composition of the invention may also be used to reduce the formaldehyde emission in materials comprising free formaldehyde, so the legal standards of the final products are met. They may be used, for example, in the manufacture of wood derived boards, fibreboards, particleboards, chipboards, oriented strand boards, or fibreglass or rock wool insulations, or any combinations thereof, as well as in industrial refining processes of lignocellulosic material. The indicated materials may comprise a formaldehyde-derived resin or adhesive.

[0078] Another aspect of the present invention is related to the use of the composition according to the invention in the manufacture of wood derived boards, fibreboards, particleboards, chipboards, oriented strand boards, or fibreglass or rock wool insulations, or any combinations thereof; especially, in the manufacture of such products comprising a formaldehyde derived resin or adhesive. The compositions of the invention do not only improve the resistance to water of the above mentioned manufactured products, but also reduce the formaldehyde emissions to values which are 0,005 mg of formaldehyde per square meter and hour, or below, as measured by using by using the gas analysis method UNE-EN ISO 12460-3:2016. Updated version from Wood-based panels - Determination of formaldehyde release - Part 3: Gas analysis method (ISO 12460-3:2015), without affecting other properties of the products, such as the internal bond.

[0079] According to particular embodiments, the formaldehyde emission is reduced to values which are 0,004 mg of formaldehyde per square meter and hour, or below, as measured by using by using the gas analysis method UNE-EN ISO 12460-3:2016, or the formaldehyde emission is reduced to values which are 0,003 mg of formaldehyde per square meter and hour, or below, as measured by using by using the gas analysis method UNE-EN ISO 12460-3:2016.

[0080] The invention also refers to wood derived boards, fibreboards, particleboards, chipboards, oriented strand boards, or fibreglass or rock wool insulations, or any combinations thereof, manufactured by using the composition of the invention, which have a formaldehyde emission below 0,005 mg of formaldehyde per square meter and hour as measured by using the gas analysis method UNE-EN ISO 12460-3:2016.

[0081] According to particular embodiments, the formaldehyde emission is 0,004 mg of formaldehyde per square meter and hour, or below, as measured by using by using the gas analysis method UNE-EN ISO 12460-3:2016, or the formaldehyde emission is 0,003 mg of formaldehyde per square meter and hour, or below, as measured by using the gas analysis method UNE-EN ISO 12460-3:2016.

EXAMPLES

[0082] In the following, the invention will be further illustrated by means of examples and comparative examples. The examples should in no case be interpreted as limiting the scope of the invention, but only as an illustration of the invention.

[0083] Throughout the Examples, a commercial paraffin suspension is repeatedly mentioned, namely FORESA WAX 2102. It is available to the public from the Spanish company FORESA, S.A. (http://www.foresa.com/en), offered under the denomination FORESA WAX 2102 (the European UFI (https://poisoncentres.echa.europa.eu/es/ufi-generator) for this suspension nowadays is 30001013/1).

[0084] FORESA WAX 2102 contains a combination of two types of paraffin, namely about 45 wt% of a paraffin with a low oil content (oil content below 6 wt%, melting point 49-58 °C), and about 11 % of a paraffin with high oil content (oil content maximum 12 wt%, melting point 42-53°C), has a solids content of 58-62wt% and a pH at 25°C between 8,5 and 10,5.

[0085] In the examples also some commercial resins are mentioned, available to the public from the Spanish company FORESA, S.A. (http://www.foresa.com/en), and offered under the denominations FORESA RES 2061, FORESA RES 1350 and FORESA RES 3250.

[0086] FORESA RES 2061 is a water-based melamine-urea-formaldehyde resin, FORES RES 3250 is a water-based phenol-formaldehyde resin, and intended for the FORESA RES 1350 is a water-based urea-formaldehyde resin, intended for their use in the manufacture of wood-based products and of lignocellulosic composites.

Preparation of compositions according to the invention

Example n° 1: Preparation of compositions of the invention comprising resorcinol and hydrogenated vegetable oil emulsion

[0087] The following O/W emulsion was prepared: 175 gr melted hydrogenated palm wax, having an iodine value of ≤ 10 gr I2/100 gr, 25 gr soy oil and 7 gr of long chain fatty acid were mixed, introduced in an oil phase reactor, and heated to about 70°C, under stirring at about 150 rpm. 275 gr water were introduced in a water phase reactor, 10 gr diethanolamine were added, in order to obtain anionic surfactant in situ by reaction with fatty acids, and the mixture was heated to about 70°C. The oil phase was added to the water phase at a rate of 30 gr/min, and dispersed at a rate of 800 rpm. Subsequently, 5 g of Tergitol 15-S-9 is added, and the mixture stirred at 800 rpm during 25 minutes. The mixture was cooled at a rate of 7°C per minute until reaching 20-25°C. The obtained suspension was kinetically stable for at least 4 months, at normal pressure and temperature conditions. The emulsion had a viscosity of about 500 cps.

[0088] The obtained emulsion was mixed with an aqueous resorcinol solution, containing about 40 wt. % resorcinol. Compositions having several different weight ratios of pure vegetable oil with regard to pure resorcinol were prepared, namely: 0:4; 1:3; 2:2; 3:1 and 4:0. The indicated weight ratios refer to pure palm oil and to pure resorcinol, as active substances.

[0089] The mixture was carried out at room temperature by using a disperser, adding the resorcinol solution to the O/W emulsion.

[0090] The values measured for particle size (Sauter diameter) and pH of the mixtures were as shown in Table 1 below:

Table 1

Palm oil : resorcinol weight ratio	4:0	3:1	2:2	1:3	0:4
Diameter Sauter in microns	1,57	1,53	1,52	1,48	coloide
pH	10,07	8,14	7,53	7,09	3,80

[0091] The shelf life of these samples was greater than one month under storage conditions at room temperature.

[0092] The solids content of the final composition was between 40 wt % and 45 wt %.

