



- (51) International Patent Classification:
C11B 3/08 (2006.01) *A23D 9/04* (2006.01)
- (21) International Application Number:
PCT/IB2017/051825
- (22) International Filing Date:
30 March 2017 (30.03.2017)
- (25) Filing Language: Italian
- (26) Publication Language: English
- (30) Priority Data:
102016000033275 31 March 2016 (31.03.2016) IT
- (71) Applicant: **VERSALIS S.P.A.** [IT/IT]; Piazza Boldrini, 1,
20097 San Donato Milanese (MI) (IT).
- (72) Inventors: **RUGGIU, Agostina Anna**; Via Sebastiano
Satta 9, 07037 Sorso (SS) (IT). **GRADELLA, Cecilia**; Via
Cavour 19, 46044 Goito (MN) (IT).
- (74) Agent: **BOTTERO, Carlo**; c/o Barzano' & Zanardo Mil-
ano S.p.A., Via Borgonuovo, 10, 20121 Milano (IT).
- (81) Designated States (unless otherwise indicated, for every
kind of national protection available): AE, AG, AL, AM,

AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY,
BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM,
DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT,
HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KH, KN,
KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA,
MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG,
NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS,
RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY,
TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN,
ZA, ZM, ZW.

- (84) Designated States (unless otherwise indicated, for every
kind of regional protection available): ARIPO (BW, GH,
GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ,
TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU,
TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE,
DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU,
LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK,
SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ,
GW, KM, ML, MR, NE, SN, TD, TG).

Published:

— with international search report (Art. 21(3))

(54) Title: PROCESS OF DECOLORATION OF OIL DERIVATIVES OF PLANT ORIGIN

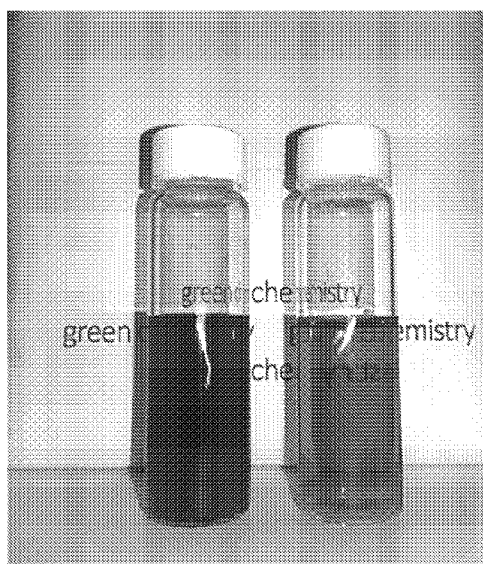


Fig. 1

(57) Abstract: The present invention relates to a process of decoloration of oil derivatives of plant origin. In particular, the present invention relates to a process of decoloration of oil derivatives of plant origin, comprising mixtures of butyl esters of medium-long chain fatty acids and oligomers thereof. The oil derivatives of plant origin thus obtained can be used for applications different from those in the traditional fields of tires, namely in those fields wherein the distinctive compositional characteristics of said derivatives are not sufficient if not also associated to suitable characteristics of color. Examples of such fields are, for example, those of the construction industry, paints, tanning industry.

PROCESS OF DECOLORATION OF OIL DERIVATIVES OF PLANT ORIGIN

5 The present invention relates to a process of decoloration of oil derivatives of plant origin.

In particular, the present invention relates to a process of decoloration of oil derivatives of plant origin, comprising mixtures of butyl esters of medium-long chain fatty acids and oligomers thereof.

10 The oil derivatives of plant origin thus obtained can be used for applications different from those in the traditional fields of tires, namely in those fields wherein the distinctive compositional characteristics of said derivatives are not sufficient if not also associated with appropriate characteristics of color. Examples of such fields are, for example, those of the construction industry, paints, tanning industry.

15 The preparation of carboxylic acids is described in the known art by the oxidative scission of plant oils. For example, US 5,399,749 discloses a process in which organic molecules containing a structural unit of formula --HC=CH-- are converted into two or more molecules containing a structural unit of formula --COOH by the reaction with ozone. Through the process of US 5,399,749, for example, the oleic acid is converted into a mixture of azelaic and pelargonic acids.

20 In order to avoid the use of a toxic and hazardous reagent such as ozone, more recently processes which allows to obtain saturated monocarboxylic acids from unmodified plant oils containing triglycerides of unsaturated fatty acids were developed. For example, US 8,222,438 discloses a process which comprises reacting the above-mentioned triglycerides of unsaturated fatty acids with an
25 oxidising compound in the presence of a catalyst, in order to obtain a reaction intermediate wherein the olefinic double bond was oxidized and provides a vicinal diol; said intermediate is then reacted with oxygen in the presence of a catalyst, such that two carboxylic groups are formed by oxidation from the vicinal diol, thus providing a reaction product comprising saturated monocarboxylic acids and
30 triglycerides of carboxylic acids having more than one acid function.

The reactions described in US 8,222,438 in sequence, as *batch* process, can

be carried out also in a continuous process, as described in US 2015/0005521 A1.

In particular, the process of US 2015/0005521 A1 comprises the same oxidation reactions of a plant oil comprising unsaturated carboxylic acids in two steps cited above and also provides a further step of separation and hydrolysis of the triglycerides of carboxylic acids having more than one acid function, in order to obtain said carboxylic acids with more than one acid function in the purified form by fractionated crystallization.

The mono- and dicarboxylic acids obtained from plant oils are used in the pharmaceutical and phyto-pharmaceutical industry, cosmetic industry and products for household care. Furthermore, some of them are constituents of the so-called biodegradable and compostable bioplastics, as well as being important intermediates in the manufacture of bio-lubricants.

