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(54) **Titre : FORMULATION POUR LE REVETEMENT DE RECIPIENTS EN VERRE**
(54) **Title: FORMULATION FOR COATING GLASS CONTAINERS**

(57) **Abrégé/Abstract:**
The invention relates to a formulation comprising at least one methyl ester of fatty acid and at least one nonionic surfactant having a HLB from 9 to 16. The invention also relates to the use of such a formulation for coating a container, to a coating composition comprising such a formulation, and to a preparation method of such a coating composition.

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Abstract:

The invention relates to a formulation comprising at least one methyl ester of fatty acid and at least one nonionic surfactant having a HLB from 9 to 16. The invention also relates to the use of such a formulation for coating a container, to a coating composition comprising such a formulation, and to a preparation method of such a coating composition.

Formulation for coating glass containers

Technical field

The present invention relates to a formulation useful for the preparation of a coating composition for glass containers, in particular for improving glass surface appearance, more particularly the external surfaces of glass containers. The invention also relates to a coating composition comprising said formulation, useful as a scratch masking coating solutions for glass bottles for enhancing appearance, and to a method for coating a container.

Technical background

Glass articles such as returnable bottles are handled a great number of times during manufacture, inspection, filling, shipping, washing etc. During such handling the bottles come into contact with various mechanical devices such as conveyors, inspection devices and the like as well as contact with other glass containers (such as bottles, jars, and the like) and surfaces such as boxes, shelves etc. This high degree of contact causes damage either by breakage, cracking, scratching or other defects of the surface.

Scratch or scuff masking agents on glass containers have been used to address this problem. Such masking agents must desirably mask scuffs and exhibit an acceptable durability and surface properties. Particularly desirable properties for scuff masking agents include water resistance and durability while being non-toxic and removable in alkaline bottle washing operations.

In single use glass containers, such protective coatings are sufficient to protect against scuffing during the life of the container. However, with returnable glass containers, which can be washed and refilled, for example 20 to 60 times or more, the original protective coating applied at the glass plant is washed off and protection is lost. As the number of return cycles increases, scuffing becomes more important, which results in an undesirable appearance.

Masking solutions may be used to improve the appearance of the bottles. Ideally, the masking solution should be food grade like, should do not cause any skin irritation, and should not be aggressive against labels that are applied on the containers. Furthermore, the masking formulations should preferably remain stable and homogeneous and avoid phase separation during storage, which would lead to high variation in concentration of the ingredients of the coating composition prepared from such formulations. An inhomogeneity in the coating

composition would have an impact on the effectiveness of the coating composition, which could result in non-sellable products due to no coating up to too high load of coating, causing unacceptable touch and/or appearance.

Document WO 2020/127922 describes a formulation comprising a mineral oil, a sorbitan ester and from 2 to 20 % of water, hydrogen peroxide or a mixture thereof. The use of a mineral oil as a main component of the formulation makes it possible to achieve a formulation that is stable over time. However, this component is not renewable and the formulation disclosed in document WO 2020/127922 is not sustainable.

There is thus a need for a formulation suitable for a use in compositions for coating glass containers that is more sustainable and environment-friendly while providing a coating exhibiting desirable properties in terms of stability, scruff masking effectiveness and touch.

Summary of the invention

It is a first object of the invention to provide a formulation comprising:

- at least one methyl ester of fatty acid; and
- at least one nonionic surfactant having a HLB from 9 to 16.

In some embodiments, the at least one nonionic surfactant is selected from the group consisting of the sorbitan esters alkoxylated or not, the alkoxylated fatty acids, the alkoxylated fatty acid esters, the alkoxylated vegetable or animal oils, the alkoxylated fatty alcohols, and mixtures thereof;
preferably is at least one sorbitan ester, alkoxylated or not, more preferably at least one ethoxylated sorbitan ester, even more preferably at least one ethoxylated sorbitan monooleate, preferably comprising an average of from 3 to 40 ethylene oxide groups, more preferably an average of from 5 to 20 ethylene oxide groups.

In some embodiments, the at least one nonionic surfactant is a mixture of an ethoxylated sorbitan monooleate comprising an average of 5 ethylene oxide groups and an ethoxylated sorbitan monooleate comprising an average of 20 ethylene oxide groups.

In some embodiments, the at least one nonionic surfactant has a HLB of from 10 to 15, preferably from 11 to 14.

In some embodiments, the at least one methyl ester of fatty acid is selected from the group consisting of castor oil methyl esters, rapeseed methyl esters, soybean ethyl esters, methyl ester of ricinoleic acid, methyl ester of oleic acid, methyl ester of linoleic acid, methyl ester of linolenic acid and combinations thereof.

In some embodiments, the formulation further comprises water.

In some embodiments, the formulation further comprises an antioxidant, preferably selected from the group consisting of butylated hydroxytoluene, propyl gallate and a mixture thereof.

In some embodiments, the antioxidant is present in an amount of from 1,000 to 10,000 ppm, preferably from 2,000 to 5,000 ppm, based on the total weight of the formulation.

In some embodiments, the at least one methyl ester of fatty acid is in an amount of from 70 to 96 % by weight, more preferably from 80 to 90 % by weight, based on the total weight of the formulation.

In some embodiments, the at least one surfactant is in an amount of from 4 to 30 % by weight, preferably from 10 to 20 % by weight, based on the total weight of the formulation.

In some embodiments, water is present in an amount of from 0.05 to 2 % by weight, preferably from 0.1 to 1 % by weight, based on the total weight of the formulation.

In some embodiments, the formulation is devoid of mineral oil.

The invention also relates to the use of the formulation as described above, in a coating composition, for coating a container, preferably a glass container.