Example n° 2. Preparation of compositions of the invention comprising resorcinol as a formaldehyde scavenger and hydrogenated vegetable oil emulsion

[0093] The following O/W emulsion was prepared: In a 4 m^3 reactor, being equipped with a disperser at 120rpm, 1405 kg water were introduced. 30 kg diethanolamine, and subsequently 35 kg of long chain fatty acid, were charged. 100 kg soy oil were charged, together with 0,5 kg of antifoaming agent. Subsequently, 25 kg Tergitol 15-S-9 were added into the reactor. Then 900 kg solid powder of hydrogenated palm wax, having a iodine value of ≤ 10 gr I2/100 gr, were added, at a rate of 50 kg/min, as well as another 2 kg of antifoaming agent. The mixture is stirred at 120 rpm, during 30 minutes at a temperature of 75 °C. While the mixture was cooled, at a rate of 1 °C per minute, until reaching a temperature of 20-25°C, 2,5 kg of a biocide (MIRECIDE® M/85) were added. Almost 2500 kg of a liquid suspension were obtained, having about 48 wt.% of solids. The suspension was kinetically stable for at least 4 months, at normal pressure and temperature conditions. Variables such as Sauter diameter were comparable to the suspension obtained at laboratory scale.

[0094] The obtained emulsion was mixed with an aqueous resorcinol solution, containing about 40 wt. % resorcinol. Compositions having several different weight ratios of pure vegetable oil with regard to pure resorcinol were prepared, namely: 0:4; 1:3; 2:2; 3:1 and 4:0. The indicated weight ratios refer to pure palm oil and to pure resorcinol, as active substances.

[0095] The mixture was carried out at room temperature by the use of a disperser, adding the resorcinol solution to the O/W emulsion.

[0096] The values measured for particle size (Sauter diameter) and pH of the mixtures were as shown in Table 2 below:

Table 2

Palm oil : resorcinol weight ratio	4:0	3:1	2:2	1:3	0:4
Diameter Sauter in microns	0,97	0,95	1,03	1,08	coloide
pH	9,89	7,88	7,39	6,79	3,80

[0097] Graphs representing the rheological profile of some of the mixtures made in this example are shown in Figures 1 to 4.

[0098] The shelf life of these samples was greater than one month under storage conditions at room temperature.

Example n° 3: Preparation of compositions of the invention comprising resorcinol and hydrogenated vegetable oil emulsion

[0099] In a 4 m^3 reactor, being equipped with a disperser at 120rpm, 1405 kg water were introduced. 30 kg diethanolamine, and subsequently 35 kg of long chain fatty acid, were charged. 100 kg soy oil were charged, together with 0,5 kg of antifoaming agent. Subsequently, 25 kg Tergitol 15-S-9 were added into the reactor. Then 900 kg solid powder of hydrogenated palm wax, having a iodine value of ≤ 10 gr I2/100 gr, were added, at a rate of 50 kg/min, as well as another 2 kg of antifoaming agent. The mixture is stirred at 120 rpm, during 30 minutes at a temperature of 75 °C. While the mixture was cooled, at a rate of 1 °C per minute, until reaching a temperature of 20-25°C, 2,5 kg of a biocide were added. Almost 2500 kg of a liquid suspension were obtained, having about 48 wt.% of solids. The suspension was kinetically stable for at least 4 months, at normal pressure and temperature conditions. Variables such as Sauter diameter were comparable to the suspension obtained at laboratory scale.

[0100] To the obtained emulsion, water is added to reduce the weight content of vegetable oil/wax to 25 wt.%, and solid resorcinol in flakes is dissolved therein:
At about 25°C, to 62,5 g of the above obtained emulsion, containing 40 wt.% vegetable wax, 12,5 g water are added, so the emulsion contains the mentioned 25 wt. % of vegetable wax. Subsequently, 25 g of solid resorcinol in flakes is added under stirring, until completely dissolved in the emulsion. The final composition has a solids content of 50 wt. %, being 25 wt.% of vegetable oils and another 25 wt.% resorcinol, with respect to the final product, and 50 wt.% water.

[0101] The resulting mixture has a Sauter diameter of 1,24 microns and a pH of 7,83.

Example n° 4. Preparation of compositions of the invention comprising resorcinol and hydrogenated vegetable oil emulsion

The final dispersion has a solids content minimum of 60%.

[0102] In a 4 m^3 reactor, being equipped with a disperser at 120rpm, 1405 kg water were introduced. 30 kg diethanolamine, and subsequently 35 kg of long chain fatty acid, were charged. 100 kg soy oil were charged, together with 0,5 kg of antifoaming agent. Subsequently, 25 kg Tergitol 15-S-9 were added into the reactor. Then 900 kg solid powder of hydrogenated palm wax, having an iodine value of ≤ 10 gr I2/100 gr, were added, at a rate of 50 kg/min, as well as another 2 kg of antifoaming agent. The mixture is stirred at 120 rpm, during 30 minutes at a temperature of 75 °C. While the mixture was cooled, at a rate of 1 °C per minute, until reaching a temperature of 20-25°C, 2,5 kg of a biocide were added. Almost 2500 kg of a liquid suspension were obtained, having about 48 wt.% of solids. The suspension was kinetically stable for at least 4 months, at normal pressure and temperature conditions. Variables such as Sauter diameter were comparable to the suspension obtained at laboratory scale.

[0103] The obtained emulsion is adjusted by adding water, so that the content of vegetable wax is reduced to 28,57 wt. %.

[0104] At a temperature of about 25 °C, 71,43 g of the emulsion obtained above, containing 40 wt.% of vegetable wax; 60 gr water are added; subsequently, 28,57 g solid resorcinol in flakes are added, at room temperatures, with stirring, until it is completely dissolved. In the composition obtained, 28,57 wt.% are vegetable wax, 28,57 wt. is resorcinol, 40 wt. % is water, and 3 wt.% are surfactants.

[0105] The resulting mixture has a Sauter diameter of 1,12 microns and a pH of 7,03.

Example n° 5. Reduction of free formaldehyde content in MDF board manufactured with urea-formaldehyde resin. Vegetable oil emulsion versus composition comprising vegetable oil emulsion and resorcinol.

[0106] In this example the capacity of acting as a formaldehyde scavenger of the compositions of the invention is shown.

[0107] The manufacture of MDF boards was performed in a pilot plant, using a commercial urea-formaldehyde resin (FORESA RES 1350); the quality results of boards obtained by using the composition of Example n° 3, comprising vegetable oil emulsion and resorcinol, and boards obtained by using the same vegetable oil emulsion but without resorcinol, were compared.