It is important to note that by the processes described in US 8,222,438 and US 2015/0005521 A1 a residue of the distillation of fatty acids comprising compounds characterized by free acid groups is obtained, which can be esterified with C₁-C₄ alcohols, preferably with n-butanol, thus allowing to obtain butyl esters of medium-long chain fatty acids and oligomers thereof having a high stability to hydrolysis and thermal oxidation.

These derivatives can be advantageously used as additives for production processes of rubber, and particularly as synthetic elastomer extender oils and as process oils for preparing elastomer blends.

For example, the patent US 8,969,454 discloses an elastomer composition comprising at least one elastomer and at least one oil derivative of plant origin selected from one or more of the following:

a) a mixture of triglycerides comprising one or more of the following oligomeric structures:



wherein R₁ is a C₂-C₂₂ alkylene, R₂ is selected from C₆-C₂₄ monocarboxylic acid residues or C₆-C₂₄ dicarboxylic acid residues, R₃ is selected from H, C₆-C₂₄ dicarboxylic acid residues and C₆-C₂₄ monocarboxylic acid residues, R₄ is an alkyl group, *n* is an integer higher than or equal to 2, wherein said C₆-C₂₄ dicarboxylic

acid residues of R_2 and R_3 , are esterified with monoalcohols, and wherein said mixture of triglycerides is characterized by a Number Average Molar Mass (M_n) comprised between 800 and 10000;

b) triglycerides of one or more long-chain carboxylic acids comprising at least one carboxylic acid containing adjacent hydroxyl groups;

c) esters of polyols with at least one C_6 - C_{24} monocarboxylic acid and at least one C_6 - C_{24} dicarboxylic acid, said esters being different from the triglycerides.

It is important to note that the derivatives described in US 8,969,454 can be characterized by a very dark color. For example, the colorimetric analysis on a sample of some of these derivatives in accordance with a standard method confers to them a color of a level exceeding the maximum level of the Gardner scale.

The Gardner color scale comprises 18 standard color levels ranging from "light yellow" to "deep red". It is widely used to establish the color of oils, paints, chemical compounds such as resins, lacquers, fatty acids, etcetera.

The Gardner scale level of a sample can be determined according to the standard methods known to the person skilled in the art, for example ASTM D1544-04, ISO 4630 or AOCS Tdla-64T.

For the aims of the present invention, a color of a level exceeding the maximum level of the Gardner scale, therefore formally higher than 18, is defined "off the chart".

Therefore, when the above-mentioned very dark oil derivatives of plant origin are subjected to colorimetric analysis according to any standard method known to the person skilled in the art, in order to assign to them a color level of the Gardner scale, they can be characterized by a "off the chart" color.

Within the elastomeric composition described in US 8,969,454, the above described oil derivatives of plant origin act as extender oils, whose function explicates by improving rubber workability, reducing the mixing time, minimizing the amount of heat generated and maximizing the dispersion of the components, and at the same time by increasing cold elasticity and flexibility of the rubber after vulcanization.

In addition to the main use in the field of tires, the above-mentioned oil

derivatives of plant origin can be used, for example, as high-stability lubricants, plasticizers for conventional plastics and bioplastics, components of polyurethane, etcetera.

Nevertheless, the application in fields different from those of tires is
5 severely limited by the very dark color of these derivatives.

For example, some oil derivatives of plant origin could be advantageously used in the construction industry, having demonstrated, for example, to be excellent release agents, namely being able to facilitate and accelerate the process of detachment of formworks after concrete pouring and solidification. Unfortunately,
10 their use is limited by the fact that they release their very dark color to the concrete and provide a permanent coloration on the handwork which is not appreciated.

Other possible applications successfully tested, for example in the field of resins (in green formulations for the manufacture of alkyd resins and polyester resins, in coil coating processes), adhesives, inks and coloring pastes, have not had
15 to date a practical realization due to the predominant coloring effect by these derivatives on the other components used in the various applications.

A further field in which some of these oil derivatives of plant origin could be advantageously used is the tanning industry, for the manufacture of oils and leather finishing intermediates. Also in this case, the coloring of these derivatives
20 make unsuitable the use on leathers with a color different from black.

Therefore, the Applicant considers the aim to identify a process of decoloration of oil derivatives of plant origin, in particular of derivatives with a very dark color (namely of a level exceeding the maximum level of the Gardner scale, namely “off the charts”), in order to extend their application field.

25 In the state of the art numerous methods of decoloration of plant oils are described. They are mostly used on plant oils intended for human nutrition.

For example, US 4,443,379 discloses a process of decoloration of plant oils using compositions comprising acid-activated sub-bentonite clays and a minor part of Y zeolite.

30 Other clays commonly used for decoloring oils are montmorillonite, kaolinite and attapulgite (also known as Fuller’s earth).

For example, US 5,151,211, discloses a composition useful to remove colored impurities from triglycerides oils, which comprises a decoloring clay of the attapulgit-smectite type and a polycarboxylic acid with chelating function.

US 4,781,864 instead describes a process for removing colored pigments
5 from plant oils comprising the treatment of said oils with acid-activated amorphous silica.

It is known to the person skilled in the art that, in general adsorbents, such as, for example activated carbon, celite, alumina, can perform a decoloring effect through the bond with chromophore molecules (chapter “Dyes – Environmental
10 Chemistry” in “Kirk-Othmer Encyclopedia of Chemical Technology”, IV Ed. 1993, vol. 8 pag. 753-783).

It is also known that some oxidizing or reducing agents can perform a decoloring effect on plant oils. Among them, for example, H_2O_2 , $NaClO$, $Na_2S_2O_4$ can be used at various concentrations (chapter “Bleaching” in “Ullmann’s
15 Encyclopedia of Industrial Chemistry”, V Ed. 1985, vol. A 4, pag. 191-199).