The invention also relates to a method for preparing a coating composition comprising mixing a formulation as described above with water.

The invention also relates to a coating composition comprising a formulation as described above and water, wherein water is preferably in an amount of from 50 to 98 % by weight, based on the total weight of the coating composition.

The invention also relates to the use of the coating composition as described above for coating a container, preferably a glass container.

The present invention enables to meet the abovementioned need. In particular the invention provides a formulation usable in compositions for coating containers that makes it possible to obtain a coating having a good shelf-life, effective in masking the scuffs of a container and pleasant to the touch. In addition, the formulation according to the invention is sustainable and thus environment-friendly.

This is achieved by the use of a specific renewable component, namely at least one methyl ester of fatty acid, in combination with a surfactant.

According to particular embodiments wherein the formulation comprises an antioxidant, the invention has the supplemental advantage of further increasing the stability and thus the shelf-life of the coating. Indeed, surprisingly, the

presence of an antioxidant in the coating composition makes it possible to slow down the evaporation of the coating.

Detailed description

The invention will now be described in more detail without limitation in the following description.

Unless otherwise mentioned, the percentages in the present text are percentages by weight.

In the present text, the amounts indicated for a given species can apply to this species according to all its definitions (as mentioned in the present text), including the narrower definitions.

Formulation

The formulation according to the invention comprises at least one methyl ester of fatty acid.

The methyl ester of fatty acid according to the invention may have a number of carbon atoms of from 6 to 30, preferably from 7 to 25, more preferably from 15 to 25.

The fatty acid moiety of the methyl ester of fatty acid are preferably unsaturated. Advantageously, the methyl ester of fatty acid is liquid at 0°C.

The formulation may comprise one methyl ester of fatty acid or a mixture of methyl esters of fatty acid. As examples of mixtures of methyl esters of fatty acid, mention can be made of vegetable oil methyl esters, obtained by transesterification of vegetable oils with methanol. Preferred vegetable oil methyl esters are castor oil methyl esters, rapeseed methyl esters, soybean ethyl esters, sunflower methyl esters and/or peanut methyl esters.

Methyl esters of fatty acid suitable for the invention also include methyl ester of caprylic acid, methyl ester of capric acid, methyl ester of palmitoleic acid, methyl ester of oleic acid, methyl ester of linoleic acid, methyl ester of linolenic acid, methyl ester of ricinoleic acid, methyl ester of gadoleic acid and/or methyl ester of arachidonic acid.

Preferably, the at least one methyl ester of fatty acid is selected from the group consisting of castor oil methyl esters, rapeseed methyl esters, soybean ethyl esters, methyl esters of ricinoleic acid, methyl ester of oleic acid, methyl ester of linoleic acid, methyl ester of linolenic acid and combinations thereof.

Preferably, the methyl ester of fatty acid has a freezing point equal to or lower than 10°C, such as from -15°C to 10°C, more preferably equal to or lower than 6°C (such as from -15°C to 6°C), even more preferably from -5°C to 5°C. In

some embodiments, the freezing point may be equal to or lower than 0°C. The freezing point may be measured according to standard ASTM D97.

The iodine value of the methyl ester of fatty acid is advantageously of from 100 to 150 g/100 g, more preferably from 105 to 135 g/100g. The iodine value may be measured according to standard GB/T5532-2008.

The methyl ester of fatty acid has preferably a kinematic viscosity at 40°C equal to or lower than 10 mm^2/s, preferably equal to or lower than 7 mm^2/s. The viscosity can be measured at a temperature of 40°C, with a shear rate of 1000 s^{-1} with a Brookfield viscometer equipped with a rotor. Low viscosity is preferred since the mobility on the glass surface is limited in case of high viscosity.

Examples of suitable methyl esters of fatty acid include those sold under the trade name Esterol A Oleris® from Arkema (castor oil methyl esters), those sold under the trade names Radia® 7956 and Radia® 7961 (rapeseed methyl esters) from Oleon, those sold under the trade name RSME from Valtris (rapeseed methyl esters) and the soybean methyl ester from Mosselman.

The methyl ester of fatty acid is preferably present in the formulation in an amount of from 50 to 96 % by weight, based on the total weight of the formulation. More preferably, the amount of the at least one methyl ester of fatty acid in the formulation is from 70 to 96 % by weight, even more preferably from 70 to 90 % by weight, even more preferably from 80 to 90 % by weight, based on the total weight of the formulation.

The formulation of the invention also comprises at least one surfactant. The surfactant is a nonionic surfactant.

Preferably, the surfactant is a food contact approved surfactant as defined by the Regulation (EC) No 1333/2008 of the European Parliament and the Council of 16 December 2008 on food additives.

The nonionic surfactant according to the invention has a HLB of from 9 to 16. The term "*HLB*" or "*HLB value*" means the hydrophilic-lipophilic balance which enables assessment of the solubility of an emulsifier in water. Preferably, the HLB is determined according to the method proposed by Griffin (Journal of the Society of Cosmetic Chemists, 5(4), (1954), 249–256). Preferably the HLB of the surfactant is from 10 to 15, more preferably from 11 to 14, even more preferably from 12 to 13. When the nonionic surfactant consists of a mixture of two or more nonionic surfactants, the above-mentioned values of HLB characterize the mixture of nonionic surfactants (and may be calculated from the mass ratio of the emulsifiers).

Advantageously, the nonionic surfactant comprises, or is, a sorbitan ester.

The sorbitan ester may be alkoxylated or not, and more particularly may be ethoxylated or not and propoxylated or not.