[0108] The boards were manufactured in a plate press, with a plate temperature of 200 ° C, the curing factor was 8,5 s / mm, the dose of urea-formaldehyde resin was 12 wt. % dry resin on dry wood fiber and the vegetable oil emulsion dose is always 0,5 wt. % of vegetable oil with respect to dry fiber; that is, the composition of Example n° 3 containing vegetable oil emulsion and resorcinol was dosed in a 1 wt. % dry mix with respect to dry fiber, that is, 0,5 wt.% of vegetable oil and 0,5 wt.% of pure resorcinol.

[0109] The results are shown in Table 3 below.

Table 3

	DENSITY BOARD SANDING			CORE BOND			WATER RESISTANCE PROPERTIES					FORMALDEHYDE
	THICKNESS	DENSITY	STANDARD DEVIATION	DENSITY BOND	INTERNAL BOND	STANDARD DEVIATION	SWELLING	STANDARD DEVIATION	ABSORPTION	INTERNAL BOND	STANDARD DEVIATION	EN 120
	mm	kg/m^3	kg/m^3	kg/m^3	N/mm^2	N/mm^2	%	%	%	%	%	mg FA/100 g ts
VEGETABLE OIL EMULSION	16,04	869	12,93	865	1,50	0,14	6,36	0,34	11,98	1,49	6,90	25,30
COMPOSITION EXAMPLE 3	16,09	902	16,66	898	1,52	0,10	6,25	0,10	10,83	0,30	8,27	14,60

[0110] In Table 3 it is shown that the application of resorcinol in the form of a mixture with the vegetable oil emulsion maintains the properties of internal traction, swelling and absorption unaltered, while it is observed that the free formaldehyde content of the board is reduced from a value of 25,30 mg of free formaldehyde per 100 g of dry board, to 14,60 mg of free formaldehyde per 100 g of dry board; adjusted in conditions of humidity of 6,5% as indicated by UNE-EN ISO 12460-5, which title is *"Boards derived from wood. Determination of the emission of formaldehyde. Part 5: Method of extraction (called perforator)*".

[0111] A reduction of 42% of the free content of formaldehyde was achieved, using the same vegetable oil emulsion without resorcinol as a reference for comparison.

Example n° 6. Reduction of free formaldehyde content in MDF boards manufactured with melamine-urea-formaldehyde resin.

[0112] For this example MDF boards using the composition according to Example n° 3, or the same vegetable oil emulsion without resorcinol, or a paraffin based commercial emulsion (FORESA WAX 2102) were manufactured.

[0113] The manufacture of MDF board in pilot plant was performed by using a commercial melamine-urea-formaldehyde resin (FORESA RES 2061), and the quality results of boards obtained with only the vegetable oil emulsion, i.e. without resorcinol, the composition of Example n° 3, as well as a commercial paraffin-based emulsion were compared.

[0114] The boards were manufactured in a plate press, with a plate temperature of 200 ° C, the curing factor was 8,5 s / mm, the dose of urea-formaldehyde resin was 12 wt. % of dry resin with respect to dry wood fiber; the hydrofugant emulsion dose was always 0,5 wt. % of vegetable oil or mineral oil with respect to dry fiber; that is, the composition of Example n° 3 was dosed in a 1 wt. % of dry mix with respect to dry fiber, therefore being 0,5 wt. % of hydrogenated palm oil and 0,5 wt. % of pure resorcinol.

[0115] The following table (Table 4) shows the quality results:

Table 4

	DENSITY BOARD SANDING			CORE BOND			WATER RESISTANCE PROPERTIES				BOND V-100	
	THICKNESS	DENSITY	STANDARD DEVIATION	DENSITY BOND	INTERNAL BOND	STANDARD DEVIATION	SWELLING	STANDARD DEVIATION	ABSORPTION	STANDARD DEVIATION	INTER BOND NAL	STANDARD DEVIATION
	mm	kg/m³	ka/m3	ka/m3	N/mm2	N/mm2	% espesor		% peso		N/mm2	N/mm2
FORESA WAX 2102	16,01	889	31,71	912	1,57	0,18	4,84	0,19	10,33	0,33	0,33	0,03
VEGETABLE OIL EMULSION	15,98	886	21,66	882	1,84	0,18	5,27	0,02	10,41	1,77	0,30	0,01
COMPOSITION EXAMPLE N° 3	16,00	873	35,96	858	1,82	0,07	5,44	0,27	13,17	2,61	0,32	0,01

[0116] With this example it was verified that the mechanical properties of the board are remarkably improved, measured as internal traction, going from 1,57 N/mm^2 to values higher than 1,8 N/mm^2, both in the case of vegetable oil emulsion allow and in the case of the composition of the invention according to Example 3. The increase in the tensile strength was 14%.

Example n° 7. Reduction of free formaldehyde content in MDF board manufactured with phenol-formaldehyde resin.

[0117] In this example the capacity as a formaldehyde scavenger of resorcinol was shown during the polymerization of the resin in the industrial application of MDF (Medium density fiberboard) board manufacturing.

[0118] The manufacture of MDF board in pilot plant was performed using a commercial phenol-formaldehyde resin (FORESA RES 3250), and the quality results were compared between a commercial wax emulsion (FORESA WAX 2102) and the composition of the invention according to Example n° 3.

[0119] The boards were manufactured in a plate press, with a plate temperature of 200 °C, the curing factor was 8,5 s/mm; the dose of urea-formaldehyde resin was 12 wt. % of dry resin with respect to dry wood fiber, and the waterproofing dose is always 0,5 wt.% of commercial paraffin wax emulsion called FORESA WAX 2102 with respect to dry fiber; also the composition of Example 3 is dosed in a 1 wt.% of dry mix on with respect to dry fiber, being therefore 0,5% of hydrogenated palm oil and 0,5% of pure resorcinol with respect to dry fiber.