Finally, it is known to the person skilled in the art the hydrotreating with hydrogen in the presence of catalyst of plant oils can cause some decoloration.

The Applicant therefore applied the above-mentioned methods known in the art in order to decolor, at least partially, said oil derivatives of plant origin, in
20 particular derivatives with a color of a level exceeding the maximum level of the Gardner scale, so as to obtain derivatives having color characteristics “suitable” for applications in fields different from, for example, those of tires, namely in those fields wherein the distinctive compositional characteristics of said derivative are not sufficient if not also associated to suitable color characteristics.

25 For the aims of the present invention, in order to determine the effectiveness of the methods of decoloration, the standard method ASTM D1544-04 was used for determining the color of transparent liquids expressed in the Gardner scale, method known to the person skilled in the art.

As described below, the known methods of decoloration, applied to oil
30 derivatives of plant origin, in particular to the derivatives having a color exceeding the maximum level of the Gardner scale, namely “off the chart”, showed to be

ineffective since they did not determine any change to the color of said derivatives, which is maintained “off the chart”.

Surprisingly, the Applicant has now found an innovative process of decoloration, never previously described, nor suggested by the known art, based on
5 the use of H_2O_2 in the presence of a suitable catalyst.

Therefore, it is an aim of the present invention to provide a process of decoloration of oil derivatives of plant origin.

An advantage of the present process is to allow the decoloration of oil derivatives of plant origin, also very dark oil derivatives, namely having a color
10 exceeding the maximum level of the Gardner scale, which in such a way can be used also in those fields different from that of the tires, such as, for example, construction industry, paints and tanning industry, and generally in those fields in which the distinctive compositional characteristics of said derivatives are not sufficient if they are not also associated to suitable characteristics of color.

15 In addition, the present process of decoloration is capable of considerably improving the transparency characteristics of the oil derivatives of plant origin.

Advantageously, the present process does not provide nor require a dilution of the oil derivatives of plant origin in organic solvents.

A further advantage of the present process is that reagents which are toxic
20 or harmful to the environment are not used.

Further characteristics and advantages of the present invention will be evident from the following detailed description and with reference to the attached figure, which illustrates the general characteristics of the process according to some embodiments of the invention and integrates the description below.

25 Particularly, Figure 1 illustrates the comparison between two samples of an oil derivative of plant origin before and after the process according to the present invention, under the conditions described in example 1.

For the aims of the present description and the following claims, the definitions of the numeric ranges always comprise the end-points unless otherwise
30 specified.

In the description of the embodiments of the present invention, the terms

“comprising” and “containing” mean that the options described, for example relating the steps of a method or a process or the components of a product or a device, are not necessarily exhaustive. However, it is important to note that also the embodiments wherein the term “comprising” referred to the described options, for example those options relating the steps of a method or a process or the components of a product or a device, is to be interpreted as “consisting essentially of” or “consisting of”, represent an object of the present application, even if not explicitly declared.

For the aims of the present invention and the following claims, the percentages are always percentages by weight, unless otherwise specified.

For the aims of the present description, the derivatives that have color characteristics “suitable” for the applications in fields different from, for example, those of tires or bitumens, or in those fields in which the distinctive compositional characteristics of the oil derivatives of plant origin are not sufficient if not also associated to suitable color characteristics, are those derivatives characterized by a color within the Gardner scale, or derivatives which are characterized by a color of a level lower than or equal to 18 of said scale when subjected to a standard analytical method known to the person skilled in the art (for example ASTM D 1544-04, ISO 4630 or AOCS Tdla-64T).

The process of the present invention is particularly suitable for the decoloration of very dark oil derivatives of plant origin, which are not transparent, in particular the derivatives having a color of a level exceeding the maximum level of the Gardner scale.

However, said process can be successfully used also for decoloring oil derivatives of plant origin having colors comprised in the levels of said Gardner scale.

In such a case, through said process, starting from an oil derivative of plant origin having a color of any level of the Gardner scale, measured according to a standard method known to the person skilled in the art (for example ASTM D 1544-04, ISO 4630 or AOCS Tdla-64T) it is possible to obtain a plant oil derivative having a color of a level of said Gardner scale lower than the starting

level.

Accordingly, for the aims of the present invention, the term “decoloration” means the transition of the color from a level of the Gardner scale to any lower level of said scale.

5 In particular, as for oil derivatives of plant origin having a color of a level exceeding the maximum level of the Gardner scale, namely a “off the chart” color, the term “decoloration” means the transition of said color from “off the chart” to any level of said scale.

Therefore, it is a first object of the present invention a process of
10 decoloration of an oil derivative of plant origin, comprising the steps of:

- i) reacting said oil derivative of plant origin with hydrogen peroxide in the presence of an oxidation catalyst at a temperature comprised in the range of 70°C-100°C in order to obtain a mixture comprising an aqueous phase and an oily phase;
- ii) separating from said mixture the aqueous phase and the oily phase, the
15 latter comprising a decolored oil derivative of plant origin.

According to a preferred aspect of the invention, the oily phase separated in step ii) consists of a decolored oil derivative of plant origin.

In a preferred aspect of the invention, step i) of said process can be carried out for a time comprised between 5 and 12 hours.

20 In a further preferred aspect of the invention, step i) of said process can be carried out for a time comprised between 6 and 10 hours, and even more preferably it is carried out for a time comprised between 7 and 9 hours.

In a preferred aspect, step i) can be carried out at a temperature comprised in the range of 80°C-95°C.

25 According to another preferred aspect of the invention, said hydrogen peroxide in step i) is in the form of an aqueous solution, preferably having a concentration comprised between 20 and 70%, more preferably between 35 and 60% by weight of hydrogen peroxide with respect to the total weight of the aqueous solution.