The sorbitan ester may be selected from the group consisting of sorbitan monostearate, sorbitan tristearate, sorbitan monolaurate, sorbitan trilaurate, sorbitan monooleate, sorbitan trioleate, sorbitan monopalmitate, sorbitan tripalmitate, alkoxylated (such as ethoxylated and/or propoxylated) or not, and combination thereof.

More particularly, the nonionic surfactant may comprise, or be, a non alkoxylated sorbitan ester selected from the group consisting of sorbitan monostearate, sorbitan tristearate, sorbitan monolaurate, sorbitan trilaurate, sorbitan monooleate, sorbitan trioleate, sorbitan monopalmitate, sorbitan tripalmitate and combination thereof.

Additionally or alternatively, the nonionic surfactant may comprise, or be, an ethoxylated sorbitan ester selected from the group consisting of ethoxylated sorbitan monostearate, ethoxylated sorbitan tristearate, ethoxylated sorbitan monolaurate, ethoxylated sorbitan trilaurate, ethoxylated sorbitan monooleate, ethoxylated sorbitan trioleate, ethoxylated sorbitan monopalmitate, ethoxylated sorbitan tripalmitate and combination thereof.

Preferably, the nonionic surfactant comprises, or is, an ethoxylated sorbitan ester.

Advantageously, the ethoxylated sorbitan ester comprises an average of from 3 to 40 ethylene oxide groups, preferably an average of from 5 to 20 ethylene oxide groups.

More preferably, the nonionic surfactant comprises, or is, a sorbitan ester selected from the group consisting of (non-ethoxylated) sorbitan monolaurate, (non-ethoxylated) sorbitan monooleate, ethoxylated sorbitan monolaurate, ethoxylated sorbitan monooleate and combinations thereof.

Even more preferably, the nonionic surfactant comprises at least one ethoxylated sorbitan monooleate, preferably comprising an average of from 3 to 40 ethylene oxide groups, more preferably an average of from 5 to 20 ethylene oxide groups. In some embodiments, the nonionic surfactant may consist in an ethoxylated sorbitan monooleate, preferably comprising an average of from 3 to 40 ethylene oxide groups, more preferably an average of from 5 to 20 ethylene oxide groups.

The formulation may comprise a combination of two or more nonionic surfactants, in particular two or more nonionic surfactants that can each independently be as described above.

The nonionic surfactant may be a combination of at least one non ethoxylated sorbitan ester and at least one ethoxylated sorbitan ester, preferably comprising an average of from 5 to 20 ethylene oxide groups. More particularly, the nonionic surfactant may be a combination of at least one non ethoxylated sorbitan monooleate and at least one ethoxylated sorbitan monooleate, preferably comprising an average of from 5 to 20 ethylene oxide groups, more preferably comprising an average of 20 ethylene oxide groups.

Preferably, the nonionic surfactant is a combination of at least two ethoxylated sorbitan esters, more preferably a combination of two or more ethoxylated sorbitan monooleates having a different average number of ethylene oxide groups, even more preferably a combination of an ethoxylated sorbitan monooleate having an average of 5 ethylene oxide groups (HLB of 10) (also called polyoxyethylene (5) sorbitan monooleate or polysorbate 81) and an ethoxylated sorbitan monooleate having an average of 20 ethylene oxide groups (HLB of 15) (also called polyoxyethylene (20) sorbitan monooleate or polysorbate 80), optionally with one or more other nonionic surfactants. Advantageously, the nonionic surfactant is a combination of from 20 to 80 % by weight, preferably from 40 to 60 % by weight, even more preferably around 50 % by weight, of an ethoxylated sorbitan monooleate having an average of 5 ethylene oxide groups and from 20 to 80 % by weight, preferably from 40 to 60 % by weight, even more preferably around 50 % by weight, of an ethoxylated sorbitan monooleate having an average of 20 ethylene oxide groups, based on the total weight of the nonionic surfactants.

Sorbitan monooleate 20 EO (*i.e.* with 20 ethylene oxide groups on average) (or polysorbate 80) is for example sold under the trade name SURFALINE SE80® (from Arkema) or Tween 80® (from Croda). Sorbitan monooleate 5 EO (*i.e.* with 5 ethylene oxide groups on average) (or polysorbate 81) is for example sold under the trade name SURFALINE SE81® (from Arkema) or Tween 81® (from Croda). Sorbitan monolaurate 20 EO (or polysorbate 20) is for example sold under the trade name Tween 20® (from Croda). Sorbitan monolaurate (non-ethoxylated) is for example sold under the trade name Span 20® (from Croda).

Other nonionic surfactants suitable for the invention include alkoxylated fatty acids (such as alkoxylated oleic acid), alkoxylated fatty acid esters (such as mono- or di-fatty acid glycol or mono-, di-, or tri-fatty acid glycerol), alkoxylated vegetable or animal oils (such as castor oil), alkoxylated fatty alcohols (such as C_{12}-C_{14} fatty acid of primary or secondary (iso) alcohol, or combinations thereof. In some embodiments, the nonionic surfactant of the invention is selected from the group consisting of the sorbitan esters (alkoxylated or not), the alkoxylated

fatty acids, the alkoxylated fatty acid esters, the alkoxylated vegetable or animal oils, and mixtures thereof. In the above-mentioned lists, the alkoxylated surfactants are independently preferably ethoxylated; more preferably, the alkoxylated surfactants are ethoxylated.

Preferably, the nonionic surfactant is present in the formulation in an amount of from 4 to 50 % by weight, more preferably from 4 to 30 % by weight, more preferably from 10 to 30 % by weight, even more preferably from 10 to 20 % by weight, based on the total weight of the formulation.

Preferably, the weight ratio of the methyl ester of fatty acid to the nonionic surfactant is from 2 to 15, more preferably from 3 to 10, even more preferably from 3 to 8.