[0120] Table 5 shows the quality results:

Table 5

	DENSITY BOARD SANDING			CORE BOND			WATER RESISTANCE PROPERTIES				BOND V-100		EMISSION
	THICKNESS	**DENSITY**	**STANDARD DEVIATION**	**DENSITY BOND**	**INTERAL BOND**	**STANDARD DEVIATION**	**SWELLING**	**STANDARD DEVIATION**	**ABSORPTION**	**STANDARD DEVIATION**	**INTERNAL BOND**	**STANDARD DEVIATION**	**EN 120**
	mm	kg/ m^3	kg/m^3	kg/m^3	N/mm^2	N/mm^2	%	%	%	%	N/mm^2	N/m m^2	mg FA/m^{2}h
FORESA WAX 2102	2,28	843	33,76	850	0,96	0,02	12,08	1,19	42,60	1,13	0,30	0,01	0,0225
COMPOSITI ON EXAMPLE N° 3	2,22	832	16,91	839	0,95	0,003	12,07	0,74	45,86	1,35	0,32	0,01	0,0031

[0121] The most interesting results that have been obtained in this example No. 7 are focused on the important reduction of the emission of formaldehyde in the board manufactured with the combination of a FORESA commercial phenol-formaldehyde type resin (FORESA RES 3250) with the composition of the invention according to Example n° 3; the reference of the resin in the manufacturing conditions of the pilot plant yields a result of 0,0225 mg of formalin emission per hour and m^2 of MDF board measured by gas analysis method UNE-EN ISO 12460-3:2016, and the resin combination phenol with the composition of Example n° 3 drops to 0,003, measured in the same test conditions: the formaldehyde emission is 7 times lower.

[0122] The natural emission of formaldehyde from pine wood according to Bohn et al. (2012), Journal of Hazardous materials, 221-222:68-79 is 5 micrograms of formaldehyde per hour and square meter, in this example of manufacture of MDF board it is shown that the mixture of Example n° 3 manages to reduce the emission of the board glued with phenol-formaldehyde resin to values inferior to the natural emission of the wood, taking as reference the pine wood.

Example n° 8. Preparation of compositions of the invention comprising resorcinol and paraffin wax emulsion

[0123] To 52,18 gr of a commercial paraffin based emulsion, comprising 60 wt. % solids, being 57,5 wt. % petroleum-derived paraffin wax, 2,5 wt.% of surfactants, at about 25°C, 17,82 gr of water are added, to adjust the solid content to about 30 wt.% of paraffin wax. Subsequently, 30 gr solid resorcinol in flakes are added, at room temperature, under stirring, until completely dissolved in the emulsion. The final composition obtained comprised 30 wt. % of paraffin wax, 30 wt. % of resorcinol, 38,7 wt. % of water and1,3 wt.% surfactants.

[0124] The solid content was 61,3 wt.%.

[0125] The resulting mixture has a Sauter diameter of less than 1 micra.

Claims

1. A hydrophobing and formaldehyde scavenging composition, comprising:

   - an O/W suspension or emulsion, which as the non-aqueous phase comprises at least one petroleum derived or at least one vegetable derived wax or oil, or a mixture of at least one petroleum derived and at least one vegetable derived wax or oil; and
   - an aqueous resorcinol solution, containing from 35 to 45 wt.% resorcinol;

   wherein the weight ratio of wax or oil with regard to resorcinol in the composition is between 4:1 and 1:4, the weight of wax or oil and resorcinol together being between 45 wt.% and 70 wt.% of the composition.

2. A composition according to claim 1, wherein the weight of wax or oil and resorcinol together is between 45 wt.% and 65 wt.% of the composition

3. A composition according to any one of claims 1 and 2, wherein the non-aqueous phase of the O/W suspension or emulsion comprises or consists of paraffin.

4. A composition according to any one of claims 1 and 2, wherein the non-aqueous phase of the O/W suspension or emulsion comprises or consists of palm oil.

5. A composition according to any one of the previous claims, comprising from 1 wt% to 5 wt% of surfactant, the surfactant being one or more selected from anionic and non-ionic surfactants.

6. A composition according to any one of the previous claims, comprising up to 25 wt.% of at least one catalyst for curing formaldehyde derived resins.

7. A composition according to any one of the previous claims, wherein the composition further comprises up to 25 wt.% of at least one formaldehyde scavenger.

8. A composition according to claim 7, wherein the formaldehyde scavenger is selected from urea, urea derivatives, urea resins, sodium metabisulfite, ammonium bisulfite. monoethanolamine, and diethanolamine.

9. Use of a composition according to any one of the previous claims, for increasing the hydrophobicity of hydrophilic materials.

10. Use of a composition according to any one of claims 1 to 8, for reducing the formaldehyde emission in materials comprising free formaldehyde.

11. Use according to claim 9 or 10, wherein the materials are selected from wood composite boards, such as wood derived boards, fibreboards, particleboards, chipboards, oriented strand boards, or fibreglass or rock wool insulations, or any combinations thereof.

12. Use of the composition according to any one of claims 1 to 8, in the manufacture of wood composite boards, such as wood derived boards, fibreboards, particleboards, chipboards, oriented strand boards, or of fibreglass or rock wool insulations, or any combinations thereof.

13. Use according to claim 11, wherein the wood derived boards, fibreboards, particleboards, chipboards, oriented strand boards, or fibreglass or rock wool insulations comprise a formaldehyde derived resin or adhesive.

14. Use according to any one of claims 11 to 13, for reducing the formaldehyde emission of the wood composite boards, such as wood derived boards, fibreboards, particleboards, chipboards or oriented strand boards; or of fibreglass or rock wool insulations, to 0,005 mg of formaldehyde per square meter and hour, or below, as measured by gas analysis method UNE-EN ISO 12460-3:2016.

15. Wood composite boards, comprising a formaldehyde derived resin or adhesive and the composition defined in claims 1 to 8, having a formaldehyde emission of 0,005 mg of formaldehyde per square meter and hour, or below, as measured by gas analysis method UNE-EN ISO 12460-3:2016.

16. Fibreglass or rock wool insulations, comprising a formaldehyde derived resin or adhesive and the composition defined in claims 1 to 8, having a formaldehyde emission of 0,005 mg of formaldehyde per square meter and hour, or below, as measured by gas analysis method UNE-EN ISO 12460-3:2016.

Patentansprüche

1. Hydrophobierende und Formaldehyd abfangende Zusammensetzung, umfassend:

- eine O/W-Suspension oder -Emulsion, die als nichtwässrige Phase wenigstens ein von Mineralöl abgeleitetes oder wenigstens ein von Pflanzen abgeleitetes Wachs oder Öl oder eine Mischung aus wenigstens einem von Mineralöl abgeleiteten und wenigstens einem von Pflanzen abgeleiteten Wachs oder Öl enthält, und
- eine wässrige Resorcinlösung, die 35 bis 45 Gew.-% Resorcin enthält,

wobei das Gewichtsverhältnis von Wachs oder Öl in Bezug auf Resorcin in der Zusammensetzung zwischen 4:1 und 1:4 liegt, und wobei das Gewicht von Wachs oder Öl und Resorcin zusammen zwischen 45 Gew.-% und 70 Gew.-% der Zusammensetzung ausmacht.