30 In a preferred aspect of the invention, the step i) of said process can comprise the sub-steps of:

- a) contacting said oil derivative of plant origin with an aqueous solution A comprising hydrogen peroxide, in the presence of an oxidation catalyst;
- b) bringing the mixture obtained in the sub-step a) to a temperature comprised in the range of 70°C-100°C;
- 5 c) adding an aqueous solution B comprising hydrogen peroxide to the mixture obtained in the sub-step b);
- d) maintaining the mixture obtained in the sub-step c), comprising an aqueous phase and an oily phase, at a temperature comprised in the range of 70°C-100°C for a time comprised between 5 and 12 hours.
- 10 Preferably, the step i) of the process according to the present invention can be carried out under stirring.
- Preferably the sub-steps from a) to d) can be carried out under stirring.
- Preferably, all the steps and/or sub-steps of the process of decoloration of the present invention are carried out without adding organic solvents.
- 15 The process of the present invention is effective not only for the decoloring effect, but also for considerably improving the transparency characteristics of the oil derivative of plant origin, and by virtue of this effect the color level can be assigned through any one of the standard methods (for example ASTM D 1544-04, ISO 4630 or AOCS Tdla-64T), specifically provided for transparent liquids.
- 20 In a preferred aspect of the invention, in order to attribute the color of the oil derivative of plant origin the Gardner color scale can be used.
- As already mentioned, in order to attribute a level of the Gardner scale to the color of the plant oil derivative, it is possible to use any one of the methods known to the person skilled in the art, for example ASTM D1544-04, ISO 4630 or
- 25 AOCS Tdla-64T. Preferably, in the process of the present invention, the Gardner scale level is attributed to the color of the oil derivative of plant origin by the standard method ASTM D1544-04.
- In a preferred aspect of the invention, the above-mentioned oil derivative of plant origin which is reacted in step i) can have a color of a level higher than level
- 30 2 of the Gardner scale. More preferably the above-mentioned derivative can have a color of a level higher than level 5 of the Gardner scale and even more preferably a

color of a level higher than level 13 of said scale.

According to a particularly preferred aspect of the invention, the above mentioned derivative can have a color of a level exceeding the maximum level of the Gardner scale.

- 5 Preferably, the oil derivative of plant origin can have a color of a level higher than level 13 of the Gardner scale or a “off the chart” color.

In a preferred aspect of the invention, when the oil derivative of plant origin has a color of a level exceeding the maximum level of the Gardner scale (namely, it is “off the chart”), the color of the decolored derivative at the end of the process
10 can be of a level lower than or equal to level 18 of the Gardner scale and even more preferably it is of a level comprised between 13 and 18 of said scale.

Preferably, the oil derivative of plant origin can be any one of the derivatives described in US 8,969,454, or comprises one or more from the following:

- 15 a) a mixture of triglycerides comprising one or more of the following oligomeric structures:



wherein R_1 is a C_2 - C_{22} alkylene, R_2 is selected from C_6 - C_{24} monocarboxylic acid residues or C_6 - C_{24} dicarboxylic acid residues, R_3 is selected from H, C_6 - C_{24}
20 dicarboxylic acid residues and C_6 - C_{24} monocarboxylic acid residues, R_4 is an alkyl group, n is an integer higher than or equal to 2, wherein said C_6 - C_{24} dicarboxylic acids residues of R_2 and R_3 , are esterified with monoalcohols, and wherein said mixture of triglycerides is characterized by a Number Average Molar Mass (M_n) comprised between 800 and 10000;

- 25 b) triglycerides of one or more long-chain carboxylic acids comprising at least one carboxylic acid containing adjacent hydroxyl groups;

c) esters of polyols with at least one C_6 - C_{24} monocarboxylic acid and at least one C_6 - C_{24} dicarboxylic acid, said esters being different from triglycerides.

In a preferred aspect, the sub-step a) can be carried out at atmospheric
30 pressure and at a temperature comprised in the range of 40°C-65°C.

In a preferred aspect, during the sub-step a), said oil derivative of plant

origin can be contacted with said aqueous solution A for a time comprised between 10 minutes and 1 hour, and more preferably for a time comprised between 15 minutes and 30 minutes.

The oxidation catalyst used in the process of the present invention belongs to the group of the transition elements. Advantageously Fe, Mn, Mo, Nb, Os, Re, Ti, V, W, Zr and acids thereof, alkaline salts and complexes, such as catalysts in homogeneous or heterogeneous phase, possibly in a supported or nanostructured form, are used.

In a preferred aspect of the invention, said oxidation catalyst can be selected from the group consisting of tungstic acid and phosphotungstic acid. Preferably, said catalyst is tungstic acid.

Said catalyst is preferably used in an amount comprised between 0.05% and 3% by weight, more preferably between 0.1% and 1.8% by weight with respect to the total weight of the oil derivative of plant origin to be decolored.

In a particularly preferred aspect, said catalyst is present in an amount comprised between 0.5 and 1.5% by weight with respect to the total weight of the derivative to be decolored.

The amount of hydrogen peroxide used in the present process can range depending on the titre of the solution used and can be comprised between 150 and 450 g of pure hydrogen peroxide (100%) per kg of oil derivative of plant origin.

In a preferred aspect of the present invention, the aqueous solution A and the aqueous solution B can comprise hydrogen peroxide at concentrations comprised between 20 and 70% by weight with respect to the total weight of the aqueous solution.

In further preferred aspect, the aqueous solution A and the aqueous solution B can comprise hydrogen peroxide at concentrations comprised between 35% and 60% and even more preferably at concentrations comprised between 45% and 55% by weight with respect to the total weight of the aqueous solution.