The formulation of the invention also advantageously comprises water.

Preferably, the formulation comprises water in an amount of from 0.05 to 2 % by weight, preferably from 0.1 to 1 % by weight, more preferably from 0.2 to 0.8 % by weight, based on the total weight of the formulation.

The weight ratio of the nonionic surfactant to water is preferably from 5 to 100, more preferably from 10 to 50, even more preferably from 20 to 40.

The formulation of the invention may consist of the at least one methyl ester of fatty acid and the at least one nonionic surfactant. In other embodiments, the formulation of the invention may consist of the at least one methyl ester of fatty acid, the at least one nonionic surfactant and water.

However, the formulation advantageously further comprises at least one antioxidant. The presence of an antioxidant in the formulation is advantageous because it makes it possible to even enhance the stability of the coating obtained based on said formulation by reducing the evaporation of the coating over time. In addition, it may make it possible to reduce the risk of stickiness and unpleasant smell occurrence of the coating during the period of use of the coated container.

The antioxidant may be any suitable antioxidant which is soluble in the formulation (at 20°C). Preferably, the antioxidant is selected from the group consisting of butylated hydroxytoluene (BHT), propyl gallate, octyl gallate, dodecyl gallate, ethyl gallate, ascorbic acid, sodium ascorbate, calcium ascorbate, potassium ascorbate, the fatty acid esters of ascorbic acid such as ascorbyl palmitate and ascorbyl stearate, guaiac resin, erythorbic acid, sodium erythorbate, potassium erythorbate, calcium erythorbate, *tert*-tutylhydroquinone (TBHQ), butylated hydroxyanisole (BHA), anoxomer, ethoxyquin, the sodium phosphates such as monosodium phosphate, disodium phosphate and trisodium phosphate, the potassium phosphates such as monopotassium phosphate, dipotassium phosphate and tripotassium phosphate, and mixtures thereof ; more preferably

from the group consisting of butylated hydroxytoluene, propyl gallate, octyl gallate, dodecyl gallate, ethyl gallate, sodium ascorbate, calcium ascorbate, potassium ascorbate, guaiac resin, erythorbic acid, sodium erythorbate, potassium erythorbate, calcium erythorbate, *tert*-tutylhydroquinone (TBHQ), butylated hydroxyanisole, anoxomer, ethoxyquin, the sodium phosphates such as monosodium phosphate, disodium phosphate and trisodium phosphate, the potassium phosphates such as monopotassium phosphate, dipotassium phosphate and tripotassium phosphate, and mixtures thereof. More preferably, the antioxidant is butylated hydroxytoluene, propyl gallate or a mixture thereof, and even more preferably propyl gallate.

The antioxidant may be present in the formulation in an amount of from 500 to 12,000 ppm, preferably from 1,000 to 10,000 ppm, more preferably from 1,500 to 8,000 ppm, even more preferably from 2,000 to 5,000 ppm, based on the total weight of the formulation.

The weight ratio of the methyl ester of fatty acid to the antioxidant is preferably from 50 to 800, more preferably from 100 to 500, even more preferably from 100 to 350.

In preferred embodiments, the formulation consists of the at least one methyl ester of fatty acid, the at least one nonionic surfactant, water and the at least one antioxidant.

The formulation may further comprise one or more other additives, preferably chosen from the group consisting of biocides, bactericides, preservatives, ester alcohols, glycol ethers, dyes, emulsion destabilizers, perfumes, odorants, UV absorbers, light absorbers, impact absorbers, other surfactants and mineral oils. In other embodiments, the additives may be selected from the group consisting of biocides, bactericides, preservatives, ester alcohols, glycol ethers, dyes, emulsion destabilizers, perfumes, odorants, UV absorbers, light absorbers, impact absorbers and other surfactants. The formulation may contain these additives in an amount of from 0 to 5 % by weight, preferably from 0 to 1 % by weight, based on the total weight of the formulation.

The formulation may comprise one or more mineral oils in an amount of from 0 to 30 % by weight, preferably from 0 to 10 % by weight, more preferably from 0 to 5 % by weight. The weight ratio of the mineral oils to the methyl ester of fatty acid may be from 0 to 0.5, preferably from 0 to 0.2, more preferably from 0 to 0.1. Preferably, the formulation is devoid of mineral oils.

Preferably, the formulation is a liquid formulation.

Preferably, the formulation is soluble in a solution of 2 % by weight of caustic soda in water (relative to the total weight of the aqueous solution of caustic soda) at 60°C and higher.

Coating composition

The present invention also relates to a coating composition comprising a formulation as described above and water. Thus, the present invention also relates to a coating composition comprising at least one methyl ester of fatty acid, at least one nonionic surfactant having a HLB of from 9 to 16 and water. The coating composition can be prepared using a formulation as described in the above section.

The coating composition according to the invention comprises preferably water in an amount of from 50 to 98 % by weight, based on the total weight of the coating composition, preferably from 80 to 97 % by weight, more preferably from 85 to 95 % by weight.

The at least one methyl ester of fatty acid, the at least one nonionic surfactant, the weight ratio of the methyl ester of fatty acid to the nonionic surfactant and the weight ratio of the mineral oils to the methyl ester of fatty acid may be as described in the above section.

The water has advantageously a hardness of from 0 to 10°dH, preferably from 1 to 4°dH.

The coating composition is preferably an emulsion. More preferably, it is an oil-in-water emulsion. In the present invention, an "*oil-in-water emulsion*" is understood as an aqueous continuous phase having an oil phase dispersed or emulsified therein, wherein the oil phase comprises at least the methyl esters of fatty acid.