2. Zusammensetzung nach Anspruch 1, wobei das Gewicht von Wachs oder Öl und Resorcin zusammen zwischen 45 Gew.-% und 65 Gew.-% der Zusammensetzung ausmacht.

3. Zusammensetzung nach einem der Ansprüche 1 und 2, wobei die nicht-wässrige Phase der O/W-Suspension oder -Emulsion Paraffin umfasst oder daraus besteht.

4. Zusammensetzung nach einem der Ansprüche 1 und 2, wobei die nicht-wässrige Phase der O/W-Suspension oder -Emulsion Palmöl umfasst oder daraus besteht.

5. Zusammensetzung nach einem der vorhergehenden Ansprüche, enthaltend von 1 Gew.-% bis 5 Gew.-% Tensid, wobei das Tensid eines oder mehrere ist, ausgewählt aus anionischen und nicht-ionischen Tensiden.

6. Zusammensetzung nach einem der vorhergehenden Ansprüche, umfassend bis zu 25 Gew.-% wenigstens eines Katalysators zur Härtung von Harzen auf Formaldehydbasis.

7. Zusammensetzung nach einem der vorhergehenden Ansprüche, wobei die Zusammensetzung ferner bis zu 25 Gew.-% wenigstens eines Formaldehydfängers enthält.

8. Zusammensetzung nach Anspruch 7, wobei der Formaldehyd-Fänger ausgewählt ist aus Harnstoff, Harnstoffderivaten, Harnstoffharzen, Natriummetabisulfit, Ammoniumbisulfit, Monoethanolamin und Diethanolamin.

9. Verwendung einer Zusammensetzung nach einem der vorhergehenden Ansprüche zur Erhöhung der Hydrophobie von hydrophilen Materialien.

10. Verwendung einer Zusammensetzung nach einem der Ansprüche 1 bis 8 zur Verringerung der Formaldehydemission bei Materialien, die freies Formaldehyd enthalten.

11. Verwendung nach Anspruch 9 oder 10, wobei die Materialien ausgewählt sind unter Holzverbundplatten, wie Platten auf Holzbasis, Faserplatten, Strangpressspanplatten, Flachpressspanplatten, Langpressspanplatten, oder unter Glasfaser- oder Mineralwolleisolierungen oder beliebigen Kombinationen davon.

12. Verwendung der Zusammensetzung nach einem der Ansprüche 1 bis 8 zur Herstellung von Holzverbundplatten, wie Platten auf Holzbasis, Faserplatten, Strangpressspanplatten, Flachpressspanplatten, Langpressspanplatten, oder von Glasfaser- oder Mineralwolleisolierungen oder beliebigen Kombinationen davon.

13. Verwendung nach Anspruch 11, wobei die Platten auf Holzbasis, Faserplatten, Strangpressspanplatten, Flachpressspanplatten, Langpressspanplatten oder Glasfaser- oder Mineralwolleisolierungen ein Harz oder einen Klebstoff auf Formaldehydbasis enthalten.

14. Verwendung nach einem der Ansprüche 11 bis 13 zur Verringerung der Formaldehydemission von Holzverbundplatten, wie Platten auf Holzbasis, Faserplatten, Strangpressspanplatten, Flachpressspanplatten, Langpressspanplatten, oder von Glasfaser- oder Mineralwolleisolierungen, auf 0,005 mg Formaldehyd pro Quadratmeter und Stunde oder weniger, gemessen mit dem Gasanalyseverfahren UNE-EN ISO 12460-3:2016.

15. Holzverbundplatten, die ein Harz oder einen Klebstoff auf Formaldehydbasis enthalten und die in den Ansprüchen 1 bis 8 definierte Zusammensetzung, mit einer Formaldehydemission von 0,005 mg Formaldehyd pro Quadratmeter und Stunde oder weniger, gemessen mit dem Gasanalyseverfahren UNE-EN ISO 12460-3:2016.

16. Glasfaser- oder Mineralwolleisolierungen, die ein Harz oder einen Klebstoff auf Formaldehydbasis enthalten und die in den Ansprüchen 1 bis 8 definierte Zusammensetzung, mit einer Formaldehydemission von 0,005 mg Formaldehyd pro Quadratmeter und Stunde oder weniger, gemessen nach dem Gasanalyseverfahren UNE-EN ISO 12460-3:2016.

Revendications

1. Composition hydrophobe et de piégeage du formaldéhyde, comprenant :

    - une suspension ou une émulsion H/E, qui, en tant que phase non aqueuse, comprend au moins une cire ou une huile dérivée du pétrole ou au moins une cire ou une huile dérivée d'un végétal, ou un mélange d'au moins une cire ou une huile dérivée du pétrole et d'au moins une cire ou une huile dérivée d'un végétal ; et
    - une solution aqueuse de résorcinol, contenant de 35 à 45 % en poids de résorcinol le rapport pondéral de la cire ou de l'huile par rapport au résorcinol dans la composition étant compris entre 4:1 et 1:4, le poids de la cire ou de l'huile et du résorcinol ensemble étant compris entre 45 % en poids et 70 % en poids de la composition.

2. Composition selon la revendication 1, dans laquelle le poids de la cire ou de l'huile et du résorcinol ensemble est compris entre 45 % en poids et 65 % en poids de la composition.

3. Composition selon l'une quelconque des revendications 1 et 2, dans laquelle la phase non aqueuse de la suspension ou de l'émulsion H/E comprend ou consiste en de la paraffine.

4. Composition selon l'une quelconque des revendications 1 et 2, dans laquelle la phase non aqueuse de la suspension ou de l'émulsion H/E comprend ou consiste en de l'huile de palme.

5. Composition selon l'une quelconque des revendications précédentes, comprenant de 1 % en poids à 5 % en poids de tensioactif, le tensioactif étant un ou plusieurs éléments choisis parmi les tensioactifs anioniques et non ioniques.

6. Composition selon l'une quelconque des revendications précédentes, comprenant jusqu'à 25 % en poids d'au moins un catalyseur de durcissement des résines dérivées du formaldéhyde.

7. Composition selon l'une quelconque des revendications précédentes, dans laquelle la composition comprend en outre jusqu'à 25 % en poids d'au moins un piégeur de formaldéhyde.