In a preferred aspect of the invention, the aqueous solution A which is contacted with the plant oil derivative during the sub-step a) of the process of the present invention can contain an amount of hydrogen peroxide comprised between

15% and 95% by weight with respect to the total weight of hydrogen peroxide added in the course of the whole process, and preferably comprised between 30% and 80%.

In a preferred aspect, during the sub-step c) the addition of the aqueous solution B can be carried out in a period of time comprised between 20 minutes and 5 hours.

More preferably, the addition of aqueous solution B in the course of sub-step c) is carried out in a period comprise between 30 minutes and 1 hour.

In a preferred aspect of the invention, the sub-step d) can be carried out for a time comprised between 6 and 10 hours, more preferably between 7 and 9 hours.

In a preferred aspect, the sub-step d) can be carried out at a temperature between 80°C and 95°C.

The separation of the aqueous phase from the oily phase of step ii) of the above-mentioned process can be carried out by any method and device known by the person skilled in the art, which are intended to separate two heterogeneous phases from each other from a mixture comprising them.

For example, said separation can be carried out by separating funnel, or by a “florentine” type continuous separator.

It is a second object of the present invention an oil derivative of plant origin decolored by means of the above mentioned process of decoloration.

In a preferred aspect, said decolored oil derivative of plant origin has a color of a level equal to or lower than level 18 of the Gardner scale, and preferably it has a color of a level comprised between 13 and 18 of said scale.

Finally, it is a third object of the present invention an oil derivative of plant origin comprising one or more of the following:

a) a mixture of triglycerides comprising one or more of the following oligomeric structures:



wherein R_1 is a C_2 - C_{22} alkylene, R_2 is selected from C_6 - C_{24} monocarboxylic acid residues or C_6 - C_{24} dicarboxylic acid residues, R_3 is selected from H, C_6 - C_{24} dicarboxylic acid residues and C_6 - C_{24} monocarboxylic acid residues, R_4 is an alkyl

group, n is an integer higher than or equal to 2, wherein said C₆-C₂₄ dicarboxylic acid residues of R₂ and R₃, are esterified with monoalcohols, and wherein said mixture of triglycerides is characterized by a Number Average Molar Mass (Mn) comprised between 800 and 10000;

- 5 b) triglycerides of one or more long-chain carboxylic acids comprising at least one carboxylic acid containing adjacent hydroxyl groups;
- c) esters of polyols with at least one C₆-C₂₄ monocarboxylic acid and at least one C₆-C₂₄ dicarboxylic acid, said esters being different from the triglycerides, characterized by the fact of having a color of a level lower than or equal to
- 10 level 18 of the Gardner scale and preferably a color of a level comprised between 13 and 18 of said scale.

In order to put into practise and better illustrate the present invention, some non-limiting examples are reported below.

Example 1 (decoloration test of an oil derivative of plant origin having a

15 color of a level exceeding the maximum level of the Gardner scale, according to the invention)

400 g of an oil derivative of plant origin having a color of a level exceeding the maximum level of the Gardner scale were loaded into a flask of 1000 ml, which was equipped with magnetic stirring and a thermometer. Said oil derivative of plant

20 origin is commercially available under the trademark Matrilox™ PF801R and has a composition comprised between those of the derivatives described in US 8,969,454. An aqueous solution, previously prepared (aqueous solution A) by mixing under stirring 4 g of tungstic acid (1% by weight with respect to the total weight of the treated plant oil derivative) and 120 g of hydrogen peroxide 50% by

25 weight in water, was added to it.

In order to promote the homogenization of the reagents, the mixture thus obtained was maintained at 55-60°C for 15 minutes under stirring.

Then, the mixture was heated at 80°C and, by a dropping funnel, further 180 g of a solution of hydrogen peroxide 50% by weight in water (aqueous solution

30 B) were added within 1 hour. Therefore, 375 g of hydrogen peroxide per kg of plant oil derivative in total were added.

At the end of the addition the reaction was left to proceed for further 7 hours by maintaining the temperature at 80°C under stirring.

After this period of time, the separation of the oily phase and the aqueous phase was carried out by transfer into a separating funnel and settling.

5 Possible residues of aqueous phase containing hydrogen peroxide in the oily phase were removed through vacuum evaporation by means of rotating evaporator.

A sample of the obtained oily phase was subjected to colorimetric analysis in accordance with the standard method ASTM D 1544-04 and compared with a sample of the same starting oil derivative of plant origin. The Gardner scale level
10 passed from the initial “off the chart” (level exceeding the maximum level of the Gardner scale) to level 13 of said scale, suitable for applications in fields different from the field of tires.

Figure 1 represents a sample of oil derivative of plant origin before and after the decoloration treatment under the conditions of example 1.

15 Example 2 (decoloration test of an oil derivative of plant origin having a color of a level exceeding the maximum level of the Gardner scale, according to the invention)

In this example the process of example 1 was repeated by using however lower amounts of oxidizing reagent.

20 250 g of Matrilox™ PF801R previously described were loaded into a flask of 500 ml, which was equipped with stirring and a thermometer. An aqueous solution, previously prepared (aqueous solution A) by mixing under stirring 1.5 g of tungstic acid (0.6% by weight with respect to the total weight of the treated plant oil derivative) and 40 g of hydrogen peroxide 50% by weight in water, was added
25 to it.

In order to promote the homogenization of the reagents, the mixture thus obtained was maintained at 55-60°C for 15 minutes under stirring.

Then, the mixture was heated at 80°C and, by a dropping funnel, further 85 g of a solution of hydrogen peroxide 50% by weight in water (aqueous solution B)
30 were added within 30 minutes. Therefore, 250 g of hydrogen peroxide per kg of plant oil derivative in total were added.