Preferably, the coating composition comprises an antioxidant, that can be as described above. The weight ratio of the methyl ester of fatty acid to the antioxidant may be as described in the above section.

The coating composition may also comprise one or more additives, preferably as described above in relation to the formulation.

Advantageously, the coating composition consists of the at least one methyl ester of fatty acid, the at least one nonionic surfactant, water and optionally the at least one antioxidant. In some embodiments, the coating composition consists of the at least one methyl ester of fatty acid, the at least one nonionic surfactant, water, optionally the at least one antioxidant and optionally one or more other additives chosen from the group consisting of biocides, bactericides, preservatives, ester alcohols, glycol ethers, dyes, emulsion destabilizers,

perfumes, odorants, UV absorbers, light absorbers, impact absorbers, surfactants and mineral oils.

Preferably, the at least one methyl ester of fatty acid is present in the coating composition in an amount of from 2 to 20 % by weight, more preferably from 5 to 10 % by weight, based on the total weight of the coating composition.

Preferably, the at least one nonionic surfactant is present in the coating composition in an amount of from 0.5 to 5 % by weight, more preferably from 0.8 to 2 % by weight, based on the total weight of the coating composition.

When present, the at least one antioxidant is preferably present in the coating composition in an amount of from 0.003 to 0.12 % by weight, more preferably from 0.007 to 0.08 % by weight, even more preferably from 0.01 to 0.06 % by weight, based on the total weight of the coating composition.

The coating composition may comprise at least one mineral oil in an amount of from 0 to 5 % by weight, more preferably from 0 to 3 % by weight, even more preferably from 0 to 1 % by weight, even more preferably from 0 to 0.05 % by weight. The weight ratio of mineral oils to the methyl ester of fatty acid may be as described in the above section. Most preferably, the coating composition is devoid of any mineral oil.

Preparation methods

The invention also relates to a method for preparing a formulation as described above, comprising mixing the at least one methyl ester of fatty acid, the at least one nonionic surfactant, the water and optionally the other components of the formulation (such as the at least one antioxidant and/or the other additives).

The mixing step may be carried out in one or more steps (some of the components may thus be premixed before being mixed with the other components of the formulation) and the components may be mixed in any order. The mixing step can be performed using any suitable mixing device. The mixing step is preferably carried out at a temperature from 5 to 50°C, preferably from 20 to 40°C.

The invention also relates to the use of a formulation as described above for preparing a coating composition, such as a coating composition as described above.

Another aspect of the invention is a method for preparing a coating composition (in particular as described above) comprising mixing a formulation as described above with water. The invention also relates to a method for preparing a coating composition as described above comprising mixing at least one methyl ester of fatty acid, at least one nonionic surfactant having a HLB of from 9 to 16, water and optionally other components (such as at least one antioxidant). The

components may be mixed in any order. The coating composition is preferably an oil-in-water emulsion.

The mixing step can be performed using any suitable mixing device such as dispersers, dynamic mixers, static mixers, ultra-sonic mixing devices or pumps. The mixing step is preferably carried out at a temperature from 5 to 50°C, preferably from 20 to 40°C.

In the above methods, the components and their amounts may be as described in the previous sections.

Applications

Another object of the invention is the use of a formulation as described above for coating a glass surface, preferably a glass container. The invention also relates to the use of a formulation as described above for coating a container. Preferably, the formulation is used in a coating composition, more preferably in a coating composition as described above. Thus, the invention also relates to the use of a coating composition as described above for coating a container, preferably a glass container. The invention also relates to a method for coating a container, preferably a glass container, comprising preparing a coating composition using a formulation as described above and applying the coating composition on the container, preferably the glass container.

The glass containers may be any glass containers, in particular bottles.

The application of a coating composition as described herein on the surface of a container, especially a glass container, more especially a returnable glass container, makes it possible to mask the scratches or the like present on the container surface which would negatively impact the commercial value of said container.

According to another aspect, the invention pertains to a method for coating a container, preferably a glass container, comprising applying a coating composition as described above on the container, preferably the glass container.

The coating composition of the invention may be applied on the container by spraying, dipping or any other contact method. Preferably, the coating composition is applied on the container by spraying said coating composition on the container.

A coating applicator can be used, such as a brush, a capillary, a sponge, a fibre or the like. When a coating applicator is used, the coating composition is advantageously applied on the surface of the container by bringing into contact the coating applicator and the surface of the container to be coated.

The coating composition is preferably applied on an outer surface of the container, to part or to the whole of the outer surface of the container.

The container may be subjected to one or more of the following steps (preferably all these steps), advantageously before the container is coated with the coating composition, and preferably in that order:

- washing the (glass) container;
- applying a lubricant onto at least a part of the surface of the (glass) container (or onto the whole surface of the container);
- filling and capping the (glass) container; and
- labelling the (glass) container.

The washing of the (glass) container may be carried out according to any method well known in the art, and for example using water, preferably hot water. Said water can contain one or more detergent, for example a base, such as sodium hydroxide, preferably at a concentration of from 1 to 5 % by weight in water, such as 2 % by weight in water, based on the total weight of the solution.

At least one lubricant can also be applied onto the outer surface of the (glass) container after washing. Such lubricants are known in the field, such as for example Kercoat® 500 provided by Arkema.

The (glass) containers are preferably then filled and capped, again according to known methods. The (glass) container may be filled with cold, tepid or warm liquids.

Labelling may be carried out before or after the coating of the (glass) container.

Any known equipment in the art may be used to carry out the coating method of the invention. The installation typically includes mixing and storage vessels, pumps, transfer and feed lines, spray apparatus and control and monitoring equipment. Preferably, the installation comprises one or more mixing vessel(s); dosing and circulating pump(s); a mixing unit (that can be the pump itself); circulation piping; and applying means, such as spraying devices.