8. Composition selon la revendication 7, dans laquelle le piégeur de formaldéhyde est choisi parmi l'urée, les dérivés de l'urée, les résines d'urée, le métabisulfite de sodium, le bisulfite d'ammonium, la monoéthanolamine et la diéthanolamine.

9. Utilisation d'une composition selon l'une quelconque des revendications précédentes, pour augmenter le caractère hydrophobe de matériaux hydrophiles.

10. Utilisation d'une composition selon l'une quelconque des revendications 1 à 8, pour réduire le dégagement de formaldéhyde dans des matériaux comprenant du formaldéhyde libre.

11. Utilisation selon la revendication 9 ou 10, dans laquelle les matériaux sont choisis parmi les panneaux composites en bois, tels que les panneaux dérivés du bois, les panneaux de fibres, les panneaux de particules, les panneaux d'aggloméré, les panneaux à particules orientées, ou les isolants en fibre de verre ou en laine de roche, ou toutes combinaisons de ceux-ci.

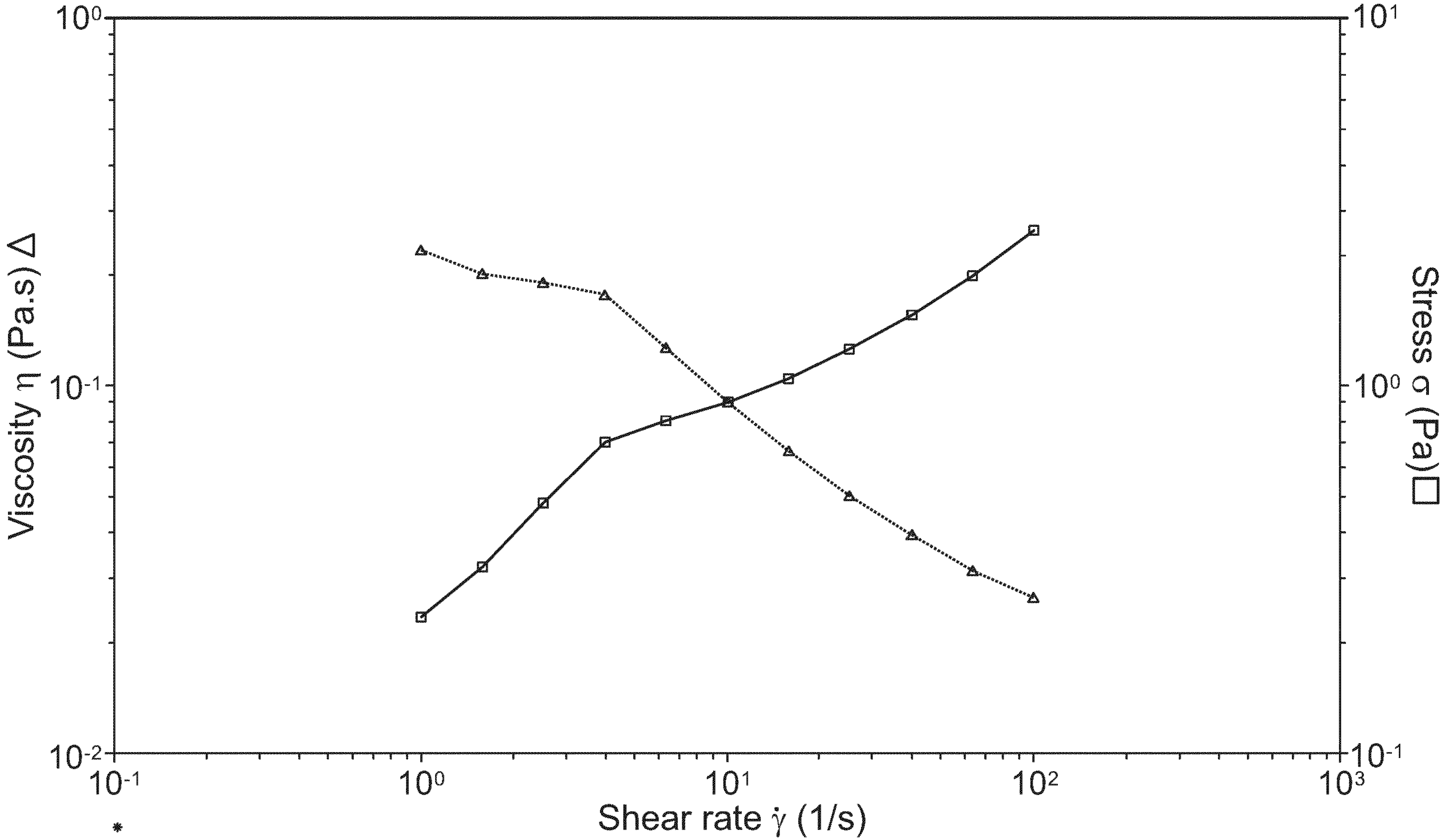
12. Utilisation de la composition selon l'une quelconque des revendications 1 à 8, dans la fabrication de panneaux composites en bois, tels que les panneaux dérivés du bois, les panneaux de fibres, les panneaux de particules, les panneaux d'aggloméré, les panneaux à particules orientées, ou des isolants en fibre de verre ou en laine de roche, ou toutes combinaisons de ceux-ci.

13. Utilisation selon la revendication 11, dans laquelle les panneaux dérivés du bois, les panneaux de fibres, les panneaux de particules, les panneaux d'aggloméré, les panneaux à particules orientées ou les isolants en fibre de verre ou en laine de roche comprennent une résine ou un adhésif dérivé du formaldéhyde.

14. Utilisation selon l'une quelconque des revendications 11 à 13, pour réduire le dégagement de formaldéhyde des panneaux composites en bois, tels que les panneaux dérivés du bois, les panneaux de fibres, les panneaux de particules, les panneaux d'aggloméré ou les panneaux à particules orientées ; ou les isolants en fibre de verre ou en laine de roche, à 0,005 mg de formaldéhyde par mètre carré et par heure, ou moins, tel que mesuré par la méthode d'analyse de gaz UNE-EN ISO 12460-3:2016.

15. Panneaux de bois composite, comprenant une résine ou un adhésif dérivé du formaldéhyde et la composition définie dans les revendications 1 à 8, ayant un dégagement de formaldéhyde de 0,005 mg de formaldéhyde par mètre carré et par heure, ou moins, tel que mesuré par la méthode d'analyse de gaz UNE-EN ISO 12460-3:2016.