At the end of the addition the reaction was left to proceed for further 7 hours by maintaining the temperature at 80°C under stirring.

After this period of time, the separation of the aqueous phase was carried out by transfer into a separating funnel and settling.

5 Possible residues of aqueous phase containing hydrogen peroxide in the oily phase were removed through vacuum evaporation by means of rotating evaporator.

A sample of the obtained oily phase was subjected to colorimetric analysis in accordance with the standard method ASTM D 1544-04 and compared with a sample of the same starting oil derivative of plant origin. The Gardner scale level
10 passed from the initial “off the chart” (level exceeding the maximum level of the Gardner scale) to level 18 of said scale, still suitable for applications in fields different from the field of tires.

Therefore, it was demonstrated that the extent of the decoloring effect can be correlated to the amount of oxidizing reagent used.

15 Example 3 (decoloration test of an oil derivative of plant origin having a color of a level exceeding the maximum level of the Gardner scale, according to the invention)

In this example the process of example 1 was repeated by using, however, a different plant oil derivative, commercially available under the trademark
20 Matrilox™ PF801D and having a composition comprised between those of the derivatives described in US 8,969,454, having a color of a level exceeding the maximum level of the Gardner scale (“off the chart” color).

177 g of said oil derivative of plant origin were loaded into a flask of 500 ml, which was equipped with stirring and a thermometer. An aqueous solution
25 previously prepared (aqueous solution A) by mixing under stirring 0.8 g of tungstic acid (0.45% by weight with respect to the total weight of the treated plant oil derivative) and 20 g of hydrogen peroxide 50% by weight in water, was added to it.

In order to promote the homogenization of the reagents, the mixture thus obtained was maintained at 55-60°C for 15 minutes under stirring.

30 Then, the mixture was heated at 90°C and, by means of a dropping funnel, further 70 g of a solution of hydrogen peroxide 50% by weight in water (aqueous

solution B) were added within 1 hour. Therefore, 254.5 g of hydrogen peroxide per kg of plant oil derivative in total were added.

At the end of the addition the reaction was left to proceed for further 7 hours by maintaining the temperature at 80°C under stirring.

5 After this period of time, the separation of the aqueous phase was carried out by transfer into a separating funnel and settling.

Possible residues of aqueous phase containing hydrogen peroxide in the oily phase were removed by vacuum evaporation by means of a rotating evaporator.

A sample of the obtained oily phase was subjected to colorimetric analysis
10 in accordance with the standard method ASTM D 1544-04 and compared with a sample of the same starting oil derivative of plant origin. The Gardner scale level passed from the initial “off the chart” (level $L > 18$) to level 18 of said scale, suitable for applications in fields different from the field of tires.

Comparative Examples 4-7 (decoloration tests of an oil derivative of plant
15 origin in accordance with the methods of the prior art)

The results of the decoloration tests of the plant oil derivative Matrilox™ PF801D previously described by some methods described in the known art are reported in the following table. For each experiment the main reagent, the use conditions and the obtained result are indicated. Each reagent was used in
20 accordance with the methods known to the person skilled in the art or following the manufacturer's instructions.

Example	Reagent	Use conditions	Result (Gardner scale)
4	Dried Engelhard® earth F24 BASF	80°C/1 hour (in accordance with the manufacturer's instructions)	Negative (off the chart)
5	Dried Engelhard® earth F54	80°C / 1 hour (in accordance with the manufacturer's instructions)	Negative (off the chart)

Example	Reagent	Use conditions	Result (Gardner scale)
	BASF		
6	Dried Engelhard® earth F54 BASF	25°C/1 hour (in accordance with the manufacturer's instructions)	Negative (off the chart)
7	H ₂ O ₂ 30%	80°C/ 24 hours (in accordance with the teaching of the prior art)	Negative (off the chart)

It is evident that none of the tested methods of the prior art are capable of decoloring the oil derivative of plant origin Matrilox™ PF801D so as to bring the level of the Gardner scale to a level lower than or equal to 18, suitable for applications in fields different from the field of tires or bitumens.

Comparative Examples 8-10 (decoloration tests of an oil derivative of plant origin in accordance with the methods of the prior art)

The results of the decoloration tests of the plant oil derivative Matrilox™ PF801R previously described by some methods described in the prior art are reported in the following table. For each experiment the main reagent, the use conditions and the obtained result are indicated. Each reagent was used in accordance with the methods known to the person skilled in the art or following the manufacturer's instructions.

Example	Reagent	Use conditions	Result (Gardner scale)
8	Trisyl® Grace	90°C/ 30 minutes (in accordance with the manufacturer's instructions)	Negative (off the chart)
9	H ₂ O ₂ 50%	80°C/ 24 hours (in accordance with the teaching	Negative (off the chart)

Example	Reagent	Use conditions	Result (Gardner scale
		of the prior art)	
10	H ₂ /Pd in ethyl acetate	80°C/ 5 hours (in accordance with the teaching of the prior art)	Negative (off the chart)

It is evident that none of the tested methods of the prior art are capable of decoloring the plant oil derivative Matrilox™ PF801R so as to bring the level of the Gardner scale to a level lower than or equal to 18, suitable for applications in
5 fields different from the field of tires.

It is finally understood that further modifications and variations without departing from the scope of the appended claims can be made to the process herein described and illustrated.