The equipment may also comprise controlling means aiming at monitoring the process of applying the coating composition. Such controlling means may be for example optical means detecting the presence or the absence of a container in front of the applying means, and/or detecting the presence and the quantity of scuff bands or scratches, so that the minimum amount of coating composition is applied on the containers to obtain the best efficiency. According to a preferred aspect, the controlling means are monitored via a computer that may interact with the dosing pump(s) and applying means.

Still preferably, the above-described equipment may be encased within a "*scratch-masking*" cabinet that can be easily adapted to existing bottling lines, comprising the necessary equipment for washing, filling, capping and labelling containers, preferably glass containers, typically returnable glass bottles.

The present invention is also relative to a glass surface, preferably a glass container, and even more preferably a glass bottle obtainable by the method of the invention. The present invention also relates to a container obtainable by the method of the invention.

Examples

The following examples illustrate the invention without limiting it.

Example 1

The stability of the following fatty acid methyl esters (FAME) was assessed:

- FAME No. 1: Esterol A Oleris® from Arkema, which is methyl esters prepared from castor oil and has an iodine value of 110, a poor point of 9°C, a kinetic viscosity at 40°C of 5.7 mm^2/s, a flash point of 173°C and a density of 0.89.
- FAME No. 2: Radia® 7956 from Oleon, which is rapeseed oil methyl esters and has an iodine value of 110, a poor point of -14°C, a kinetic viscosity at 40°C of 4.5 mm^2/s a flash point of 190°C and a density of 0.88.
- FAME No. 3: Radia® 7961 from Oleon, which is rapeseed oil methyl esters and has an iodine value of 113, a poor point of -10°C, a kinetic viscosity at 40°C of 4.2 mm^2/s, a flash point of 180°C and a density of 0.89.
- FAME No. 4: RSME from Valtris, which is rapeseed oil methyl esters containing BHT. It has an iodine value of 120, a poor point of -9°C, a kinetic viscosity at 40°C of 4 mm^2/s, a flash point of 173°C and a density of 0.89.
- FAME No. 5: soybean methyl esters from Mosselman which have an iodine value of 130, a poor point of -4°C, a kinetic viscosity at 40°C of 4 mm^2/s, a flash point higher than 150°C and a density of 0.875.

Samples of 10 g of the fatty acid methyl esters were placed in a small glass beaker in a ventilated oven, at 40°C, for 105 days and their weight over time was measured.

The results are shown in the table below.

[Table 1]

FAME No.	Weight (in % of the initial weight)	
	Maximum weight achieved (day at which it is achieved)	Weight at day 105
1	102,60 % (day 15)	95.45 %
2	103.96 % (day 35)	98.76 %
3	103.70 % (day 49)	99.61 %
4	100 % (day 0)	98.53 %
5	104.20 % (day 79)	100.56 %

The fatty acid methyl esters kept at least 95 % of their weight 105 days after the start of the test. Therefore, the evaporation rate of the FAMEs is sufficiently low to result in a satisfactory coating during the whole period of use of the container coated using said FAMEs.

It should be noted that apart from FAME No. 4, the FAMEs underwent a weight increase during the test before losing weight due to evaporation.

The following basic formulations were prepared by mixing the components in the amounts indicated in the table below.

[Table 2]

Formulation No.	Used FAME	Amount of FAME (% by weight)	Amount of Surfaline SE81® (% by weight)	Amount of Surfaline SE80® (% by weight)	HLB	Amount of water (% by weight)
A'	1	84.5	7.5	7.5	12.5	0.5
B'	2	84.5	7.5	7.5	12.5	0.5
C'	3	84.5	7.5	7.5	12.5	0.5
D'	4	84.5	7.5	7.5	12.5	0.5
E'	5	84.5	7.5	7.5	12.5	0.5
F'	4	84.5	12	3	11	0.5
G'	4	84.5	9	6	12	0.5
H'	4	84.5	6	9	13	0.5
I'	4	84.5	3	12	14	0.5
J'	4	89.5	8	2	11	0.5
K'	4	87	10	2.5	11	0.5
L'	4	89.5	6	4	12	0.5
M'	4	87	7.5	5	12	0.5

N'	4	89.5	4	6	13	0.5
O'	4	87	5	7.5	13	0.5

In the above table, the HLB indicated is the HLB of the mixture of surfactants.

Surfaline SE80® is a nonionic surfactant that is sorbitan monooleate 20 EO (HLB 15). Surfaline SE81® is a nonionic surfactant that is sorbitan monooleate 5 EO (HLB 10).

The basic formulations were prepared by mixing and stirring the ingredients for 5 minutes at room temperature.

Then, coating compositions were prepared by diluting the above-mentioned formulations in tap water (having a hardness of 3°dH) at a concentration of 7 % by weight or 10 % by weight, using a disperser Dispermat® at 25 % stirring power for 5 minutes.

A volume of 0.4 mL of said coating compositions was sprayed on the scuff band present on the shoulder of a bottle. For each coating compositions, the test was performed on 5 bottles at 20°C and 5 bottles at 30°C.

The coated bottles were then stored at room conditions for 24 hours. The masking effect was assessed by visual inspection (human eye) and rated from 0, which stands for no masking effect, to 5, which stands for full excellent masking effect. Touch was assessed by visual inspection and by hand touch, and was rated from 0, which stands for visible oil droplets and fatty touch, to 5, which stands for pleasant glass like touch. The rating is given in the table below.