16. Isolants en fibre de verre ou en laine de roche, comprenant une résine ou un adhésif dérivé du formaldéhyde et la composition définie dans les revendications 1 à 8, ayant un dégagement de formaldéhyde de 0,005 mg de formaldéhyde par mètre carré et par heure, ou moins, tel que mesuré par la méthode d'analyse de gaz UNE-EN ISO 12460-3:2016.



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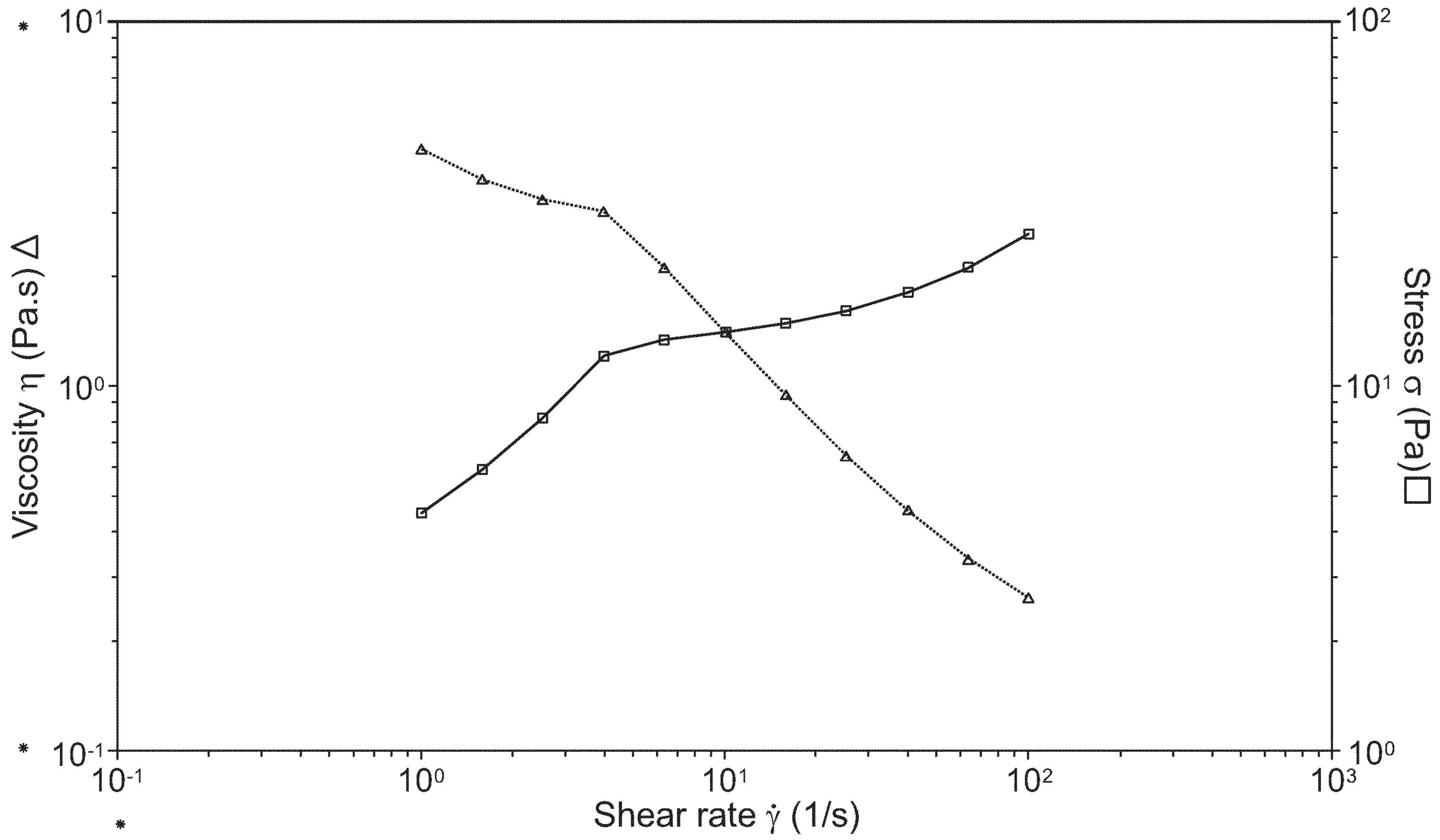
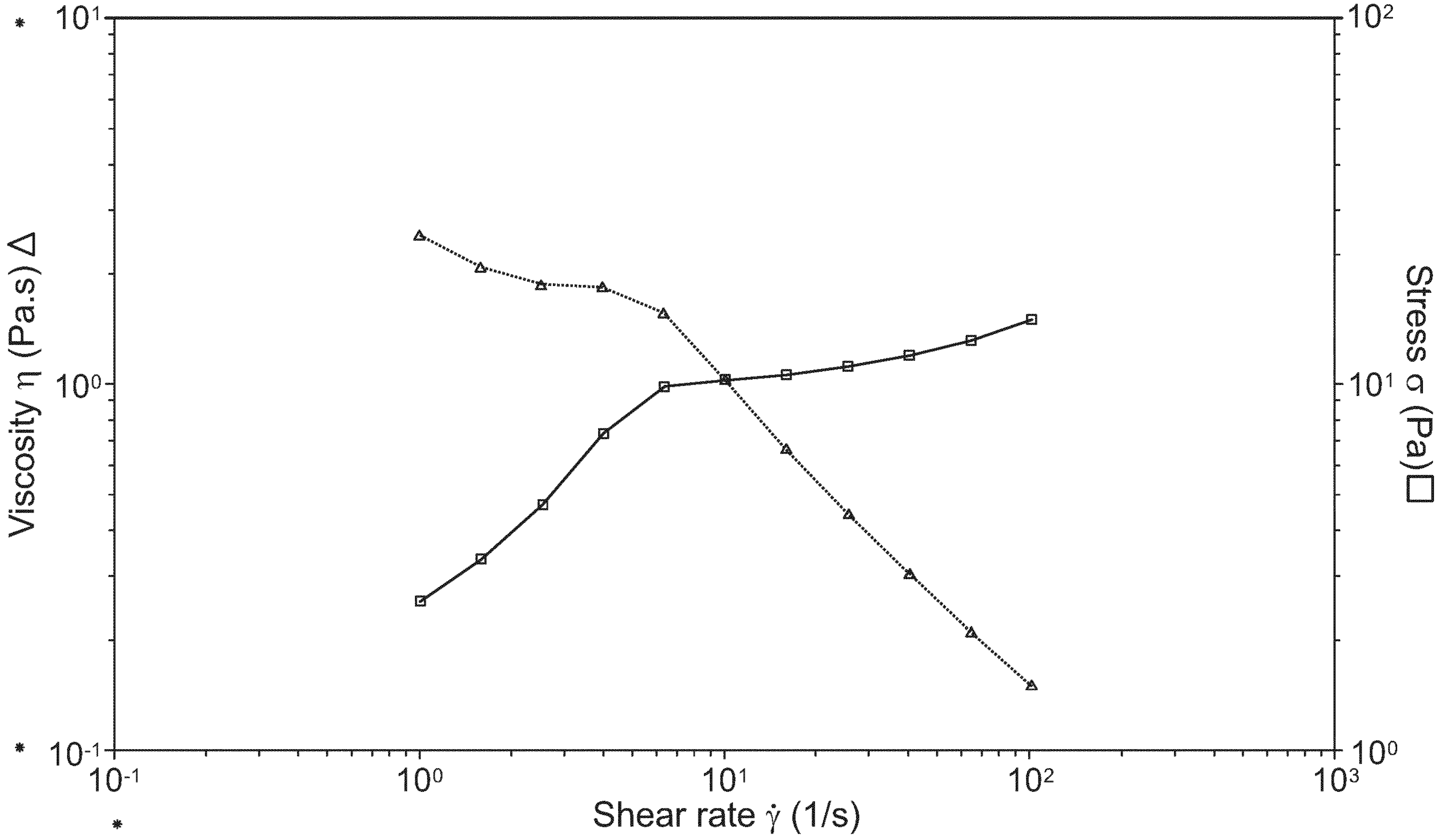
Example nº 2: Weight ratio 1:3 between pure vegetable oil and pure resorcinol