CLAIMS

1. Process of decoloration of an oil derivative of plant origin, comprising the steps of:
 - i) reacting said oil derivative of plant origin with hydrogen peroxide in the presence of an oxidation catalyst at a temperature comprised in the range of 70°C-100°C in order to obtain a mixture comprising an aqueous phase and an oily phase;
 - ii) separating from said mixture the aqueous phase and the oily phase, the latter comprising a decolored oil derivative of plant origin.
2. Process according to claim 1, wherein the step i) is carried out for a time comprised between 5 and 12 hours.
3. Process according to claim 1 or 2, wherein the step i) comprises the sub-steps of:
 - a) contacting said oil derivative of plant origin with an aqueous solution A comprising hydrogen peroxide, in the presence of an oxidation catalyst;
 - b) bringing the mixture obtained in the sub-step a) to a temperature comprised in the range of 70°C-100°C;
 - c) adding an aqueous solution B comprising hydrogen peroxide to the mixture obtained in the sub-step b);
 - d) maintaining the mixture obtained in the sub-step c) at a temperature comprised within the range of 70°C-100°C for a time comprised between 5 and 12 hours.
4. Process according to any one of the claims from 1 to 3, wherein the step i) and/or the sub-steps from a) to d) are carried out under stirring.
5. Process according to any one of the claims from 1 to 4, wherein all the steps and/or sub-steps are carried out without adding organic solvents.
6. Process according to any one of the claims from 1 to 5, wherein said oil derivative of plant origin has a color of a level exceeding the maximum level of the Gardner scale.
7. Process according to any one of the claims from 1 to 6, wherein when said oil derivative of plant origin has a color of a level exceeding the maximum level of

the Gardner scale, the color of said decolored derivative at the end of the process is of a level lower than or equal to level 18 of the Gardner scale, and preferably it is of a level comprised between 13 and 18 of said scale.

8. Process according to any one of the claims from 1 to 7, wherein said oil derivative of plant origin comprises one or more from the following:
- a) a mixture of triglycerides comprising one or more of the following oligomeric structures:
- $$R_4[O-C(O)-R_1-C(O)-O-CH_2-CH(OR_2)-CH_2]_n-O-R_3,$$
- wherein R_1 is a C_2 - C_{22} alkylene, R_2 is selected from C_6 - C_{24} monocarboxylic acid residues or C_6 - C_{24} dicarboxylic acid residues, R_3 is selected from H, C_6 - C_{24} dicarboxylic acid residues and C_6 - C_{24} monocarboxylic acid residues, R_4 is an alkyl group, n is an integer higher than or equal to 2, wherein said C_6 - C_{24} dicarboxylic acid residues of R_2 and R_3 , are esterified with monoalcohols, and wherein said mixture of triglycerides is characterized by a Number Average Molar Mass (M_n) comprised between 800 and 10000;
- b) triglycerides of one or more long-chain carboxylic acids comprising at least one carboxylic acid containing adjacent hydroxyl groups;
- c) esters of polyols with at least one C_6 - C_{24} monocarboxylic acid and at least one C_6 - C_{24} dicarboxylic acid, said esters being different from the triglycerides.
9. Process according to any one of the claims from 3 to 8, wherein the sub-step a) is carried out at atmospheric pressure and at a temperature comprised in the range of 40°C-65°C.
10. Process according to any one of the claims from 3 to 9, wherein during the sub-step a) of said process, said oil derivative of plant origin is contacted with said aqueous solution A for a time comprised between 10 minutes and 1 hour.
11. Process according to any one of the claims from 1 to 10, wherein said oxidation catalyst is selected from the group consisting of tungstic acid and phosphotungstic acid and preferably it is tungstic acid.
12. Process according to any one of the claims from 1 to 11, wherein said catalyst is used in an amount comprised between 0.05% and 3% by weight with respect

to the total weight of the oil derivative of plant origin to be decolored.

13. Process according to any one of the claims from 3 to 12, wherein during the sub-step c) the addition of aqueous solution B is carried out in a period of time comprised between 20 minutes and 5 hours.
- 5 14. Process according to any one of the claims from 3 to 13, wherein the sub-step d) is carried out for a time comprised between 6 and 10 hours.
15. Process according to any one of the claims from 3 to 14, wherein the sub-step d) is carried out at a temperature comprised between 80°C and 95°C.
16. Process according to any one of the claims from 1 to 15, wherein the oily phase
10 separated in the step ii) is consisting of a decolored oil derivative of plant origin.
17. Derivative of oil of plant origin decolored through the process of decoloration according to any one of the claims from 1 to 16.
18. Derivative of oil of plant origin according to claim 17 having a color of a level
15 equal to or lower than level 18 of the Gardner scale and preferably of a level comprised between 13 and 18 of said scale.
19. Oil derivative of plant origin comprising one or more from the following:
- a) a mixture of triglycerides comprising one or more of the following oligomeric structures:
- 20
$$R_4[O-C(O)-R_1-C(O)-O-CH_2-CH(OR_2)-CH_2]_n-O-R_3,$$

wherein R_1 is a C_2 - C_{22} alkylene, R_2 is selected from C_6 - C_{24} monocarboxylic acid residues or C_6 - C_{24} dicarboxylic acid residues, R_3 is selected from H, C_6 - C_{24} dicarboxylic acid residues and C_6 - C_{24} monocarboxylic acid residues, R_4 is an alkyl group, n is an integer higher than or equal to 2, wherein said
25 C_6 - C_{24} dicarboxylic acid residues of R_2 and R_3 , are esterified with monoalcohols, and wherein said mixture of triglycerides is characterized by a Number Average Molar Mass (Mn) comprised between 800 and 10000;
- b) triglycerides of one or more long-chain carboxylic acids comprising at least one carboxylic acid containing adjacent hydroxyl groups;
- 30 c) esters of polyols with at least one C_6 - C_{24} monocarboxylic acid and at least one C_6 - C_{24} dicarboxylic acid, said esters being different from the

triglycerides,
characterized by the fact of having a color of a level lower than or equal to level 18 of the Gardner scale and preferably a color of a level comprised between 13 and 18 of said scale.