[Table 3]

Rating	**Masking efficiency**	**Touch performance**
0	No masking effect	Fatty touch, droplets visible
1	Very little masking	Fatty touch, no droplets visible
2	Little masking	Little fatty touch
3	Poor masking	Organic touch
4	Nearly good masking	Nearly perfect but little different from glass touch
5	Excellent masking	Pleasant, glass like touch

The masking and touch performances of the compositions according to the invention were compared to the masking and touch performances of coating compositions comprising 7.5 % by weight or 10 % by weight of Opticoat® 240

(prepared in the same manner as the coating compositions of the invention). Opticoat® 240 is a commercial formulation from Arkema comprising mineral oil.

A global score was calculated for each tested coating composition by summing the average rating of the masking performance of the bottles at 20°C, the average rating of the masking performance of the bottles at 30°C, the average rating of the touch performance of the bottles at 20°C and the average rating of the touch performance of the bottles at 30°C. This global score was then converted into percentages (where the possible maximum score 20 corresponds to 100% and the possible minimum score 0 corresponds to 0 %).

The results are displayed in the following table.

[Table 4]

Formulation on which the coating composition is based	Concentration of the formulation in the coating composition	Mask and Touch performance
No. A'	7.5 % by weight	88 %
	10 % by weight	92 %
No. B'	7.5 % by weight	80 %
	10 % by weight	91 %
No. C'	7.5 % by weight	79 %
	10 % by weight	91 %
No. D'	7.5 % by weight	83 %
	10 % by weight	89 %
No. E'	7.5 % by weight	83 %
	10 % by weight	88 %
No. F'	7.5 % by weight	83 %
	10 % by weight	85 %
No. G'	7.5 % by weight	89 %
	10 % by weight	89 %
No. H'	7.5 % by weight	88 %
	10 % by weight	88 %
No. I'	7.5 % by weight	86 %
	10 % by weight	91 %
No. J'	7.5 % by weight	89 %
	10 % by weight	93 %
No. K'	7.5 % by weight	90 %
	10 % by weight	84 %
No. L'	7.5 % by weight	89 %

	10 % by weight	91 %
No. M'	7.5 % by weight	87 %
	10 % by weight	84 %
No. N'	7.5 % by weight	86 %
	10 % by weight	89 %
No. O'	7.5 % by weight	86 %
	10 % by weight	88 %
Opticoat® 240	7.5 % by weight	86 %
	10 % by weight	86 %

The coating compositions according to the invention all exhibit good making and touch performances, that are similar to those achieved with compositions based on the Opticoat® 240 formulation.

The label sensitivity (i.e. extraction of the dye from print and deformation of the label) was also assessed. AMSTEL® BEER labels were put between filter paper and saturated with 10 % by weight of the tested coating composition. The wet labels between filter paper were hold between two glass sheets for 24 hours. Then, the filter paper was checked for any colour extracted from the label (which is called ghost print). Wearing a disposable glove, the label was touched with a finger and a swipe off movement was made, and the presence of a smear was checked.

For each bottle, a rating was given, from 0 to 5, according to the table below.

[Table 5]

Rating	Label sensitivity	
	Ghost print	**Smear**
1	Ghost print all colours	Severe smear (all colours)
2	Ghost print more colours	Smear more colours
3	Ghost print one colours	Smear one colour
4	Minor ghost print	Minor smear
5	No ghost print	No smear

All the coating compositions according to the invention displayed mild label attack (that is to say, with a rating of about 4), comparable to that of the compositions based on the Opticoat® 240 formulation.

Example 2

In the test described in example 1, the FAMEs No. 1, 2, 3 and 5 showed an increase in weight before they lose weight over time due to evaporation. The gain in weight may take place from the beginning of the test (FAME No. 1) or after several days, after a first loss of weight over time due to evaporation (FAMEs No. 2, 3 and 5). The increase in weight is thought to be a result of the oxidation of the FAME. The antioxidant BHT present in the FAME No. 4 protected the methyl esters of fatty acid since no increase in weight was observed.

Therefore, the effect of the combination of an antioxidant with the fatty acid methyl esters was studied. To the above-mentioned FAMEs, BHT was added as indicated below:

- FAME No. A: FAME No.4 supplemented with 2,000 ppm of BHT;
- FAME No. B: FAME No.5 supplemented with 1,000 ppm of BHT;
- FAME No. C: FAME No.2 supplemented with 1,500 ppm of BHT;
- FAME No. D: FAME No.3 supplemented with 1,500 ppm of BHT;
- FAME No. E: FAME No.1 supplemented with 2,000 ppm of BHT;

Samples of 10 g of the fatty acid methyl esters were placed in a small glass beaker into a ventilated oven, at 40°C, for 76 to 100 days and their weight over time was measured.

The results are shown in the table below.

[Table 6]

FAME No.	Weight (in % of the initial weight)	
	Maximum weight achieved (day at which it is achieved)	Weight at the end of the test (day of the end of the test)
A	100 % (day 0)	98.05 % (day 97)
B	100 % (day 0)	98.19 % (day 90)
C	100 % (day 0)	98.26 % (day 83)
D	100 % (day 0)	97.94 % (day 76)
E	100 % (day 0)	96.57 % (day 100)

At the end of the test, all the FAMEs maintained a weight higher than 96 % of their initial weight. No increase in weight was detected for each of the tested FAMEs over the whole duration of the test.

The loss of weight per day of the above-mentioned FAMEs was calculated and compared with the loss of weight per day obtained for the same FAMEs devoid of antioxidant. The results are summarized in the table below. For the

FAMEs displaying an increase in weight due to oxidation, the loss of weight per day measured was the one occurring after said increase in weight.