FIG. 1



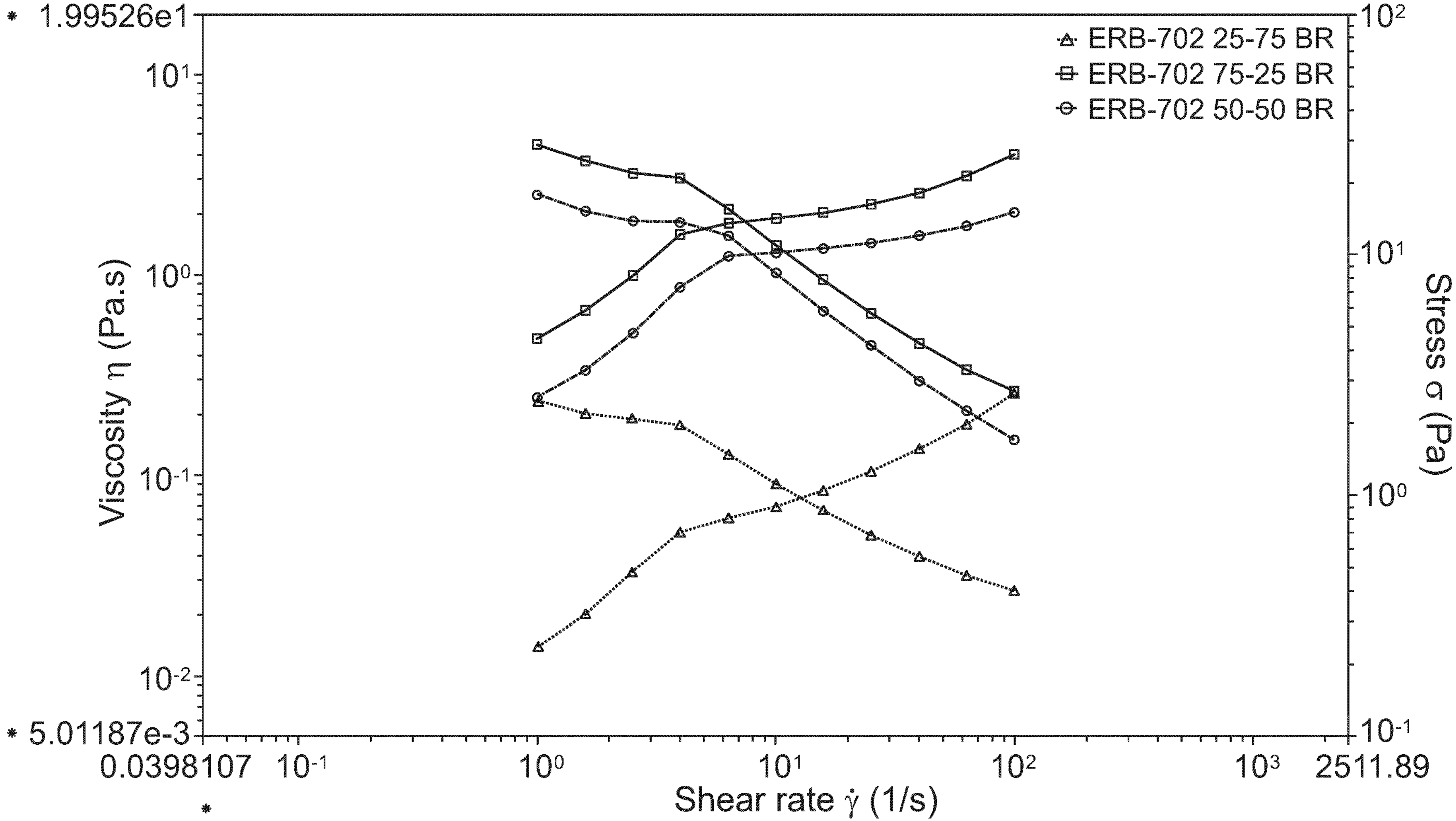
Example n° 2: Weight ratio 3:1 between pure vegetable oil and pure resorcinol

FIG. 2



Example nº 2: Weight ratio 2:2 between pure vegetable oil and pure resorcinol

FIG. 3



Example nº 2: comparative figure of weight ratios 1:3, 3:1, 2:2 between pure vegetable oil and pure resorcinol

FIG. 4

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