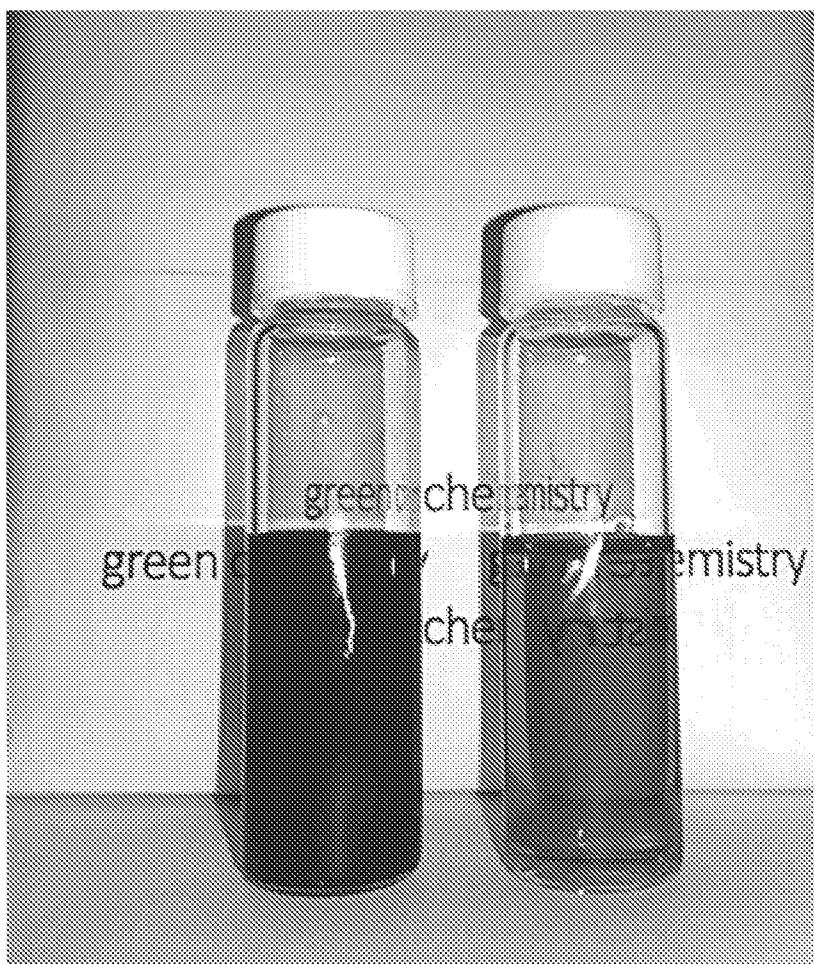


Fig. 1

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2017/051825

A. CLASSIFICATION OF SUBJECT MATTER
INV. C11B3/08 A23D9/04
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)

C11B A23D

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)

EP0-Internal, WPI Data, FSTA

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 581 468 A2 (ROHM & HAAS [US]) 2 February 1994 (1994-02-02) claims 1-10; example 15 -----	1-19
X	GB 226 818 A (NAAML00ZE VENNOOTSCHAP ANT JUR) 10 September 1925 (1925-09-10) the whole document -----	1-19
X	GB 2 068 404 A (UNILEVER LTD) 12 August 1981 (1981-08-12) claims 1-23; examples 1-19 -----	1-19
X	US 8 399 693 B2 (YALAMANCHILI SRIKANTH [US] ET AL) 19 March 2013 (2013-03-19) claims 1-22; examples 1-3 ----- -/--	1-19



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

21 June 2017

Date of mailing of the international search report

30/06/2017

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

Adechy, Miriam

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2017/051825

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2 524 056 A (VAGN JESPERSEN) 3 October 1950 (1950-10-03)	17-19
A	the whole document -----	1-16
X	US 8 350 070 B2 (CASPER DAVID [US] ET AL) 8 January 2013 (2013-01-08)	17-19
A	example 9 -----	1-16
X	US 2 358 866 A (DOUGLAS MACMAHON JAMES) 26 September 1944 (1944-09-26)	17-19
A	claims 1-8; examples I-IX -----	1-16

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/IB2017/051825

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0581468	A2	02-02-1994	AT 132893 T 15-01-1996
		AU 675787 B2 20-02-1997	
		BR 9302976 A 01-03-1994	
		CA 2100507 A1 28-01-1994	
		CN 1081707 A 09-02-1994	
		DE 69301289 D1 22-02-1996	
		DE 69301289 T2 29-08-1996	
		DK 0581468 T3 12-02-1996	
		EP 0581468 A2 02-02-1994	
		ES 2083253 T3 01-04-1996	
		GR 3018637 T3 30-04-1996	
		HU 215240 B 30-11-1998	
		IL 106332 A 12-09-1996	
		TR 26937 A 24-08-1994	
		US 5371254 A 06-12-1994	
		ZA 9305228 B 27-01-1994	

GB 226818	A	10-09-1925	NONE

GB 2068404	A	12-08-1981	NONE

US 8399693	B2	19-03-2013	CA 2736688 A1 07-10-2011
		US 2011251411 A1 13-10-2011	
		US 2012178949 A1 12-07-2012	

US 2524056	A	03-10-1950	NONE

US 8350070	B2	08-01-2013	US 2011313124 A1 22-12-2011
		US 2012172610 A1 05-07-2012	

US 2358866	A	26-09-1944	BE 464370 A 21-06-2017
		CH 260569 A 31-03-1949	
		DE 843394 C 07-07-1952	
		FR 916090 A 26-11-1946	
		GB 588040 A 13-05-1947	
		US 2358866 A 26-09-1944	