[Table 7]

FAMEs without antioxidant		FAMEs comprising BHT	
FAME No.	**Loss of weight per day (%)**	**FAME No.**	**Loss of weight per day (%)**
1	0.079	**E**	0.034
2	0.074	**C**	0.021
3	0.073	**D**	0.027
5	0.140	**B**	0.020
		4	0.014
		A	0.020

We can see that the presence of an antioxidant makes it possible to significantly reduce the loss of weight per day of the FAMEs and thus to slow down the evaporation of the FAMEs. Therefore, the shelf-life of a coating may be further improved by adding an antioxidant in the coating composition.

Another test was performed with propyl gallate being added to the fatty acid methyl esters as an antioxidant instead of BHT.

To the FAME No. 1 (as described in example 1), propyl gallate was added as indicated below:

- FAME No. F: FAME No.1 supplemented with 3,500 ppm of propyl gallate;
- FAME No. G: FAME No.1 supplemented with 4,000 ppm of propyl gallate;
- FAME No. H: FAME No.1 supplemented with 4,500 ppm of propyl gallate;
- FAME No. I: FAME No.1 supplemented with 10,000 ppm of propyl gallate.

Samples of 10 g of the fatty acid methyl esters were placed in a small glass beaker in a ventilated oven, at 40°C, for 105 days and their weight over time was measured.

The results are shown in the table below.

[Table 8]

FAME No.	Weight (in % of the initial weight)	
	Maximum weight achieved (day at which it is achieved)	Weight at day 105
F	100 % (day 0)	94.53 %
G	100 % (day 0)	94.90 %
H	100 % (day 0)	95.23 %
I	100 % (day 0)	95.56 %

After 105 days, all the FAMEs maintained a weight higher than or equal to 94 % of their initial weight. In contrast to FAME No. 1 containing no antioxidant, that exhibited an increase in weight due to the oxidation of the fatty acid methyl esters (until it reached a weight of 102.60 % of its initial weight at day 15), the FAMEs No. F, G, H and I containing from 3,500 to 10,000 ppm of propyl gallate did not undergo oxidation.

The loss of weight per day of the FAMEs No. F, G, H and I containing propyl gallate was calculated and compared with the loss of weight per day obtained for the FAME No. 1 devoid of antioxidant (measured after the peak of weight increase). The results are summarized in the table below.

[Table 9]

FAME without antioxidant		FAMEs comprising propyl gallate	
FAME No.	Loss of weight per day (%)	FAME No.	Loss of weight per day (%)
1	0.079	F	0.052
		G	0.049
		H	0.045
		I	0.042

The addition of propyl gallate to the fatty acid methyl esters results in a significant reduction in the loss of weight of the fatty acid methyl esters per day, which suggests that the coating will have an even improved life-shelf.

Claims

1. A formulation comprising:
   - at least one methyl ester of fatty acid; and
   - at least one nonionic surfactant having a HLB from 9 to 16.

2. The formulation of claim 1, wherein the at least one nonionic surfactant is selected from the group consisting of the sorbitan esters alkoxylated or not, the alkoxylated fatty acids, the alkoxylated fatty acid esters, the alkoxylated vegetable or animal oils, the alkoxylated fatty alcohols, and mixtures thereof;
preferably is at least one sorbitan ester, alkoxylated or not, more preferably at least one ethoxylated sorbitan ester, even more preferably at least one ethoxylated sorbitan monooleate, preferably comprising an average of from 3 to 40 ethylene oxide groups, more preferably an average of from 5 to 20 ethylene oxide groups.

3. The formulation of claim 1 or 2, wherein the at least one nonionic surfactant is a mixture of an ethoxylated sorbitan monooleate comprising an average of 5 ethylene oxide groups and an ethoxylated sorbitan monooleate comprising an average of 20 ethylene oxide groups.

4. The formulation of any one of claims 1 to 3, wherein the at least one nonionic surfactant has a HLB of from 10 to 15, preferably from 11 to 14.

5. The formulation of any one of claims 1 to 4, wherein the at least one methyl ester of fatty acid is selected from the group consisting of castor oil methyl esters, rapeseed methyl esters, soybean ethyl esters, methyl ester of ricinoleic acid, methyl ester of oleic acid, methyl ester of linoleic acid, methyl ester of linolenic acid and combinations thereof.

6. The formulation of any one of claims 1 to 5, further comprising water.

7. The formulation of any one of claims 1 to 6, further comprising an antioxidant, preferably selected from the group consisting of butylated hydroxytoluene, propyl gallate and a mixture thereof.

8. The formulation of claim 7, wherein the antioxidant is present in an amount of from 1,000 to 10,000 ppm, preferably from 2,000 to 5,000 ppm, based on the total weight of the formulation.

9. The formulation of any one of claims 1 to 8, wherein the at least one methyl ester of fatty acid is in an amount of from 70 to 96 % by weight, more preferably from 80 to 90 % by weight, based on the total weight of the formulation.

10. The formulation of any one of claims 1 to 9, wherein the at least one surfactant is in an amount of from 4 to 30 % by weight, preferably from 10 to 20 % by weight, based on the total weight of the formulation.

11. The formulation of any one of claims 6 to 10, wherein water is present in an amount of from 0.05 to 2 % by weight, preferably from 0.1 to 1 % by weight, based on the total weight of the formulation.

12. The formulation of any one of claims 1 to 11, that is devoid of mineral oil.

13. Use of the formulation of any one of claims 1 to 12, in a coating composition, for coating a container, preferably a glass container.

14. A method for preparing a coating composition comprising mixing a formulation of any one of claims 1 to 12 with water.

15. A coating composition comprising a formulation of any one of claims 1 to 12 and water, wherein water is in an amount of from 50 to 98 % by weight, based on the total weight of the coating composition.

16. Use of the coating composition of claim 15 for coating a container, preferably a glass container.